

Short communication

Early stages of the lead-acid battery discharge

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Received 1 May 2004; accepted 8 June 2004

Available online 28 July 2004

Abstract

New electrochemical investigations of the Pb/PbO₂/PbSO₄ electrode are reported. In this study we focus on two related phenomena: an anodic peak that appears on cathodic sweep, which we regard as a reactivation peak and a voltage dip that appears in galvanostatic discharges, commonly known as “coup de fouet”. It was possible to demonstrate that the commonly accepted interpretation for the “coup de fouet” as PbSO₄ nucleation over PbO₂ surface is incorrect. From the comparison between galvanostatic and voltammetric experiments, the connection between the “coup de fouet” and the reactivation peak is elucidated and a model that explains the overall behavior is proposed. © 2004 Elsevier B.V. All rights reserved.

Keywords: Lead-acid batteries; “Coup de fouet”; Reactivation peak; State-of-charge; State-of-health; Grid corrosion

1. Introduction

Stationary applications of rechargeable batteries have received increased attention as the demand for uninterruptible power supply (ups) and remote area power supply (raps) expands. The fact that the lead-acid battery has a low cost and accumulates over 100 years of technological development make it the most attractive option among several battery types. To assure the reliability of the system, an important requirement in ups and raps applications, continuous monitoring of the battery state-of-charge and state-of-health is necessary. The development of simple and “in situ” electrical estimation of these parameters is an important technological challenge, which has stimulated new investigations about the electrochemistry of the lead-acid system [1–6].

A great number of papers have correlated the electrical response of lead-acid batteries with physical and chemical transformation into the active material, grids and interfaces between them [7–17]. The main processes are now well characterized but some details remain unclear. One interesting point about voltammetric response, which is a subject of discussion in the literature, is an anodic peak that appears only on cathodic sweep (so we refer to it as reactivation peak) before the PbO₂ reduction to PbSO₄. Different explanations to the appearance of this reactivation peak have been proposed [18–23]. The most accepted interpretation attributes the reactivation peak to the lead oxidation, but why this

oxidation does not occur during the anodic sweep is still an open question.

Another electrical response, which has received attention in some recent publications, is a voltage dip that occurs in the start of the discharge and is commonly known as the “coup de fouet” [24]. The “coup de fouet” appears only if a fully charged battery is discharged which has led to the assumption that the PbSO₄ nucleation on the PbO₂ surface causes the dip [25,26].

Both the reactivation peak and the “coup de fouet” occur in the initial stages of the discharge before PbSO₄ formation and seem to be related. We investigate both processes in a variety of experimental conditions and explain the connection between them in this paper.

2. Experimental

A conventional three electrode cell was used. The working electrode was a Pb–2.5%Sb rod with 0.038 cm² of exposed geometrical area, mechanically polished with 600-grit emery paper. All potentials were measured against the Hg/Hg₂SO₄/H₂SO₄ reference electrode in the same concentration of the working solution. The counter electrode was an industrial negative plate cut out with about 4 cm² of geometrical area. All solutions were prepared with analytical grade sulfuric acid and ultra-pure water. Electrochemical measurements were performed by a Gamry® PC4-300 potentiostat/galvanostat.

In some experiments, an electrodeposited PbO₂ electrode was used. The PbO₂ deposition on carbon electrode was

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made through five voltammetric cycles between 0.4 V and 1.6 V (versus Ag/AgCl) in a 0.02 M $\text{Pb}(\text{NO}_3)_2$ and 0.165 M HClO_4 solution (the last cycle was interrupted after the anodic run).

Before the start of the voltammetric experiments, the lead electrode was reduced at the potential of hydrogen evolution for 10 min. Triangular sweep voltammetry (TSV) with different sweep rates (1 mV s^{-1} – 50 mV s^{-1}), different cathodic and anodic limits and several H_2SO_4 concentrations (0.05 M–5 M) were performed. In order to investigate the anodic process in the oxygen evolution region, a modification of the TSV experiment was implemented. In this experiment, after the anodic sweep, the potential was maintained constant in the upper limit for a predetermined time interval before the start of the cathodic sweep (trapezoidal sweep voltammetry, TpSV).

Galvanostatic charge/discharge experiments were performed on Pb/PbO₂ electrodes with different charge/discharge currents and several H_2SO_4 concentrations (0.05 M–5 M). The Pb/PbO₂ electrodes were obtained by Pb electrode oxidation through five voltammetric cycles between 0.6 V and 1.6 V (the last cycle was stopped after the anodic run). Before voltammetric oxidation, the Pb electrode was polarized in the hydrogen evolution potential for 10 min.

Since the occurrence of the “coup de fouet” depends on the charge state of the electrode, preliminary experiments were conducted to establish the influence of overcharge in the magnitude of the voltage dip. We were particularly interested in the difference between the discharge plateau potential and the minimum potential on the dip, as sketched in Fig. 1 (for the sake of conciseness, we refer to the minimum potential as dip potential and to the difference between the plateau and the minimum potentials as dip overpotential).

Fig. 2 summarizes the results obtained, showing that a great overcharge of about 800% (approximately 300 mC in this case) is necessary for the occurrence of the “coup de fouet”. At greater overcharge than this threshold value the

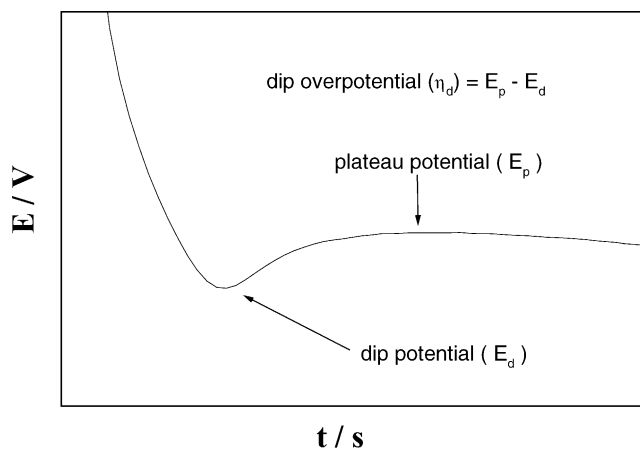


Fig. 1. Detail of the potential transient of a Pb/PbO₂ electrode galvanostatic discharge showing the “coup de fouet”.

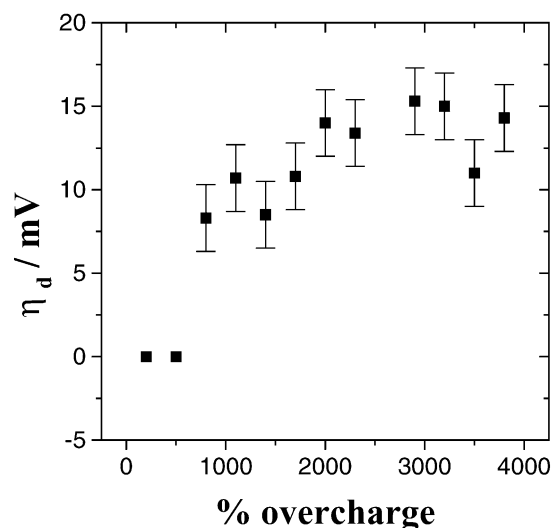


Fig. 2. Dip overpotential in galvanostatic discharges at 26.3 mA cm^{-2} in $0.86 \text{ M H}_2\text{SO}_4$ vs. overcharge.

dip overpotential is practically independent from the overcharge. As a constant overcharge is maintained, repetitive galvanostatic discharges were realized and the reproducibility of the dip overpotential was estimated in $\pm 2 \text{ mV}$.

3. Results and discussions

3.1. Galvanostatic discharge

Several authors attribute the “coup de fouet” to the nucleation of PbSO₄ on PbO₂ surface in completely charged electrodes [25,26]. Thus, the overcharge required to observe the phenomenon is explained as we realize that it is necessary to eliminate the PbSO₄ completely, which otherwise will act as a nucleation site, suppressing the nucleation overpotential.

That being the case, we must analyze the potential transients on the basis of the nucleation and growth theories. Roughly speaking, we must identify the potential drop with the PbSO₄ supersaturation to form critical nuclei and the recovery of the potential after the minimum with the lowering of the current density due to the nucleus growth. Similarly, we realize that as nuclei collide, the reaction area becomes constant and, consequently, the plateau potential is attained. Actually, we would expect a further decaying in potential because the reaction area diminishes when the nuclei coalesce, but this behavior is never observed.

Fig. 3a shows the initial potential transients in several galvanostatic discharges with current densities from $0.4 \mu\text{A cm}^{-2}$ to 30 mA cm^{-2} . Clearly, the dip potential and the plateau potential shift cathodically as current density increases. As can be seen in Fig. 3b, the dip potential drop is larger, indicating an additional polarization. The dip overpotential is plotted against discharge current density in Fig. 3c. In Fig. 3d the charge until the plateau in the final of the dip is plotted against the discharge current density.

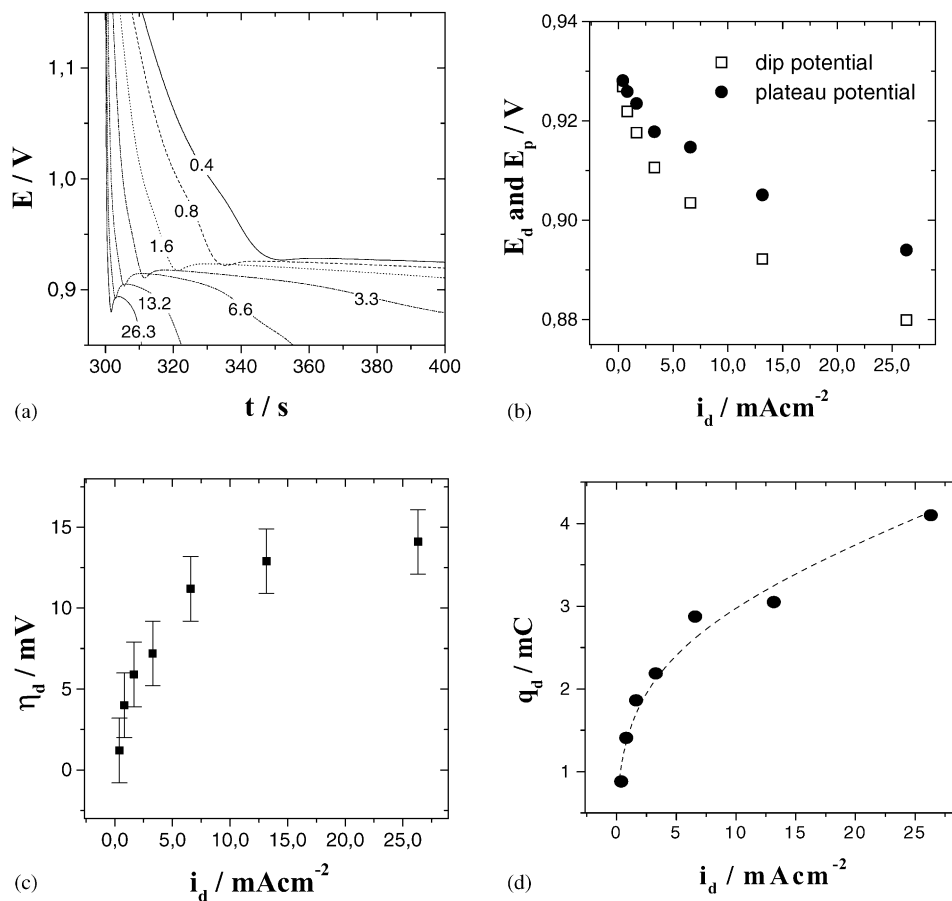


Fig. 3. Galvanostatic discharges of the Pb/PbO₂ electrode at several current densities in 0.86 M H₂SO₄. (a) Potential profiles. Numbers over the lines indicate the discharge current density in mA cm⁻². (b) Dip potential and plateau potential vs. discharge current density. (c) Dip overpotential vs. discharge current density. (d) Total dip charge vs. discharge current density. The line is a guide for the eye.

Considering the results in Fig. 3c, it is reasonable to suppose that, as current increases, due to the higher overpotential, a large number of PbSO₄ nuclei is formed leading to smaller PbSO₄ crystals. Sauer and Garche [27] who propose that the size of PbSO₄ crystals could be controlled by initial current discharge make a similar point. Nevertheless, the higher the number of PbSO₄ crystals the lower the amount of charge evolved until the coalescence of the nuclei. Therefore, we must expect that as current density increases the total charge of the dip decreases, but in Fig. 3d we observe the opposite behavior.

In order to study the concentration effects in dip overpotential, the experiments reported in Fig. 3 were repeated with different H₂SO₄ concentrations in the 0.5 M–5 M range. The general trends observed were the same for all concentrations and did not differ significantly from that showed in Fig. 3. Fig. 4 collects the results for some concentrations. In Fig. 5 the dip overpotential is plotted against H₂SO₄ concentration for some discharge current densities. Again, drawing on the nucleation theories, we must expect that, for a constant current density, the minimum in overpotential coincide with the maximum in the PbSO₄ solubility (about 1 M H₂SO₄). Con-

trasting this, Fig. 5 shows a decreasing overpotential until 3.2 M. It is worth to mention that the maxima H₂SO₄ conductivity is at 3.2 M, indicating that the potential drop in the “coup de fouet” is mainly determined by the iR drop in electrolyte. All of the above considerations must be viewed with caution, once the porosity of the electrode and the dielectric nature of the PbSO₄ complicate the analysis.

A most conclusive result is obtained when PbO₂ electrodeposited on carbon is discharged. Fig. 6 shows typical discharge curves for this kind of electrode where the “coup de fouet” is not observed. Several discharge currents and H₂SO₄ concentrations are explored without the occurrence of the “coup de fouet”. Therefore, the “coup de fouet” is associated with a process occurring in the Pb/PbO₂ interface. Consequently, the idea of nucleation over the entire PbO₂ surface determining the final PbSO₄ crystal size must be abandoned.

In order to explain the overcharge required to observe the “coup de fouet” (see Fig. 2) we must propose a new model once the PbSO₄ elimination hypothesis must be discarded. During overcharge, the substrate oxidizes by a solid state mechanism involving a PbO intermediate [16,17].

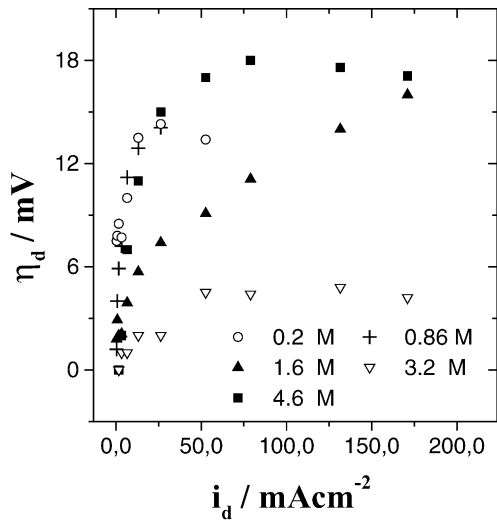


Fig. 4. Dip overpotential vs. discharge current density for several H₂SO₄ concentrations.

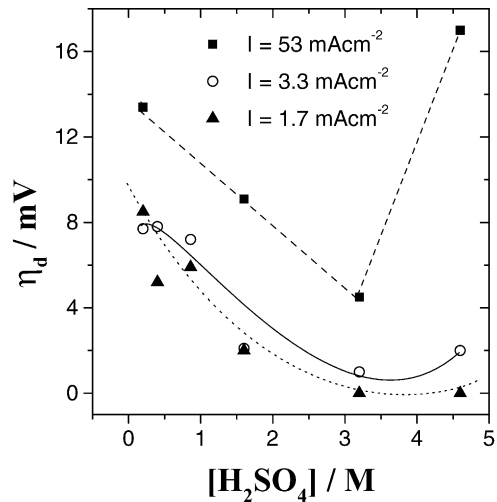


Fig. 5. Trough overpotential vs. H₂SO₄ concentration for several current densities. The lines are guides for the eye.

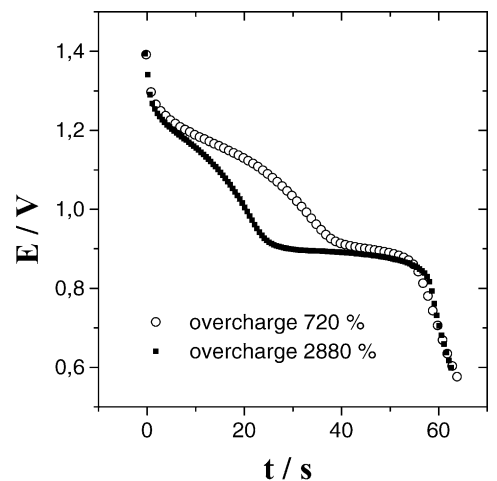


Fig. 6. Typical discharge potential profiles for electrodeposited PbO₂.

Consequently, the PbO₂ layer formed is morphologically distinct of the PbO₂ formed by PbSO₄ oxidation, which occurs via dissolution–precipitation mechanism. Therefore, after overcharge, the electrode presents two PbO₂ layers: an external and porous layer originated from PbSO₄ oxidation and a barrier layer recovering the substrate. The discharge would initiate locally in the later and the potential drop would be determined by the larger current density and by the *iR* drop in electrolyte inside the pores. Once the PbSO₄ is formed, the local electric resistance increases and the discharge gradually extends to the entire PbO₂ surface. Blood and Sotiropoulos [5] have proposed a similar mechanism to explain the appearance of some shoulders resembling “coup de fouet” in discharges obtained with a small probe pressed onto a restricted area of a positive plate. According to the authors, a partial local discharge under the probe area occurs initially, spreading over the entire plate surface as PbSO₄ is formed.

This interpretation apparently contradicts the classical papers of Takehara et al. [28,29], which established that the PbSO₄ is formed in the Pb/PbO₂ interface only in the final of deep discharges. Nevertheless, these authors have studied electrodes in which PbO₂ are electrodeposited or obtained by oxidation of the 3PbO·PbSO₄ pasted onto the Pb surface. In these arrangements the PbO₂ is not resulting of the direct Pb oxidation and, consequently, the barrier layer, firmly adhered and in close electrical contact with the substrate, is absent.

Another important result appears in Fig. 7. When consecutive charge/discharge cycles are applied, maintaining a constant overcharge, the dip potential shifts cathodically. The increase of the discharge time observed in the Fig. 7 is caused by the increase in the amount of the PbO₂ due to the substrate oxidation during overcharge. Therefore, the actual discharge current density decreases and, consequently, the plateau potential shifts to less cathodic potentials. Despite this, the dip overpotential increases, which is not consistent with a nucleation mechanism.

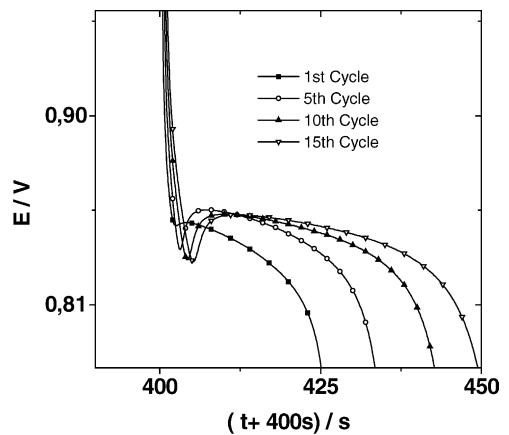


Fig. 7. Discharge potential profiles obtained in consecutive discharges maintaining constant overcharge (800%). *i_d* = 16 mA cm⁻². [H₂SO₄] = 0.86 M.

Pascoe and Anbuky [24] showed that magnitude of the “coup de fouet” (the dip overpotential in our terminology) is controlled by several experimental conditions including the battery state-of-health. This fact indicates that the phenomenon observed in Fig. 7 is complex and claims for new investigations. The central point here is that the dip overpotential is controlled not by the real current density (as can be seen in Fig. 7) but by the geometrical current density (as can be seen in Fig. 3). This fact is consistent with our model once we suppose that the “coup de fouet” is determined by the reduction of the PbO_2 barrier layer film, which recover the substrate surface.

3.2. Voltammetric discharge

Fig. 8 shows the reactivation peak. Clearly, when the anodic sweep goes throughout the peak region, the electrode surface is completely passivated. It is normally accepted that a PbO film formed below PbSO_4 holds the protective character responsible for this passivation [30,31]. In the cathodic sweep, the reactivation peak appears just before the PbO_2 reduction to PbSO_4 .

Czerwinski et al. [22] advocate that this peak is always preceded by a cathodic peak attributed to the reduction of some part of the PbO_2 formed at high anodic potentials. According to the authors, the formation of PbSO_4 , which has a much greater molar volume than PbO_2 , generates cracks on the surface layer, exposing a bare metal surface. Some authors mentioned that the exposing of metal substrate is determined by pH changes in the interior of the passive film [15,30]. We believe that the mechanism that leads to the

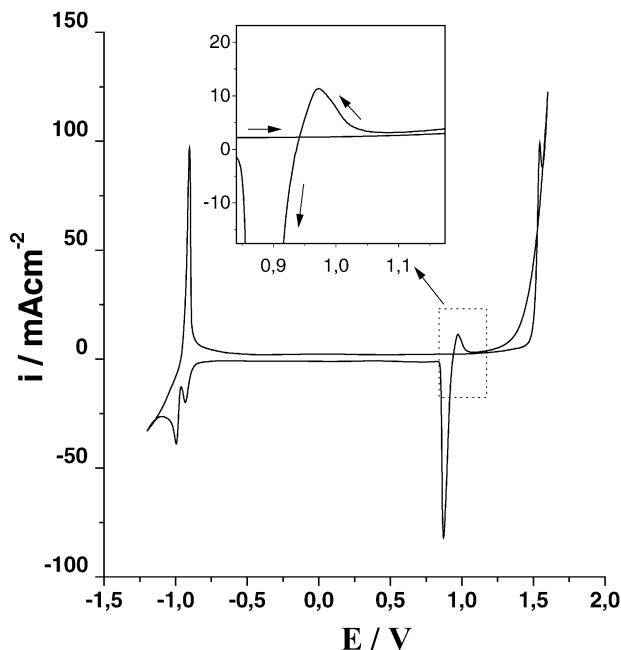


Fig. 8. Typical voltammogram for Pb–2.5%Sb electrodes in 0.86 M H_2SO_4 solutions. The inset shows reactivation peak region magnified.

exposure of the metal substrate is more complex and must account for the multi-layer structure of the films formed during anodic sweep.

We have investigated the reactivation peak under several experimental conditions, varying anodic and cathodic potential limits, H_2SO_4 concentrations and sweep rates. The peak dependence with the experimental parameters we have encountered was the same found in reference [22], but we have not observed any cathodic peaks before the reactivation peak.

Fig. 9a shows results of TpSV performed with different potentiostatic polarization times in 1.4 V. We found a complex behavior of the reactivation peak current density (i_r) regarding the polarization time. In Fig. 9b both the current transient during potentiostatic polarization and i_r (right y-axis) are plotted. It is interesting to note that the alternating increasing and decreasing pattern of the current transient in potentiostatic polarization is accompanied by i_r , suggesting that the reactivation of the substrate is connected with the processes that occur during anodic polarization in a complex manner. At greater polarization times, the current in potentiostatic transient increases monotonically and the reactivation peak current density begins to decrease. This indicates that, at that time, the passivation film has been partially removed and the lead substrate has been partially oxidized. We expect that at high anodic potentials this process will be completed and the reactivation peak disappears. In Fig. 10 we have observed results of TpSV performed with different potentiostatic polarization times in 1.6 V. As shown in this figure, the current in potentiostatic polarization increases monotonically and the reactivation peak current density decreases toward zero, showing that the substrate is completely oxidized at high anodic potentials. According to Bullock [16,17] this oxidation occurs via solid-state mechanism. As oxidation advances the t - PbO layer between Pb and PbO_2 is narrowed until a stationary thickness is attained. Such stationary state occurs because the rate of PbO to PbO_2 conversion equals the rate of Pb to PbO conversion, owing to the oxygen transport limitation throughout the PbO_2 barrier layer.

If the interpretation of the “coup de fouet” described in Section 3.1 is correct, we must expect that, as the barrier PbO_2 layer is formed and the reactivation peak disappears, the “coup de fouet” appears. In order to verify this hypothesis we repeated the anodic part of the experiments reported in Fig. 10, adding a galvanostatic discharge immediately after the potentiostatic polarization. In Fig. 11 the dip overpotential observed in these galvanostatic discharges has been plotted against the time of potentiostatic polarization. The reactivation peak current densities observed in Fig. 10 have also been plotted (right y-axis) for comparison. Clearly, just when the reactivation peak vanishes, the “coup de fouet” emerges. Therefore, we can assert that the previous formation of a PbO_2 layer on the lead substrate is a necessary condition to the appearance of the “coup de fouet”.

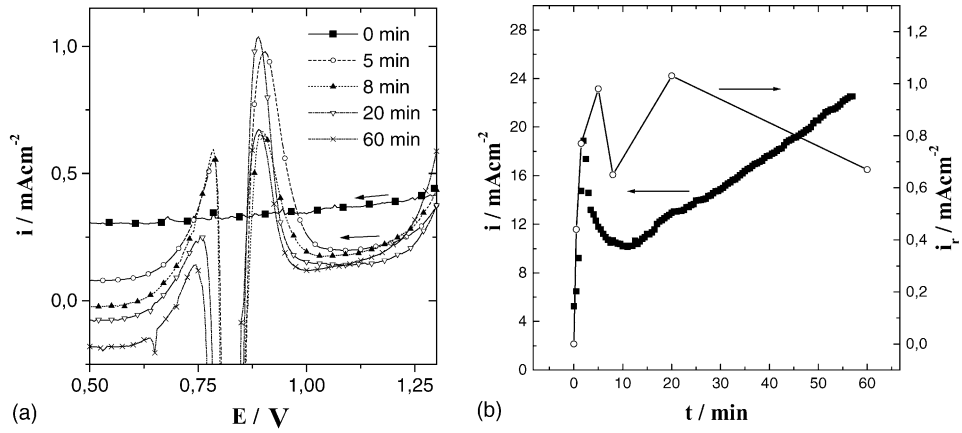


Fig. 9. Results of TpSV in 0.5 M H_2SO_4 showing the influence of the potentiostatic polarization time (1.4 V) on reactivation peak. (a) Detail of the voltammograms in the reactivation peak region for several polarization times. (b) Current transient during potentiostatic polarization (left axis) and reactivation peak current density (right axis) vs. polarization time.

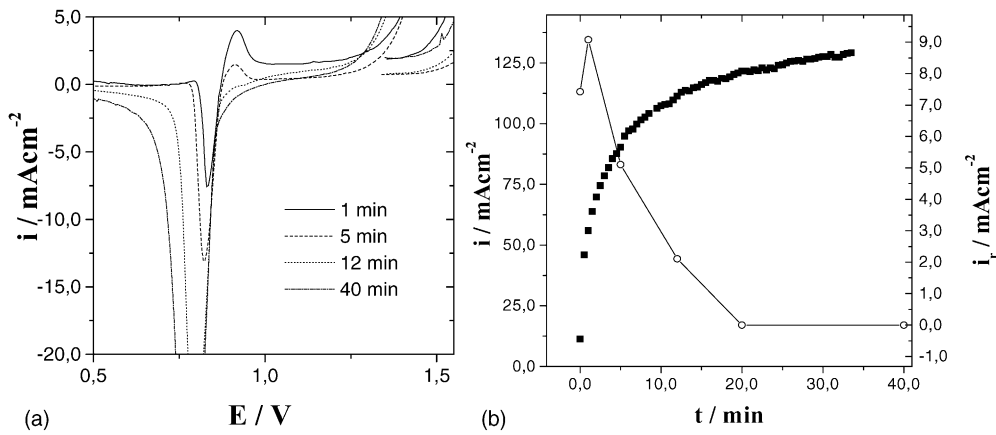


Fig. 10. Results of TpSV in 0.5 M H_2SO_4 showing the influence of the potentiostatic polarization (1.6 V) time on reactivation peak. (a) Detail of the voltammograms in the reactivation peak region for several polarization times. (b) Current transient during potentiostatic polarization (left axis) and reactivation peak current density (right axis) vs. polarization time.

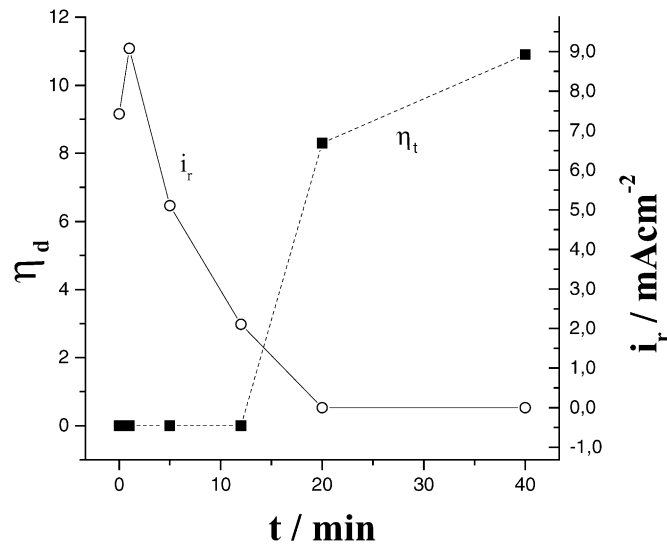


Fig. 11. Dip overpotential in galvanostatic discharges (left axis) and reactivation peak current density in voltametric discharges (right axis) vs. potentiostatic polarization time.

4. Conclusions

The present study shows that the commonly accepted interpretation of the “coup de fouet” as PbSO₄ nucleation over PbO₂ surface must be abandoned. It was demonstrated that the “coup de fouet” only appears when a PbO₂ barrier layer on the Pb substrate is formed. A qualitative model to explain this phenomenon has been proposed with the following main features. When the Pb/PbO₂ electrode is overcharged, a barrier layer firmly adhered and in close electrical contact with Pb substrate is formed. When discharge starts, the first PbO₂ to be reduced is that of this layer. As PbSO₄ is formed the discharge spreads over the entire PbO₂ surface. The formation of PbSO₄ causes the rupture of the barrier layer due to the volume variations and a new overcharge is required to observe the “coup de fouet”.

Acknowledgements

FINEP and Fundação Araucária financially supported the research. C.P. Oliveira wishes to express gratitude to CNPq for her scholarship.

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