

# Disruption processes in films grown and reduced electrochemically on metals

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**Abstract** New aspects characterizing the disruption process are discussed, based on an analysis of a proposed disruption model and on a review of previously reported voltammetric and galvanostatic anodic growths of films on metals and their consequent reduction. For voltammetric cases of Pb and Zn, it is shown that the formation charge is not always recoverable, leading to irreversible processes. The total formation charge of Zn can never be totally recovered, but that of Pb is totally recoverable if the reduction rate trends to zero, rendering the process reversible. Furthermore, disruption always causes part of the film to remain adhered to the metal, which is why it is only partially disrupted. Increasing the reduction rate causes the disruption process to increase and the remaining film adhered to the metal to trend toward a minimum constant value, which differs in Pb and Zn but is equal in voltammetric and galvanostatic experiments with Pb. The conclusions are the same with regard to the galvanostatic results for Pb, except that the film charge density is always totally reversibly recovered if the reduction rate is lower than the formation rate. Moreover, the reduction rate does not necessarily have to trend to zero in this case. It needs only to be lower than or

equal to the formation rate. All these facts are discussed based on the disruption model. The paper also discusses in detail how to experimentally obtain highly reproducible measurements, which are fundamental for the conclusion's validity. These experimental discussions and propositions are also based on the disruption model. High reproducibility is achieved even in the case of Pb, a metal whose reproducibility is notoriously difficult.

## Introduction

In this paper, disruption is understood as the possible partial rupture of a given film phase into very small particles while the other part remains adhered to the metal. The film's total thickness can be nanometric. According to this concept, continuous films grown electrochemically on metals may become disrupted after the formation of only a few monolayers. This disruption may be due to interruption of the forming electrical field (after galvanostatic, potentiostatic, or voltammetric growths), to the reduction of the electrical field during potentiostatic growths (very common in atmospheric corrosion), or to constraints occurring during the reduction process of the film (very common in batteries), rendering the entire forming-reduction process in the three cases partially irreversible.

In many cases reported in the literature, the films were much thicker than those referred to here and were grown potentiostatically. The disruptions, if at all possible, had already occurred during the films' growth. Under a potentiostatic growth, the increase in film thickness is accompanied by a reduction of the electrical field inside the film, causing it to fall below the minimum critical value necessary to stabilize the film as a continuous one. These thicker potentiostatic films will not be discussed here.

This paper is dedicated to Professor Francisco Carlos Nart, in memoriam.

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Voltammetric or galvanostatic grown films, the subject of this paper, are usually too new to undergo this disruption process during their growth because these are transient techniques. They correspond to the initial states of those thicker potentiostatic films when they are still very thin (up to a maximum of 20 monolayers or less). These thin films are usually present underneath the cracked thicker ones, remaining adhered to the metal surfaces.

It must be noted that it is not stated here that all films grown on metals undergo disruption. Even those that could become disrupted do not always do so because disruption depends on the experimental conditions as well as on the metal, as will be shown later.

Only electrochemical experiments that indicate disruption processes will be focused on here, particularly insofar as the reduction process of the film is concerned. The reason we use only electrochemical measurements at this time is that there are practically no studies of this phenomenon in electrochemistry; this is our second paper on the subject [1]. To this end, some metals were selected: zinc (voltammetric results) and lead (galvanostatic and voltammetric results).

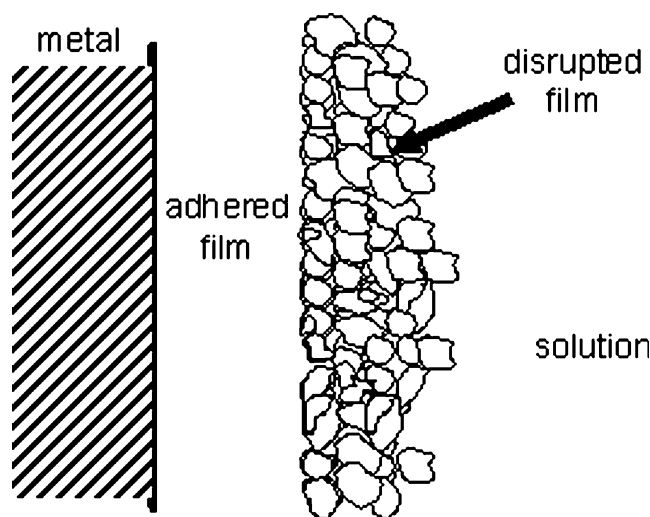
A last important point is that the solutions used here must cause practically no dissolution of grown films. Dissolution is a phenomenon to be precluded. These kinds of studies of such films require that the solution play only a fundamentally current-conducting role. Otherwise, the film's dissolution will unnecessarily complicate the experimental results, making them difficult to understand.

#### The disrupted film model

To increase the thickness of an initial monolayer film at room temperature requires the application of high electrical fields through which the ions can move. At the same time, these fields stabilize the films in their current thickness through electrostriction forces [2]. This is necessary because disruptive forces are produced by the molar partial volumes of films, which are usually higher than those of the original metals.

When these high fields are reduced, inverted, or interrupted, the disruptive forces can exceed the electrostriction forces [3]. The films can then become partially disrupted, giving rise to disrupted particles, which form an external film, with particles attached to the surface of the remaining adhered film by superficial tensile forces (see Fig. 1).

The remaining adhered films are stuck to the metal surface because an inner potential difference always remains at any metal–film–solution interface, in this case, between the metal and the solution. This inner potential difference always produces a remanent electrical field inside the adhered film, which stabilizes it through electrostriction forces.



**Fig. 1** Schematic representation of a metal/film/solution interface of a partially disrupted film showing also the remaining adhered film

The partial disruption produces very fine disrupted particles (possibly nanometric ones). Because these particles have high surface curvatures, they give rise to high chemical potentials (through the Laplace equation). As a result, the disrupted particles will recrystallize, even in solutions in which the films are highly insoluble (where recrystallization under other conditions may take larger times). That is why SEM observations of the surface of these films may reveal particles of reasonably different sizes and characteristic shapes produced by dissolution–precipitation processes, giving rise to cracked film patterns.

One important aspect of this model is that, because the inner adhered film can be subjected to oriented electrical fields, it can be voltammetrically or galvanostatically reduced through a solid-state reaction. This process will be called the solid-state reaction mechanism.

On the other hand, because it is impossible to apply a given oriented electrical field through the particles of the disrupted film (because the current tends to pass through the solution between the particles), these particles cannot be reduced voltammetrically or galvanostatically directly through a solid-state reaction. To reduce them, they must dissolve into the solution between the particles, with the metal ions diffusing and reaching the metal surface, where they become reduced. This process will be called the dissolution/precipitation mechanism.

#### Preexisting facts about the disruption phenomenon

Few experimental facts about these disruptive processes, involving systems in which the metal ions are highly insoluble and, thus, where dissolution of the disrupted films is impossible, are reported. One experimental fact comes from the combination of cyclic voltammetry and ellipso-

metric measurements of Fe in alkaline solution [4], although the authors may not have realized the disruption problem. In these experiments, after a given period of applying cycle voltammetry in the potential region of film formation and reduction, when ellipsometric measurements were taken at an anodic potential ( $E_{\lambda,a}$ ) in relation to film formation peaks, the measurements reveal two films: an inner one with a dielectric constant near that of an iron oxide and an external one with a dielectric constant similar to but lower than that of water. On the other hand, when ellipsometric measurements were taken at a cathodic potential ( $E_{\lambda,c}$ ) to the reduction peaks, only the external film was observed, also with its dielectric constant similar to but lower than that of water. The inner film detected at  $E_{\lambda,a}$  presents always the same thickness, independent of the number of cycles, but the external film thickness increases with the increase of the number of voltammetric cycles. The film detected at  $E_{\lambda,c}$  also increases with the number of cycles. The inner film is evidently the adhered continuous one, while the external film is the disrupted one.

Another general experimental fact pointing to disruption is that the anodic charge densities ( $q_a$ ) of the anodic growths are generally found higher than the cathodic corresponding charge densities ( $q_c$ ) of the respective reduction process. That this is a demonstration of disruption holds true only if the system is seen during the first growing cycle; the voltammetry begins at a sufficiently high initial cathodic potential ( $E_i$ ) for the electrode to have no film grown on it; the film is grown in a solution in which it is practically insoluble, thus precluding unnecessary complications, and cycle voltammetry is applied at a suitable potential sweep interval, including the oxidation and reduction peaks. Under these conditions, the question is: where has the excess of  $q_a$  gone? Evidently, it has gone to the disrupted film, through which a highly oriented field cannot be applied, so it cannot be reduced directly through a solid-state mechanism. It can only be reduced through a dissolution/precipitation mechanism. This dissolution/precipitation mechanism will take longer times than those of voltammetric measurements, due to the low solubility of the films in the selected solutions. This explains, for example, why normal recharging of industrial batteries takes longer times than discharging (their films are insoluble in their solutions).

Disruption can also be demonstrated indirectly by the experimental fact that all nonnoble metal/solution electrodes submitted to multiple film formation and reduction voltammetries reach a constant current density/potential ( $i/E$ ) pattern. These results can be understood as the formation of a specific stationary solution in between the particles of the disrupted external growing film determining the pattern of the  $i/E$  plots. The adhered film grows in each voltammetric anodic sweep and, during the subsequent cathodic sweep, is then partially disrupted, with the remaining

adhered film reduced through the solid state reaction mechanism. This set of phenomena acts to produce an external disrupted growing film, with its solution in between the particles reaching a constant composition through mass transport processes and an inner adhered film, which appears and disappears at each cycle. This explains the evolution of these kinds of cyclic voltammetry to an always-stationary  $i/E$  pattern.

A final experimental fact indicative of disruption phenomena is the kind of films that appear in atmospheric corrosion. In general, these films appear cracked, even microscopically, especially when they become directly visible, when they have grown sufficiently. That is why it has been stated, in several cases, that they display a quasilogarithmic relation between thickness and growth time [5]. Under potentiostatic conditions such as those that usually prevail in atmospheric corrosion, the field inside the film decreases as the film grows because the difference in inner potential through the film is constant. This causes it to reach a minimal critical value at which its stabilizing electrostriction effects become lower than the disruptive effects due to the differences in partial volumes. As a consequence, the film becomes partially disrupted. Nevertheless, in the remaining adhered film, the electrical field will regain sufficient strength to restart the process recursively. The disruption model can then explain the cracked atmospherically corroded films.

## Materials and methods

The electrodes were Pb or Zn with purity higher than 99.9% in weight, keeping an electroactive area of 0.4 cm<sup>2</sup> for both. The solutions were 4.6 M H<sub>2</sub>SO<sub>4</sub> for Pb and 0.3 M H<sub>3</sub>BO<sub>3</sub> plus 0.15 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O for Zn, deoxygenated. The reference electrodes were Hg/Hg<sub>2</sub>SO<sub>4</sub>/4.6 M H<sub>2</sub>SO<sub>4</sub> for Pb and Hg/HgO/1.0 M NaOH for Zn, respectively, to which all the potentials are referred.

The working electrodes for voltammetric measurements were always initially polished with 600 emery paper at the beginning of any set of experiments. Then, they were introduced cathodically polarized with the aid of a fourth Pt electrode at a potential of –1.3 V for Pb and also –1.3 V for Zn. At this initial potential, it was waited up to the stabilization of the initial current density (0.5 mA cm<sup>–2</sup> for Pb and 0.05 mA cm<sup>–2</sup> for Zn). The cathodically polarized electrode introduction was performed to inhibit any spontaneous film growth in the short time during which the electrode could be at a free potential. After obtaining the corresponding initial current densities, both metals were subjected to repetitive cycles as pretreatment. They consist of several voltammetric cycles plus a potential arrest at –1.3 V for 5 min, between the sets of voltammetric cycles.

This was done up to the moment when, in successive first anodic voltammetric sweeps of the following voltammetric cycles, the anodic peak become totally reproducible. Only after attaining this stabilization (from 5 to 10 sets of these cycles, depending on the history of the electrode) was the electrode considered ready because this allows for the increased reproducibility of the measurements.

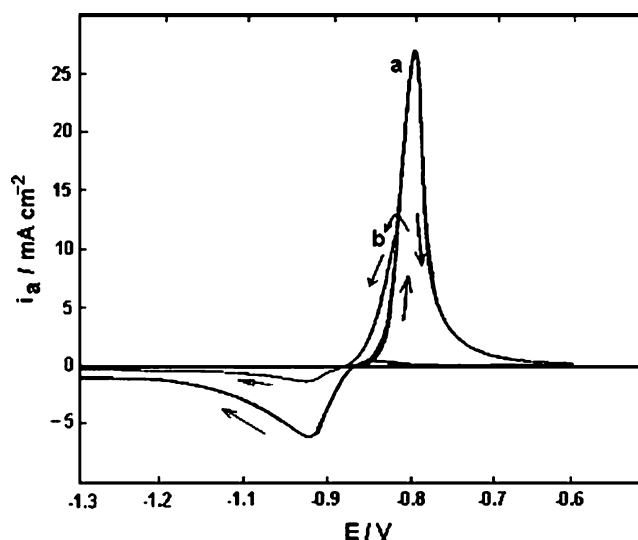
The mentioned pretreatment was originated from the idea that, during the cathodic sweeps, only the adhered films are reduced. While waiting at an appropriate cathodic potential, through the dissolution/precipitation mechanism, the disrupted film can be reduced. The entire multiple complete formation/reduction process assures the stabilization of the metal/solution interface. The effectiveness of this procedure has already been proved in several metals in our laboratories.

Each set of voltammetric experimental results, after the pretreatment, comprises several formations always at a given  $v_a$ , immediately followed by their respective reduction at different  $v_c$ , followed by a 5-min waiting period at  $-1.3$  V between each formation/reduction cycle. The anodic ( $v_a$ ) and cathodic ( $v_c$ ) sweep voltammetries used in this work will be described in the “Results and discussions” section of this paper. The anodic ( $q_a$ ) and cathodic ( $q_c$ ) peak charge densities were determined by integrating the anodic ( $i_a$ ) or cathodic ( $i_c$ ) current densities vs the voltammetric potential ( $E$ ).

For Pb voltammetric experiments, an alternative method to know that reproducibility was attained has also been employed. This second method is based on the fact that, as in several other cases, when a growing film is not an oxide (in a Pb/H<sub>2</sub>SO<sub>4</sub> system the film is PbSO<sub>4</sub>), its nucleation phenomenon can always be detected by inverting the anodic sweep in a given initial potential region of the growing peak during the voltammetry (when the nuclei have not yet overlapped). The nucleation shows the previous inexistence of the film phase.

The reproducibility for Pb can be seen in Fig. 2 where curves “a” show the result of the first method (the reproducibility of the formation peak, with two superposed curves). In the curve “b” in Fig. 2, the effect of nucleation is observed through the higher current during the cathodic return, showing the results of the second method. The nucleation phenomenon is not observed if the electrode has not been held for 5 min at  $-1.3$  V. It is the holding of the electrode at a sufficiently negative cathodic potential which allows us to observe the nucleation phenomenon, as well as to achieve the reproducibility of the first voltammetric anodic peak.

The fact that nucleation has never been observed in oxide films makes it impossible to use this second method in the case of Zn. This is because either nonnoble metals in contact with a water solution are never free of some kind of

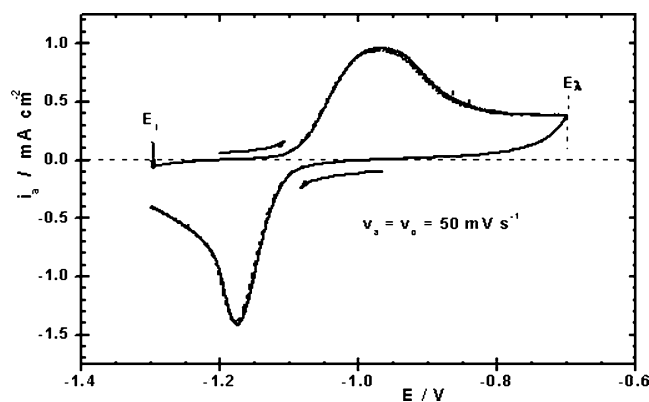


**Fig. 2** Voltammetric results showing (a) the reproducibility of anodic and cathodic total peaks after the pretreatment and (b) the reappearance of nucleation after the cathodic polarization at  $-1.3$  V for 5 min.  $v_a=20$  mV s<sup>-1</sup>,  $v_c=20$  mV s<sup>-1</sup>,  $E_i=-1.3$  V, holding potential of  $-1.3$  V for 5 min. Deoxygenated 4.6 M H<sub>2</sub>SO<sub>4</sub> solution. Reference Electrode (RE) Hg/Hg<sub>2</sub>SO<sub>4</sub>/4.6 M H<sub>2</sub>SO<sub>4</sub>

monolayer oxide film, thus making nucleation unnecessary, or the number of nuclei is so large that their overlapping can hardly be observable. However, the nucleation aspects of these films will not be discussed in this paper.

Figure 3 illustrates the reproducibility of Zn results only with the first method. The reproducibility is particularly important in the case of Pb electrodes because it is difficult to obtain it when the electrodes have to be polished between measurements due to the low tensile strength of this metal.

In galvanostatic experiments, only Pb was studied, using the same solution of the voltammetric measurements. For all the aforementioned reasons, the process involved po-



**Fig. 3** Two voltammetric results for Zn after the pretreatment, showing the reproducibility of the first anodic (formation of ZnO film) and cathodic (reduction of ZnO) peaks.  $v_a=v_c=v=50$  mV s<sup>-1</sup>, deoxygenated solution 0.3 M H<sub>3</sub>B<sub>3</sub>O<sub>3</sub> plus 0.15 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O. Reference Electrode (RE) Hg/HgO/1.0 M NaOH



lishing the electrodes with 600 emery paper with their introduction without polarization (the fourth electrode is useless under galvanostatic conditions). Their polarizing were done as soon as possible at a sufficiently high cathodic current density, then waiting 30 min at this current density to reduce any kind of formed film during these procedures. Finally, the electrodes were cycling as pretreatment for stabilization. Each pretreatment cycle consisted of a galvanostatic formation plus the corresponding reduction of the film, followed by holding the electrode, another time, at a sufficiently cathodic current density to reduce the disrupted film. This cycling was performed until the successive anodic and cathodic galvanostatic transients were totally reproducible. After that, the electrode was ready for the measurements. For the pretreatment,  $i_{g,a}$  was always  $0.4 \text{ mA cm}^{-2}$  up to a potential of  $-0.7 \text{ V}$  (the cutting potential) and  $i_{g,c}$  was always  $0.2 \text{ mA cm}^{-2}$  until the beginning of the hydrogen evolution, where this  $i_{g,c}$  was maintained for 5 min to reduce the disrupted film.

Each set of measurements, after the pretreatment, consists of always applying to each time a constant galvanostatic anodic current density,  $i_{g,a}$ , always giving rise to the same film charge density, followed each time by different galvanostatic cathodic current densities,  $i_{g,c}$ . For each formation and reduction experiment, a holding of the electrode at a high cathodic current density for 5 min was always interposed to reduce the disrupted film.

For each set of experimental results, the respective  $q_{g,a}$  and  $q_{g,c}$  values, the anodic and cathodic galvanostatic charge densities, were obtained from the respective transition times ( $\tau$ ) in the  $E$  vs  $t$  plots. Different sets of experiments use different constant  $i_{g,a}$  with variable  $i_{g,c}$ . The  $i_{g,a}$  of different sets of experiments are given in the respective charge density figures as a function of the subsequent  $i_{g,c}$ .

## Results and discussions

### Voltammetric growth and disruption

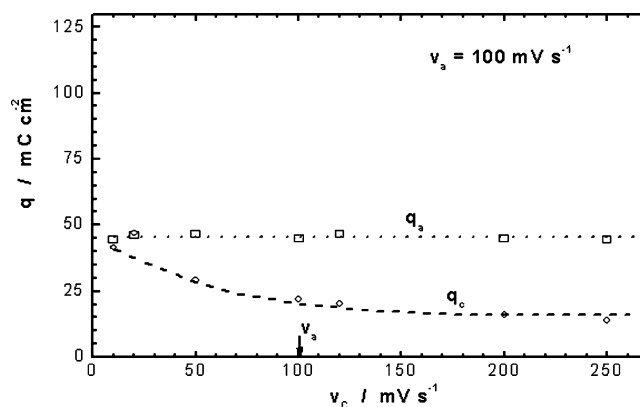
What characterizes the voltammetric growth of films on metals is the fact that they are produced under variable anodic current densities giving rise to a peak (see Figs. 2 and 3). This probably influences the disruption processes. Voltammetric anodic peaks, after the nucleation, have been quantitatively understood [6–8] only recently. They result from the decrease of ionic resistivity due to the injection of recombining point defects, which are produced by the passage of current. This is followed by a new increase of the ionic resistivity due to recombination of the point defects, giving rise to an ionic resistivity minimum and, consequently, a current density maximum. This is accompanied by a high anodic electrical field inside the film. All

these phenomena also occur in the voltammetric reduction process of a film, giving rise also to voltammetric peaks (see Figs. 2 and 3). Nevertheless, these kinds of reduction processes, which are important for the disruption processes, have received very few quantitative studies.

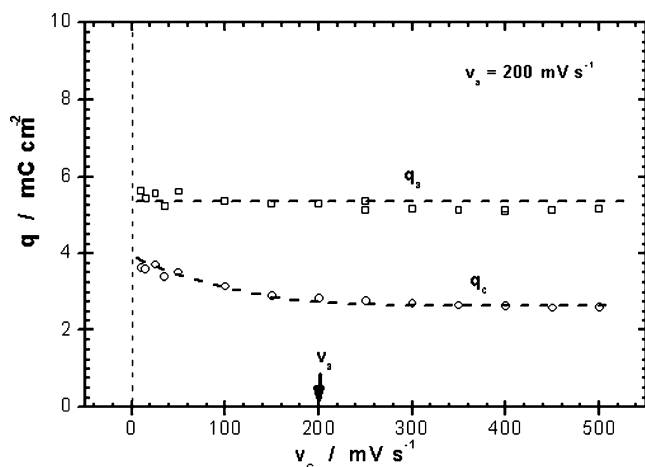
During the reduction [7], where the disruption takes place, there is the injection of the recombining point defects, giving rise, also at the initial steps, to the reduction of the ionic resistivity. This is also followed by its increase, in this case not only due to the recombination but also to the reduction of the film thickness. It produces the consequent increasing of collapses of point defects at the two limiting film interfaces. In this case, the high electrical field is cathodic.

From the standpoint of the disruption phenomenon for the two metals, it is important that the variation of  $v_c$ , after a constant  $v_a$ , always implies a decrease in  $q_c$ . This decrease also always finishes in a minimum constant value. This is illustrated in Fig. 4 for Pb and in Figs. 5 and 6 for Zn, for special values of constant  $v_a$  (particular grown films). In these figures, the corresponding previous  $q_a$  has also been plotted to be able to graphically see the disruption process. The  $q_a$  value for a given metal depends on  $v_a$  (compare Figs. 5 and 6 for Zn). This is because as it is well known [6–8] that  $q_a$  depends on  $v_a$  for any metal. It decreases with the increase of  $v_a$ . The reasons for this are discussed and explained in the cited papers.

In this context, in both cases (Pb and Zn), regardless of the applied sweep velocities, the low solubility of the films in the solutions makes it impossible to explain a lower  $q_c$  than  $q_a$  through dissolution. It is evident that the disruption phenomenon can easily explain these results as it was able to explain the stabilization cycles in the “Material and methods” section.

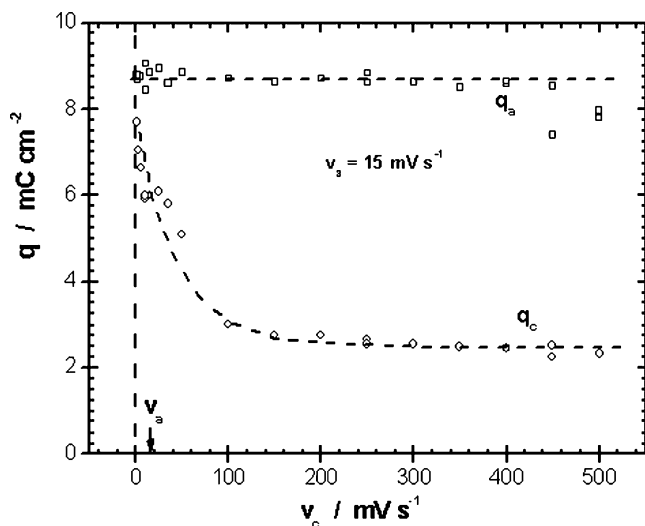


**Fig. 4** Pb electrode, anodic charge densities ( $q_a$ ) at constant  $v_a$  ( $100 \text{ mV s}^{-1}$ ), showing the reproducibility afforded by the pretreatment and the corresponding subsequent cathodic charge densities ( $q_c$ ), both vs  $v_c$ . Each pair of cathodic/anodic results corresponds to one experiment

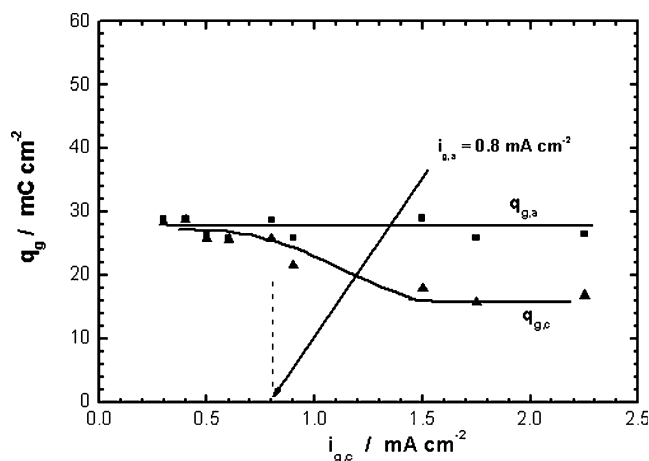


**Fig. 5** Zn electrode, anodic charge densities ( $q_a$ ) at constant  $v_a$  ( $200 \text{ mV s}^{-1}$ ), showing the reproducibility provided by the pretreatment and the corresponding subsequent cathodic charge densities ( $q_c$ ), both vs  $v_c$ . Each pair of cathodic/anodic results corresponds to one experiment

An important point related to Figs. 4, 5 and 6 is that, when  $v_c$  reaches a sufficiently high value, as it was pointed out previously, the  $q_c$  values trend toward a constant minimum value. This is independent of the conditions in which the film has been grown. It is practically a characteristic of the metal and the solution. The value for Pb in  $\text{H}_2\text{SO}_4$  4.6 M is about  $17 \text{ mC cm}^{-2}$  (see Fig. 4) (the same value obtained galvanostatically for high growing rates; see, for example, Fig. 7) and about  $2.6 \text{ mC cm}^{-2}$  (compare Figs. 5 and 6) for Zn in  $\text{H}_3\text{B}_3\text{O}_3$  0.3 M plus  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  0.15 M solution. From the standpoint of the disruption model, the constancy of  $q_c$  at a sufficiently



**Fig. 6** Zn electrode, anodic charge densities ( $q_a$ ) at constant  $v_a$  ( $15 \text{ mV s}^{-1}$ ), showing the reproducibility given by the pretreatment and the corresponding subsequent cathodic charge densities ( $q_c$ ), both vs  $v_c$ . Each pair of cathodic/anodic results corresponds to one experiment



**Fig. 7** Pb electrode, anodic charge density ( $q_{g,a}$ ) at constant  $i_{g,a}$  ( $0.8 \text{ mA cm}^{-2}$ ), showing the reproducibility resulting from the pretreatment and the corresponding subsequent cathodic charge density ( $q_{g,c}$ ), both vs  $i_{g,c}$ . Each pair of cathodic/anodic results corresponds to one experiment

high  $v_c$  results from the fact that there is always a remanent inner potential difference,  $\Delta\phi_{m/s}$ , between a metal and a solution. This remanent inner potential difference can always give rise to the same stabilizing electrical field, due to electrostriction forces, through a remaining adhered film with constant thickness.

On the other hand, the reasons for the fact that  $q_c$  decreases as  $v_c$  increases need to be more carefully studied. It must be related to the fact that the increasing  $v_c$  implies an increase of the involved  $i_c$  values. In any voltammetric film reduction, the increase of  $v_c$  is followed by an increase in the involved current densities [7]. The disruption process in its dependence on the forming conditions, on the maximum potential attained, on the reduction conditions, and so on, requires more in-depth experimental and theoretical studies.

Even so, the results presented here reveal typical behaviors that are dependent on the type of metal. In the case of Pb, it is possible to recover practically the entire anodic charge density provided the cathodic sweep rate is very slow (see Fig. 4). However, this does not seem possible in the case of Zn. Even at very low cathodic sweep rates, the recovered  $q_c$  does not reach the original value of  $q_a$ . It is as if Pb can become reversible in the formation/reduction process but Zn always seems to have an irreversible component. The reversible part is evidently the part connected to the adhered film through which a direct reduction electrical field can be applied (the solid state mechanism). Hence, depending on the procedure, there may be no disruption in Pb, but in Zn, part of the film always seems to suffer disruption. Studies involving other metals as well as theoretical studies are needed to gain a more overall viewpoint.

## Galvanostatic growth and disruption

When one shifts one's attention from the voltammetric to the galvanostatic results, other important facts can be stated about the disruption processes. However, one of the problems of galvanostatic transients is the small amount of theoretical quantitative literature. In general, only the transition time  $\tau$  is related with the galvanostatic current density, but transient processes are never analyzed.

The galvanostatic transient plots [9] show, during the film's formation, an initial high increase of potential, followed by a linear or quasilinear increase of  $E$ , depending on the  $i_{g,a}$ . This linear region ends in a new final high increase of  $E$ . The first increase of  $E$  is given by the initial charge of the interface, which acts as a capacitor, in parallel with the initial stages of the film formation. The linear region is the result that, in this case, there is a constant injection of point defects (a constant current density) together with the constant increase of thickness. Parallel reactions are very rare in anodic growth, at least at fairly low potentials. A linear region evidently indicates a quasiconstant ionic resistivity of the growing film. When there is sufficient defect mobility, the concentration of defects in the film can be seen as constant throughout the film's thickness. Such films are called ultrathin transient films [10]. When defect concentration gradients appear inside films, they are called normal transient thin films. The last increase of potential is due to point defect recombination as well as film aging, probably related with the dehydration process. In the case of Zn, the transient region has been the object of a theoretical and quantitative analysis in a recent paper [9].

What characterizes galvanostatic film growth as different from voltammetric ones, and probably influencing the disruption process, is the constancy of  $i_{g,a}$ , as will be seen. When a galvanostatically grown film is immediately reduced galvanostatically through a cathodic current density  $i_{g,c}$ , the  $E/q_{g,c}$  plot shows [9] an initial instantaneous decay, followed by a new linear and now decreasing potential region. It ends with a new final high-potential decrease.

The initial instantaneous potential decrease is necessary to charge the metal–film–solution interface, enabling the potential to shift to the reduction zone but taking into account the ohmic drop through the film. The linear region also corresponds to a constant ionic resistivity of a reducing-in-thickness film. The final potential decrease is due to a film's increased ionic resistivity. It results from the recombination of the point defects together with the increasing collapse of them at the film interfaces, due to the reduction of the film thickness.

Under this context, interesting facts about the disruption processes become observables when galvanostatic experiments are conducted using an equivalent procedure as that

described earlier herein for voltammetric measurements. Figure 7 illustrates results of  $q_{g,c}$  and the corresponding previous  $q_{g,a}$  for Pb. The  $q_{g,a}$  was plotted for comparison. The films were always grown at the same  $i_{g,a}$ , always growing the same film. The intercalated reduction processes, each time, were made with variables  $i_{g,c}$ , against which the data are represented in Fig. 7.

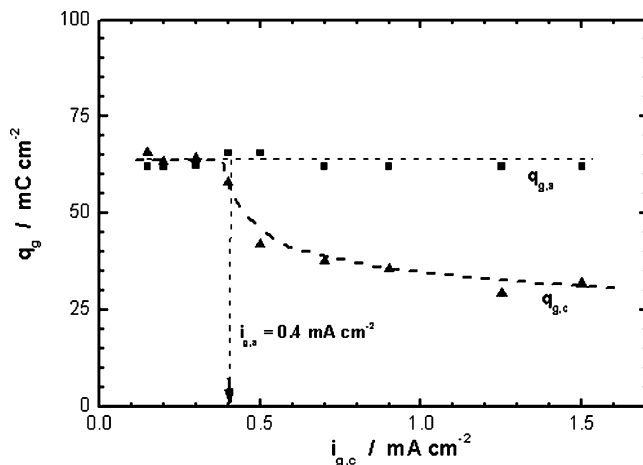
In Fig. 7, when  $i_{g,c} \leq i_{g,a}$ , the entire formed film is recovered. On the other hand, when  $i_{g,c} > i_{g,a}$ , the disruption phenomenon appears, another time trending to a low constant  $q_{g,c}$  value for high reduction rates. This low constant value at high reduction rates, which is identical to that shown in Fig. 4 for an equivalent solution in the voltammetric experiments, corresponds here also to about  $17 \text{ mC cm}^{-2}$  (Pb in 4.6 M  $\text{H}_2\text{SO}_4$ ). As can be seen, this value is independent of the technique employed to grow the film. This fact corroborates the proposed explanation about the remaining inner film due to the consistently remaining inner potential difference between a given metal and the corresponding solution.

A comparison of Fig. 7 with Fig. 4 reveals a clear difference in relation to the reversibility of the processes. Figure 7 suggests that galvanostatically grown films appear to have something resembling a memory that enables them to detect where the reduction current densities are higher than or equal to/lower than the anodic formation current densities. This memory is not present in voltammetric films. As far as we know, this is the first experimental demonstration that there could be important differences between voltammetric and galvanostatic films, even during transient conditions.

In the Pb/ $\text{H}_2\text{SO}_4$  system subjected to voltammetry, the fact that the recovery of the entire grown film occurs, when possible, only when  $v_c$  trends to zero (involved current densities trend to very low values) emphasizes how important the reduction current densities are to the disruption process. In the voltammetric case, the films are formed in slices that grow at different current densities so the condition in galvanostatic experiments cannot be applied in voltammetric experiments. In galvanostatic experiments, the constant current is possibly the cause of no disruption. All these facts confirm the necessity for more in-depth experimental and theoretical studies involving film disruptions.

To demonstrate that the above galvanostatic results are typical ones, Fig. 8 shows plots of some other set of equivalent data but with a different constant  $i_{g,a}$ . This figure shows the same phenomena as those illustrated in Fig. 7. Nevertheless, due to the low maximum attained of  $i_{g,c}$ , the  $q_{g,c}$  has not yet reached its minimum value at high growing rates; even the data trend to it.

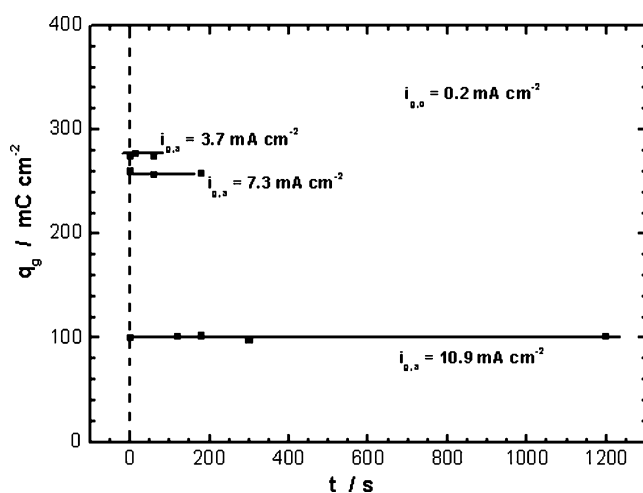
Finally, the galvanostatic experimental data on Pb show that the results on  $q_{g,c}$  do not change when the polarization of the electrode is arrested for different waiting times



**Fig. 8** Pb electrode, anodic charge density ( $q_{g,a}$ ) at constant  $i_{g,a}$  ( $0.4 \text{ mA cm}^{-2}$ ), showing the reproducibility provided by the pretreatment and the corresponding subsequent cathodic charge density ( $q_{g,c}$ ), both vs  $i_{g,c}$ . Each pair of cathodic/anodic results corresponds to one experiment

between anodic growths and cathodic reductions. This fact is illustrated in Fig. 9 for different  $i_{g,a}$  with the same  $i_{g,c}$  ( $0.2 \text{ mA cm}^{-2}$ , always lower than the various used  $i_{g,a}$ , to have no disruption).

From the advanced viewpoint, the results in Fig. 9 imply that the interruption of polarization, after the film's galvanostatic growth, does not cause disruption of the film. Figure 9 proves this finding for different  $i_{g,a}$ . The film's charge density reduction at increasing  $i_{g,a}$  lies inside the well-known [6–9] fact that increasing the film's growth rate (galvanostatically or voltammetrically) always leads to a reduction of the film involved charge densities for passivation.



**Fig. 9** Cathodic galvanostatic charge density ( $q_{g,c}$ ) vs different holding times without polarization between the anodic growth and the cathodic reduction of the film. The experiments were always conducted at the same  $i_{g,c}$  ( $0.2 \text{ mA cm}^{-2}$ ) and the same grown film for each  $i_{g,a}$ . Data for different  $i_{g,a}$  always have  $i_{g,a} > i_{g,c}$

## Conclusions

Based on a description of the disruption phenomenon, using voltammetric and galvanostatic experiments for which established interpretations are reviewed, various new aspects of the disruption processes are pointed out. In the case of films grown voltammetrically on Pb and Zn, it is shown that, depending on the metal, it may or may not be possible, during the reduction process, to totally recover of the previous charge density used to form the film. When it is possible, this total recovery (reversibility of the process) only occurs voltammetrically at very low reduction rates. An interesting point is that this analysis is valid for Pb experiments, but for Zn experiments, even at voltammetric reduction rates tending to zero, complete recovery of the formation charge density is never possible (a portion of the process is always voltammetrically irreversible). On the other hand, in the case of both metals, increased reduction rates always cause an increased loss of part of the formation charge density, which is explained here by the disruption phenomenon. In fact, these losses cannot be attributed to the dissolution phenomenon because of the low film solubility of the employed solutions. Moreover, in voltammetric cases, it is also shown that, when the reduction rate is sufficiently increased, recovery of the charge density in the reduction process always arrives at a minimum constant value, which seems to depend only on the selected metal and solution. All these facts are interpreted and discussed from the standpoint of the proposed disruption model. Finally, for voltammetric measurements, a method for reducing the disrupted film is proposed and applied to attain high reproducibility, also based on the disruption model.

In the case of galvanostatic experiments on Pb, it is shown that complete recovery of the whole formation charge density can always be achieved under a variety of reduction conditions. To this end, the only necessary condition is that the galvanostatic formation current density must be higher than the galvanostatic reduction current density. The same measurements are presently being applied to Zn to discover if these results are general or only applicable to Pb or to other specific metals. At present, it can only be stated that, in the case of Pb treated galvanostatically, the process can be totally reversible. This fact has important technological implications, for example, in the field of industrial batteries or atmospheric corrosion problems, which will be discussed elsewhere. In galvanostatic experiments, when the reduction rate is higher than the formation rate, again as in voltammetric experiments, the detected reduction charge density diminishes up to a minimum constant value, which is attained only at high reduction rates (as in voltammetry). A proposal put forward here explains it, also on the base of the disruption phenomena. Finally, based on the ideas advanced herein,



a method for reducing the disrupted film is also proposed and applied in galvanostatic experiments, achieving high levels of reproducibility with this technique too.

An important point is that, for Pb, the minimum film remaining at high reduction rates is the same whether the measurements are voltammetric or galvanostatic. This is an important support for the disruption model. All these facts indicate the generality of the phenomena discussed in this paper with respect to the disruption theory.

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