Electrochimica Acta 93 (2013) 44–52

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

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

Electrochemical characterization of reduced graphene oxide-coated polyester fabrics

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ARTICLE INFO

Article history:
Received 17 October 2012
Received in revised form 8 January 2013
Accepted 15 January 2013
Available online xxx

Keywords:
Graphene
Graphene oxide
Conducting fabric
Polyester
Scanning electrochemical microscopy

ABSTRACT

Reduced graphene oxide (RGO) coated fabrics were obtained by chemical reduction of GO on polyester (PES) fabrics. Conducting fabrics that have different applications were obtained by applying several layers of RGO. Electrochemical techniques not traditionally used for the characterization of these materials were used to test their electrical and electrochemical properties. Electrochemical impedance spectroscopy was used to measure the electrical properties. The resistance of the original PES was more than 10^{11} Ω cm^2, but when coated with three RGO layers, the resistance decreased to 23.15 Ω cm^2. Phase angles changed from 90° for PES and PES-GO (capacitative behavior) to 0° for all the RGO coated samples (resistive behavior). Electro-activity was measured by cyclic voltammetry (CV) and scanning electrochemical microscopy. An increase in electro-activity was observed when the inactive GO was reduced to RGO. With CV an increase of electro-activity was observed with an increasing number of RGO layers. The contact between the different RGO sheets is responsible for the electric conduction in the fabrics. The techniques used showed that with only one RGO coating, the contact between the RGO sheets is not good and more coatings were needed to assure good electrical and electrochemical properties.

1. Introduction

Graphene has attracted a great deal of attention during recent years due to its electronic, mechanical and thermal properties, as well as other exciting properties [1–8]. Different methods have been used for the production of graphene [7–9], and mechanical exfoliation was the first method used to produce graphene layers [1]. However, the production by this method is not very effective, so other methods such as chemical vapor deposition or chemical methods have been developed [7–9]. The use of graphene composites with other materials has been also proposed as an alternative solution to the large-scale production of graphene-based materials [10].

In this paper we have used a chemical method to obtain graphene-coated fabrics, where graphene oxide (GO) is reduced chemically to obtain reduced graphene oxide (RGO) on the surface of the fabrics. Textile materials have several advantages over conventional materials such as film, such as having good flexibility and mechanical properties. In addition, they are light materials that have a large surface area. This large surface area makes these materials good substrates on which to deposit other materials for different applications. For example fabrics have been coated with conducting polymers to produce conductive fabrics [11,12], with silver or TiO_2 nanoparticles to produce antibacterial fabrics [13], with single walled nanotubes and MnO_2 [14] or graphene and MnO_2 [15] to produce super-capacitors.

Graphene-coated fabrics have usually been obtained by placing the fabrics in contact with solutions containing GO [16,17]. GO sheets are adsorbed on the surface of the fabrics due to the attraction forces between the functional groups of the fabrics and the oxidized groups of the GO sheets. The process is similar to a dying process where an adsorption process occurs [16]. Once the fabric is coated with GO, it is then reduced to RGO using reducing agents such as sodium hydrosulfite [16] or hydrazine [17]. GO coated fabrics have also generated interest due to the photo-catalytic activity of GO and also to its antibacterial activity [18]. Directly coated graphene fabrics have also been obtained in other works referenced in the bibliography [15]. Graphene fabrics have also been produced by depositing graphene by chemical vapor deposition on a Cu mesh, after which the Cu mesh was dissolved by an acid solution and graphene fabrics were obtained [19]. Regarding graphene fibers, different methods such as wet spinning [20] or obtaining hydrothermally [21] using GO as a precursor material have been used in the past. The fibers formed were later reduced chemically [20] or thermally [21] to obtain graphene fibers.

The fibers used to deposit graphene or GO have been polyarylate [16] or cotton [17]. Polyester (PES) is one of the most used fibers in industry so it would be of interest to use it to study the production of graphene-coated fabrics. In addition, the presence of polar groups

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http://dx.doi.org/10.1016/j.electacta.2013.01.071

on its structure makes this family attractive because the adhesion of GO is better in fibers with polar groups (C—O and C═O groups are present in PES).

In the present work, graphene-coated fabrics were obtained by reducing GO on the surface of the fabrics. Traditional characterization techniques such as Fourier transform infrared spectroscopy with total attenuated reflection (FTIR-ATR) were used for chemical characterization, while scanning electron microscopy (SEM) was used to observe the morphology of the coatings and the samples. There is a lack of characterization of these materials by electrochemical techniques, so electrochemical techniques not usually used for the characterization of these materials were used in this work. Electrochemical impedance spectroscopy (EIS) was used for the measurement of the electrical resistance ($\Omega\,cm^2$) and the surface resistivity ($\Omega/\square$) of the fabrics and also to obtain the phase angle (°), which gives an indication of the insulating/conducting behavior of the fabrics. Scanning electrochemical microscopy (SECM) was used to measure the electrochemical activity by means of approach curves. SECM is a relatively novel (1989) and powerful technique that is becoming more popular among researchers [22–24]. Its applications range for example from the study of corrosion of metals [25] to the study of biological systems [23]. Cyclic voltammetry (CV) was also used to measure the electro-activity of these materials.

2. Experimental

2.1. Reagents and materials

All reagents used were of analytical grade. Sodium dithionite ($Na_2S_2O_4$) and sulphuric acid (H_2SO_4) were supplied by Merck. Hexaammineruthenium (III) chloride ($Ru(NH_3)_6Cl_3$), 98% and potassium chloride (KCl), were used as received from Acrōs Organics and Merck respectively.

Monolayer GO powders were supplied by Nanoinnova Technologies S.L. (Spain).

PES fabrics were supplied by Viatex S.A. and their characteristics were: fabric surface density, 140 g m^{-2}; warp threads per cm, 20 (warp linear density, 167 dtex); weft threads per cm, 60 (weft linear density, 500 dtex). These are specific terms used in the field of textile industry and their meaning can be consulted in a textile glossary [26]. The estimated diameter of polyester fibers was around 17 μm (estimated employing SEM). The effective area of the fabric was also estimated employing the values of density (1.37 g cm^{-3}), fabric surface density and diameter of the fibers. The value obtained was around 24 cm^2 per geometrical cm^2 of the fabric.

Where necessary, solutions were deoxygenated by bubbling nitrogen (N_2 premier X50S). Ultrapure water was obtained from an Elix 3 Millipore-Milli-Q Advantage A10 system with a resistivity near to 18.2 MΩ cm.

2.2. Synthesis of RGO on PES fabrics

RGO coated fabrics were obtained with the same method used by Fugetsu et al. [16]. Solutions of 3 g L^{-1} of GO were prepared by mixing monolayer GO powders with water in an ultrasound bath for 30 min. Then the PES fabric was placed in contact with the GO solution for 30 min to allow the dyeing of the fabric. Fabrics were allowed to dry for 24 h. After this time, they were placed for 30 min in a solution containing sodium dithionite at approximately 90 °C to perform the reduction of GO to RGO. Finally, the fabrics were washed several times with ultrapure water. RGO powders from solution were also filtered to perform FTIR-ATR measurements in order to assure the reduction of GO to RGO. Several samples with a different number of RGO coatings (1, 2, 3, 4) were obtained (PES-G1, PES-G2, PES-G3, PES-G4) repeating the same procedure mentioned above. One sample coated with GO (PES-GO) was also obtained for comparison of the different results.

2.3. FTIR-ATR

FTIR-ATR with horizontal mono-rebound attenuated total reflection was performed with a Nicolet 6700 Spectrometer equipped with deuterated triglycine sulfate detector. An accessory with pressure control was used to equalize the pressure in the different solid samples. A prism of ZnSe was used. Spectra were collected with a resolution of 4 cm^{-1} and 100 scans were averaged for each sample. GO and RGO powders were characterized. PES fabrics uncoated and coated with GO and RGO were also characterized by FTIR-ATR.

2.4. SEM

A Jeol JSM-6300 scanning electron microscope was used to observe the morphology of the samples. SEM analyses were performed using an acceleration voltage of 10 kV. Samples for SEM measurements were coated with Au using a sputter coater Bal-Tec SCD 005.

2.5. Electrical measurements

An Autolab PGSTAT302 potentiostat/galvanostat was used to perform EIS analyses. EIS measurements were performed in the 10^5–10^{-2} Hz frequency range. The amplitude of the sinusoidal voltage used was ±10 mV. Measurements were carried out in a two-electrode arrangement. Two types of configuration were used to carry out the measurements. In the first one, the sample was located between two round copper electrodes ($A = 1.33\ cm^2$), while in the second configuration, two rectangular copper electrodes (0.5 cm × 1.5 cm) separated by 1.5 cm and pressed on the fabric sample were used. The measured area of the fabric with this configuration was a square of 1.5 cm so the measured impedance modulus (Ω) was equal to the surface resistivity ($\Omega/\square$) [27,28].

2.6. CV

An Autolab PGSTAT302 potentiostat/galvanostat was used to perform CV measurements of the RGO coated fabrics in 0.5 M H_2SO_4 solutions. The conducting fabric sample was located between two Ti plates to connect the sample with the potentiostat/galvanostat. The measurements were performed in a three-electrode arrangement. The counter electrode used was made of stainless steel; the pre-treatment consisted of polishing, degreasing with acetone in an ultrasonic bath and washing with water in the ultrasonic bath. The working electrode was made by cutting a strip of the RGO coated conducting fabric, the exposed area of the fabric to the solution was 1 cm^2. Potential measurements were referred to Ag/AgCl (3 M KCl) reference electrode. Oxygen was removed from solution by bubbling nitrogen gas for 10 min and then a N_2 atmosphere was maintained during the measurements. The ohmic potential drop was measured and introduced in the Autolab software (GPES). The measurements were done between −0.2 V and +0.8 V. The characterization by means of CV has been taken at different scan rates as previous authors have corroborated the influence of this parameter on the electrochemical response obtained [11,27]. The scan rates used were 50 mV s^{-1}, 5 mV s^{-1} and 1 mV s^{-1}.

2.7. SECM

SECM measurements were carried out with a Sensolytics scanning electrochemical microscope. The three-electrode cell