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ORIGINAL PAPER

Cyclic voltammetry and impedance spectroscopy analysis for graphene-modified solid-state electrode transducers

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Abstract The transducer of solid-state electrodes based on an epoxy-graphite composite was modified by two different methods, such as direct mixed and layer deposition of graphene (commercial and synthesized by electrochemical exfoliation of graphite). The modified electrodes were characterized by cyclic voltammetry and impedance spectroscopy. Also, scanning electron microscopy (SEM) was carried out to acquire information concerning the morphology of the composite electrode. Voltammetric measurements, in presence of $[Fe(CN)_6]^{3-}$ as electroactive standard, determined a *quasi*-reversible electrochemical behavior under linear diffusion control. Electronic transference for modified and unmodified electrodes was compared. Solid-state electrode modified by inclusion of synthesized graphene showed a better electronic transference at electrode surface, due to the lower potential difference between anodic and cathodic peaks (ΔE = 125 mV) with respect to unmodified electrode (ΔE = 160 mV). Impedance spectroscopy characterization of electrode bodies in solid-state it was revealed a higher electronic conductivity and a supercapacitive behavior for the modified composites (values of intrinsic capacitances in the order of nanofarads) due to inclusions of graphite and graphene in the epoxy matrix. These inclusions were verified through SEM microscopy. The electronic conductivity and the supercapacitive character contributed both to the enhancement of electronic transference at electrode surface.

Keywords Graphene · Solid-state electrode · Cyclic voltammetry · Impedance spectroscopy

Introduction

Ion-selective electrodes (ISEs) have become a well-established electroanalytical method for environmental and clinical monitoring. These sensors are robust, easy to build and sensitive to many species as heavy metals and enzymes [1–4]. Since the early 1970s, when a coated-wire electrode (CWE) [5] was reported, great attention has been paid to all-solid-state ion-selective electrodes (ASS-ISEs). This interest has been motivated by the possibility of miniaturization, simplicity, robustness, and low cost of production for practical applications. In this way, sensors based on carbon polymer composites have been developed for electroanalytical measurements [6–9]. These new materials combine the easy modification of polymers such as methacrylate and the conducting properties of graphite in a single piece, which result in attractive electrochemical, physical, mechanical, and economical features than those of classic conductors (gold, platinum, graphite, etc.) [10–12].

The progress in the nanomaterials field has opened new horizons in the design of integrated electrochemical systems, allowing to the development of new generations of chemically modified electrodes. In recent years, carbon-based nanomaterials such as carbon nanotubes [13, 14], three-

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dimensionally ordered macroporous carbon [15, 16], fullerenes [17, 18], and graphene [19–22] have been used as solid contacts for the fabrication of solid-state electrodes. These sensors have showed high stability in the potential response and low-ohmic resistance, without an interfacial aqueous layer between the polymeric sensing membrane and the underlying contact, due to the large double layer capacitances and hydrophobic properties of carbon materials.

ISEs based on PVC membrane with thiourea derivatives as ionophores has been employed for potentiometric determination of heavy metals using an epoxy-graphite composite as conducting phase [23–25]. These sensors are stable for weeks without any divergence in potentials, show fast response time, Nernstian response over a wide concentration range (approximately between 10^{-6} and 10^{-2} M) and acceptable selectivity for several transition metals. However, lower detection limits and better transducer characteristics are still requires for application of these sensors in environmental samples.

In this work, solid-state electrodes based on an epoxy-graphite conducting composite material were modified with commercial and synthesized graphene by two methods for its posterior application in the construction of ion-selective electrodes. The electrical response of the resulting materials was evaluated by cyclic voltammetry using $K_3[Fe(CN)_6]$. For the first time, impedance spectroscopy measurement of isolated electrode bodies was used in order to investigate the influence of graphene on the conducting properties of the final composite.

Experimental

All reagents were of analytical grade and used without further purification. The experiments were conducted under ambient conditions of temperature and pressure. Bidistilled water (conductivity ≤ 1.5 μS/cm) was obtained from an Aquatron model A4D apparatus.

Electrode construction and modification

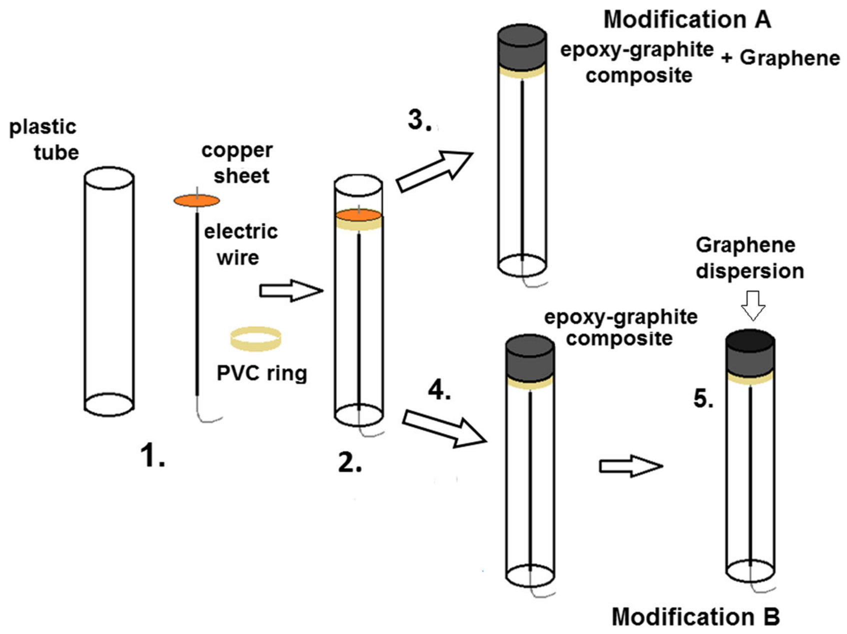
Electrodes were assembled with poly(methacrylate) tubes (8 mm internal diameter, 9.0 cm length), electric wire (no. 16) and copper sheets (99.9%, Merck) with 0.1 mm of thickness. Graphite-epoxy composite was prepared using graphite powder (1–2 μm, Aldrich), Araldite adhesive and hardener (Ciba-Geigy).

Modification of conductive composite was made with a graphene dispersion in terpineol and ethyl cellulose [26] (Aldrich). Also, it used graphene sheets synthesized by electrochemical exfoliation method presented by Ching-Yuan Su et al. [27] with a graphite rod (5 mm internal diameter, 4.0 cm length) (99.9%, Merck) and a Pt electrode as working and reference electrodes, respectively, in a H_2SO_4 (0.5 M) solution.

Ohmic resistance of the composite electrodes was estimated by means of an YFE multimeter, model YF-2100. Graphene dispersion was treated by ultrasound in an SB-3200DT ultrasonic cleaner. The epoxy-conducting composite was dried in a BGZ-Boxun oven.

Electrodes were constructed according to the method, which has been reported by Lima and Machado for all-solid-state PVC membrane electrodes [28]. It has been also followed the procedure of Lazo-Fraga and coworkers for construction of solid-contact ion-selective electrodes based on thiourea derivatives [23]. Modification of epoxy-graphite composite

Fig. 1 Scheme of electrodes construction procedure



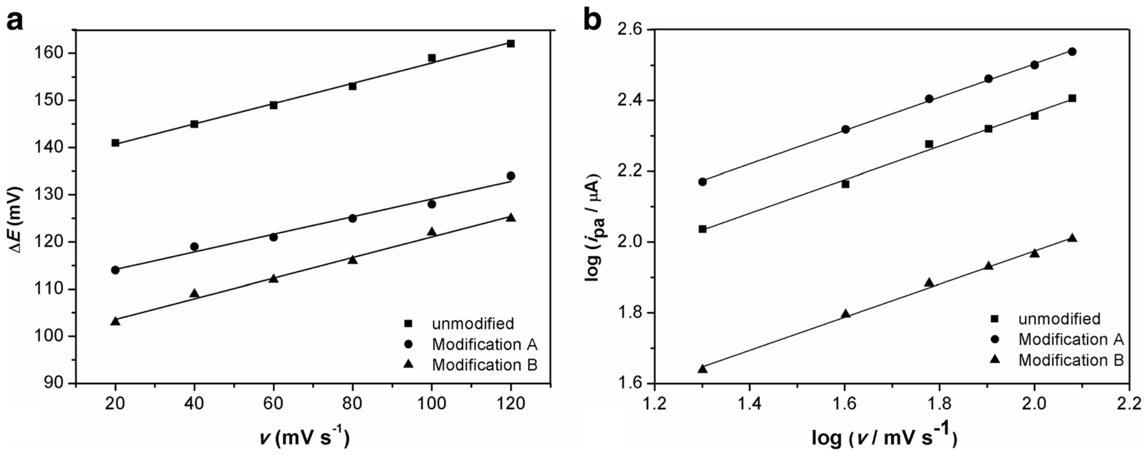


Fig. 2 **a** Potential difference between anodic and cathodic peaks (ΔE) vs. scan rate (ν). **b** Dependence of log of the anodic peak current (i_{pa}) with the log of scan rate from cyclic voltammograms for a solution of $K_3[Fe(CN)_6]$ (0.01 M) using an unmodified electrode (square), a modified electrode—Modification A (circle) and a modified electrode—Modification B (triangle) as working electrodes

was carried out by different paths and with both graphene types (commercial dispersion and synthesized sheets).

Scheme in Fig. 1 shows the main sections of electrodes construction: 1.—The components, 2.—The electric contact, 3.—Modification A, 4.—Modification B (in two steps).

Firstly, electric wire in contact with copper sheet were introduced in the plastic tube and supported onto a PVC ring (8 mm of internal diameter, 1 mm of thickness) (Fig. 1, step 2). Conducting composite was prepared by mixing the epoxy resin (araldite and hardener) with graphite powder and graphene. The mixture was homogenized, the paste was inserted into the poly(methacrylate) tube filling 2 mm of thickness from surface to electric contact (Fig. 1, step 3). The electrodes were dried for 12 h at 50 °C for complete the curing of composite. Surface of electrodes was thoroughly polished previously with a sand paper and then with alumina (5 μm).

The other modification method consisted in prepare epoxy-graphite composite with the elementary components (graphite powder, araldite, and hardener) in the same proportion, which was previously described (Fig. 1, step 4). The working sensor was prepared by first polishing the electrodes surface after the cured of composite, followed by deposition of a graphene dispersion. An aliquot of 25 μL of graphene in THF (1 mg/mL) was coated onto the clean electrode with a micro-pipette and dried in air for 24 h (Fig. 1, step 5).

Ohmic resistance has also been measured for all cases, showing values lower than 2 kΩ, which is an acceptable result [28]. In order to compare the obtained results, epoxy-graphite electrodes without graphene were also prepared.

Impedance measurements Impedance measurements, without solution, were carried out by using an Automatic LCR-meter (WAYNE KERR 4270) in the frequency range between 500 Hz and 1 MHz applying 1 V of ac. Collected data were analyzed by Origin 8.0 software. For the measurements, a silver painting (Laque Ag, L-200N, CDS Electronique) were deposited onto the surface of the constructed electrodes bodies in circular shape

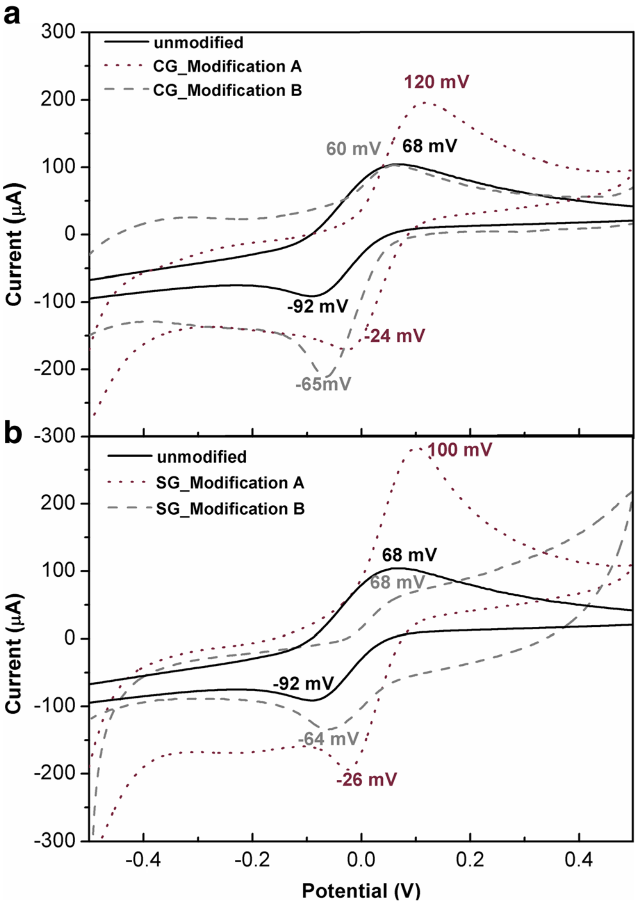


Fig. 3 CV for redox system $[Fe(CN)_6]^{3-}$ (0.01 M) at 100 mV s^{-1} using an unmodified electrode (solid plot), a modified electrode—Modification A (dot plot) and a modified electrode—Modification B (dash plot): **a** commercial graphene, **b** synthesized graphene

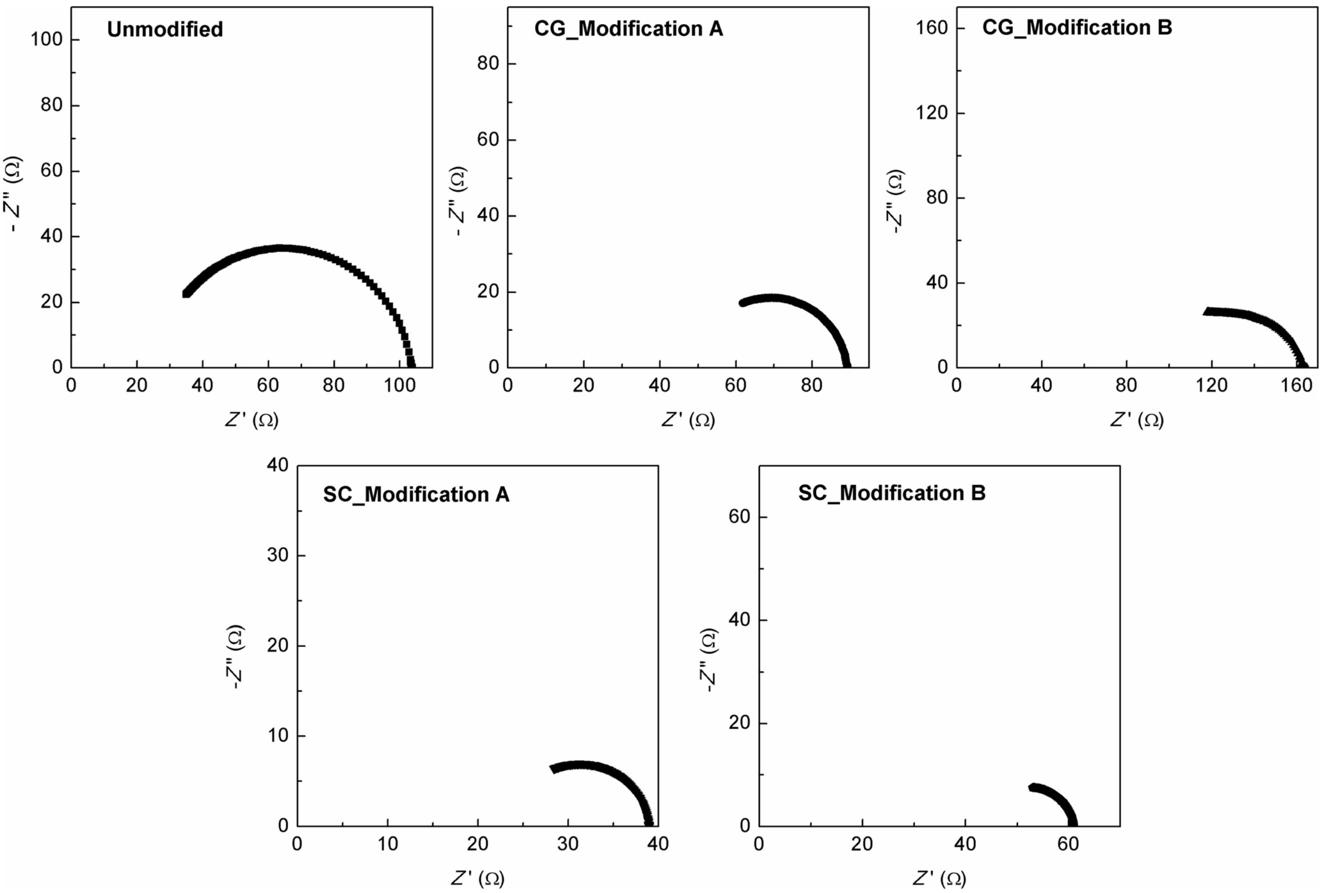


Fig. 4 Bode plots (*Z*″ vs *Z*′) (Impedance measurements were performed from 500 Hz to 1 MHz applying 1 V of ac)

with 3 mm of diameter and an electric wire were fixed to the silver contact. Wires of the fixed contact and the electrode were connected to the terminals of the equipment.

Cyclic voltammetry Electrochemical experiments were carried out by cyclic voltammetry (CV) with a three electrode configuration using a pontentiostat (384B EG&G, Princenton Applied Research Polarographic Analyzer) connected to a computer with Origin 8.0 software. A double junction Ag/AgCl electrode (Russell 90-00-29) and a Pt electrode were used as reference and auxiliary electrodes, respectively. The constructed electrodes were employed as working electrodes.

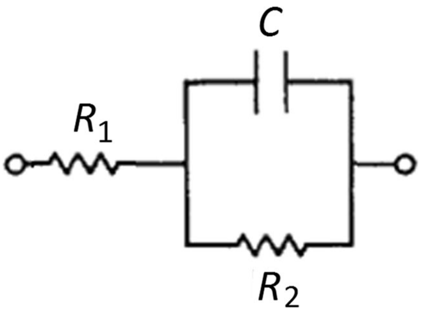


Fig. 5 Proposed equivalent circuit

The measurements were made in 50.0 mL of $NaSO_4$ (0.1 M) containing 0.01 M of $K_3[Fe(CN)_6]$. Cyclic voltammograms were carried out at different scan rates (20, 40, 60, 80, 100, and 120 mV s^{-1}). The working electrodes were treated in NaOH (0.1 M) taking at least three cycles between − 1 and 1 V at scan rate of 100 mV s^{-1}, until a reproducible voltammetry curve was recorded.

Scanning electron microscopy Microscope images were acquired with a scanning electron microscope (TESCAN Vega, 5130 SB3), in the Laboratorio Universitario de Caracterización y Estructura de la Sustancia (LUCES), IMRE, Universidad de La Habana, Cuba. The image was captured at 10 kV.

Results and discussion

Voltammetric characterization of modified composite electrodes

In order to characterize the electrochemical behavior of the modified composites in the different electrodes constructed, cyclic voltammograms were carried out in presence of an

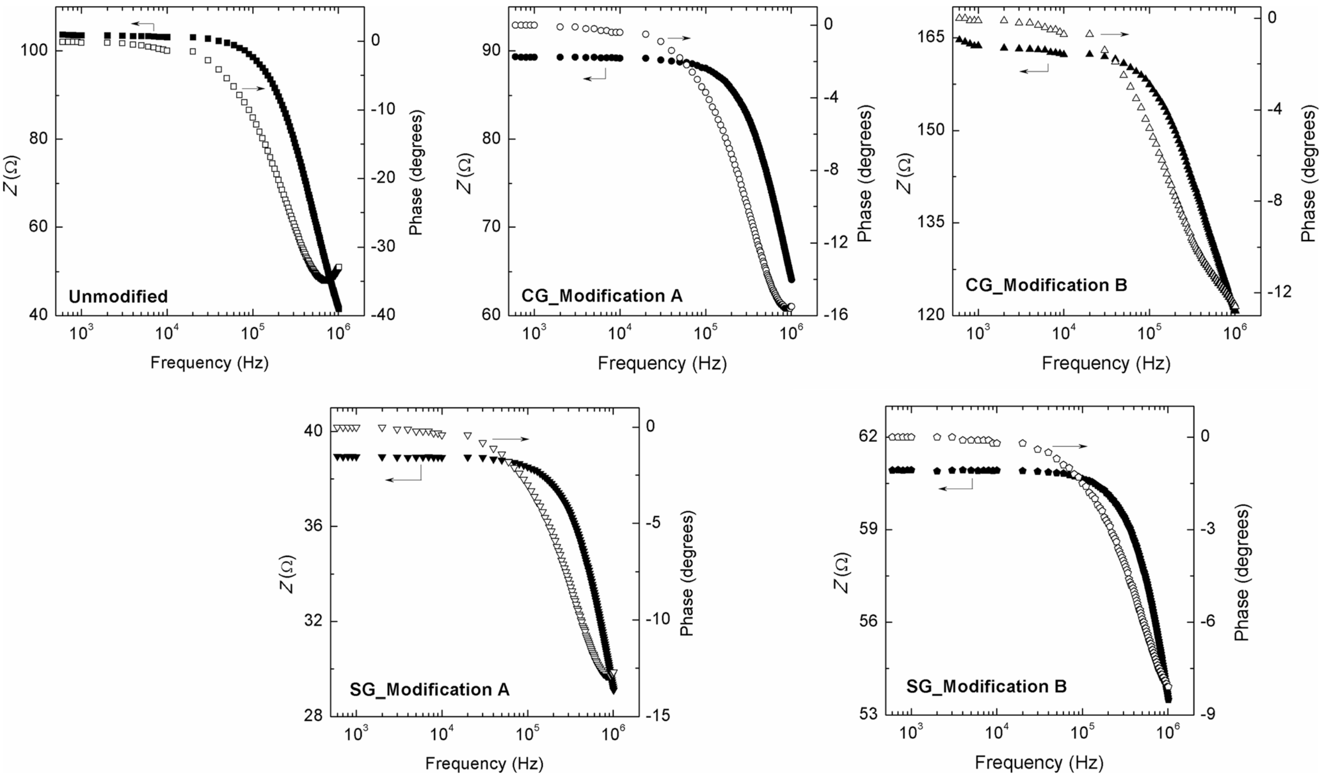


Fig. 6 Frequency dependence for the impedance modulus and the phase

electroactive standard, $K_3[Fe(CN)_6]$ (0.01 M) using different scan rates (20–120 mV s^{-1}) (See Online resource 1).

The anodic and cathodic peaks for the redox pair (Fe^{3+}/Fe^{2+}) are well-defined in all cases and the position of these peaks depends on the applied scan rate. From the previous results, reversibility of the electrochemical process in the surface of the constructed electrodes was studied. Difference between anodic and cathodic peak potential values (ΔE) increases with scan rate (Fig. 2) in the unmodified and modified electrodes. Values of ΔE are far from ideal value of 59 mV for rapid kinetic systems [29].

Electronic transference process of the electroactive substance $[Fe(CN)_6]^{3-}$ (0.01 M) at electrodes surface were also studied. It was established a linear dependence between cathodic and anodic peak currents with square root of the scan rate for $[Fe(CN)_6]^{3-}$ (0.01 M) (Online resource 2), which is consistent with a diffusion-controlled transference process of the electroactive species [29]. In all cases, slopes of the curves

Table 1 Fitting parameters of the experimental data using the equivalente electrical circuit given in Fig. 5

	R_1 (Ω/cm^2)	R_2 (Ω/cm^2)	C (nF/cm^2)
Unmodified	529.5 ± 0.4	932.5 ± 0.8	82.01 ± 0.04
CG_Modification A	409.1 ± 0.2	570.3 ± 0.5	81.88 ± 0.04
CG_Modification B	975.1 ± 0.8	1060.8 ± 0.9	48.17 ± 0.03
SG_Modification A	381.1 ± 0.2	216.9 ± 0.1	207.6 ± 0.6
SG_Modification B	399.3 ± 0.2	236.4 ± 0.2	127.7 ± 0.5

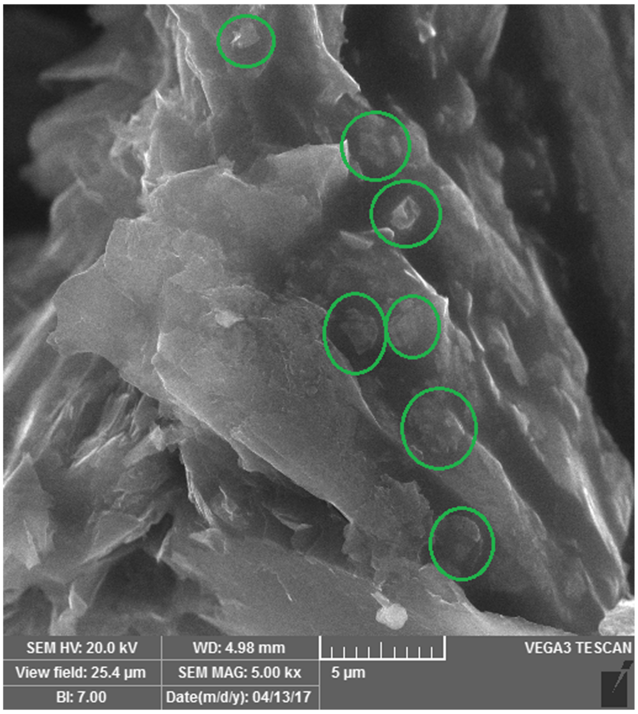
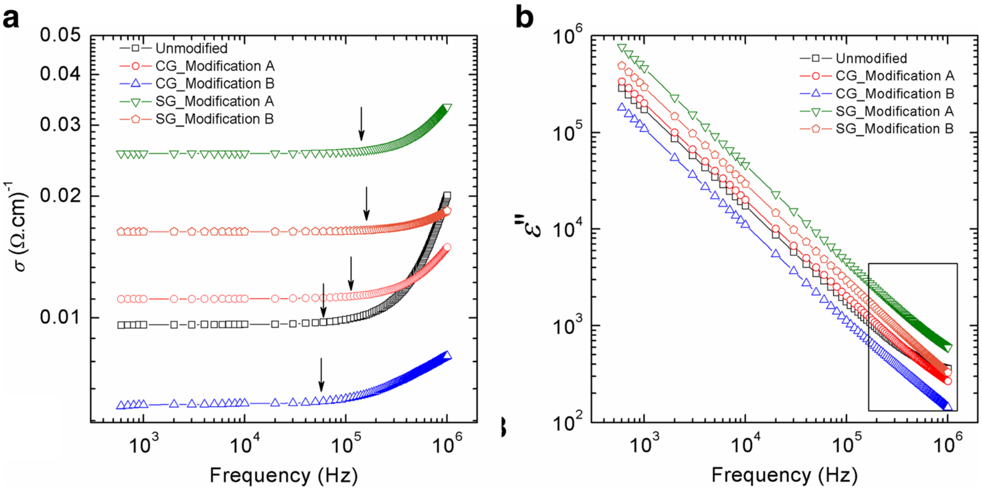


Fig. 7 SEM for graphite-epoxy composite modified with SG

Fig. 8 Frequency dependence for **a** losses factor, **b** electrical conductivity



log i_{pa} vs. log v were determined using the modified Randles-Sevcik equation [30]. The results for unmodified and modified electrodes with modification A and B were 0.475 ± 0.017 (R^2 = 0.993), 0.472 ± 0.007 (R^2 = 0.998), and 0.469 ± 0.015 (R^2 = 0.995), respectively. The obtained values are closer to ideal value of 0.5 for a process under linear diffusion conditions [29]. Moreover, the current ratio $ip_a/ip_c > 1$ was determined. All these aspects suggests a *quasi*-reversible behavior in the electronic transfer process of the constructed electrodes.

Figure 3 compares the cyclic voltammograms in $K_3[Fe(CN)_6]$ (0.01 M) recorded at 100 mV s^{-1} using an unmodified and modified electrodes in both cases with CG and SG. As is shown, the values of ΔEp with both graphenes (modification A and B) decrease respect to the unmodified electrode. In addition, it can be observed that current intensity of these peaks increase significantly in the modified sensors. Electrochemical response of the modified electrodes in the presence of the standard $K_3[Fe(CN)_6]$ is indicative of an increase in the electronic transfer at the surface of the modified electrodes due to the conducting characteristics of graphene. In addition, capacitive effects can be observed in the form of voltammograms which could be attributed to the manual process of construction of the electrode bodies.

Impedance measurements

Figure 4 shows the Z'' vs Z' dependence (Bode plot) for the studied electrodes. The scale for both axes is the same in any case for better understanding of the obtained results. Frequency increases from right to left.

It can be analyzed the presence of capacitive and resistive components considering the incomplete arcs, which are displaced from the origin. From this point of view, the equivalent electrical circuit given in Fig. 5 could be proposed to describe the obtained behavior. It is also supported by using the frequency dependence of the impedance modulus and the phase (Fig. 6). It can be also noted that the arcs are not perfect, i.e., their centers are below the Z'-axis, even depressed. On the other hand, it can be evaluated an important influence of the kind of electrode on the obtained results. The electrodes constructed according modification A (these included CG and SG in the epoxy-graphite composite) seems to increase the electrical conductivity because the resistance at the lowest frequency decreases, being the synthetized graphene which exhibits the lower value. However, both deposited graphenes show higher resistance values than that of the above case.

The equivalent electrical circuit was tested by non-linear least-squares fitting of the experimental data, showing very good agreement between theoretical and experimental values. Table 1 shows the obtained results. R_1 can be associated to the response of the interface between the copper sheet and the conductive composite; R_2 and C_2 to the polarization resistance an intrinsic capacitance of the composite electrode, respectively.

The values of R_1 and R_2 exhibit a similar behavior in the different constructed electrodes. R_2 indicates that the presence of graphene improves the electric conductivity of the composite regarding to the unmodified electrodes and the lowest values were obtained when SG is used in modification A. If the values obtained for modification B are analyzed when GC is deposited, these are even higher than the values for unmodified electrodes.

This result may be related with the chemical nature of the species that compose the dispersion of the CG (ethyl cellulose and terpineol). The presence of these non-conductive materials in the dispersion affects the conducting composite.

On the other hand, the high capacitance values, contrary to what should be expected in order the low values of permittivity of the epoxy matrix [31], suggests that the material performs as an assembly of small capacitors due to the conducting graphite and graphene grains, which are randomly dispersed in the insulating epoxy matrix, leading the system to a super-capacitor behavior. This arrangement can be observed in the Fig. 7 as an example for all the modifications. The mentioned figure shows a heterogeneous material, with some lighter areas, associated with the graphite conducting micro-structures and darker areas, related to the insulating polymer. The isolated particles were dispersed in epoxy matrix and some agglomerates or bundles were detected, which suppose an advantage forming the large microcapacitor network and suppressing the leakage current.

Figure 8 shows the frequency dependence of the losses factor (Fig. 8a) and the electrical conductivity (Fig. 8b), respectively. The losses factor shows a clear linear dependence, suggesting a DC conductivity behavior. Note also that the curves are almost parallels suggesting an important influence of the electrode on the dc component; the electrode modified with CG in the modification A exhibits the higher values for the studied frequency range. For the highest frequency range (inside the square), the linear dependence is less clear because of less influence of the DC components of the electrical conductivity.

These results are confirmed in Fig. 8b. The electrical conductivity follows the known Universal Relaxation Law, given by Eq. (1), where σ_{dc} is dc conductivity, $\omega_{\underline{\mathrm{H}}}$ is characteristic frequency of hopping of carriers, n is an exponent, and A is a term, which shows a weak dependence with the temperature. It can be seen that a strong dc component (the first term in Eq. 1) dominates the electrical behavior in a wide frequency range following by the ac dependence (the second term in Eq. 1) whose component appears at different frequencies depending of the kind of electrode (marked by arrows).

$$\sigma(\omega) = \sigma_{dc}\left[1 + \left(\frac{\omega}{\omega_H}\right)^n\right] + A\omega \tag{1}$$

It is also noted that the kind of electrode and the way of preparation has an influence on the electrical conductivity results. The SG shows higher σ_{dc} values, but the results for the modification B are lower, which is in agreement with the previous analysis made from Fig. 4.

The results obtained are related to those obtained by VC, in general, the modified electrodes presents values of σ_{dc} higher than the unmodified one. It indicates that graphene increases the concentration of conducting particles in the composite, which make contact, to form effective conductive paths and, thus, make the whole compound conductive. This percolation process may be responsible for the increase of the electrical conductivity of composite materials with graphene [32]. Therefore, inclusion of SG in conductive composite is the modification that most favors the conductive properties of the transducer. These results turn the modified electrodes into potential devices for the development of ion-selective electrodes.

Conclusions

Cyclic voltammetry and impedance spectroscopy measurements have demonstrated that the inclusion of graphene in the composite of the constructed electrodes results in the best modification way and the graphene synthesized by electrochemical exfoliation allows to obtain the transducer with higher conductivity.

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