

EFFECTS OF ULTRASOUND ON THE ELECTRODEPOSITION OF LEAD DIOXIDE ON GLASSY CARBON ELECTRODES

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ABSTRACT

The electrodeposition of lead dioxide from lead(II) nitrate in an acid medium has been used as a test reaction to study the effects of an ultrasound field. The different behaviours found between platinum and glassy carbon electrodes have been compared by means of cyclic voltammetry and simple potential steps. The current-time response for platinum has not been affected by the presence or absence of ultrasound, but in the case of glassy carbon, by contrast, significant changes have been observed in the characteristic regions of these curves (induction time t_0). Scanning electron microscopy (SEM) has been employed to follow changes in the surface topography after the electrodes had been exposed to ultrasound. Results indicate that neither pits nor structural modifications that may increase the electrode surface occur with the device used. It is concluded that the activation of glassy carbon electrodes by the action of an ultrasound field for electrodeposition of lead dioxide is associated with the surface functionalization caused by the reaction of OH^\cdot radicals (derived from aqueous sonolysis) with the carbon surface.

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INTRODUCTION

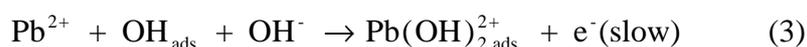
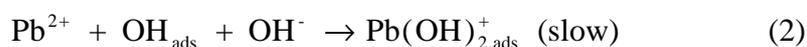
Nowadays, the influence of ultrasound on the electrochemical behaviour of different systems is a very active field of research [1]. Thus, there have been found beneficial effects on mass transport [2, 3], on activation of the electrode surface [4], on adsorption processes [5], and on the modifications which occur in the mechanisms of reaction due to the generation of radicals [6, 7] when electrochemical processes are carried out in presence of ultrasonic irradiation. In most of these studies the reduction of ferricyanide anion [8], methylviologen [9], p-benzoquinone [10], copper sulphate [11], and the oxidation of pyrrole [12] have been used as test reactions in order to obtain information on changes which occur in the different types of electrochemical processes. It has also been studied the influence of ultrasound on the electrode surface of different materials [13]. Coury et al have studied substrates such as glassy carbon, Ebonex, Pt, Au, W and Pd, and they have laid great stress on the effects of ultrasound on glassy carbon.

A wide diversity of methods have been reported for treatment and activation of surfaces of carbon electrodes. There are very different and even controversial opinions about the reproducibility of results [14, 15]. Anyway, it seems that there is agreement as to the fact that the oxidation of the surface of glassy carbon provides an increase in the activity of the electrode [16 - 18].

In this context, we can also find in the literature other studies in which a pretreatment with ultrasound of the electrodic surface, in order to be used in Electrochemistry, provides a more activated surface [19]. In that particular paper [19], glassy carbon electrodes which had been irradiated with ultrasound in dioxane exhibited an increase of activity in the heterogeneous electronic transference for a variety of aqueous redox probes. However, when sonication was performed in water, no significant enhancement was observed, but severe surface pitting was noticeable. In addition, it was evident an increase in the density of electroactive surface oxides, which

was probably produced as a result of the reaction between OH[•] radicals generated in the aqueous sonolysis and the surface [20, 21].

In this paper we propose the electrodeposition of lead dioxide from soluble salts of Pb(II) as a test reaction to study the effects of ultrasound on the electrode surface. Fleischmann et al [22 - 25] were the first to investigate the mechanism for electrodeposition of lead dioxide. They suggested the following mechanism:



Several authors, like Johnson et al. [26, 27] and Velichenko et al. [28] have recently proposed some modifications to this mechanism. Thus, they suggest that the mechanism involves the generation of some soluble intermediates which can be withdrawn from the electrode surface by means of convective-diffusional processes. Anyhow, it should be noted that the first step in the mechanism (generation of OH_{ads}) has been widely accepted [29 - 35].

EXPERIMENTAL

All experiments were carried out using a Voltalab Electrochemical system consisting of a DEA 332 potentiostat and an IMT 102 Electrochemical Interface. The system was connected to a personal computer for recording and treatment of curves.

Electrochemical experiments were performed in a typical all-glass two-compartment voltammetric cell (50 mL volume) placed just over the transducer of a Selecta commercial ultrasonic bath (30 kHz-100 W). The cell was immersed in such a way that the level of both liquids (bath and electrolyte) was the same. The level of the bath liquid was 6 cm. from the bottom, and this was the separation distance between the transducer and the electrode surface (Fig. 1). Thermostatting of the system was accomplished by means of recirculating water at a constant temperature of 25 °C.

The working electrodes were a polyoriented platinum electrode and a glassy carbon rod. A platinum wire acted as the counter electrode. Platinum electrodes were cleaned by heating to red heat and quenching in water prior to each experiment. Before each experiment, glassy carbon electrodes were polished first with fine emery paper, followed by polishing decreasing size alumina particles in suspension on a polishing cloth until a mirror finish was obtained. In both cases, electrodes were thoroughly rinsed with water. A SCE served as the reference electrode.

The chemicals were Analar quality. Aqueous solutions of 0.1 M lead(II) nitrate + 1M nitric acid were prepared using ultrapure water obtained from a Millipore Milli-Q system. Solutions were thoroughly purged of oxygen prior to sweeping by bubbling with Nitrogen N50 (Air Liquide) for 20 minutes. Nitrogen N50 (Air Liquide) was also used for saturation gassing of the solutions before each experiment. During measurements a flow of gas was passed over the solution surface.

A JSM-840 JEOL Scanning electron microscope was employed to obtain topographical views of the electrodes surfaces.

RESULTS

Voltammetry

Figure 2 shows the cyclic voltammogram of the electrodeposition of lead dioxide from 0.1M $\text{Pb}(\text{NO}_3)_2$ + 1M HNO_3 on a platinum electrode recorded under silent (a) and ultrasonic (b) conditions. Figure 3 shows the same experiment on a glassy carbon electrode. Voltammetric response for platinum is the same under both silent and ultrasonic conditions, except for the mass transport control region, as might be expected. Analogous behaviour is observed for a glassy carbon electrode. However, the potential at which electrodeposition begins is different for each electrode. It can, therefore, be deduced that the activation overpotential for platinum is significantly less than that for glassy carbon. This same behaviour, which has also been observed in oxygen evolution process, is consistent with the conclusion drawn by plenty of researchs [26, 36, 37], whereby initial step (1) in the lead dioxide electrodeposition mechanism is the same than that for the oxygen evolution on a lot of electrodes. It is noteworthy that the electric charge of the stripping process of lead dioxide on platinum ($E \approx 1130$ mV vs ECS) is less than the electric charge on glassy carbon. This is a consequence of the poor adherence of lead dioxide to the platinum electrode, as it is demonstrated by the presence of lead dioxide flakes at the bottom of the cell during the experiment.

Chronoamperometry

Potential step experiments were performed in two stages. At the first stage, the electrode is held in open circuit ($j=0$) for 30 seconds. In a second stage, and immediately after, a potential step which has been fixed beforehand is carried out. In some experiments (fig. 7), the electrode underwent additional pretreatment with ultrasound in which the variable to study was the duration of this pretreatment.

Figure 4 shows the j - t profiles for lead dioxide deposition on a polyoriented platinum electrode under silent (a) and ultrasonic conditions (b) for two steps of

different amplitudes. It can be seen that both transients curves are very similar but with slightly lower j values in presence of ultrasound.

Figure 5 shows the chronoamperometric transients for a glassy carbon electrode under silent (a) and ultrasonic conditions (b) for two steps of different amplitudes. In this case, a strong influence of the ultrasound field can be pointed out. Thus, the induction time in ultrasonic conditions is less than in silent conditions and the current density is higher under ultrasound than under silent conditions. Coury et al. [13] have shown that glassy carbon and Ebonex electrodes are severely pitted under ultrasound in aqueous media. This is one of the reasons they argue against the use of glassy carbon for sonoelectrochemical studies in aqueous media. Figure 6 shows the microphotograph of a glassy carbon electrode surface before and after sonication in electrolytic medium for 20 minutes. No damage of the surface is observed. A very plausible explanation of this different behaviour is the experimental approach used in both experiments. Thus, Coury et al. used a sonoelectrochemical reactor which permits to locate a sonic horn directly a very short distance away from the electrode surface. In our work, we immersed the electrochemical cell into the ultrasonic bath, and it is known that in this configuration the ultrasound power transmitted is much lower than in the other arrangement [38].

Figure 7 shows the superposition of j - t profiles recorded in a quiescent solution on a glassy carbon electrode (pretreated in situ with ultrasound of different time duration) and in solution under ultrasound. On increasing pretreatment times, the j - t curve recorded under quiescent conditions becomes similar to the response recorded under ultrasound.

Figure 8 shows the superposition of potential-time curves prior to the chronoamperometric experiment of the curve pretreated for 20 minutes and the curve

recorded under ultrasound shown in figure 7. The electrode potential for surfaces pretreated with ultrasound is always held constant within a short interval.

Figure 9 shows the scanning electron micrographs (SEMs) corresponding to a graphite surface before (a) and after (b) sonication (20 minutes) in the same electrolytic medium. No appreciable surface effect is evident.

Figure 10 shows the SEMs of the lead dioxide electrodeposition process at the induction period (400 s) under quiescent conditions (a) and under ultrasound (b). It is evident that the influence of ultrasound increases considerably the number of particles of lead dioxide deposited at the same potential.

DISCUSSION

The interpretation of cyclic voltammetry curves provides little information about the effects of an ultrasonic field on the electrodeposition process. However, other electroanalytical techniques like chronoamperometry have been useful to contribute details of the process.

Chronoamperometric experiments have shown that the results obtained for platinum and glassy carbon are different. No noticeable effect is produced on platinum electrodes. The little decrease in the current density has also been observed by other workers [26, 27] in convective conditions. By contrast, the response for glassy carbon electrode shows a more complex reaction. This fact makes evident the existence of effects located on the electrode surface. SEMs confirm that the surface of the sonicated electrode does not exhibit any signs of superficial pitting or damage. Therefore, no modifications of the geometric area must be expected for electrochemical measurements.

On the other hand, some new signs have been found regarding the formation of functional groups on the surface of the electrode during sonication. These functional groups persist with time. This phenomenon had previously been observed by L. A. Coury et al. using other test reactions and techniques [13, 19]. Still, when lead dioxide electrodeposition is used as a test reaction, these functional groups play a very active role in the electrodeposition mechanism (step 1) as an intermediate product, and they can be consumed within the lead dioxide deposition. This is evident in the decreasing induction time produced by the pretreatment time increase (or recording the curve under ultrasound) and by current density increases in the steady-state period. In addition, the idea of the functionalization of the glassy carbon electrode surface as a consequence of the action of ultrasound on the surface is reinforced by the different behaviour in the E-t response for pretreated and non-pretreated electrodes. The fact that potential remains constant with time for pretreated electrodes is an evidence that that treatment provides a stable surface, in contrast with non-pretreated electrodes, whose surfaces undergo changes with time, as the spontaneous variation of potential at open-circuit indicates. The reaction of the hydroxyl radical OH^\cdot , derived from aqueous sonolysis, with the free carbon surface catalyses the nucleation process on the surface, decreasing the induction time for a constant step potential. This decrease depends on pretreatment time.

CONCLUSION

The results described in this paper show that the application of an ultrasound field activates the lead dioxide electrodeposition on glassy carbon surfaces. The enhancement of this process is probably associated with an increase in the density of electroactive superficial oxides. Thus, glassy carbon is a suitable material for kinetics studies of these processes and for other studies in which step 1 occurs.

The design of the experiment used in this work can be appropriate for mechanistic studies in Sonoelectrochemistry with non-metals, which are severely damaged by sonic horns located a short distance away from electrodes.

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Figure and Table Captions

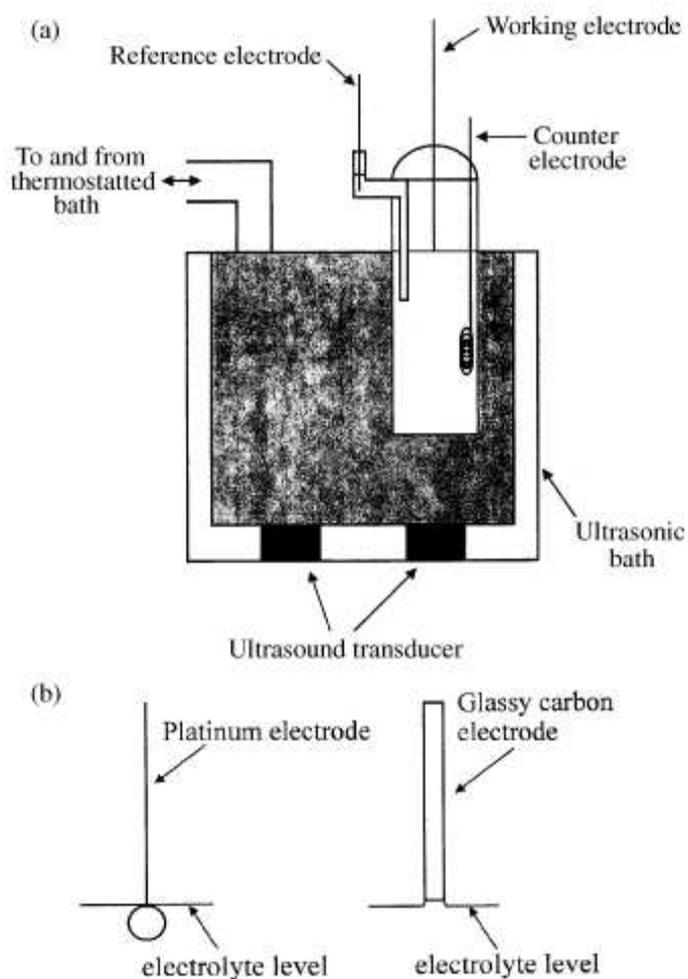


Figure 1.- (a) Diagram of the experimental cell and the insonation arrangement.
 (b) Electrode location at surface electrolyte in the electrochemical cell.

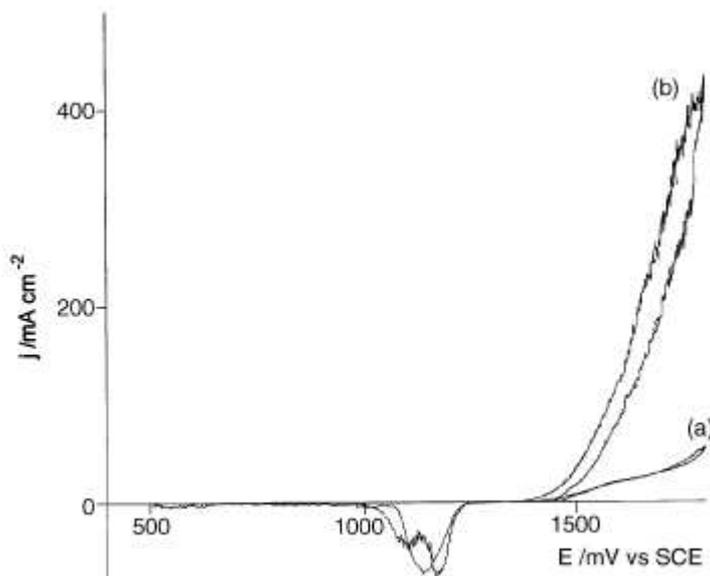


Figure 2.- Cyclic voltammogram in 1M HNO₃ + 0.1M Pb(NO₃)₂ at a polyoriented platinum electrode, $\nu = 5 \text{ mV s}^{-1}$. (a) Silent, (b) ultrasonic conditions.

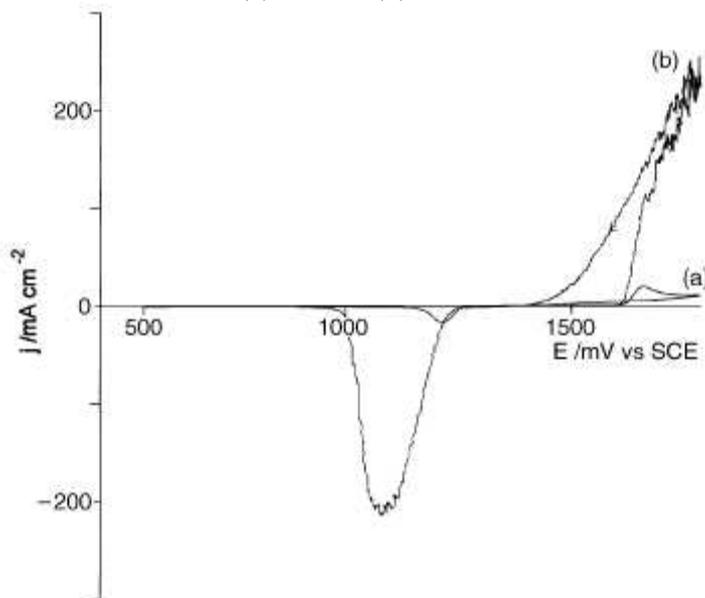


Figure 3.- Cyclic voltammogram in 1M HNO₃ + 0.1M Pb(NO₃)₂ at a glassy carbon electrode, $\nu = 5 \text{ mV s}^{-1}$. (a) Silent, (b) ultrasonic conditions.

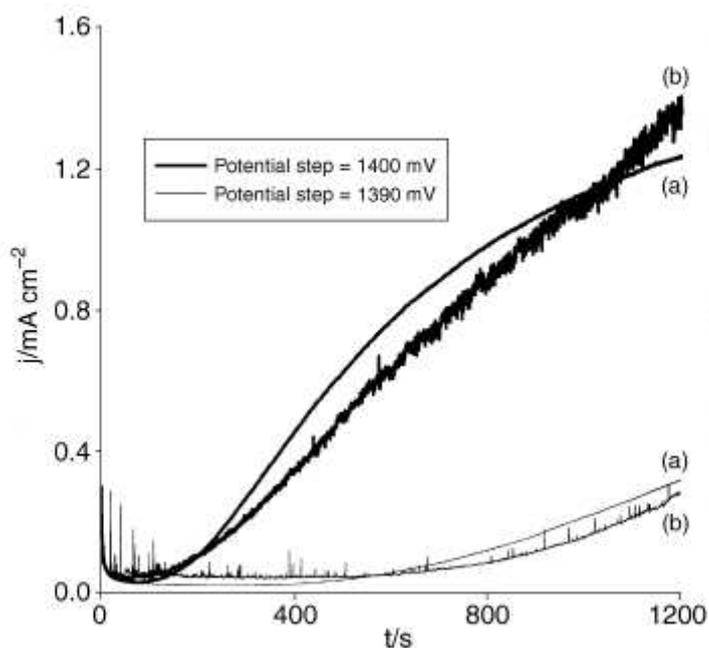


Figure 4.- Chronoamperometric curves for PbO_2 deposition in 1M HNO_3 + 0.1M $\text{Pb}(\text{NO}_3)_2$ at a polyoriented platinum electrode. (a) Silent, (b) ultrasonic conditions.

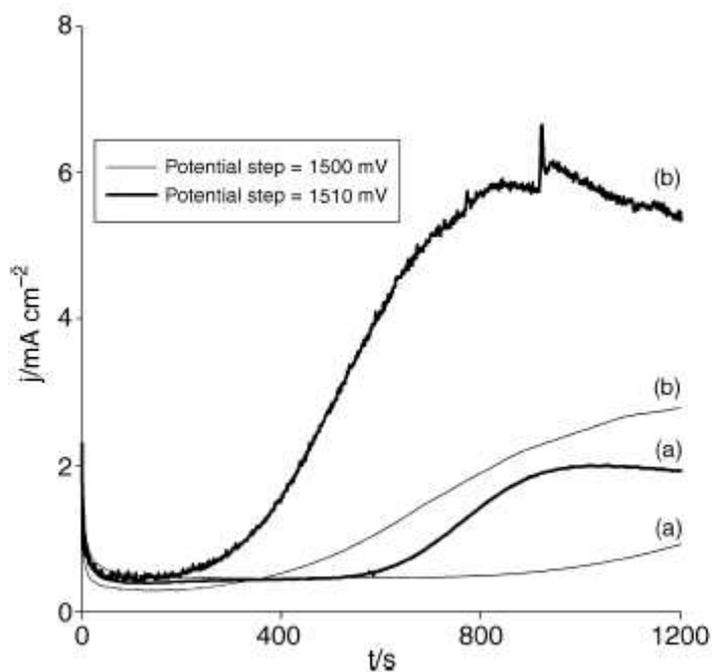


Figure 5.- Chronoamperometric curves for PbO_2 deposition in 1M HNO_3 + 0.1M $\text{Pb}(\text{NO}_3)_2$ at a glassy carbon electrode. (a) Silent, (b) ultrasonic conditions.

- | | | | |
|-------|----------------------------------|-------|-------------------------------------|
| ————— | pre-treatment time=0 min. Silent | | pre-treatment time=5 min. Silent |
| - - - | pre-treatment time=10 min. | ----- | pre-treatment time=15 min. |
| | pre-treatment time=20 min. | ————— | non pre-treatment. Under ultrasound |

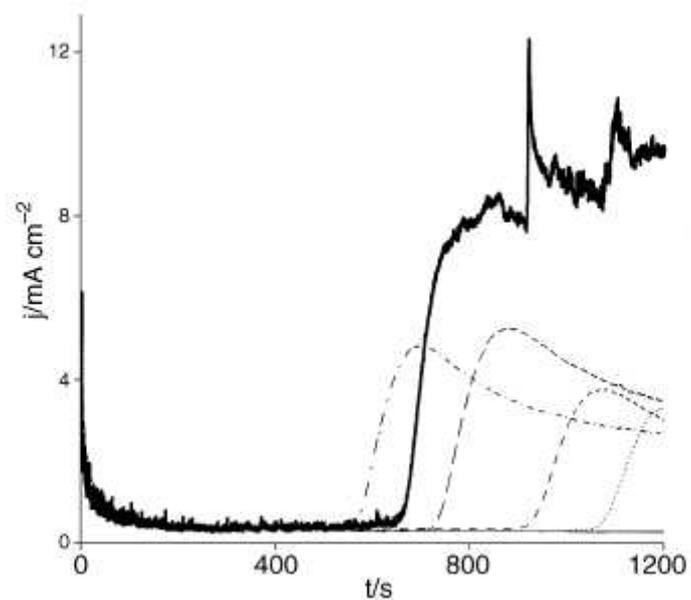


Figure 6.- Chronoamperometric curves for PbO_2 deposition in $1\text{M HNO}_3 + 0.1\text{M Pb(NO}_3)_2$ at glassy carbon electrode with different ultrasonic pre-treatment time, (Details in figure).

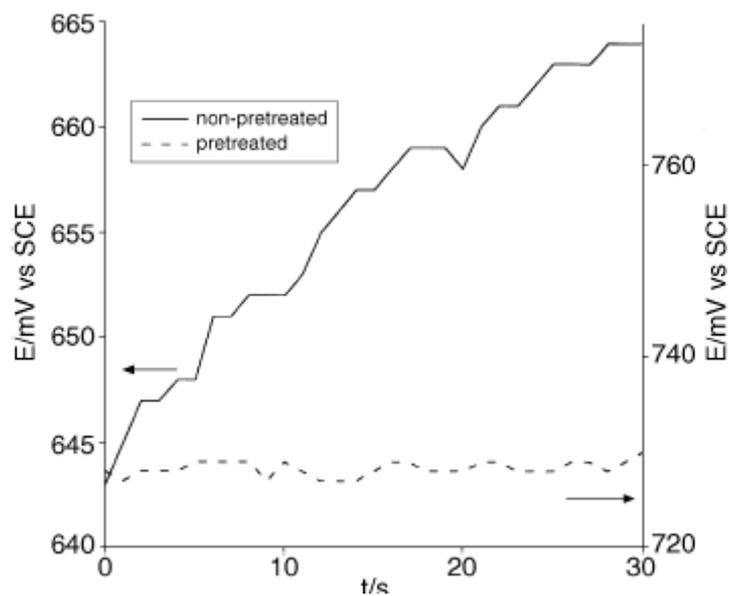


Figure 7.- E-t Curves in $1\text{M HNO}_3 + 0.1\text{M Pb(NO}_3)_2$ at glassy carbon electrodes. (Details in figure).

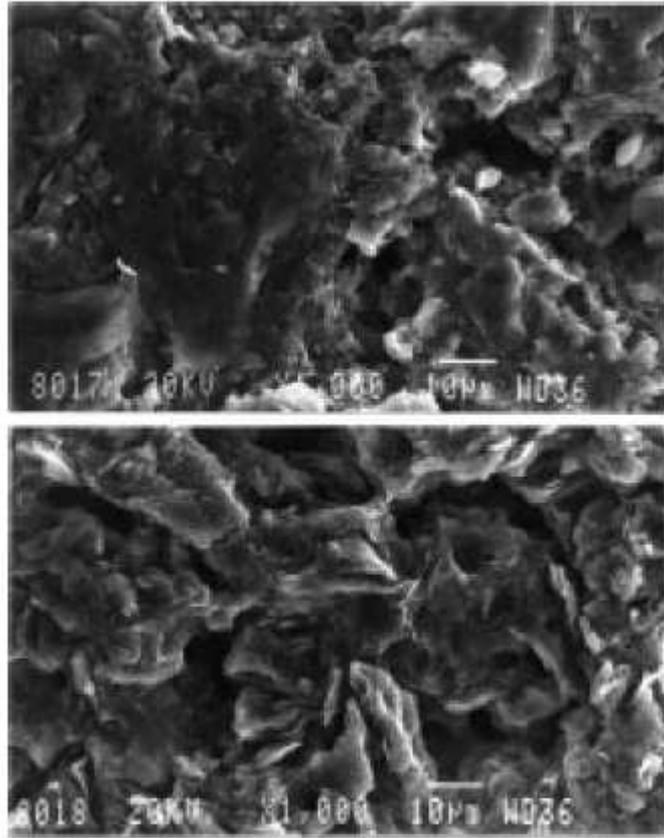


Figure 8.- Scanning electron micrographs of a graphite surface (a) before (b) after sonication in the electrolytic medium for the experiment time (20 min).

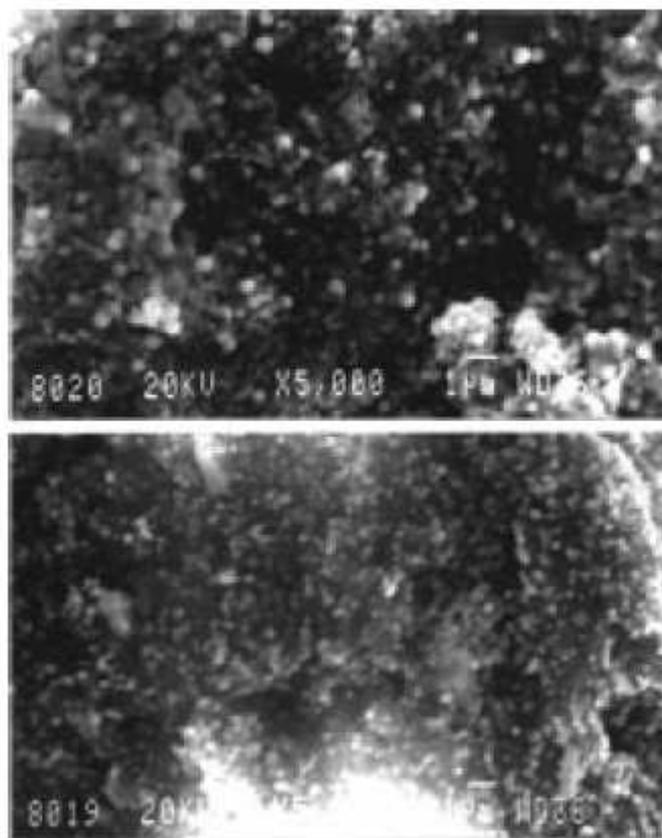


Figure 9.- Scanning electron micrographs of a graphite surface at induction time (400s) during a lead dioxide electrodeposition chronoamperometric experiment under (a) silent (b) ultrasonic conditions.