



Electrochemical synthesis of polypyrrole doped with graphene oxide and its electrochemical characterization as membrane material



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ARTICLE INFO

Article history:

Received 3 May 2016

Received in revised form 24 June 2016

Accepted 28 June 2016

Available online 12 July 2016

Keywords:

Polypyrrole

Graphene oxide

Hybrid material

Membrane

Scanning electrochemical microscopy

Electrochemical impedance spectroscopy

ABSTRACT

Polypyrrole (PPy) doped with graphene oxide (GO) has been electrochemically obtained by potentiostatic synthesis and its electrochemical behavior as membrane material has been studied for the first time. Fourier transform infrared spectroscopy with attenuated total reflection showed the formation of the hybrid material due to presence of PPy and GO bands. Field emission scanning electron microscopy micrographs showed the effective incorporation of GO sheets and the formation of a 3-D porous material with high surface area. Scanning electrochemical microscopy of PPy/GO films showed positive feedback close to the ideal conducting behavior, indicating a good electroactivity. Electrochemical impedance spectroscopy (EIS) was employed to measure the electrochemical properties of the coatings by two-, three-, and four-electrode configurations. The electronic conductivity of PPy/GO film, measured between two metallic conductors, was $4.7 \cdot 10^{-6}$ S/cm. Its ionic conductivity was superior ($1.6 \cdot 10^{-3}$ S/cm) due to the high porosity of the material as demonstrated by cyclic voltammetry and EIS measurements, where the PPy/GO film was employed as a free-standing membrane. The diffusion-migration rate of tetramethylammonium chloride was very similar to sodium chloride when present in the same concentration, which indicated no influence of the size of the electrolyte conductor due to the high porosity.

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1. Introduction

The discovery of conducting polymers in the 1970s led to a revolution in the field of materials science and different applications such as supercapacitors, LEDs, solar cells, field effect transistors, biosensors, etc., have been reported for the family of conducting polymers [1]. The isolation of graphene by K.S. Novoselov and A.K. Geim [2] has led to the last revolution in materials science due to its outstanding electronic, mechanical, optical and thermal properties [3]. Different applications in electronics, photonics, composite materials, energy storage, sensors or bio-applications have been studied [3]. The family of graphene materials is comprised of a range of different materials (graphene, graphene oxide, reduced graphene oxide, nitrogen doped graphene, etc.). Among the production methods of graphene derivatives, chemical methods for the production of graphene oxide (GO) have received particular attention due to its ease of operation and high capacity production [4]. This processing

technique has the drawback that GO is an insulating material due to the disrupted sp^2 structure. However, its posterior reduction leads to the partial restoration of the conducting sp^2 structure of graphene [5].

During the polymerization of pyrrole (Py) to form polypyrrole (PPy) (either chemically or electrochemically), positive charges are created in its structure (polarons and bipolarons). These charges need to be neutralized to maintain the electroneutrality principle; the charge compensation is produced by a counter ion (anion). Traditionally, organic counter ions (such as anthraquinone sulfonic acid) have been employed for such purpose [6], although the employment of inorganic counter ions has also been reported [6,7]. GO presents negative charges in its structure due to the presence of functional groups (carboxylic acids, hydroxyl groups, etc.) [8], reason why GO presents negative Zeta potential [9]. Its negative nature allows the incorporation of GO in the PPy matrix during polymerization, and the large size of GO sheets (typically in the order between hundreds of nm and several μm) prevents its expulsion from the PPy structure. This would be an advantage when compared with the employment of traditional organic counter ions (such as anthraquinone sulfonic acid with a size in the order of several Å), which suffer migration and are partially expelled from the PPy structure, especially after deprotonation of

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PPy in basic media [10]. The combination of PPy with GO has been shown of interest for the production of composites with interesting properties for the development of supercapacitors [11,12], microbial fuel cells [13], counter electrode for dye-sensitized solar cells [14], Cr (VI) removal [15], etc. Chemical [15] and electrochemical methods of synthesis [11–14] of PPy/GO composites have been reported previously in bibliography.

Several studies have studied the transport properties across PPy films doped with organic [16–19] or inorganic counter ions [7]. However, up-to-date no study of this type has been performed on PPy/GO films. The main objective of this work is to characterize the PPy/GO nanocomposite as a membrane material for the first time, to study the transport properties across it. Electrical characterization has been performed by electrochemical impedance spectroscopy (EIS) with the symmetrical metal-PPy/GO-metal configuration. The electrochemical characterization of the free-standing PPy/GO films has been performed in solution by EIS and cyclic voltammetry (CV). Scanning electrochemical microscopy (SECM) has also been applied for the first time to study the electroactivity of PPy/GO hybrid materials obtained electrochemically.

2. Experimental

2.1. Reagents and materials

All reagents used were of analytical grade.

For the synthesis: Monolayer graphene oxide (GO) powder was acquired from Nanoinnova Technologies S.L. (Spain). The thickness of the GO flakes was in the order of 0.7–1.2 nm which demonstrates its monolayer nature, typical values for monolayer GO are around 1 nm [4]. Other characteristics of the GO employed in this work can be consulted on the web of the provider [20]. Analytical grade pyrrole (Py) was purchased from Merck.

For the characterization: Sulphuric acid (H_2SO_4) and potassium chloride (KCl) were purchased from Merck. Sodium chloride (NaCl) was supplied by Fluka. Hexaammineruthenium (III) chloride ($\text{Ru}(\text{NH}_3)_6\text{Cl}_3$), potassium ferrocyanide (III) $\text{K}_3\text{Fe}(\text{CN})_6$ were used as received from Acrōs Organics. Tetramethylammonium chloride was purchased from Panreac.

When needed, 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 $\text{M}\Omega\text{ cm}$.

2.2. Synthesis of PPy/GO films

All electrochemical experiments were performed at room temperature with an Eco-Chemie Autolab PGSTAT302 potentiostat/galvanostat. Electrochemical synthesis of PPy/GO was performed in 2 g L^{-1} GO/0.2 M Py aqueous solution. Firstly, the synthesis was performed on stainless steel (SS) electrodes employing a three-electrode configuration. When needed, the PPy/GO film was detached from the SS surface with the help of a sharp blade to obtain the membranes. The characteristics of SS electrode plates employed were: (plates of $2\text{ cm} \times 3\text{ cm} \times 0.1\text{ cm}$); the chemical composition in weight (%) was: C ≤ 0.050 , Si 0.750, Mn ≤ 2.000 , P 0.040, S 0.015, Cr 18–19, Cu 8.5–9, the rest of the composition corresponds to Fe. Before the electrosynthesis, SS electrodes were degreased with acetone, mechanically polished to obtain a smooth surface and then, cleaned with ultrapure water in an ultrasonic bath. The counter electrode was a SS mesh with cylindrical geometry to equalize the electric field around the working electrode. Electrochemical potential was referred to the Ag/AgCl (3.5 M KCl) reference electrode. Firstly, cyclic voltammetry (CV) technique was employed to determine the synthesis potential

(0.86 V was the potential selected). Thereafter, potentiostatic synthesis was performed at 0.86 V until an electrical charge of 1 C cm^{-2} was achieved.

2.3. Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR)

FTIR-ATR with horizontal mono-rebound attenuated total reflection accessory 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 and spectra were collected with a resolution of 4 cm^{-1} , 64 scans were averaged for each sample. GO powders were characterized to assign their different contributions.

2.4. Field emission scanning electron microscopy (FESEM) and energy dispersive X-ray analysis (EDX)

A Zeiss Ultra 55 FESEM was used to observe the morphology of the samples using an acceleration voltage of 3 kV. Energy dispersive X-ray (EDX) measurements were performed between 0 and 10 kV. An optical microscope Zeiss Discovery V.8 was employed to observe the mounting of the membrane on an adhesive tape.

2.5. Electrochemical impedance spectroscopy measurements

A two-electrode configuration was employed to measure the electronic conductivity of the PPy/GO films. The PPy/GO sample was located between two metals; one was the SS electrode where the film was grown and the other was Hg, applied as drops on the surface of the PPy/GO film. Hg is liquid and adapts to the surface topography of the electrode, thus allowing a better interfacial contact with the electrode material than when employing rigid metallic electrodes.

A standard three-electrode design was used to measure the EIS response of SS-PPy/GO electrodes in 0.1 M H_2SO_4 solutions. An asymmetrical configuration metal-sample-electrolyte was used. An Ag/AgCl (3.5 M KCl) electrode and Pt wire were used as reference electrode and counter electrode, respectively.

A four-electrode configuration was employed to measure the transport properties across the PPy/GO free-standing membrane. A two-compartment symmetrical electrochemical cell was employed to carry out the measurements. The membrane separated the two compartments. Two Pt electrodes were employed as auxiliary electrodes and two Ag/AgCl (3.5 M KCl) reference electrodes were employed to measure the potential. The measurements were performed in 0.50 M, 0.10 M, 0.05 M and 0.01 M NaCl solutions. 0.1 M tetramethylammonium solutions were used to test the effect of size of the ion on the diffusion-migration through the membrane.

EIS measurements were performed in the 10^5 – 10^{-2} Hz frequency range by using an Autolab PGSTAT302 potentiostat/galvanostat. The amplitude of the sinusoidal voltage was $\pm 10\text{ mV}$. Each measurement was carried out at a constant imposed potential equal to the stabilized open circuit potential at the beginning of the experiment. The experimental results were also fitted using a non-linear least squares fitting minimization method by ZView software (version 2.7).

2.6. Scanning electrochemical microscopy (SECM)

SECM measurements were carried out with a scanning electrochemical microscope of Sensolytics. A three-electrode configuration cell consisting of a 25- μm -diameter Pt

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