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Towards to the improvement of the analytical response in voltammetric sensors based on rigid composites

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ABSTRACT

In order to increase the efficiency of voltammetric transducers we have studied the use of alternative strategies to characterize and optimize the composition of composite electrodes based on graphite and epoxy. The electroanalytical properties such as limit of detection and sensitivity have been improved by optimizing the distribution of the graphite particles inside the composite materials. The composites were characterized and optimized by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements. EIS measurements provide information about the electron-transfer rate, the double-layer capacitance, contact resistance and resistance of the solution. These optimized parameters are directly related with the response time, signal-to-noise ratio (limit of detection) and sensitivity, respectively. In addition, morphological and conductance characterization was performed by atomic force microscopy and complemented with scanning electron microscopy. The improvement of the electroanalytical response was evaluated by means of hydrodynamic amperometry measurements using different reference analytes.

1. Introduction

The development of composites based on a conductive phase as graphite or carbon nanotubes and dispersed in a polymeric matrix (epoxy, methacrylate, Teflon, etc.), has led to important advances in the analytical electrochemistry field, particularly in the development of sensors devices. Sensors devices provided complementary solutions without needing complex instruments or huge support infrastructure. A composite results from the combination of two or more dissimilar materials. Each individual component keeps its original nature while giving the composite distinctive chemical, mechanical and physical qualities, different from those shown by individual components [1]. Conducting composites, such as carbon–epoxy composites, are an interesting alternative for the construction of electrochemical sensor. The capability of integrating various materials is one of their main advantages since it can provide added values in the increase of the sensitivity and selectivity if compared to more traditional electrodes [2]. Furthermore, carbon–epoxy composite electrodes play an important role in biomedical applications because of their good biocompatibility, low cost, and ease of construction [3–8]. They can be bulk modified with stabilized enzymes [9,10] to make biofuel cells or used in electroanalytical application to detect acids [11], glucose [12,13] and enzymes [14]. In the literature it has been widely described development of voltammetric sensors and biosensors using epoxy resin in the electrode fabrication in order to be applied in electroanalysis [15].

The characterization and optimization of composites based on graphite–epoxy have been widely studied using different strategies based in several techniques as well as by the percolation theory [16,17] or chronoamperometry [16,18]. Up to now, the optimization of these composite materials has been done from the point of view of maximum conductivity [16] and maximum electron-transfer [19]. These parameters have always been associated to the development of composites with the maximum conductive particle loading into the insulating matrix without losing their physical and mechanical properties. The maximum conductivity is directly related to the improvement of sensitivity; meanwhile the maximum electron-transfer is associated with the improvement of response time. However, the optimization of the signal-to-noise ratio, which is directly related to the limit of detection, was not considered.

It is well-known that the sensors based on an array of microelectrodes owe their extraordinary electrochemical characteristics to an optimized distribution of the conductive microsurfaces [20]. While an excessive separation between microelectrodes supposes a drastic decrease of the signal, an excessive approximation

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between microelectrodes implies a conductive surface with properties of a macroelectrode, increasing considerably the analytical signal despite increasing drastically the noise too [20,21].

In composites based on a homogeneous dispersion of conductive microparticles in a polymeric matrix, frequently the maximum conductive particle loading does not correspond to the optimal loading in terms of signal-to-noise ratio. In the present work, this parameter was optimized by varying the conductive material loading in the insulating matrix and using powerful strategies to characterize the electrodes. We have demonstrated that if the composite proportions are optimized the response of the electrode is improved. The electroanalytical properties required by an electrode are high electron-transfer rate, the lowest ohmic resistance and double-layer capacitance in order to guarantee high sensitivity and a high signal-to-noise ratio and, consequently, low detections limits.

EIS measurements provide, in an easy way, information about the electron-transfer rate, the double-layer capacitance, contact resistance and resistance of the solution [22,23]. Using EIS technique it is possible to determine the optimal composite composition that exhibits these electrochemical properties associated with the improvement of the analytical properties. The results obtained by EIS technique can also be complemented with voltammetric measurements performed by cyclic voltammetry (CV).

The main goal of this study is the use of alternative strategies of characterization, previously used in transducers based on composite electrodes with carbon nanotubes [24], to characterize and optimize composite composition based on graphite–epoxy. Moreover, in order to complement the electrochemical results, atomic force microscopy (AFM) in the current sensor mode and scanning electron microscopy (SEM) were used to gain insights on the surface characteristics of graphite composites studied.

We have systematically varied the graphite loading from the percolation threshold zone obtained by means of percolation curve and constructed the corresponding composites. In a first stage of characterization, electrochemical impedance spectroscopy has been used to determine the composite which provides the best electrochemical properties. These results are later compared with the cyclic voltammetry measurements. Then and in order to evaluate the electroanalytical response of the optimized composites different analytes are used. Finally, microscopy techniques are used to study the electrode surface.

2. Experimental

2.1. Apparatus

Electrochemical impedance spectroscopy and voltammetric measurements were performed using a computer controlled Autolab PGSTAT12 potentiostat/galvanostat (EcoChemie, Utrech, The Netherlands) with a three-electrode configuration. A platinum-based electrode 53–671 (Crison instruments, Alella, Barcelona, Spain), an AgCl covered silver wire and the constructed graphite composite electrodes were used as a counter, reference, and working electrodes, respectively.

Linear-sweep voltagramms were performed using a computer controlled Autolab PGSTAT12 potentiostat/galvanostat (EcoChemie, Utrech, The Netherlands) with a three-electrode configuration. A single junction reference electrode Ag/AgCl Orion 900100 (Thermo Electron Corporation, Beverly, MA, USA) and platinium-based electrode were used as reference and auxiliary, respectively and graphite composite electrodes as working electrodes.

Amperometric measurements were done using an amperimeter LC-4C (Bio Analytical Systems Inc., West Lafayette, IN, USA), connected to a personal computer by data acquisition card ADC-42 Pico Technology (St. Neots, Cambridgeshire, UK) for data registering and visualization. Electroanalytical experiments were carried out in 20 mL glass cell, at room temperature (25 °C), using three-electrode configuration. A single junction reference electrode Ag/AgCl Orion 900100 (Thermo Electron Corporation, Beverly, MA, USA) and platinium-based electrode were used as reference and auxiliary, respectively. The graphite composites electrodes were used as working electrode. A magnetic stirrer provided the convective transport during the amperometric measurements.

Atomic force microscopy (AFM) images were taken with the Agilent 5500LS AFM/SPM (Agilent Technologies, USA) operated in current sensing mode.

Scanning electron microscopy (SEM) images were obtained with the EVO unit with an acceleration voltage of 15 kV.

2.2. Chemical reagents

Graphite powder (particle size 50 μm) was received from Merk (Merk Millipore, Darmstadt, Germany). Epoxy resin Epotek H77A and hardener Epotek H77B were obtained from Epoxy Technology (Epoxy Technology, Billerica, MA, USA). Potassium ferricyanide/ferrocyanide (99.8%), potassium chloride (99.5%), potassium phosphate monobasic (99.5%), nitric acid (65%), potassium phosphate dibasic-anhydrous (98%), ascorbic acid (99.5%), hypochlorite sodium (10–13%), hydrogen peroxide (30%), were supplied from Sigma–Aldrich (St. Louis, MO, USA) and used without further purification. All the dissolutions were prepared using deionised water from Milli-Q system (Millipore, Bellerica, MA, USA).

2.3. Fabrication of the composites electrodes

Handmade epoxy–graphite electrode composites were prepared as followed: a resin Epotek H77 and their corresponding hardener compound were mixed in the ratio 20:3 (w/w). The graphite composite was prepared by loading different amounts of graphite (13%, 14%, 15%, 16%, 17%, 18%, 19% and 20% (w/w)) into the epoxy resin before hardening. The composite was homogenized for 30 min. For the electrode construction the composite was placed into a cylindrical PVC tube (6 mm i.d., 20 mm length) containing a copper disk soldered to an electrical connector end. Composites were hardener during 24 h at 60 °C and then the electrode surface was polished with different sandpapers of decreasing grain size. The final electrode dimensions were 28 mm^2 for its geometric area and the final pasta-filled cavity was 3 mm long inside the PVC tube.

2.4. Preparation of the devices for electrical measurements

For the construction of the electrical measurement devices, the composites were placed into PVC cylindrical bodies (6 mm i.d.; 10 mm length). A piece of copper in each extreme of the cylindrical bodies completed the electrical contact. Composites were hardened during 24 h at 60 °C and finally the copper surface was polished with 0.8 mm sand paper to remove the generated oxide layer. Electrical resistance was then measured between the two pieces of copper with a digital multimeter (Fluke, Everett WA, USA).

2.5. Characterization of composites

2.5.1. Electrochemical characterization

EIS and voltammetric measurements were made in a 0.1 M potassium chloride solution containing 0.01 M potassium ferricyanide/ferrocyanide under quiescent condition.

Amperometric detection of the different reference analytes was made under force convection by stirring the solution with magnetic stirrer.