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Electrochemical behaviour and electrical percolation in graphite–epoxy electrodes

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The electrochemical properties of mouldable graphite–epoxy composite electrodes have been studied as a function of graphite content. The shape of ferri–ferrocyanide voltammograms relates to the ratio of graphite and an adsorption process. The dielectric constant from spectroelectrochemical impedance measurement of this composite electrode is maximum when the proportion of graphite is ca. 60 wt%. An electrochemical equivalent circuit is proposed. The graphite–epoxy composite acts as a multi-microelectrode near this proportion.

1. Introduction

In the past decade composites formed by a mixture of conductor and insulator materials have been used for electronics [1], electrochemical transducers [2], antistatic materials [3] and chemical sensors [4]. The properties of these materials are understood through percolation theory. The electrical conductance of composites depends on individual conductances of each component.

The electrical conduction in a conductive/insulator composite is explained by the existence of an open path between two distant points for electron transport. The percolation theory explains the size and geometry of this open path by defining an occupancy probability in a regular lattice that simulates the dispersion of the conductor in the polymeric insulator matrix. Under these conditions there is a critical probability, or a critical concentration of the conductive load, where the composite conductivity changes several orders of magnitude. The percolation threshold is the key phenomenon of percolation theory, defined as the critical probability, that an infinite open cluster appears [5].

The electrical conductance of a composite depends on individual conductances and volume ratios of each component. The conductivity is an increasing function of the conductive load proportion, its size and geometry (spheres, flakes, spheroids, etc.). If the conductive particles are considered to be spheres, the total resistance between two adjacent particles is due to two contributions [6]: the constriction resistance (due to current flow through a small contact area between particles) and tunnelling resistance (due to electron hopping between two particles separated by a film).

One of the most common composites used for electroanalytical chemistry is the graphite–polymer mixture. Its performance and behaviour are functions of polymer composition, graphite structure (powder, sphere fibre) and the interaction between them [7]. In this work the electrochemical behaviour of a graphite–epoxy mouldable composite electrodes is described. The spectroelectrochemical impedance provides information about the composite and the electrode–interface solution. Voltammetric experiments were done to obtain information about a well-known ferricyanide/ferrocyanide system as a model of a reversible faradaic process.

The results suggest that this system can be considered as a multi-microelectrode.

2. Experimental procedure

The calorimetric measurements were taken with Mettler DSC 30 differential scanning calorimeter coupled with a TC11 data processor. The experimental stoichiometric ratios were found with dynamic scans at 10 K min^{-1}, searching for maximum reaction enthalpy per mass unit. Once the resin was cured, the glass-transition (T_g) was determined. The SEM microphotographs were taken with a JSM 25S JEOL scanning microscope.

Potentiodynamic measurements were done with a PAR 373A potentiostat (EG&G), and connected to a lock-in amplifier for impedance measurements. For all experiments in this work, the frequency scans were taken between 0.05 Hz to 100 KHz, the applied potential was 0 V, referred to Ag/AgCl, KCl (sat.) electrode, and the superimposed alternating potential was $\Delta E = \pm 5$ mV. In all potentiodynamic measures the scan rate was 20 mV s^{-1} and the temperature 293 K.

Composite electrodes were prepared by dispersing graphite (Merck), with particle sizes < 50 μm, in an epoxy resin (EPOSIER 7020, SIER S.A.), curing the mixture with diethylenetetramine (ND 0702, SIER S.A.). The paste was introduced into cylindric polyethylene moulds of 0.9 cm diameter and cured by

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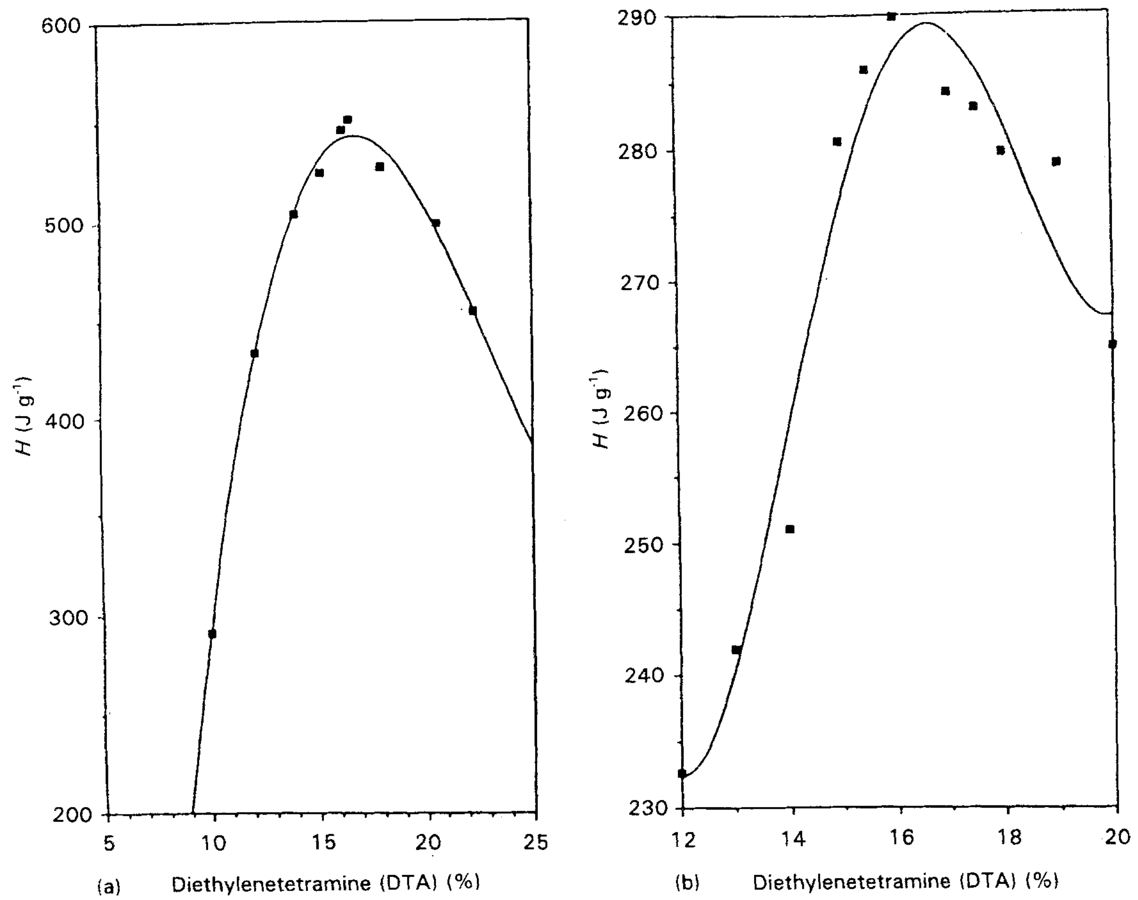

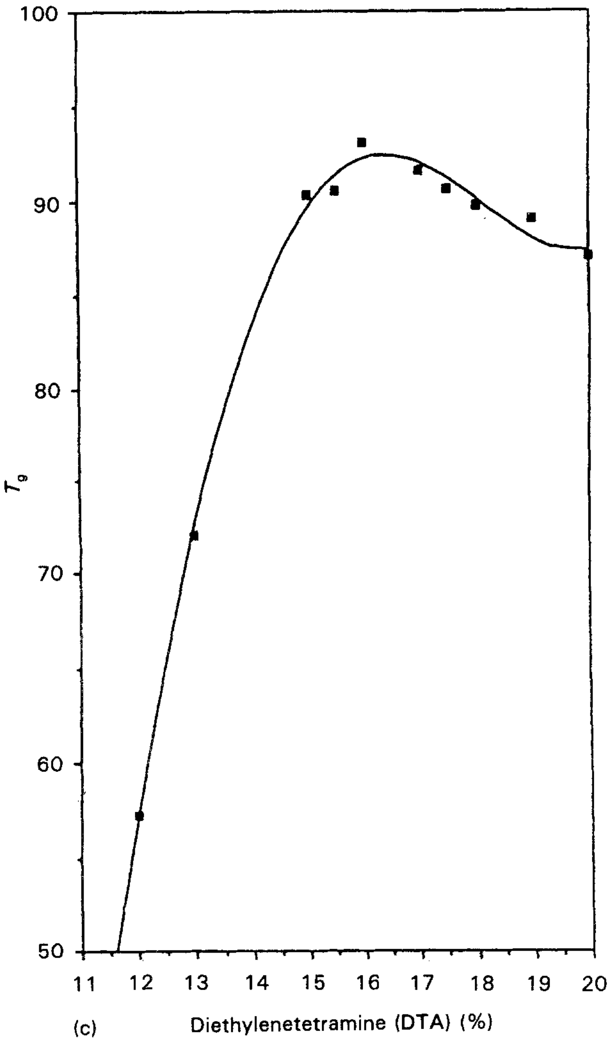

Figure 1 Determination of stoichiometric proportions of cross-linking (diethylenetetramine) and epoxy resin in graphite–epoxy composites. (a) Reaction enthalpy versus diethylenetetramine content in absence of graphite. (b) Reaction enthalpy that characterizes the cross-linking of graphite epoxy–composite at 1:1 with different amounts of diethylenetetramine. (c) Dependence of the glass-transition temperature (T_g) on the cross-link concentration of composite electrodes.

exposing the sample to 90 °C for 15 min. Electrodes were cut with a circular diamond saw so that the surfaces were parallel, they were 0.5 cm thick. Contact with the conductor was achieved using highly conductive silver paint (BIORAD A 1208), and then sealing with an epoxy adhesive.

Water used in all experiments was distilled and deionized with MilliQ (Millipore) equipment. In all experiments a Ag/AgCl, KCl(sat.) reference electrode with a KCl 0.4 M salt bridge was used.

3. Results

To minimize the possible effects of the inactive polymer surface on electrochemical behaviour it was necessary to establish the experimental conditions necessary to make the material. The optimal cross-link proportion was determined by differential scanning calorimetry (DSC) [8, 9]. Maximum enthalpy values were obtained for proportions of 16.5%, referred to as the epoxy resin weight. The maximum vitreous transition temperature confirmed this proportion (Fig. 1) as the optimum for maximum cross-linking. At this point the existence of end-chain reactive epoxy-groups, were avoided in the polymer and on the composite surface.

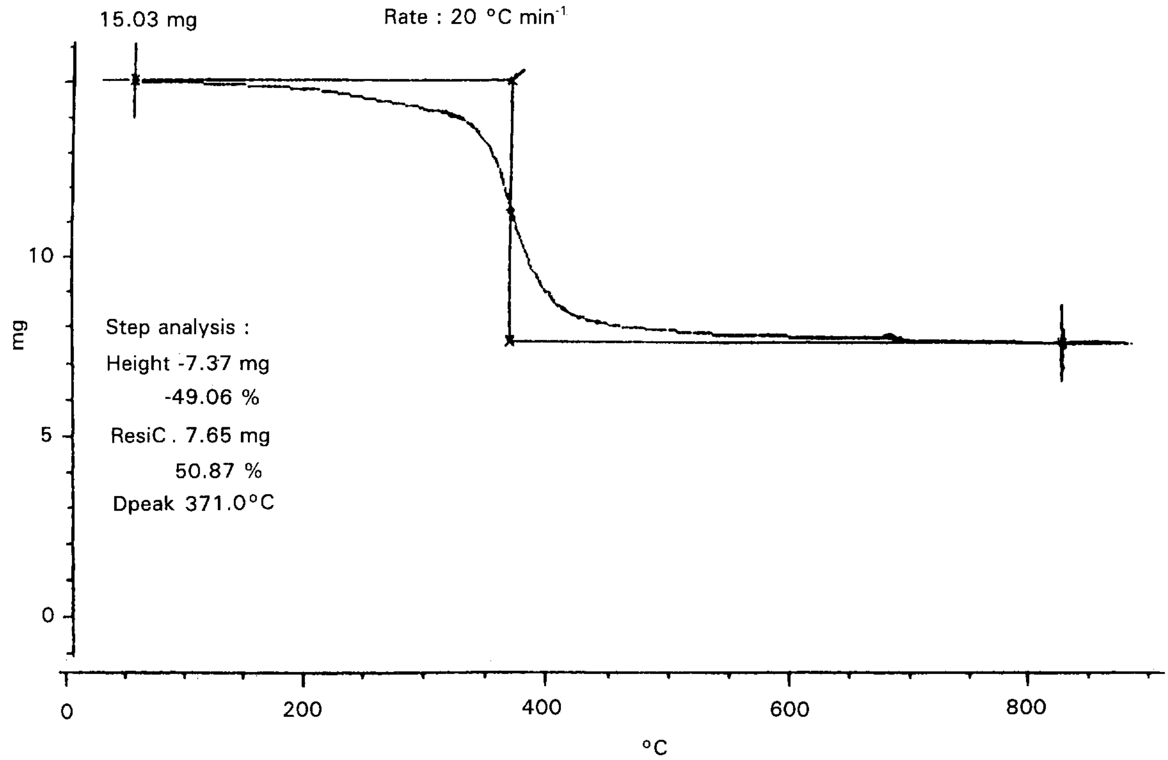

Figure 2 Thermogravimetric analysis of graphite–epoxy composite at 1:1.

Thermogravimetric analysis (TGA) [9] showed the cured graphite–epoxy system to be thermally stable below 200 °C, reaching total decomposition of the resin at a temperature ca. 400 °C (Fig. 2). Under these conditions the solid obtained had good electric conductivity but low mechanical strength.

The superficial morphology of this composite can be described as a group of small graphite sheets dispersed in the resin (Fig. 3), as the photomicrograph obtained by SEM shows.

In order to electrochemically characterize these materials comparative studies with graphite electrodes were carried out. Fig. 4 shows the ratios between faradaic current and charging current, i_p/i_c, for a commercial graphite electrode (PAR) and a composite electrode, revealing that the ratio is larger in the composite than in the graphite. Therefore, voltammetric peaks of potassium ferricyanide are better defined in a graphite–epoxy electrode than in a graphite electrode.

A strong adsorption of ferricyanide on the composite electrodes was observed. To prove this, the electrode was immersed in a 7 mM potassium ferricyanide solution and its voltammetric response between 0.8 and -0.4 V recorded. Subsequently, the electrode and the electrochemical cell were washed with distilled water and a ferricyanide-clear KCl 0.4 M solution was placed in the cell. Under these conditions the voltammetric experiment was repeated and a redox ferri–ferrocyanide couple signal was observed (see Fig. 5).

Accepting that adsorption occurs, this system can be described with an appropriate adsorption isotherm. For each graphite proportion the current and peak potentials depend on concentration:

$$i_p = kC^n \qquad (1)$$

Figure 3 SEM photomicrograph of the graphite–epoxy surface.

This experimental equation (see Fig. 6a and b) is obtained if the system behaves as a Freundlich-like adsorption isotherm [10].

Supposing the adsorption rate is faster than the diffusional transport towards the electrode then:

$$i_p = \xi(g)\theta \qquad (2)$$

where θ is the fraction of the graphite surface occupied by ferricianyde, $\xi(g)$ depends on the mass transfer from solution to the electrode surface and is also a function of the graphite amount, g, contained in the electrode.

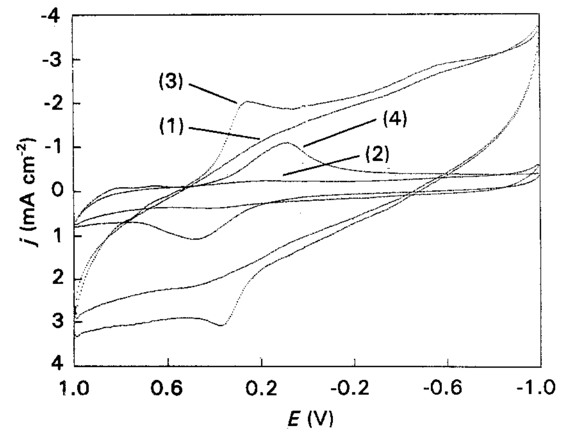

Figure 4 Voltammograms of $K_3[Fe(CN)_6]$ solutions. (1) Commercial graphite electrode in 0.4 M KCl solution. Area, $S = 0.327$ cm^2. (2) Graphite–epoxy composite (60 wt%) = in 0.4 M KCl solution. (3) Commercial graphite electrode in 2.4 mM $K_3[Fe(CN)_6]$/0.4 M KCl solution. (4) Graphite–epoxy composite (60 wt % in 2.4 mM $K_3[Fe(CN)_6]$/0.4 M KCl solution.

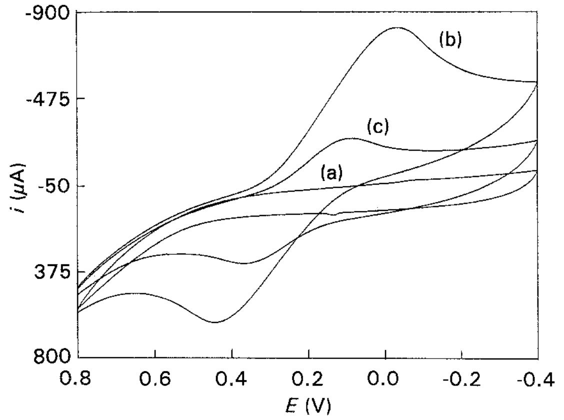

Figure 5 Ferricyanide adsorption on graphite–epoxy electrode (55 wt %) in KCl 0.4 M solution. (a) Voltammogram of medium. (b) Voltammogram of 7 mM $K_3[Fe(CN)_6]$. (c) Voltammogram recorded after washing the electrode used in (b) in 0.4 M KCl.

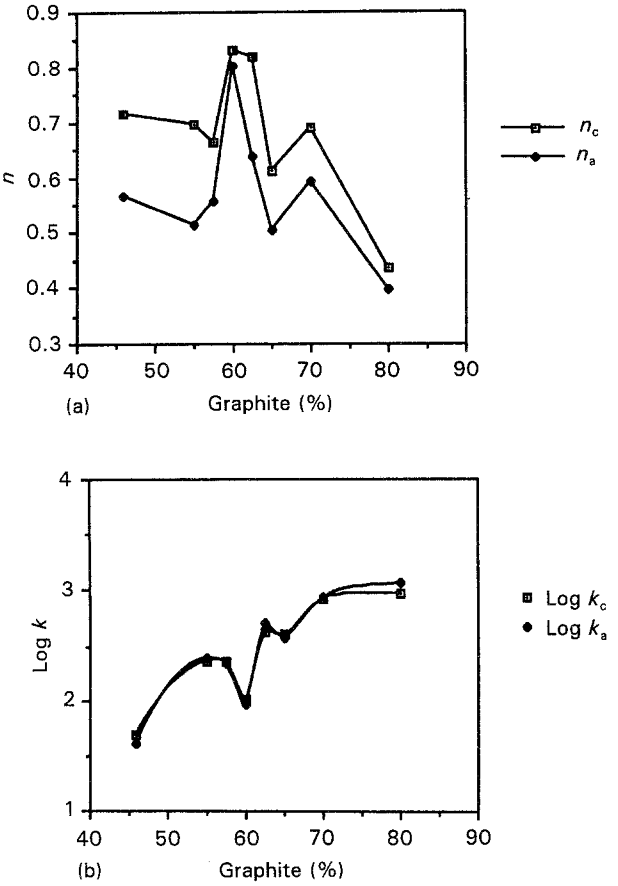

Figure 6 Dependence of $1/a$ (a) and log k (b) Freundlich isotherm coefficients with graphite content g, in composite electrodes: □, cathodic peaks; ◆, anodic peaks.

This term includes the contribution of the total effective area of the electrode. Assuming that the Freundlich isotherm is verified, the following equation will give the peak intensity.

$$i_p = \xi(g)\, RTab \exp\left[-\frac{Q}{RT}\right] C^{1/a} \qquad (3)$$

were $\xi(g)$ is the function of the electrode mass transfer, R is the gas constant, T is the absolute temperature, a is a parameter related to the number of adsorbate sites, b is a frequency parameter, Q is the adsorption heat and C is the bulk concentration. The experimental results agree with the meaning of each term of Equations 1 and 3. In fact, by plotting $n = 1/a$ and log k from Equation 1 versus the graphite proportion two different zones can be observed. Below 60% the high resistivity of the material suggests the rate determining process be the electron transport through the composite, in other words, the electrical percolation. Above this concentration the only rate determining process is the ferricyanide transport towards the electrode.

On the other hand, from Fig. 7a and b information about the different ferrocyanide and ferricyanide behaviour of these electrodes can be extracted. The constant k in Equation 1 is related to mass transfer and adsorption energy of electroactive species, which is the same for both ferrocyanide and ferricyanide. That implies the same rate determining process for current flow in the electrochemical cell (electrical percolation or diffusional transport) and equivalent adsorption energy as well. But, it cannot be concluded that the adsorption sites are equal, as shown in Fig. 6a the concentration exponent of Equation 1 for both oxidized and reduced species is different at different load proportions.

It is also observed that when the graphite content decreases, the separation between the anodic and the cathodic peak potentials increases (Fig. 8). Plotting i_p versus E_p for varying ferricyanide concentrations gives a straight line for each electrode (Fig. 9). The slope gives the conductance, which gives the resistance of the material (Table I).

The impedance measurements reveal that both their modulus ($|Z|$) and phase (θ) are dependent on the graphite content in the composite electrode. Fig. 10 shows that for 60 wt % of graphite at low frequencies, $|Z|$ and θ have a local maxima. Two effects should be considered for the interpretation of impedance data: (1) the electrode internal structure; (2) the interfacial structure.

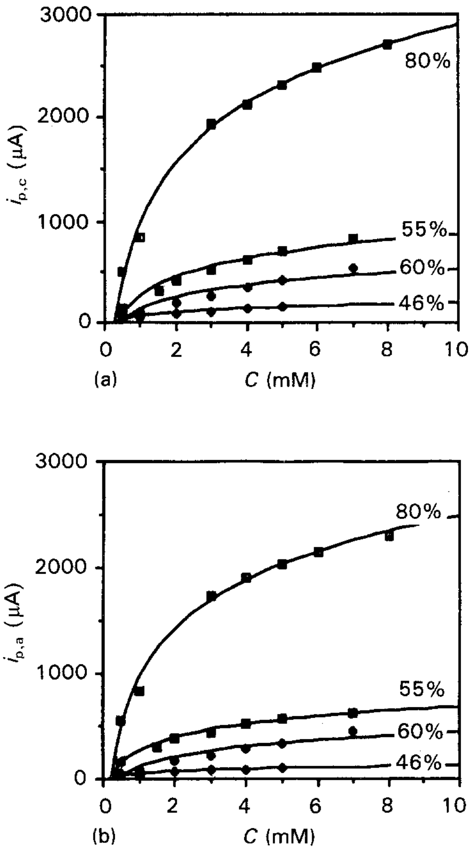

Figure 7 Cathodic (a) and anodic (b) peak currents versus ferricyanide concentration for different composite electrodes. The proportion of graphite (wt %) is indicated on the curves.

TABLE I Slope and intercept values from the lines plotted in Fig. 9 at different graphite proportions.

Graphite (wt %)	Cathodic slope ($\mu A\, mV^{-1}$)	Cathodic intercept (μA)	Anodic slope ($\mu A\, mV^{-1}$)	Anodic intercept (μA)
46	0.15	42.7	0.26	− 80.6
55	3.64	683.4	3.55	− 949.9
60	15.57	3484	11.56	− 3337
65	6.39	1680	7.49	− 1728
70	14.61	3571	12.95	− 2728
80	37.31	6594	33.53	− 8710

4. Discussion

On electrochemical reduction of potassium ferricyanide the best relation between faradaic and charging currents is obtained at 60 wt % of graphite content, which is slightly higher than the theoretically expected percolation threshold [5] for a bicomponent insulator/conductor system. On the other hand, the impedance technique at this graphite ratio shows that the system has optimal electric properties for use as an analytical electrode. Also, from analysis of the impedance spectra, it is deduced that at this critical proportion a maximum value of the electric permittivity [14] is produced (Fig. 11).

The results obtained for the graphite–epoxy system that the equivalent circuit which produces its behaviour is composed of a Debye circuit (which explains the solid conductivity [15, 16]) and a modified Randles type circuit (which explains the electrode–solution

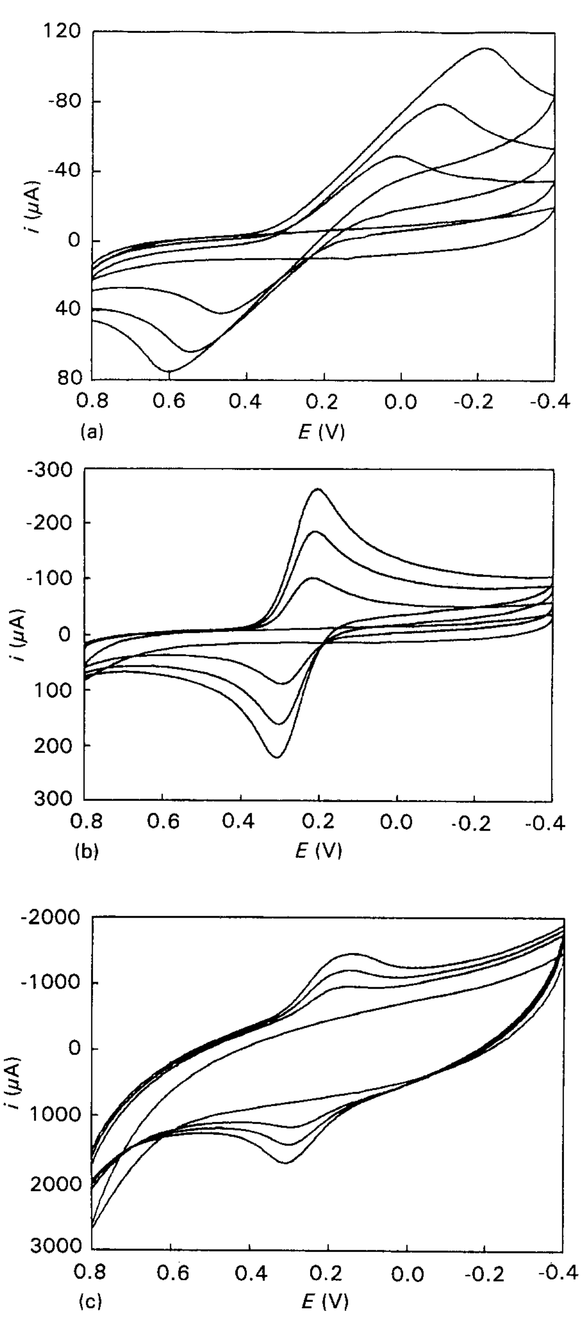

Figure 8 Voltammograms of ferricyanide solutions at 0, 1, 2 and 3 mM concentrations in 0.4 M solution. Scan rate $v = 20\ mV\, s^{-1}$. (a) 46 wt % of graphite; (b) 60 wt % of graphite; (c) 80 wt % of graphite.

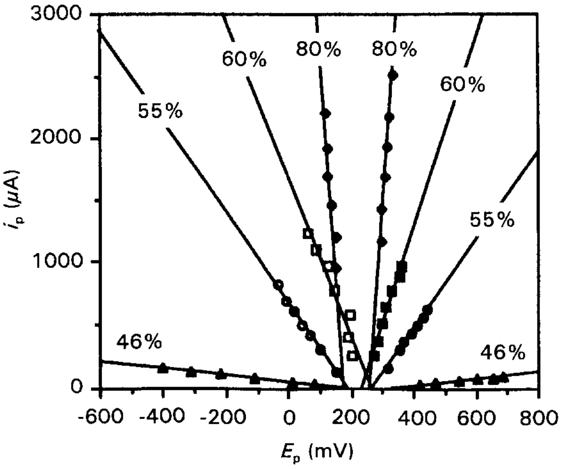

Figure 9 i_p versus E_p plots from ferricyanide voltammograms when their concentration and electrode composition are varied. The slopes characterize the conductivity of the electrodes. The filled and blank dots correspond to anodic and cathodic waves, respectively.

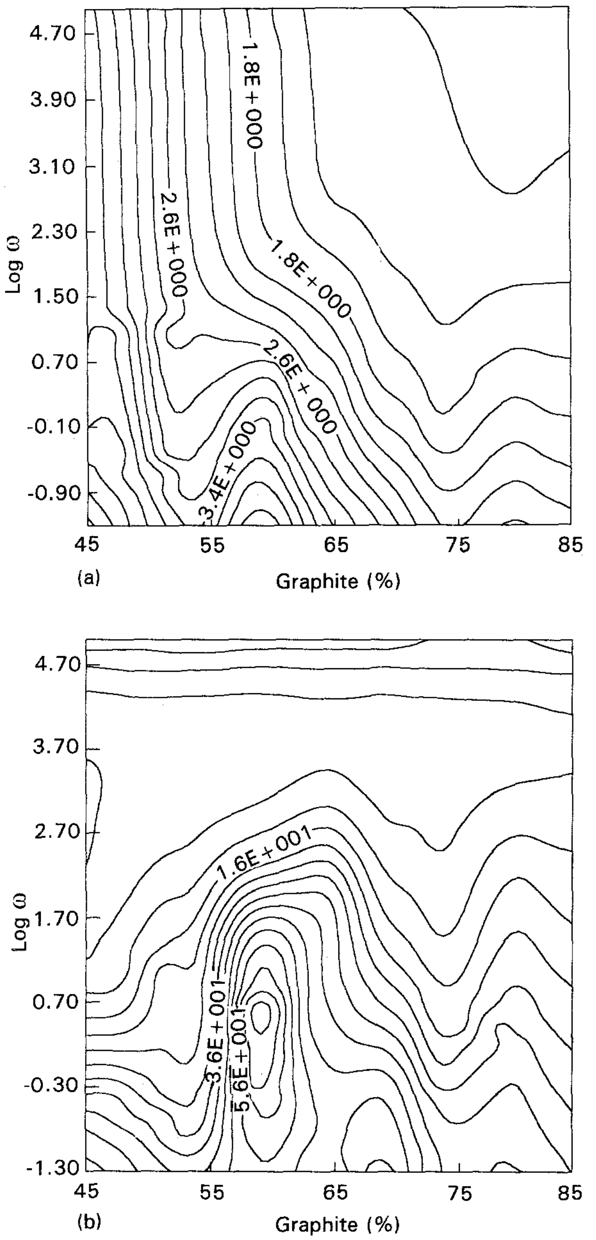

Figure 10 Impedance spectroscopic characterization of the composite electrodes. (a) Tridimensional plots of log |*Z*| versus log ω and graphite content in wt %. Each level curve corresponds to 0.2 logarithmic units. (b) Tridimensional plots of phase angle (θ) versus log ω and graphite content in wt %. Each level curve corresponds to 0.5°.

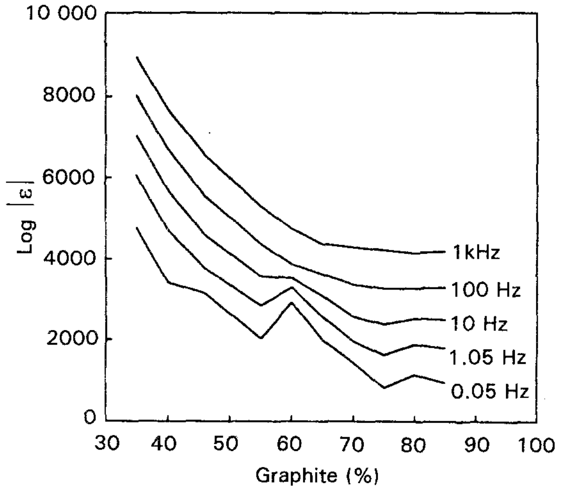

Figure 11 Dependence of the modulus of the electrical permittivity with the frequency for different graphite–expoxy electrodes.

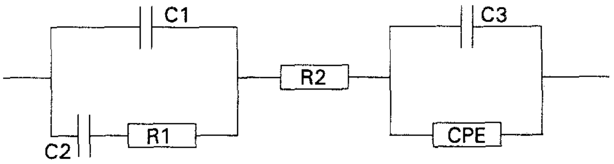

Figure 12 Electrical equivalent circuit for a composite–solution interface.

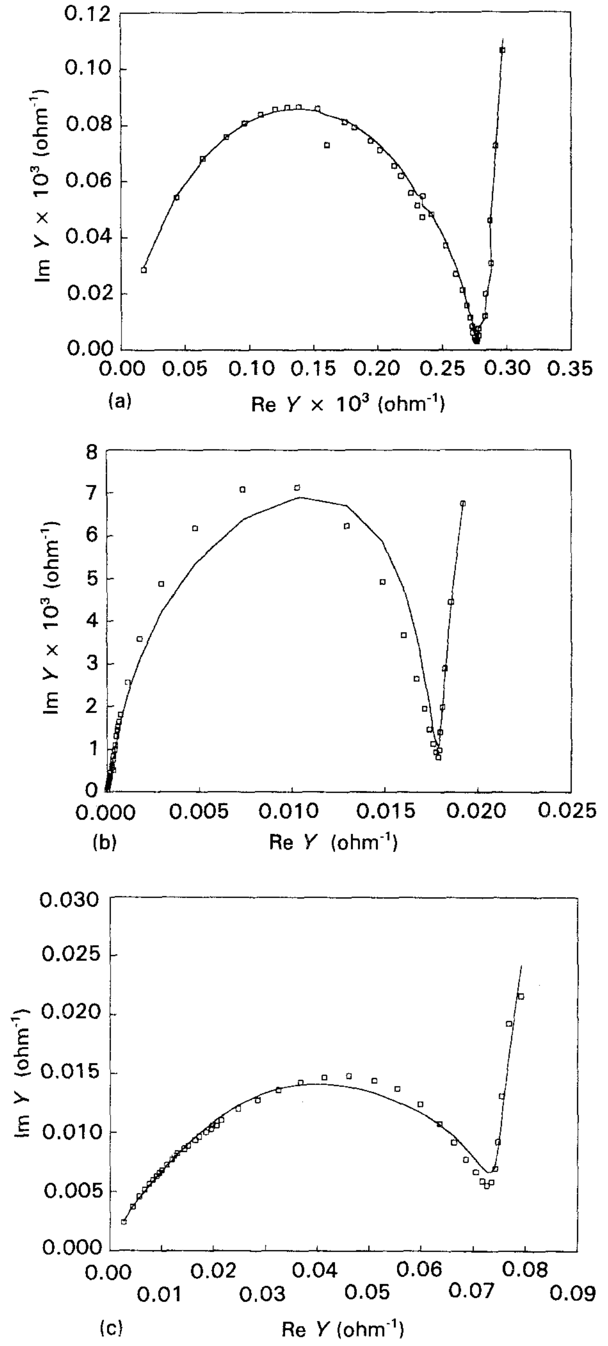

Figure 13 Admittance plots in the complex plane. The solid line corresponds to the simulation of equivalent circuit and the dots to the experimental results. (a) 46 wt % of graphite; (b) 60 wt % of graphite; (c) 80 wt % of graphite.

interaction [17]) (Fig. 12). A constant phase element (CPE) of value A explains in a phenomenological way the graphite–solution interaction. The impedance of this element depends on the frequency to which the element is exposed:

$$Z_{\mathrm{CPE}} = A^{-1}(\mathrm{j}\omega)^{-\eta} \qquad (4)$$

where A is a constant; $j^2 = -1$ and ω is the frequency of the input signal [18]. Recently a geometric interpretation to the exponent η has been assigned, by means of which it is related to the surface fractality. This explains the modification of electrode behaviour by varying the graphite content. The remaining parameters have the following meaning: C1, intraparticle capacitance; C2, interparticle capacitance; R1, interparticle resistance; R2, electrolyte resistance; C3, double layer capacity.

An adequate representation for this system is the admittance (Fig. 13). A well-defined loop can be observed for a broad frequency range between 0.05 and 100 Hz, but at high frequencies, the beginning of another loop corresponding to the Debye circuit can be distinguished. At this frequency zone more information about the composite–solution interface is obtained than about the spectral response of the composite material.

From electrochemical results it has been concluded: (1) ca. 60 wt % of graphite gives a maximum value of i_p/i_c in anodic and cathodic voltammetric scans of ferricyanide solutions; (2) the electrochemical impedance of the composite/KCl 0.4 M system reveals a local maxima in phase angle, impedance modulus and electric permittivity. All these phenomena suggest that when the composite material is close to this critical concentration it can function as a multi-microelectrode [20]. Below this critical concentration the interaction between graphite microelectrodes is negligible compared to the material conductivity, but for higher proportions an increase in the effective electrode surface means that the graphite–solution interface becomes more important. The graphite proportion where this irregular behaviour appears is ca. 43 vol %, assuming that the density of the epoxy resin and graphite are equal to 1:1 and 2.25 g cm^{-3}, respectively [21]. The preceding results justify the use of these materials as electrodes, with compositions ca. 60 wt % having the optimum analytical characteristics.

Acknowledgements

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