Sensor development exploiting graphite-epoxy composite as electrode material

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Abstract. This study presents some results regarding the development and characterization of graphite-epoxy composites for use as working electrodes in electroanalysis. Such composites were preliminary assessed by TGA-DTA, AFM, XDR and cyclic voltammetry (CV), standing for a suitable stable and low cost material for electroanalytical purposes. The described material was used, in its best proportion (65% graphite m/m), to build a cell electrochemistry.

1. Introduction

Since the incipient and historical application of Sir Humphrey Davy[1], carbon electrodes have been extensively exploited for both electrochemical and electroanalytical purposes. Despite this, however, with the advent of polarography, many reducible analytes, including metal ions, could be better determined by using mercury as a working electrode. Observing the wide range of oxidizable compounds and considering the limitations of mercury for such analysis Adams, in 1958, revisited some of first carbon-based electrodes and proposed the use of carbon-insulator dispersions as electrode materials, a new material capable of complementing the existing technique[2].

Composites are hybrid materials consisting of a conducting phase, usually graphite powder, mixed in different proportions with an insulating phase, being such product homogeneous on macroscopic level but with clearly defined zones in microscopic dimensions[3]. Mechanical characteristics of the material are often controlled by the insulating phase selected, since the conductive phase generally employed is graphite powder. Among the insulating materials used, some should be highlighted: organic solvents[2], mineral oil[4], paraffin[5], poly(4-vinyl pyridine)[6], epoxy [7] and polyurethane resins[8], [9]. Generally solid composite electrodes exhibits higher mechanical stability than those found for paste-like electrodes[10], fundamental aspect when building robust and reproductive sensing systems. From the simplest to the most sophisticated applications, there are many good examples of how useful are graphite-epoxy composites: starting from the determination of metals[11], covering many biochemical and pharmaceutical analysis such as the simultaneous determination of dopamine and ascorbic acid[12], melamine[13], atenolol[14], and urea[7], reaching the recent developments in electronic tongue systems[15]. Polymers used can be incorporated by simply dissolving in a corresponding solvent[10] or the polymerization can be carried out in situ[9].
2. Experimental procedures

One disposable electrochemical cell comprising working electrode, counter electrode of stainless steel, silver conductive epoxy reference (pseudo-reference) electrode was constructed. The electrodes were mounted on a plunger of a 5 mL syringe, being then the syringe filled by insulating polymers for mechanical purposes (Figures 1 and 2).

The working electrode was a graphite-epoxy composite prepared through the conventional method described by Swofford e Carman[16], being the polymerization carried out in situ, by mechanical dispersion of suitable amounts of graphite powder (Sigma-Aldrich, USA, 2-20 µm) in epoxy resin (Avipol, Brasil, Silaex SQ 2126-3024); the system was left to cure for 24 hrs under pressure and polished with suitable tools. A copper wire was inserted through the composite to establish electrical contact. The frame utilized to construct was based on an insulin syringe 0.50 mL with 3.1 mm internal diameter. Different compositions were prepared (55-80%, w/w graphite content) and characterized by thermogravimetric analysis (TGA-DTA), atomic force microscopy (AFM), X-ray diffraction (XDR) and cyclic voltammetry (CV) according to current-potential responses (5.0 x 10$^{-3}$ mol L$^{-1}$ K$_3$[Fe(CN)$_6$] in 0.5 mol L$^{-1}$ KCl)[17], showing suitable long-term stability.

![Figure 1. Body of working electrode](image1)

![Figure 2. Arrangement of electrodes in electrochemical cell](image2)

3. Results and discussion

3.1. Preliminary characterization

The results revealed that the material has a thermal stability up to 150°C, besides this, no chemical relevant interaction between graphite and epoxy was observed (Figure 3). By means AFM studies and calculation, main qualitative and quantitative aspects such as topography and roughness (Figure 4) were assessed and taken into account during global evaluation of electrode performance and stability.

![Figure 3. Thermal analysis of different compositions](image3)

![Figure 4. Calculated roughness (rms) found by AFM results and topography](image4)
XRD measurements reveal that even with adding an amorphous compound, graphite phase with hexagonal crystal system is maintained (Figure 5)[18]. Although fast and simple, the procedures used for surface polishing and cleaning do not compromise the surface homogeneity, as presented by Figure 6; experiments carried out by AFM provided a roughness (RMS) of circa 0.261. Electroactive areas for composite electrodes (55 to 80%) were determined by cyclic voltammetry. Such studies aimed to evaluate the composition of best electrochemical performance, through a well-known redox probe (Figure 7).

Figure 5. XRD for graphite powder in (a), epoxy in (b) and graphite-epoxy 65% composite in (c)

Figure 6. Surface of graphite-epoxy 65% composite by AFM.

3.2. Electroanalytical performance
The composite electrodes showed reliable responses, with linear dependence between both currents, cathodic and anodic, and scan rates assessed, as expected. Best results for stability, mechanical and electrical properties were found to be 65% (w/w) (64.4% graphite, characterized via TGA), being these close to the previously described by Trijuque et al.[19] (62% graphite). Potential window and applicability in diverse pH media were also assessed and compared to a commercial glassy carbon electrode with similar geometric surface, leading to equivalent results, but with much lower costs. Besides these, the obtained surface showed to be excellent for chemical modifications aiming to increasing sensitivity, and/or selectivity, which are being currently developed by our group in many different fields.

Figure 7. Electrochemical performance assessed by cyclic voltammetry in different scan rates, using outer sphere probe (5.0 x 10^-3 mol L^-1 K3[Fe(CN)6] in 0.5 mol L^-1 KCl)
4. Concluding remarks
A suitable stable and low cost material for electroanalytical application is hereby described. Its hardness facilitates polishing, and subsequently recovery of the surface, allowing stable but transient chemical modifications as well as renewal. The methodology of polishing on abrasive surface resulted on low roughness topography. Economically such material showed to be easy to build and cost-effective when compared to glassy carbon commercially available sensors. For analytical purpose such composite is being evaluated as substrate for gold-nanoparticles immobilization in chitosan-modified and cellulose acetate films, with good preliminary results. The electrochemical cell developed can be directly used to determinate many inorganic and/or organic compounds in real samples or even undergoes to chemical modification to more specialized situations.

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