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Strategies for the optimization of carbon nanotube/polymer ratio in composite materials: Applications as voltammetric sensors

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ABSTRACT

Multiwall carbon nanotubes and resin epoxy have been used to fabricate a composite electrode for electroanalytical purposes. The optimum composite proportions for high electrode sensitivity, low limit of detection and fast response were investigated. Compositions were characterized by percolation theory, electrochemical impedance spectroscopy, cyclic voltammetry, scanning electron microscopy, atomic force microscopy and chronoamperometry. We found that around the optimum composite proportion, the electrode performance is less affected by small variations in the composition of the composite. These composite electrodes provide easy surface renewal, low background current, an efficient mass transport and are suitable for chemical modification. The potentiality of this approach in terms of electroanalytical response is demonstrated by means of the amperometric detection of ascorbic acid in water solution.

1. Introduction

Composite materials based on different forms of carbon as conductive phase have played a leading role in the analytical electrochemistry field, particularly in sensor devices. Pioneering work in this area was done by Adams [1] by using carbon paste electrodes. Considering carbon composite in general, their electrochemical properties present improvements over conventional solid carbon electrode, such as glassy carbon. This is due to some interesting advantages, such as easy surface renewal, as well as low background current since the electrode capacitance is strongly influenced by the exposed carbon. Depending also on the conductive load, composites can behave as microelectrode arrays which are known to provide efficient mass transport of the electroactive species due to radial diffusion on the spaced carbon particles. Such improved mass transport favors the sensitive electroanalysis of a variety of reagents, including electrocatalysts, enzymes and chemical recognition agents. Moreover, the carbon chemical surface influences significantly the electron transfer processes at these electrodes [2–4].

During the past few decades, the electrochemical properties of different carbon paste electrodes have been studied in detail [5–7]. Indeed, in the last years our research group has developed different composite materials based on different kinds of polymeric matrices, obtaining interesting electrochemical applications by using graphite powder as conductive phase [8–11].

Nowadays, high interest is focused on composites based on carbon nanotubes (CNTs). They are attractive materials due to their remarkable mechanical and electrical properties [12–14]. They have a highly accessible surface area, low resistance, high mechanical and chemical stability and their performance had been found to be superior to the other kinds of carbon material in terms of reaction rates and reversibility. Several configurations of CNT electrodes are found in the literature, such as those randomly adsorbed on glassy carbon electrodes [15,16] or dispersed in an inert matrix [17–20]. The last configuration presents attractive electrochemical properties because the CNT improves the electric conductivity and the polymeric matrix confers mechanical robustness to the composite electrode [21,22]. Many papers have reported the outstanding electrochemical behavior of CNT composite electrodes, especially for the detection of compounds such as total cholesterol [23], glucose [20], NADH [17], ascorbic acid [24] and hydrogen peroxide [25].

The main drawback in CNT composite materials reside in the lack of homogeneity of the different commercial CNT lots due to different amounts of impurities in the nanotubes, as well as dispersion in their diameter/length and state of aggregation (isolated, ropes, bundles). These variations are difficult to quantify and make mandatory a previous electrochemical characterization of the composite [26–28], before being used as a chemical sensor. More recently, Zhao and O'Hare [29] have characterized, using voltammetric techniques, the electrochemical behavior of conductive–nonconductive phase composites as a function of different parameters such as thickness, proportion ratio and resistance of the composite electrode. Under this context, another important point of consideration is the optimization of the CNT

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loading in the composite materials for improving their electrochemical properties and analytical applications.

Up to now in our research group, the optimization of the composite proportions has been done under the criteria of maximizing the conductive particle loading, without losing its physical and mechanical stability [8,17,30,31]. In composite materials the type of carbon used can affect the maximum attainable carbon loading [32] and the goal of that approach was to achieve the maximum conductivity value. However and taking into account the low reproducibility of the composite electrochemical performance due to the heterogeneity of the different commercial lots of CNT, it is important to consider not only the conductivity of the composite material (percolation theory [33–37]), but also the reproducibility regarding their electrochemical properties.

Therefore, the main goal of this study is to develop composite material electrodes optimized for their use in electroanalysis. Multiwall carbon nanotube (MWCNT) and resin epoxy have been used to fabricate these composites. From the analytical point of view, the requirements to achieve a good electrode performance are high sensitivity, rapid response time and low limit of detection. They are related with some physical parameters such as material resistivity, heterogeneous electron transfer rate and double-layer capacitance. For this reason, in this work, we have characterized these physical parameters for each electrode composition to determine the optimum CNT loading composite.

First, we have systematically varied the MWCNT loading and measured the bulk and dry state resistivity of the resulting composite. These data are described by the percolation theory and have allowed us to identify the different MWCNT loadings at which the resulted composite is conductor. That is an important step because the main requirement for materials used as voltametric sensors, is that they are conductors. Furthermore, it is known that, depending on the nature of the phases that compose it, the maximum and minimum amount of carbon loading capable of producing a conductive composite can vary. Consequently, it produces changes in the electrical behavior [38] of the composite. In a second stage, the electrochemical impedance spectroscopy has been used to characterize each resulting conductive composite. This technique provides, in an easy way, information about the electron transfer rate, double-layer capacitance, contact resistance and resistance of the solution. Thereby, we can determine the composite that exhibits the highest electron transfer rate, the lowest double-layer capacitance and ohmic resistance. These results were contrasted with voltammetric measurements. Additionally, the microscopy techniques are used to gain more insights about the electrode surface.

Finally the benefits of using this approach in terms of analytical performance are demonstrated by means of successful analytical results based on the detection of ascorbic acid. The optimized composite electrode combines the ease of fabrication, low background current and the improved response compared to other traditional carbon paste electrode with a higher loading.

2. Experimental

2.1. Apparatus

Electrochemical impedance spectroscopy (EIS) and voltammetric measurements were performed using a computer controlled Autolab PGSTAT30 potentiostat/galvanostat (EcoChemie, Utrech, The Netherlands) with a three-electrode configuration. A platinum-based electrode 52-671 (Crison Instruments, Alella, Barcelona, Spain), a AgCl covered silver wire and the constructed MWCNT composite electrode were used as counter, reference, and working electrodes, respectively.

Scanning electron microscope (SEM) images were obtained with the Hitachi S-570 unit with an acceleration voltage of 15 kV. Atomic force microscopy (AFM) images were taken with the PicoSPM unit (Molecular Imaging, USA) operated in current sensing mode. Electrical resistance was measured with a digital multimeter (Fluke, Everett, WA, USA). Amperometry measurements were done using an amperimeter LC-4C (Bio analytical Systems Inc., West Lafayette, IN, USA.), connected to a personal computer by a data acquisition card ADC-42 Pico Technology (St. Neots, Cambridgeshire, UK) for data registering and visualization. Electroanalytical experiments were carried out in a 10 mL glass cell (home made), at room temperature (25 °C), using a three-electrode configuration. A single junction reference electrode Ag/AgCl Orion 900100 (Thermo Electron Corporation, Beverly, MA, USA) and a platinum-based electrode 52-671 were used as reference and auxiliary, respectively. The MWCNT composite electrodes were used as working electrode. A magnetic stirrer provided the convective transport during the amperometric measurements.

2.2. Chemicals and reagents

All dissolutions were prepared using deionised water from a Milli-Q system (Millipore, Billerica, MA, USA). Potassium ferricyanide/ferrocyanide (99.8%), ascorbic acid (99.5%), potassium nitrate (99.0%), potassium chloride (99.5%) and nitric acid (65%), were purchased from Sigma–Aldrich (St. Louis, MO, USA) and were of the highest grade available and used without further purification. Purified multiwall carbon nanotubes fabricated by chemical vapor deposition (MWCNTs purity >95%, length 5–15 μm, outer diameter 10–30 nm) were purchased from Ses Research (Houston, TX, USA). Epotek H77 and its corresponding hardener which was supplied from Epoxy Technology (Billerica, MA, USA) were used as polymeric matrix.

2.3. Fabrication of the MWCNT electrodes and devices for electrical measurement

Working electrodes were prepared following the conventional methodology previously established in our research group [39]. A resin Epotek H77 and its corresponding hardener compound were mixed in the ratio 20:3 (w/w). The MWCNT composite was prepared by loading different amounts of carbon nanotube (0.5, 1, 2, 3, 4, 5, 6, 8, 10, 12, 15, 17 and 20% (w/w)) into the epoxy resin before hardening. The composite was homogenized for 60 min. The composite paste electrode was allowed to harden during 24 h at 80 °C [17]. Electrode surface was then polished with different sandpapers of decreasing grain size. The final electrode dimensions were 28 mm^2 and 3 mm for its geometric area and thickness, respectively.

For calculation of the resistivity we designed MWCNT composite devices reported in a previous work [38].

2.4. Procedure

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 was made under force convection by stirring the solution with a magnetic stirrer. A daily-prepared 0.01 M ascorbic acid solution was used as stock solution. Standard solutions were prepared by dilution of the stock solution. Solutions of 0.01 M potassium nitrate/nitric acid were used as a background electrolyte in amperometric detection of ascorbic acid.