

Processes involved in charging of discharged lead-acid battery electrodes by pulse methods

I. Qualitative analysis for flat negative electrodes

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Abstract

In general, a relatively large part of the PbSO_4 of lead-acid battery electrode discharge products can be seen as particles at the end of the discharge and thus their reduction, on the negative electrode, or oxidation, on the positive electrode, must involve the dissolution of the Pb^{2+} . In this paper, the processes occurring on flat negative electrodes during the galvanostatic charge transients are studied in detail, especially in relation to where and how much the PbSO_4 and Pb^{2+} are reduced. The understanding of these processes is fundamental for the understanding of any pulse charging process. Thus, it is shown for a single discharge/charge cycle, that during the charging process a disruption of the PbSO_4 film, giving rise to a continuous glued non-disrupted film and to a disrupted film attached by surface tension forces to the electrode surface can occur. Further, it is shown that the amount of disruption depends on the charging current conditions and it decreases with decreasing charging currents. It is also demonstrated that the reduction of the Pb^{2+} dissolved from the disrupted particles takes place simultaneously to the reduction of the non-disrupted glued part of the film. On the basis of these facts, it is finally shown, for the case of multiple discharge/charge cycles, how the charge associated with the disrupted film changes with cycling and why and how it is possible to determine the amount disrupted PbSO_4 film formed.

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1. Introduction

1.1. Kinetic theories regarding discharge/charge mechanisms

Recently we have published a paper in which the two most different kinetic mechanisms for positive and negative plate electrodes were reviewed [1]. One was the solid-state model with disruption and recrystallization, based initially on a solid-state reaction for the formation of the film followed by its partial disruption and the dissolution/precipitation of the disrupted particles (recrystallization). The other model was the simple dissolution/precipitation mechanism, based always on the passage of the reaction through the Pb^{2+} in solution, followed by its precipitation as PbSO_4 particles. For the case of

the dissolution/precipitation mechanism, passivating films have been proposed taking into account the possibility of existence of micropores inside the film [2–4].

While the present paper is limited to flat electrodes, it should be noted that in the previous paper [1] the problem of a discharge in conducting porous electrodes was discussed, showing it must be related to a zone reaction mechanism, where any of the above kinetic mechanisms act only in the reaction zone, transforming an active region, consisting of the internal surface of spongy Pb or porous PbO_2 , into a final non-conducting discharged surface covered by the film products. The reaction zone moves from the external to the internal part of the plates. Based on these ideas, a battery plate can be seen as a system of interpenetrating materials of different conductivities (the active material and the solution inside the pores). These materials conduct the current in parallel, depending on the evolution of their relative resistivities and the resistivities of the corresponding interfaces. The idea of the reaction zone was also based on results obtained with galvanostatically discharged battery plates [5]. In this last study, before cutting the discharge current, the H_2SO_4 solution, even

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that inside the pores, was substituted by water, and the amount of PbSO_4 formed was analyzed, in different plates, for various discharge levels. This amount was compared, for each discharge level, with the equivalent amount formed when the substitution by water was omitted, and where higher amounts of PbSO_4 were detected. The result of that work was a demonstration of the existence of a zone-reaction mechanism in porous electrodes made of conducting materials that form non-conducting surface layers during discharge.

1.2. The solid-state model with disruption and recrystallization

To understand the kinetic mechanism of the discharge in the solid-state model with disruption and recrystallization, it is necessary to take into account that during formation of a film at a metal/solution interface [6], an inner continuous film forms which adheres to the substrate electrode surface due to the existence of the electrostriction forces (which counteract the disruption tensions provoked by the higher partial volume of the films), and an external disrupted film, attached to the electrode by superficial tension forces. The disrupted film occurs because of the loss (or inversion) of the forming electrical field inside the film, eliminating or varying the electrostriction forces. The electrostriction forces have been discussed in the passivity context by Sato and Okamoto [7], in order to explain the pitting potential.

The inner continuous part of the film can be directly reduced [6] by a solid-state reaction, by applying the appropriate electrical field to bring about the movement of the ions inside the film and the corresponding processes at the two film interfaces. On the other hand, the external disrupted film particles (nanoparticles), which suffer recrystallization to bigger ones, can only be reduced (negative electrode) or oxidized (positive electrode) under the correct potential or current electrode conditions, through a reducing or oxidizing dissolution mechanism. In these mechanisms, the metal ion is firstly dissolved and then, after diffusion and/or migration to the electrode surface, it is reduced or oxidized, depending on the electrode.

There have been several demonstrations of the presence of both the continuous adhered and disrupted films, after the electrochemical growth of a film on a metal [6]. Nevertheless, we will mention only one recent demonstration referring to the problem of Pb in H_2SO_4 [8]. The authors show, by a voltammetric technique on a flat Pb electrode in H_2SO_4 , in the PbSO_4 potential region, that for a given anodic sweep velocity v_a followed by various cathodic v_c , the cathodic charge density q_c is always equal to or lower than the anodic one, q_a . q_c is lower than q_a for $v_c > v_a$, it decreases with increasing v_c (for constant v_a), reaching a constant value of about 20 mC cm^{-2} at sufficiently high v_c . On the other hand, for $v_c \leq v_a$, q_c is equal to q_a within the experimental error. The question is: where has the remaining charge density associated with the PbSO_4 formation gone if, for the H_2SO_4 solution, it cannot be dissolved in the short time of the voltammetry? The PbSO_4 solubility is of the order of 10^{-5} M . The explanation is that the grown film has been partially disrupted. At the same time, the remaining voltammetric reduction

charge shows that some part of the film has been retained glued on the metal surface and thus, it has been able to be reduced directly through a solid-state reaction by the application of a convenient electrical field.

In the case of Pb or PbO_2 electrodes, the presence of disrupted film products and their recrystallization is the reason why the surface films on flat electrodes when are observed by electron microscopy, show disrupted structures [9] (one of the fundamental bases for the dissolution/precipitation models).

1.3. Problems with the simple dissolution/precipitation model

Several authors have taken the results from rotating ring-disk electrodes to argue in support of the simple dissolution/precipitation mechanism. Nevertheless, it is necessary to consider firstly that, when simple rotating disk electrodes are used, the dissolution/precipitation mechanism would imply that the current in the first anodic voltammetric sweep depend on the rotation. This has never been experimentally observed.

Further, in relation to the rotating ring-disc electrode, an aspect that has been disregarded [4,10,11] is the fact that, when the current in the disk is calculated from that in the ring (using the collection coefficient) at most only 5% of the experimental observed current in the disk is obtained. This wide discrepancy is a problem for the dissolution/precipitation mechanism as presently proposed. From the point of view of the solid-state mechanism with disruption and recrystallization, this only reflects the fact that during the formation of PbSO_4 film, its dissolution current would be higher than that in stationary conditions.

Associated with these problems there are some other aspects that have been disregarded and would need to be explained by a complete formulation of a simple dissolution/precipitation mechanism.

It has not been explained in the dissolution/precipitation mechanism how different current densities can give rise to distinct PbSO_4 crystal morphologies, if in some way, the dissolution must destroy the memory of the system. Finally, it has not been explained why regions of the lead surface remain free of film at the bottom of the PbSO_4 precipitate structures and how Pb^{2+} ions can pass through the pores between the PbSO_4 particles without being incorporated into the PbSO_4 walls, blocking the path.

In the light of problems identified above the results presented in this paper are discussed in terms of the solid-state reaction model followed by disruption and dissolution/precipitation (recrystallization).

1.4. The studied problem

From the point of view of the solid-state model with disruption and recrystallization, to understand pulse charge processes it is firstly necessary to understand when and how the reduction (negative) or oxidation (positive) of the continuous adherent film occurs by solid-state reaction and when and how the reduction or oxidation, respectively, of the disrupted film occurs through dissolution of Pb^{2+} . To do that, one fundamental question is, for

the negative electrodes, when and how reduction of continuous adherent PbSO_4 film and Pb^{2+} ions (which must be dissolved from the disrupted film particles into the solution between them) can be observed. The present study tries to answer these last questions for flat negative electrodes and results are given that support the solid-state model with disruption and recrystallization against the simple dissolution/precipitation model.

2. Experimental

The working electrodes were of high purity polycrystalline lead in the form of a cylinder embedded in epoxy resin, with an exposed flat area of 0.7 cm^2 of electroactive surface which was polished before each measurement. In all the experiments, the electrodes, after being polished with 600 emery paper, washed and dried, were introduced into the electrolyte cathodically polarized with an initial cathodic current density of 0.2 mA cm^{-2} . Under these conditions the electrode potential was monitored until it reaches the initial potential of -1.2 V . This initial procedure was followed to prevent any growth of PbSO_4 film, and at the same time, to minimize the hydrogen evolution reaction, which otherwise would produce bubbles interfering in the processes under study.

Two kinds of galvanostatic experiment were carried out. In the first, the electrodes were submitted to only one discharge/charge cycle. In the second, the electrodes were submitted to several discharge/charge cycles controlled by selected cutoff potentials.

In single discharge/charge cycle experiments, after establishing the above initial condition, the electrodes were submitted to an anodic discharge current density (i_d) up to the cutoff potentials of -0.7 V . At this moment, selected cathodic charge current densities (i_{ch}) were applied up to the hydrogen evolution reaction. In some experiments, between the anodic discharge and the cathodic charge stages, an interval of 4.5 s was established during which the electrodes were free to drift to their rest free potential.

In multiple discharge/charge cycling experiments, the electrodes were also prepared up to the initial condition, and then cycled with various discharge and charge current densities up to pre-selected anodic and cathodic cutoff potentials.

In several runs, to verify the accuracy of the potential/time results, an oscilloscope with memory was connected directly to the electrodes in the cell.

The reference electrode in all experiments was $\text{Hg}/\text{Hg}_2\text{SO}_4/4.6 \text{ M H}_2\text{SO}_4$ solution and all the potentials given are referred to this electrode. The solution used was always $4.6 \text{ M H}_2\text{SO}_4$, deoxygenated. The temperature was $25 \pm 2 \text{ }^\circ\text{C}$.

3. Results and discussions

3.1. Results from a single discharge/charge cycle

In Fig. 1a there is a typical galvanostatic transient on a flat Pb electrode for only one discharge current density (i_d). In Fig. 1b, various charging processes are plotted, with different charge current densities, i_{ch} , following the same previous complete dis-

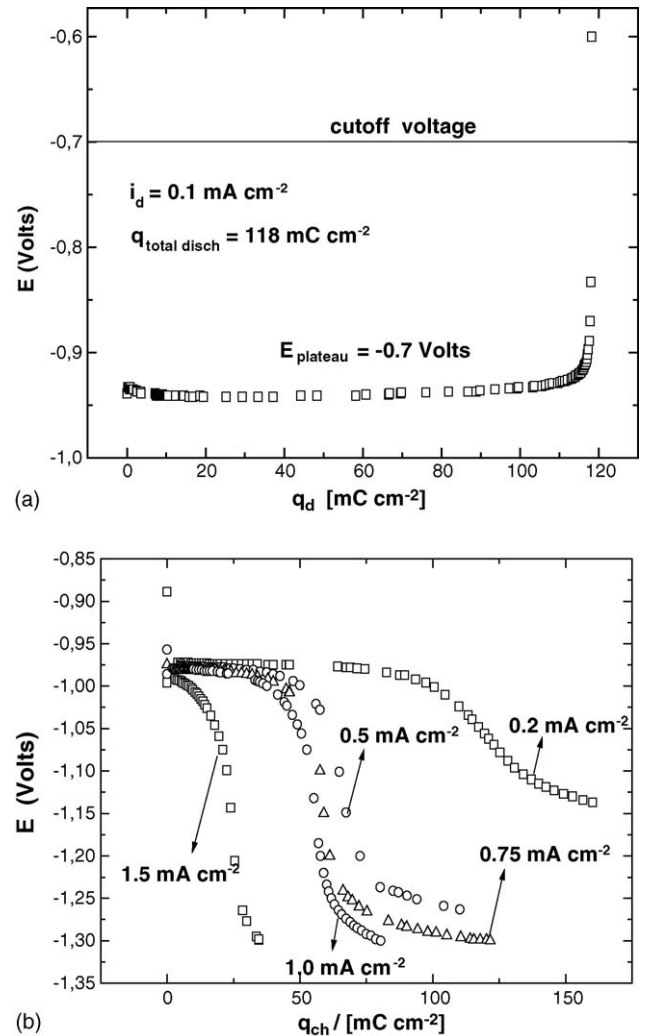


Fig. 1. Typical galvanostatic discharging (a) and charging (b) curves. Before each measurement, the electrode was polished and introduced cathodically polarized. Solution: $4.6 \text{ M H}_2\text{SO}_4$; reference electrode $\text{Hg}/\text{Hg}_2\text{SO}_4/4.6 \text{ M H}_2\text{SO}_4$.

charge, at an i_d of 0.1 mA cm^{-2} (that of Fig. 1a). The i_{ch} was varied in Fig. 1b from 0.2 to 1.5 mA cm^{-2} .

The discharge processes always show the nucleation phenomenon as an anodic peak in the initial part of the discharge (Fig. 1a), proving that there was no PbSO_4 at the beginning of the discharge. The observed total discharge density (q_d) is 120 mC cm^{-2} for this i_d .

The evolution of the charge density of recharge (q_{ch}) for different i_{ch} , after the same discharge process of Fig. 1a, can be seen in Fig. 2, derived from data in Fig. 1b. The q_{ch} depends on the i_{ch} . The observation that q_{ch} is lower than q_d , at i_{ch} higher than i_d , cannot be explained by dissolution of the PbSO_4 , due to its low solubility. Thus, where has the remaining of the PbSO_4 formed during the discharge gone? This can be answered by the disruption of the grown film giving rise to disrupted particles which cannot be reduced directly. The disruption depends not only on the growing conditions (the q_d depends on i_d in a way which is not discussed in the paper), but also on the reduction conditions, as can be seen in Fig. 2. For i_{ch} of the same order or lower than i_d , the q_d is practically all recovered and q_{ch} is equal

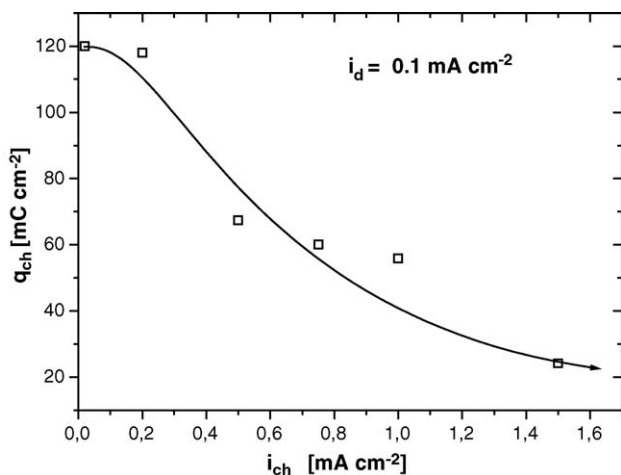


Fig. 2. Charge densities (from Fig. 1b) for the charging processes of identical discharge films vs. various discharge current densities. Data from Fig. 1b. Discharge current density i_d of 0.1 mA cm^{-2} (see Fig. 1a). Solution: $4.6 \text{ M H}_2\text{SO}_4$.

to q_d (there is no film disruption). When the i_{ch} becomes higher than i_d , the q_{ch} decreases, as the disruption increases.

An important point is that in the galvanostatic case, as in the voltammetric case [8], the q_{ch} falls to a constant value. These results are reinforced by those seen in Fig. 3, representing another slightly different condition. In this figure once again the q_{ch} becomes equal to q_d for i_{ch} equal or lower to i_d and decreases for i_{ch} higher than i_d , reaching a constant 20 mC cm^{-2} for very high i_{ch} .

The small decay of q_d detected in Fig. 3 with the increase in the number of experiments (data for increasing values of i_{ch} in Fig. 3) must be related to small variations (reduction in this case) of the electrode area with successive polishing, during the experiments. This shows that q_d can be used, for a flat electrode, as a normalizing factor for possible changes in real electrochemical area, when different measurements have to be compared.

Returning to q_{ch} , it should be noted that the values of constant q_{ch} for high i_{ch} in Figs. 2 and 3 are the same. This is in

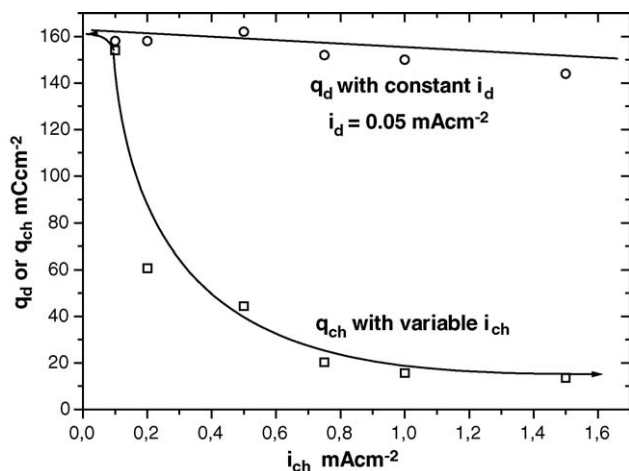


Fig. 3. Charge densities for discharge and charge processes vs. discharge current density, i_{ch} , for identical discharge films. $i_d = 0.05 \text{ mA cm}^{-2}$ and i_{ch} variable. Solution: $4.6 \text{ M H}_2\text{SO}_4$.

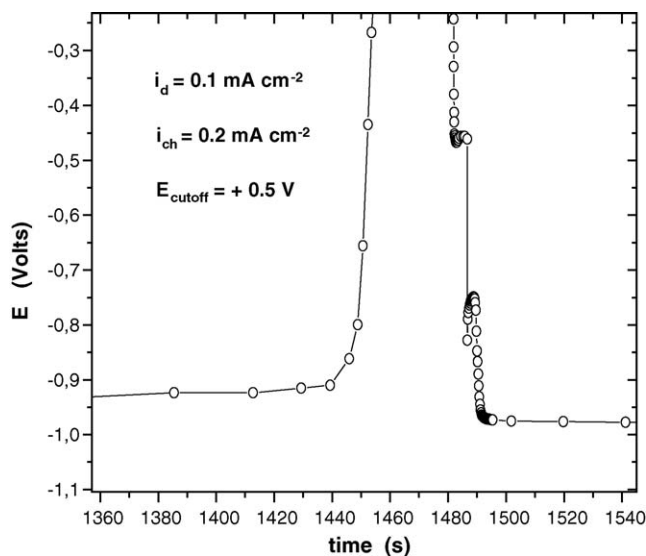


Fig. 4. Typical galvanostatic final stage of the discharge and initial stages of the charge during an E/t transient with 4.5 s of free potential between the discharge and the charge. Solution: $4.6 \text{ M H}_2\text{SO}_4$; reference electrode $\text{Hg}/\text{Hg}_2\text{SO}_4/4.6 \text{ M H}_2\text{SO}_4$.

agreement with the general behavior of passivity transients [6] and corresponds to a q_d of constant minimal remaining non-disrupted film. This occurs because at any electrode interface there always remains an inner potential difference and thus, a electrical field which, through electrostriction, would stabilize the same remaining film at the metal/remaining film/solution interfaces. This is an indirect demonstration of the stabilizing role of the electrostriction forces produced by electrical fields.

From the point of view of the solid-state model with disruption and recrystallization, an increase of the rate of reduction increases the amount of disrupted film which remains unreduced (see Figs. 1b, 2 and 3). This occurs because the increase in i_{ch} increases the point defect injection above the values which have been accepted by the film during its formation. This is one of the reasons that it is always convenient to execute the charging process at an equal or lower i_{ch} than the i_d . When the injection of defects produced by the passage of i_{ch} becomes slow enough (compared to those produced by the i_d as the film was formed), the disruption disappears.

The reduction of q_{ch} with increasing i_{ch} does not present difficulties for a qualitative interpretation in terms of the simple dissolution/precipitation mechanism. It can be attributed to the reduction in the amount of the Pb^{2+} recovered from the solution between the PbSO_4 particles. Nevertheless, the quantitative interpretation does present some problems, due to the low Pb^{2+} solubility and the slowness of the diffusion processes. Besides, there are two other problems for this theory. One is to understand the constancy of q_{ch} for low i_{ch} (equal or lower than i_d), taking into account the diffusion processes. The second is to explain why the q_{ch} becomes constant at high i_{ch} . Why does it not present an asymptotic approach to zero, as would be the case if the diffusion of Pb^{2+} at low concentrations is considered to be the fundamental basis of this process.

In Fig. 4 is shown a typical amplification of the end of a discharge process followed by the beginning of the charge process, between which has been added 4.5 s of free, rest potential. The rest potential is seen as a plateau at -0.45 V during the 4.5 s of free potential. When the application of i_{ch} an arrest is seen at -0.75 V, showing an initial cathodic potential peak, after which the potential falls to a final plateau for the reduction of the $PbSO_4$ continuous non-disrupted adherent film (discussed in Figs. 2 and 3), at -0.980 V. The problem to be discussed is what is the reason for the -0.75 V plateau? It may be due to the reduction of the Pb^{2+} formed by the dissolution of the disrupted particles or the result of the formation of a new phase beneath the $PbSO_4$ continuous adherent film, which must be reduced first. It must be beneath the $PbSO_4$ continuous film because the possible new phases (PbO , PbO_n or basic $PbSO_4$ phases) are not stable in the presence of 4.6 M of H_2SO_4 .

It is experimentally observed that the appearance of the arrest at -0.75 V depends on the cutoff potentials during the discharge being high enough. Nevertheless, this does not resolve the controversy. Both explanations (a new phase or Pb^{2+}) continue to be acceptable. The fact that resolves the controversy is the form of this plateau. If the free rest potential of the $Pb/PbSO_4$ film, in the presence of enough Pb^{2+} , is -0.45 V, a slow potential decay from this potential should be observed on application of the i_{ch} . This would be due to the time taking for the reduction of Pb^{2+} . Instead of that, what happens is an instantaneous fall of the potential from -0.45 V to the first arrest at -0.75 V, as can be seen in Fig. 4. This must correspond to a newly formed film. In the literature, there are papers pointing out this interpretation [12,13]. They attribute this process to the reduction of basic $PbSO_4$ underlying films, for some cutoff potentials, or to a PbO film for higher ones.

On the other hand, the evolution of potential during this first arrest at -0.75 V can be interpreted as nucleation and growth and some authors have pointed this out [14]. Nevertheless, it is very strange that the reduction of a lead compound on lead exhibits nucleation: the metallic lead is already present. An initial cathodic peak of an arrest, followed by a decrease in the overpotential, in a galvanostatic experiment (or a peak current in a potentiostatic one), may correspond typically to a process of a thin-film reduction through a solid-state mechanism [15]. At the beginning of the reduction process, the thin film is highly resistive: the point defects collapse at the two film interfaces and the point defects are then in very low concentrations. After the injection of point defects by the passage of current, the film growth and the ionic resistivity of the film decreases, as does the overpotential. Finally, the recombination of point defects makes the ionic resistivity increase again and then, the system seeks for a more cathodic potential, in the present case, in the direction of the $PbSO_4$ continuous adherent film reduction plateau, at -0.98 V (Fig. 4).

In any case, there is no Pb^{2+} reduction before the reduction of the $PbSO_4$ continuous adherent film and thus, this reduction must occur during or at the end of the reduction of the $PbSO_4$ continuous non-disrupted film. This is a very important point for the design of a pulse charging process.

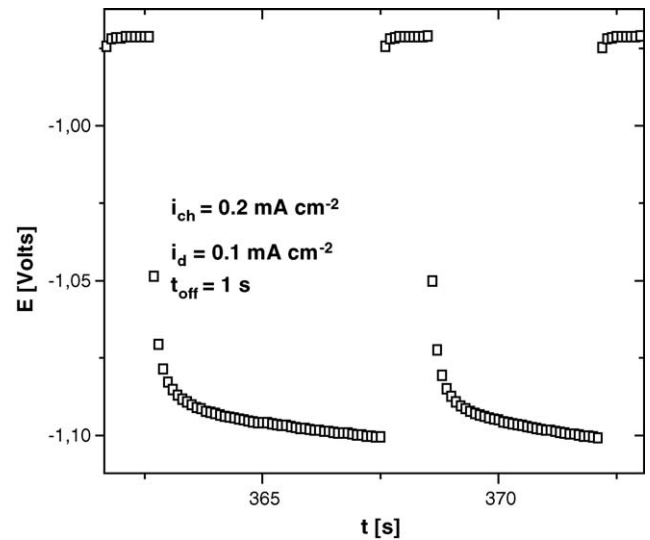


Fig. 5. Details of a galvanostatic transient. Different arrests for 1 s (t_{off}) of i_{ch} , in the middle of a charging process when the non-disrupted $PbSO_4$ film is under reduction. Firstly the electrode was totally discharged. Discharge current density i_d of 0.2 mA cm^{-2} . Anodic cutoff potential: -0.7 V. Charge current density i_{ch} of 0.1 mA cm^{-2} . Solution: 4.6 M H_2SO_4 ; reference electrode $Hg/Hg_2SO_4/4.6$ M H_2SO_4 .

To resolve the question of where the Pb^{2+} is reduced in Fig. 5 is shown the evolution of the potential if, during a given charging process, when the reduction of the continuous adherent film is occurring, the i_{ch} is stopped for 1 s, permitting the potentials to go to the free potential of the remaining non-disrupted $PbSO_4$ film (under the disrupted film). When the i_{ch} is reestablished, no arrest is seen in Fig. 5 before the plateau for the reduction of the remaining non-disrupted $PbSO_4$ film. In addition, the rest free potential in this case is found to be near -0.97 V, indicating the presence of $PbSO_4$ on the Pb electrode practically without Pb^{2+} . It is cathodic in relation to the -0.45 V of the free potential arrest of Fig. 4. This is why it shows that in this experiment there is no remaining appreciable concentrations of Pb^{2+} . It must be assumed that it has been already reduced, together with the non-disrupted $PbSO_4$ film already reduced. Thus, an important new conclusion is that it has been established that the Pb^{2+} , in the solution between the disrupted $PbSO_4$ particles, is reduced together with the non-disrupted continuous film and the new free rest potential comes from a $Pb/PbSO_4/H_2SO_4$ electrode.

3.2. Results from discharge/charge cycling processes

In Fig. 6a for i_d of 0.1 mA cm^{-2} and i_{ch} of 0.2 mA cm^{-2} and in Fig. 6b for i_d and i_{ch} equal to 1.5 mA cm^{-2} , in both cases for different cutoff potentials, the first several cycles of discharge/charge processes are shown. In both cases, it is clearly seen the reduction plateau of the $PbSO_4$ adherent non-disrupted continuous film at -0.777 ± 0.002 V for the low i_{ch} values (Fig. 6a) and at -1.086 ± 0.010 V for the high i_{ch} values (Fig. 6b), before the potential begins to shift to the hydrogen evolution reaction. These values cannot be compared with those of single cycles, because now the solution in front of the reducible film is that between the disrupted particles of $PbSO_4$.

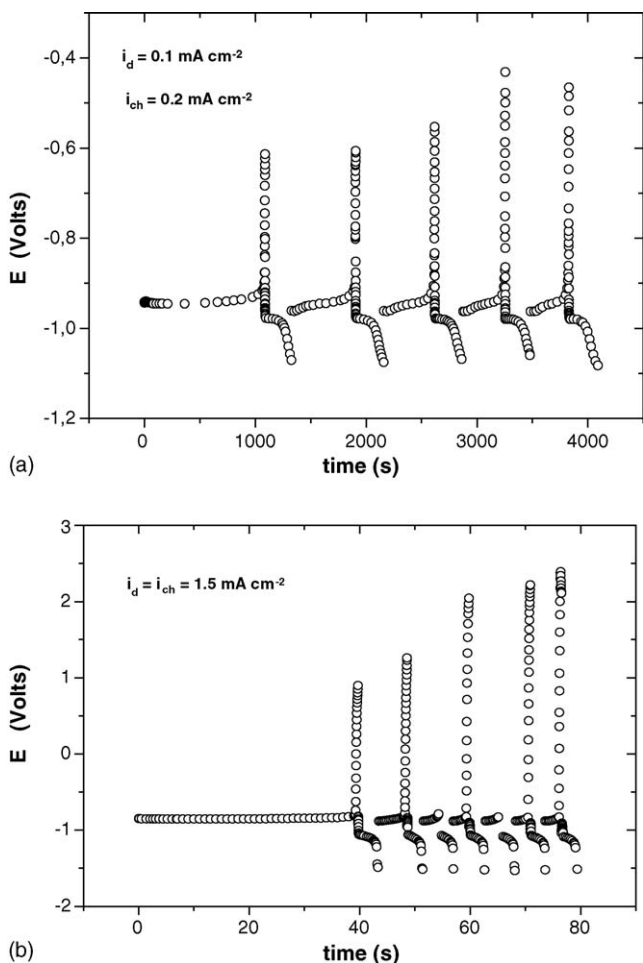


Fig. 6. Two typical E/t galvanostatic initial charge/discharge cycling for PbSO_4 film formation (discharge) and reduction (charge) on Pb. Charge/discharge conditions shown in the figures. Solution: 4.6 M H_2SO_4 ; reference electrode $\text{Hg}/\text{Hg}_2\text{SO}_4/4.6\text{ M H}_2\text{SO}_4$.

This solution must reach a stationary composition produced by the discharge/charge regime and the diffusion. It cannot be considered equal to the composition of the external solution during the experiments.

The interesting point derived from Fig. 6a and b is the evolution of the q_d together with that of q_{ch} . This can be seen in Fig. 7a and b for the two analyzed conditions (high and low i_d and i_{ch} values). From the differences in each cycle between q_d and q_{ch} , it is possible to calculate the accumulated disrupted charge related to the PbSO_4 disrupted film (the sum of the differences, in each cycle, between q_d and q_{ch}) for Fig. 7a and b, separately. These data give 47 mC cm^{-2} for Fig. 7a and 59 mC cm^{-2} for Fig. 7b. It is otherwise seen in Fig. 7a and b that for charging cycles of flat electrodes, the biggest difference between q_d and q_{ch} , which constitutes the charge related to the disrupted film, comes practically from the initial cycles and depends slightly on the discharge/charge process conditions and the involved times.

The growth of the disrupted film during successive cycles reaches a point at which the only process contributing to the discharge/charge cycle is associated with the continuous non-disrupted adherent film on the metal (the disrupted one reaches

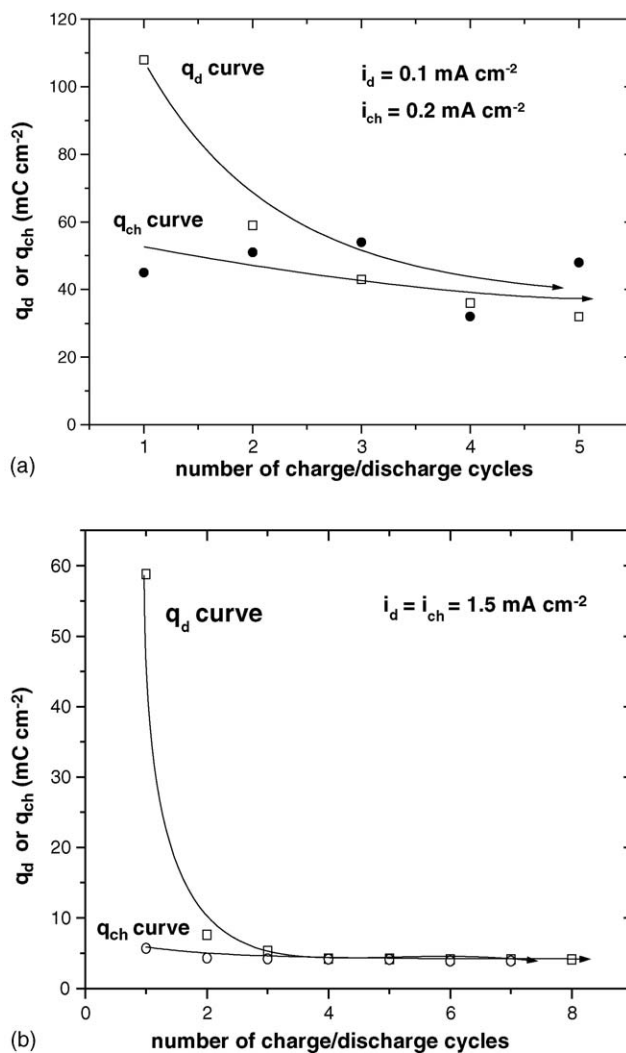


Fig. 7. Discharge and charge densities with the number of cycling. Data from Fig. 6a and b. Discharge and charge conditions in the figures.

a constant value associated with the above charge densities). This is the reason why in both cases (low and high i_d/i_{ch}) the q_d and q_{ch} converge to constant, different values, depending on the discharge/charge conditions. These constant values are about 40 mC cm^{-2} for low i_d/i_{ch} (Fig. 7a) and only 10 mC cm^{-2} for higher ones (Fig. 7b). These results are in total agreement with what is observed in the transient formation and reduction of passivating films, when the experiments are carried out in solutions in which the corresponding metal ions are highly insoluble [6]. This is the kind of situation to which the PbSO_4 formation process must be related, owing to the low solubility of the PbSO_4 in H_2SO_4 .

In Fig. 7a and b, the first discharges are bigger in charge density in the anodic parts of the cycles, because the disrupted film has not yet been formed, partially or completely. The way in which the formation of the PbSO_4 disrupted particle layer affects the discharge/charge cycling must be related to evolution of the solution composition between the disrupted particles during the cycling. This is different from that of the external solution, despite diffusion from outside. For the same reason, in

equivalent voltammetric experiments of formation and reduction of passivating films on metals, with solutions with very low solubility for metallic cations, it is well known that the i/E plots always reach stationary curves. It cannot be forgotten that the thickness to which an anodic film grows depends on the concentration of its forming anion in the forming solution [6] (here the SO_4^{2-} concentration in the solution between the disrupted particles).

4. Conclusions

Several phenomena observed during charging of negative flat electrodes have been analyzed and discussed. This was done employing the results of discharge/charge galvanostatic experiments with single or multiples cycles, with or without disconnecting the electrodes for several seconds to eliminate galvanostatic condition between discharging and charging, so as to permit the electrode to come to its free potential. The discussion is based on the solid-state mechanism with disruption and recrystallization and an understanding of the charging and discharging processes. Comments are made in parallel on the interpretation of these results in terms of the simple dissolution/precipitation model. In general, it is shown that the solid-state mechanism with disruption and recrystallization proposes better explanations for the observed facts.

When charging current densities are higher than the discharging ones, the charge recovered decreases with increasing charging current densities, reaching a minimal constant value. This is hard to explain from the point of view of a simple dissolution/precipitation model. The solid-state model with disruption and recrystallization, however, provides an easy understanding of the phenomenon by differentiating between an inner continuous PbSO_4 adherent film on the metal, stabilized by electrostriction forces and which can be reduced directly by high electrical-field mechanisms, and an external PbSO_4 disrupted film, which suffers recrystallization processes and can only be reduced by the dissolution/precipitation mechanism over much longer times. The fall in recover charge density with rising charging current densities is attributed to a higher level of disruption during charging of the film formed during the previous discharging.

On the other hand, for an identical discharge process, it is shown that in the case of charging current densities equal to or lower than the previous discharging current density, the whole discharge density can be recovered. This result is also hard to

explain through a simple dissolution/precipitation mechanism, but this can be easily done by the solid-state model with disruption and recrystallization, with the idea of the non-disruption of the previously grown film.

Still, the experiments with single discharge/charge cycle, with interruption of the current before charging, show the possibility of appearance of a plateau before the reduction of the continuous non-disrupted film. It is demonstrated that this plateau cannot be attributed to the reduction of the Pb^{2+} in solution between the disrupted PbSO_4 particles. It is demonstrated that these Pb^{2+} ions are reduced in parallel with the continuous non-disrupted adherent PbSO_4 film. The plateau in question is related to the reduction of a film formed at the Pb/PbSO_4 interface of the PbSO_4 continuous adhered film.

Finally, analyzing the results of multiple discharge/charge pulses, it is shown and discussed how (and how much of) the disrupted PbSO_4 film is formed in this type of experiment and how the solid-state model with disruption can explain these results, opening a way to development of pulse charging methods.

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