Electrochemical Impedance Spectroscopy applied to the optimization of composites based on graphite/epoxy to be used as amperometric sensor

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The mail goal of this study is the use of alternative strategies of characterization, previously used in transducers based on composite electrodes with carbon nanotubes [1], to characterize and optimize the composite composition based on graphite-epoxy. Moreover, in order to complement the electrochemical results, atomic force microscopy (AFM) was used to gain insights on the surface characteristics of graphite composites and, finally, the electroanalytical response of the optimized composites were evaluated by hydrodynamic amperometry.

The development of composites based on conductive phase (graphite, carbon nanotubes, etc.), 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. The characterization and optimization of composite based on graphite-epoxy has been widely studied using different strategies based on several techniques as well as percolation curve or chronoamperometry [2]. Up to now, optimized composites used to have a maximum conductivity with the maximum conductive particles loading into the insulating matrix without losing their physical and mechanical properties. However, the optimization of the signal to noise ratio was not considered. In this work, this parameter was optimized by means of the variation of conductive material loading in the insulating matrix and using novel alternative strategies of characterization which demonstrates that if the composite portions are optimized the response of the electrode is improved [1]. These techniques are electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). EIS measurements provides, in an easy way, information about the electron transfer rate, double layer capacitance, contact resistance and resistance of the solution [3, 4]. The electroanalytical properties required by an electrode are high electron transfer rate, the lowest double layer capacitance and ohmic resistance in order to guarantee a high signal/noise ratio, high sensitivity and low detections limits. By this technique it is possible to determine the composite composition that exhibits these electroanalytical properties. These results can also be contrasted with voltammetric measurements.

By means of EIS measurements we can obtain different parameters as ohmic resitance (R_Ω), charge transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}). These parameters were obtained by fitting the impedance spectra to an equivalent circuit (Figure 1). This circuit was sufficiently suitable to interpret the R_Ω, R_{ct} and C_{dl} values in terms of interfacial phenomena that occur at the electrochemical cell [2]. In order to achieve the properties required for an electrode with electroanalytical purposes, such as a rapid response time, low limit detection and a high sensitivity, we are looking for low R_Ω, R_{ct} and C_{dl} values.

Figure 2A and Figure 2B present the most significant images obtained during the electrode surface study of the composite with 15% and 20% of graphite load. The composite with 20% of graphite loading showed slightly more conductive areas than in the case of the composite with 15% of graphite loading. Moreover, the distance between the conductive microzones was slightly controlled by a decrease or increase of the graphite loading.

Working electrodes based on graphite-epoxy composites were fabricated, characterized and hence optimized by means of EIS and CV techniques, as well as hydrodynamic amperometry and AFM. Such optimal graphite loading values allow us to fabricate attractive and robust composite electrodes with very interesting application as amperometric sensors at low electroanalyte concentration.

[1] Olivé-Monllau, R., Esplandiu, M.J., Bartrolí, J., et al., Actua. B- Chem., **146** (2010), 353-360.
[2] Ramírez-García, S., Alegret, S., Céspedes, F., Forster, R.J., Anal. Chem, **76** (2004), 503-512.
[3] Pacios, M., del Valle, M., Bartrolí, J., et al., *J.* Electroanal. Chem., **619-620** (2008), 117-124.
[4] Espandiu, M.J., Pacios, M., Cyganek, L., et al., Nanotechnology, **20** (2009), 355-502.

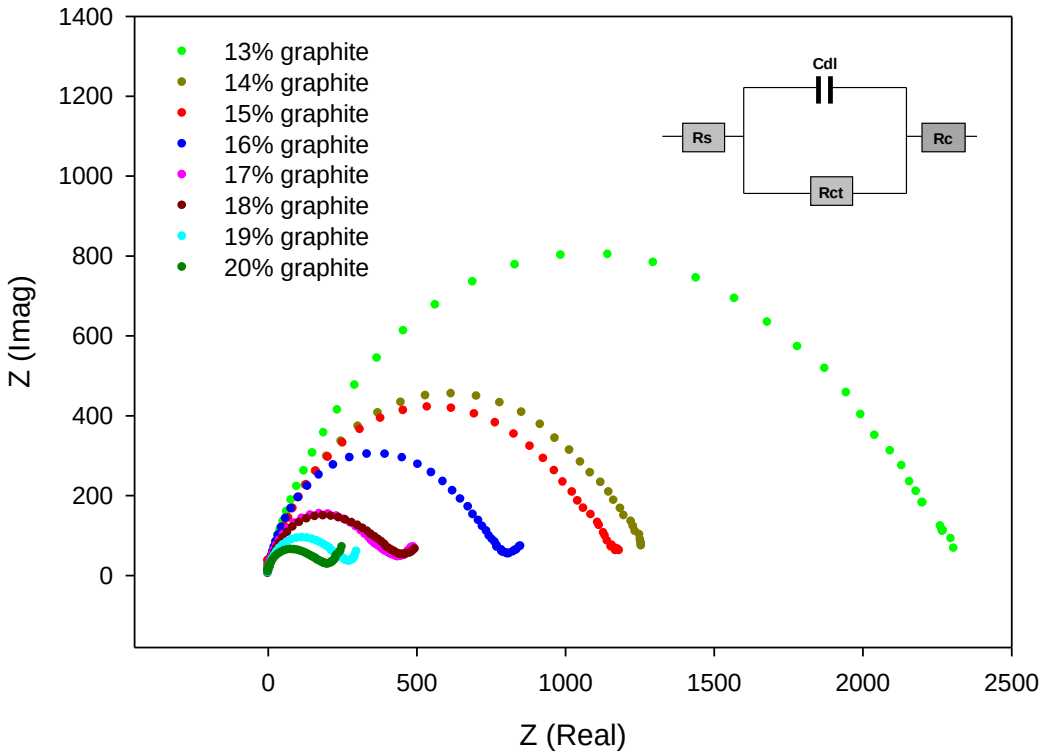

Figure 1: Nyquist plots for different graphite loading electrodes in presence of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$. The insets figure show the equivalent circuit used for the impedance spectra fitting.

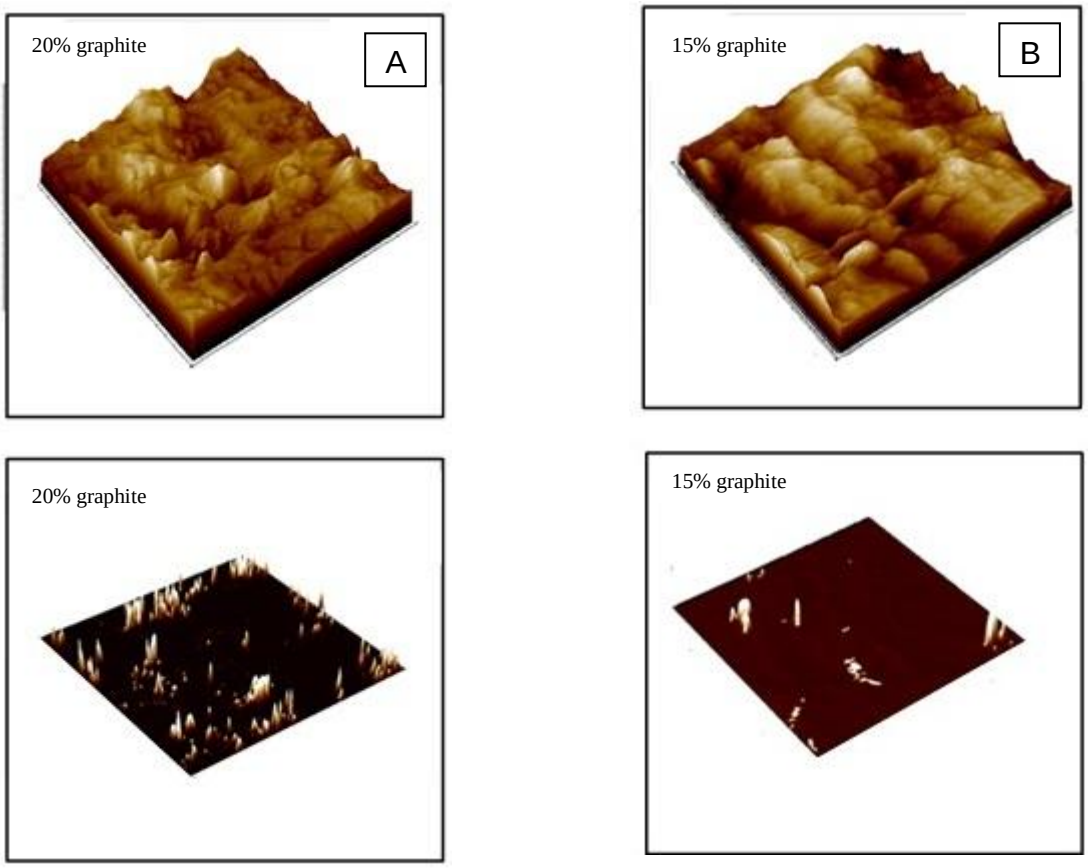

Figure 2. Topographical AFM images with their corresponding conductance mapping (20x20µm) for (A) 20% of graphite loading and (B) 15% of graphite loading.