

Electrochemical behavior of lead in sulfuric acid solutions

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Abstract

The electrochemical behavior of the lead electrode has been studied by cyclic voltammetry (CV) in sulfuric acid solutions, with concentrations ranged from 0.05 to 5 M. Also, the effect of a sweep rate, the range of potential polarisation and temperature has been examined. Special attention has been paid to unusual anodic processes, i.e., “anodic excursion” peaks that accompany the main reduction peak. The presence of a small, and previously unrecognized cathodic peak, preceding “anodic excursion” peaks, has been documented. Since all these peaks appear on the CVs only when the electrode potential is cycled in a wide potential range, limited by hydrogen and oxygen evolution, it has been proposed that they are related to the reduction of the lead dioxide to the bare metal, occurring at high negative potentials. The presence of a small reduction peak preceding “anodic excursion” peaks, as well as the presence of the main reduction peak of the lead dioxide has also been related to the exposure of the bare metal. When the lead dioxide, formed at high positive potentials, is reduced ($\text{PbO}_2 \rightarrow \text{PbSO}_4$), a large increase of the molar volume is expected and, as a result, the surface cracks, exposing the bare metal. These parts of the surface are then oxidized in “anodic excursion” peaks. To repeat these redox processes, the electrode has to be reduced again at high negative potentials, i.e., at the conditions when reduction to the metal occurs. The CVs performed only in a positive potential range confirmed that the reduction of PbO_2 to PbSO_4 , which follows the formation of PbO_2 , is not related to the “anodic excursion” peaks and it also means that no cracks of the surface occur, as long as the potential cycling of the electrode to high negative potentials, and the resulting reduction to the metal, are avoided. Therefore, when the lead electrode is used as a positive electrode in a battery, no corrosion due to the exposure of the bare metal is expected. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Although the behavior of the lead electrode in sulfuric acid solutions has been studied for almost 150 years, some of the surface processes are still not fully understood and are the subject of discussion in the literature. One of the curiosities of the redox reactions of the lead electrode is the appearance of small oxidation peaks that accompany the main reduction process, i.e., the reduction of the lead dioxide to lead sulfate [1–14]. These small anodic peaks, sometimes [3,4] called “anodic excursion” peaks, appear either before [2,8] or after [3,4] the main reduction peak

and depend significantly on the conditions of the experiment.

The presence of the “anodic excursion” peaks has been explained in the literature in many different ways [1–14]. At the beginning of the 1970s the appearance of the anodic peak at the tail of the main reduction peak was attributed by Panesar [1] to the formation of tetravalent lead compounds in 5 M H_2SO_4 . A few years later, Sunderland [2] found that the “anodic excursion” peak is visible in cyclic voltammetry (CV) experiments before the main reduction peak. He postulated that this oxidation reaction is due to water oxidation by Pb^{3+} species generated during surface reduction of PbO_2 . This view was supported by Fletcher and Matthews [3], who performed photoelectric experiments and showed that the formation of “anodic excursion” peaks is not accompanied by the photocurrent, and, therefore, might be related to the photoinactive Pb(III)

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species. Then, Deutscher et al. [4] proposed that the “anodic excursion” peaks, situated on the CVs obtained in 5 M H_2SO_4 after the main reduction peaks, are related to the reduction reaction, in which β -lead oxide is reduced to lead sulfate. This reaction is accompanied by a large increase of molar volume, from 25 cm^3/mol for $\beta\text{-PbO}_2$ to 48 cm^3/mol for PbSO_4 . Such change in the molar dimensions of the surface layer might generate cracks on the electrode surface and the exposure of the metallic lead, which is instantly oxidized by sulfuric acid, giving rise to the “anodic excursion” current. Similarly, Danel and Plichon [12] interpreted the presence of these anodic peaks as due to the corrosion of the Pb sublayer. They found that the position of these peaks does not change with the concentration of sulfuric acid in the range from 3.6 to 8.2 M. Also Laitinen et al. [5,6] studies of the lead electrode in 4.5 M H_2SO_4 pointed to the possible oxidation of lead and/or partially oxidized lead in the “anodic excursion” reactions. Similarly, Mattesco et al. [7] explained the presence of unusual oxidation peaks as due to partial oxidation of lead to PbO_2 , probably to basic lead sulfate.

Recent papers on the behavior of the lead electrode in sulfuric acid solutions pointed out [8–10] that both “anodic excursion” peaks, one occurring before and the other after the main reduction peak, can be seen on cyclic voltammograms at certain experimental conditions. Metikoš-Huković et al. [8] observed two “anodic excursion” peaks during lead polarisation in 0.5 M H_2SO_4 and attributed the presence of the anodic peak following the reduction reaction as due to the process $\text{Pb}, \text{PbO}_2 \rightarrow \text{PbSO}_4, \text{PbO}_2$, i.e., the oxidation of metallic lead, but the presence of the preceding anodic peak was not explained. In fact, it is difficult to explain the occurrence of this preceding anodic reaction as due to the cracks in the sulfate layer, formed during the reduction of lead dioxide to the sulfate, since the reduction has not commenced yet. Yamamoto et al. [9] have studied the “anodic excursion” reaction in a wide range of sulfuric acid concentrations (0.5–6.0 M) and in various potential regions of electrode polarization [10]. They found that in relatively dilute sulfuric acid solutions (> 1.0 M), the “anodic excursion” peaks are situated before the PbO_2 reduction and in concentrated acidic solutions the anodic peak appears after the reduction process. They also found the relationship between the appearance of “anodic excursion” peaks and the presence of sulfates generated on the lead surface [10]. These authors, as well as Sunderland [2], did not find any sweep rate dependence of the placement of the “anodic oxidation” peaks. Again, the presence of the anodic peak, situated before the reduction peak, has not been accounted for.

Various reports on the position of the “anodic oxidation” peaks versus the main reduction peak, as well as different opinions on the mechanism of the process, call for regular and complex studies of the behavior of lead electrode in sulfuric acid solutions with respect to the following experimental variables: sulfuric acid concentra-

tion, sweep rate in cyclic voltammetric experiments, range of potential polarization and temperature.

2. Experimental

The working electrode was a lead wire (99.99% purity, 0.5 cm^2 geometric area). Before the experiment, the electrode was mechanically polished with abrasive paper (P 500 and P 1000), washed in acetone and thoroughly rinsed in triply distilled water. Before the start of the CV experiments, i.e., prior to each run, the lead electrode was reduced at the potential of hydrogen evolution for about 5 min. The counter electrode was a platinum black foil (ca. 4 cm^2 geometric area) and the reference electrode was a $\text{Hg}|\text{Hg}_2\text{SO}_4|\text{K}_2\text{SO}_4(\text{sat})$.

The sulfuric acid solutions with various molar concentrations (0.05, 0.5, 1.0, 3.0 and 5.0) were used as the electrolytes. These solutions were deaerated with argon and the experiments were carried out in a glass cell. The cyclic voltammograms were obtained at sweep rates ranging from 10 to 50 mV s^{-1} . Usually, the potential of the lead electrode was cycled between -2.0 and 2.4 V. In some experiments, the potential range was limited, either to positive potentials from 0.0 to 2.4 V, or was not extended beyond 1.6 V.

Most of the experiments were carried out at room temperature (25°C , 298 K), but some were performed at elevated temperatures (20 – 90°C). To avoid any possibility of a photoelectric effect [15], the electrochemical cell was kept in the dark during all experiments.

3. Results and discussion

The redox reactions occurring on the Pb electrode in sulfuric acid solutions are complex and depend on many variables, like the concentration of the acid, the sweep rate in CV experiments and the temperature. Particular attention will be paid to the potential range of the not fully understood “anodic excursion” processes, which accompany the main reduction peak.

3.1. Sulfuric acid concentration

Fig. 1 shows a typical cyclic voltammogram, at 40 mV s^{-1} , of a pure lead wire electrode cycled in 0.5 M H_2SO_4 in a potential range limited by the evolution of hydrogen and oxygen at ca. -1.8 and $+1.8$ V, respectively. The main redox processes of the lead electrode are as follows: (a) the reduction of Pb (II) ions to the metallic Pb and subsequent oxidation to Pb (II) ions which occurs at high negative potentials in the potential range from -1.4 to 0.6 V, and (b) the oxidation of Pb(II) to Pb(IV) seen at highly positive potentials ca. $+1.8$ V. The shape of these peaks does not change significantly with the concentration of

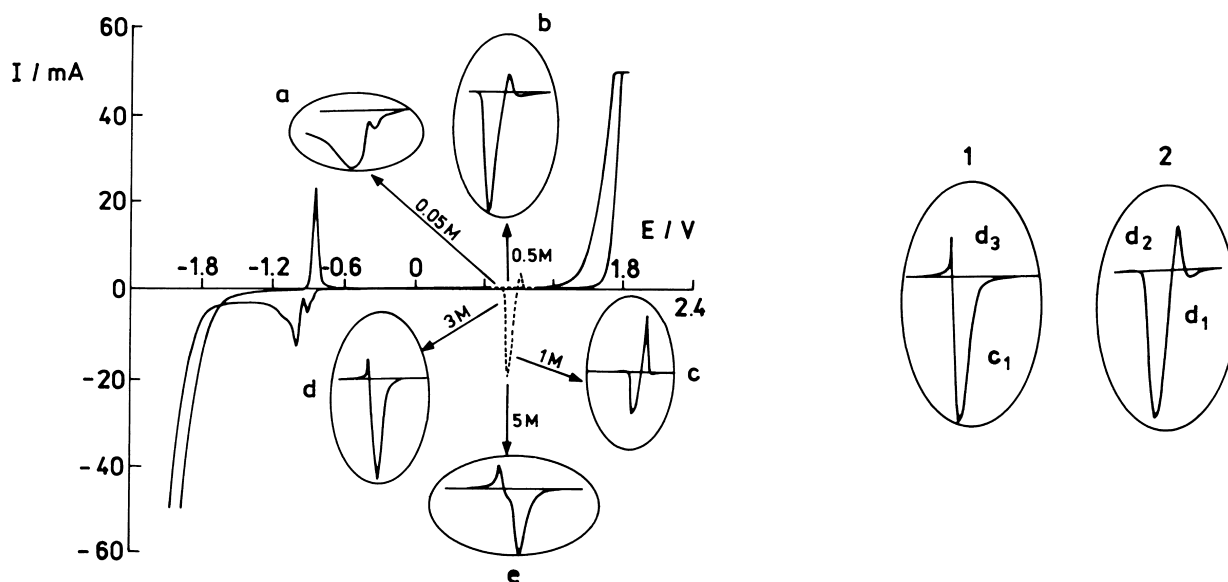


Fig. 1. Cyclic voltammograms, at 40 mV s^{-1} , of the Pb electrode in various H_2SO_4 solutions: (a) 0.05, (b) 0.5, (c) 1.0, (d) 3.0, (e) 5.0 M. The “anodic excursion” peaks are separated and magnified in circles. In separated circles labeled as 1 and 2 the possibilities of “anodic excursion” peak locations are shown (see in the text).

sulfuric acid. This is contrary to the behavior of the main reduction peak, c_1 , occurring at the potential close to $+0.8 \text{ V}$. Moreover, this peak is usually associated with small oxidation (d_2, d_3) and reduction (d_1) peaks, which appear $100\text{--}200 \text{ mV}$ positive or negative of the c_1 peak. Since the existence and the position of c_1 peak and the other small accompanying peaks depend to a great extent on the concentration of sulfuric acid, their CVs obtained in sulfuric solutions with various concentrations, from 0.05 to 5 M, were magnified and are shown in Fig. 1 in circles (a–d).

To further clarify the classification of the small oxidation and reduction peaks associated with the c_1 peak, two model CVs are additionally shown in Fig. 1 in separate circles (Fig. 1, circles 1 and 2). It can be seen from these diagrams that two oxidation peaks d_2 and d_3 , as well as one additional reduction peak d_1 , appear on the CVs under various conditions of the experiment. It should be noted, however, that the anodic peak d_2 is always preceded by the cathodic peak d_1 . The appearance of the anodic peaks, d_2 and d_3 , has been documented in previous works [3,4], and referred to as “anodic excursion”. In contrast, the existence of the additional cathodic peak, d_1 , has only been briefly mentioned [4,14] and its origin has not been explained, yet the presence of the d_1 peak offers important additional information on the mechanism of redox reactions occurring on the lead electrode in d_2 and d_3 processes.

The presence of the d_2 and d_3 “anodic excursion” peaks has been a subject of discussion since the early 1970s [1–14]. These oxidation peaks, which might be responsible for the increased corrosion of pure lead electrodes, are usually interpreted [3,4] as reflecting oxidation

of metallic lead, which is uncovered in a preceding reduction reaction (peak c_1). In fact, the surface might be uncovered even earlier in the main anodic reaction when PbSO_4 is oxidized to PbO_2 and the molar volume is reduced, exposing the bare metal, but these metal sites are probably instantly oxidized to PbO_2 at these high anodic potentials. Then, the main reduction reaction (peak c_1) most probably reflects the reduction of the β -lead dioxide to the sulfate. The molar volume of the $\beta\text{-PbO}_2$ is $25 \text{ cm}^3 \text{ mol}^{-1}$, a much smaller value than the molar volume of PbSO_4 , which equals $48 \text{ cm}^3 \text{ mol}^{-1}$ [4] and, for this reason, this transition can result in a large increase of the molar volume of the surface layer. This, in turn, might cause cracks in the surface layer, thus exposing a bare metal surface, which is instantly oxidized.

The above interpretation might be used to explain the presence of one of the “anodic excursion” peaks, namely d_3 peak, which appears after the reduction peak c_1 , but not the d_2 peak, which appears before the reduction in c_1 and, therefore, has no preceding reduction reaction leading to cracks and to the exposure of the bare metal surface. The experiments presented in this work clearly show the existence of another small reduction peak, namely the d_1 peak, that always precedes the d_2 peak (Fig. 1, circles b and c) and the c_1 peak as well. Therefore, this additional, and previously unrecognised, peak d_1 might be the missing reduction peak needed to explain the existence of the oxidation peak d_2 . This observation lends strong support to the notion that both “anodic excursion” peaks, i.e., d_2 and d_3 peaks, that appear after initial reduction in the d_1 and/or c_1 peak, are related to the oxidation of a bare lead surface that was uncovered during the reduction in the d_1 or c_1 processes that involved reduction of lead dioxide to

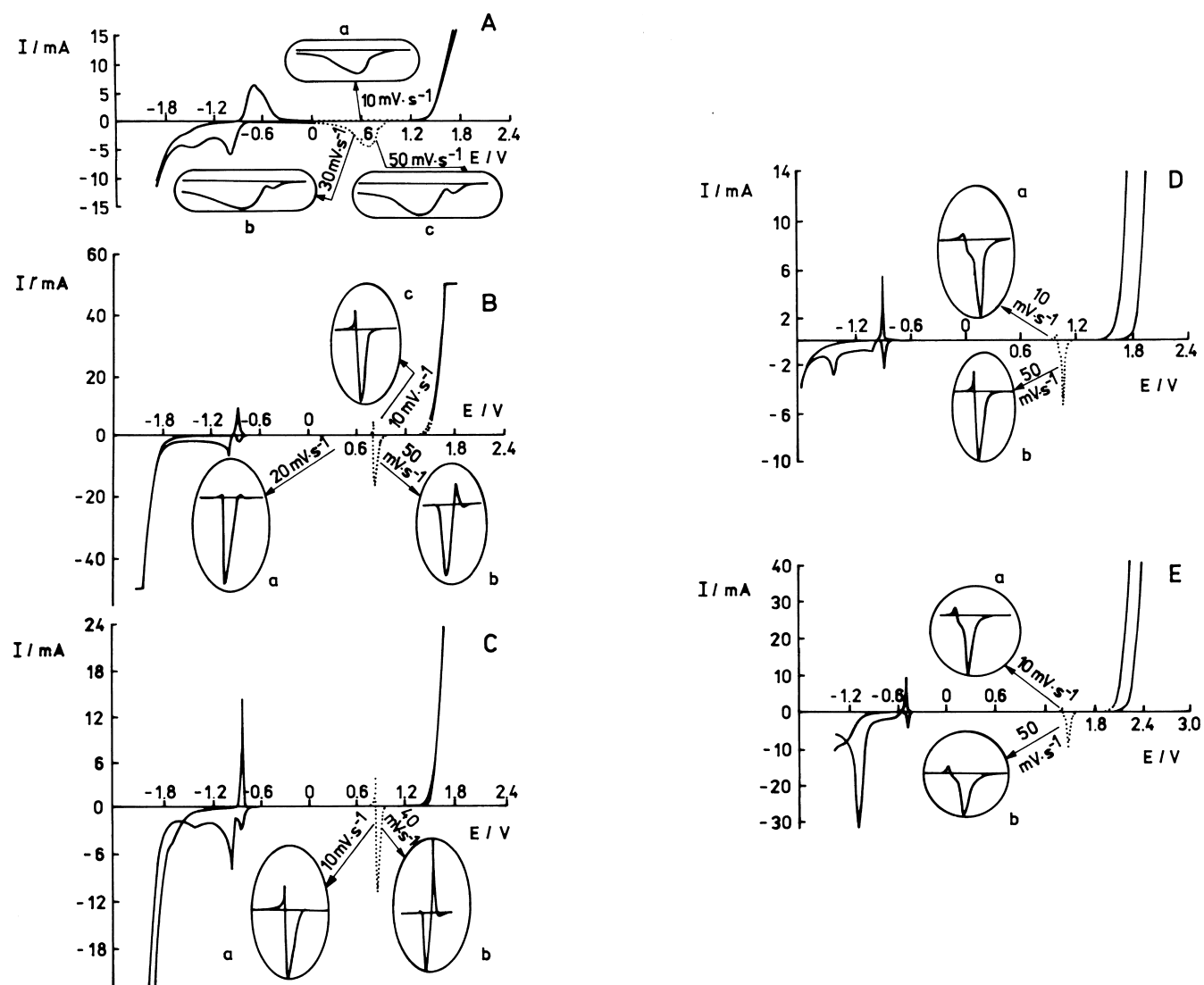


Fig. 2. Cyclic voltammograms of the Pb electrode in H_2SO_4 solutions, at different sweep rates. The “anodic excursion” peaks are separated and magnified in circles. The “main” curves in all figures were obtained at $v = 10 \text{ mV s}^{-1}$. (A) $c = 0.05 \text{ M H}_2\text{SO}_4$, (a) $v = 10 \text{ mV s}^{-1}$, (b) $v = 30 \text{ mV s}^{-1}$, (c) $v = 50 \text{ mV s}^{-1}$. (B) $c = 0.5 \text{ M H}_2\text{SO}_4$, (a) $v = 20 \text{ mV s}^{-1}$, (b) $v = 50 \text{ mV s}^{-1}$, (c) $v = 10 \text{ mV s}^{-1}$. (C) $c = 1.0 \text{ M H}_2\text{SO}_4$, (a) $v = 10 \text{ mV s}^{-1}$, (b) $v = 40 \text{ mV s}^{-1}$. (D) $c = 3.0 \text{ M H}_2\text{SO}_4$, (a) $v = 10 \text{ mV s}^{-1}$, (b) $v = 50 \text{ mV s}^{-1}$. (E) $c = 5.0 \text{ M H}_2\text{SO}_4$, (a) $v = 10 \text{ mV s}^{-1}$, (b) $v = 50 \text{ mV s}^{-1}$.

sulfates and the subsequent cracking of the sulfate layer due to a significant difference in molar volumes of lead oxide and lead sulfate.

The unusual d_1 peak, as well as the “anodic excursion” peaks, d_2 and d_3 , appear on the CVs of the lead electrode only when certain concentrations of the sulfuric acid are used in the experiments. It can be seen from Fig. 1 that, at a sweep rate of 40 mV s^{-1} , the d_1 peak is visible on the CVs when the concentration of the acid is below 1 M, i.e., in dilute acidic solutions (circles a–c). This result points to the role of sulfates in the above mentioned processes, thus supporting the idea of the cracks in the surface layer caused by the formation of lead sulfate.

It is important to note that at moderate concentrations of sulfuric acid, i.e., at 0.5 and 1 M (circles b and c) the cathodic peak d_1 is followed by the anodic peak d_2 and the d_3 peak does not appear, i.e., only one cathodic and one anodic peak is seen. This is similar to the situation at high sulfuric acid concentration when only the main cathodic peak c_1 is seen and it is accompanied by the anodic peak d_3 (circles d and e). The $d_2 \leftrightarrow d_3$ transition takes place then (Fig. 1, circles 2 to 1) with the increase of sulfuric acid concentration.

The peak pairs d_1, d_2 and c_1, d_3 may reflect independent processes occurring at the Pb surface, like, for instance, redox reactions of mixed valence oxides, which differ by the amount of sulfate incorporated into the structure. However, it might as well be that the reduction potential of d_1 is shifted negatively with the increase of the acid concentration and, then, the d_1 peak might be related to the other small oxidation peak, i.e., to the d_3 peak [it will be explained later that a small irregularity, seen at the tail of the c_1 peak (Fig. 1, circle d) does not seem to be related to the d_1 peak]. Also, it is not clear from the experiment shown in Fig. 1 whether the oxidation of a bare metal can occur simultaneously in d_2 and d_3 . More information about the position of the d_1, d_2, d_3 and c_1 peaks can be obtained by CV, when various sweep rates are used.

3.2. Sweep rate dependence

Fig. 2A–E show how the position of the oxidation/reduction peaks of the lead electrode changes with various sweep rates in the CV experiments. The experiments are performed in a wide range of sulfuric acid concentrations from 0.05 (Fig. 2A) to 5 M (Fig. 2E) and the most interesting potential region which covers reactions d_1, d_2, d_3 and c_1 is magnified in circles (a to b or c). It can be seen from Fig. 2A, circles a–c, that, at low concentrations of sulfuric acid, the change of a sweep rate does not influence to a great extent the shape of the CVs. As suggested before, the concentration of sulfates is presumably too low to cause the complete change of the oxide to the sulfates. Both d_1 and c_1 reduction peaks are present, but not the oxidation peaks d_2 or d_3 . Only the potential

range of the d_1 peak is changed, and the peak potential shifts positively with the increase of a sweep rate and the two reduction peaks are more clearly separated then. Also, at high concentrations of sulfuric acid, 3 and 5 M, the sweep rate in a CV experiment does not change the position of the oxidation/reduction peaks. The peaks d_1 and d_2 are absent and only c_1 and d_3 are seen (Fig. 2D and E, circles a–b). It could be argued that at such high sulfate concentrations, the formation of lead sulfate is complete and does not change with the conditions of the experiment, and, therefore, the transition from d_2 to d_3 does not occur.

A significant change in the reaction scheme with a sweep rate occurs only at intermediate sulfuric acid concentrations 0.5 and 1.0 M (Fig. 2B and C). When the sweep rate in the CV experiment shown in Fig. 2B and C is lowered from 40 or 50 mV s^{-1} to 10 mV s^{-1} , the d_1 reduction peak and the corresponding d_2 peak disappear

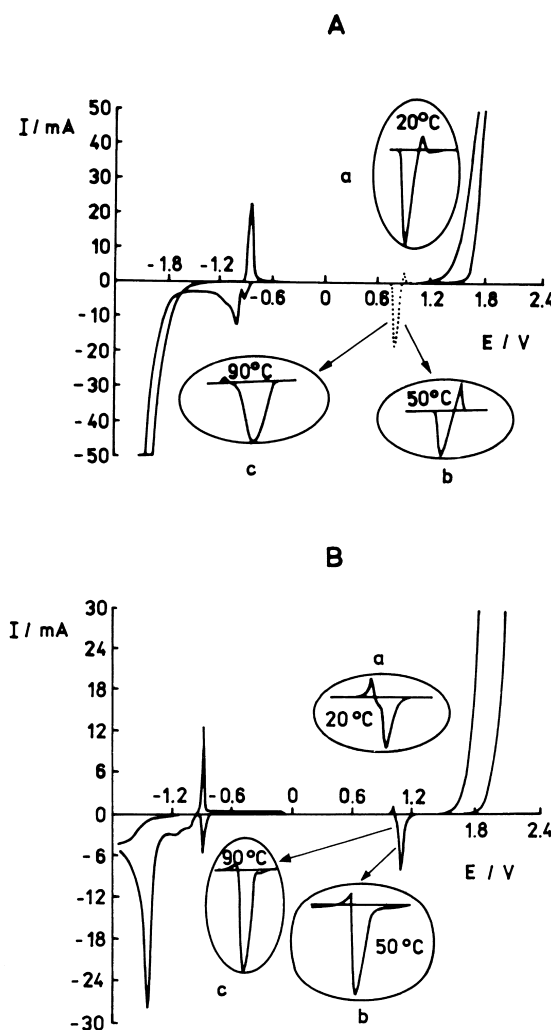


Fig. 3. The temperature dependence of the cyclic voltammograms of the Pb electrode in H_2SO_4 solutions. The “anodic excursion” peaks are separated and magnified in circles. The “main” curves in all figures were obtained at $v = 50 \text{ mV s}^{-1}$. (A) $c = 0.5 \text{ M H}_2\text{SO}_4$, (a) 20°C , (b) 50°C , (c) 90°C . (B) $c = 5 \text{ M H}_2\text{SO}_4$, (a) 20°C , (b) 50°C , (c) 90°C .

and the d_3 peak is formed ($d_2 \rightleftharpoons d_3$ transition). This is similar to the situation when the acid concentration is increased (Fig. 1). Presumably, the reaction leading to the formation of lead sulfates, reflected in peak d_3 , is slow and is more visible when the sweep rate is lowered. Contrary to that, the d_1 and d_2 processes are favored at high sweep rates, as was observed in Fig. 1 at high concentrations of sulfuric acid. In other words, the lowering of the sweep rate has the same effect on the d_2 to d_3 transition as the increase of the sulfuric acid concentration.

Interestingly, at 20 mV s^{-1} in 0.5 M sulfuric acid all four peaks d_1 , d_2 , c_1 and d_3 can be observed on cyclic voltammograms. The c_1 peak is always present, but peaks d_2 and d_3 are interchangeable. This result suggests that these are independent processes, which can occur simultaneously on the Pb electrode. The lowering of the sweep

rate and the increase of the acid concentration only change the equilibrium between d_2 and d_3 processes, but do not influence to a great extent the c_1 process.

3.3. Temperature dependence

Additional evidence that the d_1 peak always precedes the d_2 peak and that the $d_2 \rightleftharpoons d_3$ transition occurs on the lead surface comes from the temperature dependence of the redox processes c_1 , d_1 , d_2 and d_3 . If the temperature is increased from 20°C to 90°C in the sulfuric acid solution of a medium concentration (0.5 M , Fig. 3A), similar changes are observed as if the concentration of the sulfuric acid is increased or the sweep rate is lowered, i.e., the d_2 to d_3 transition is seen. At high sulfuric acid concentration (5 M , Fig. 3B), the temperature has a small influence on

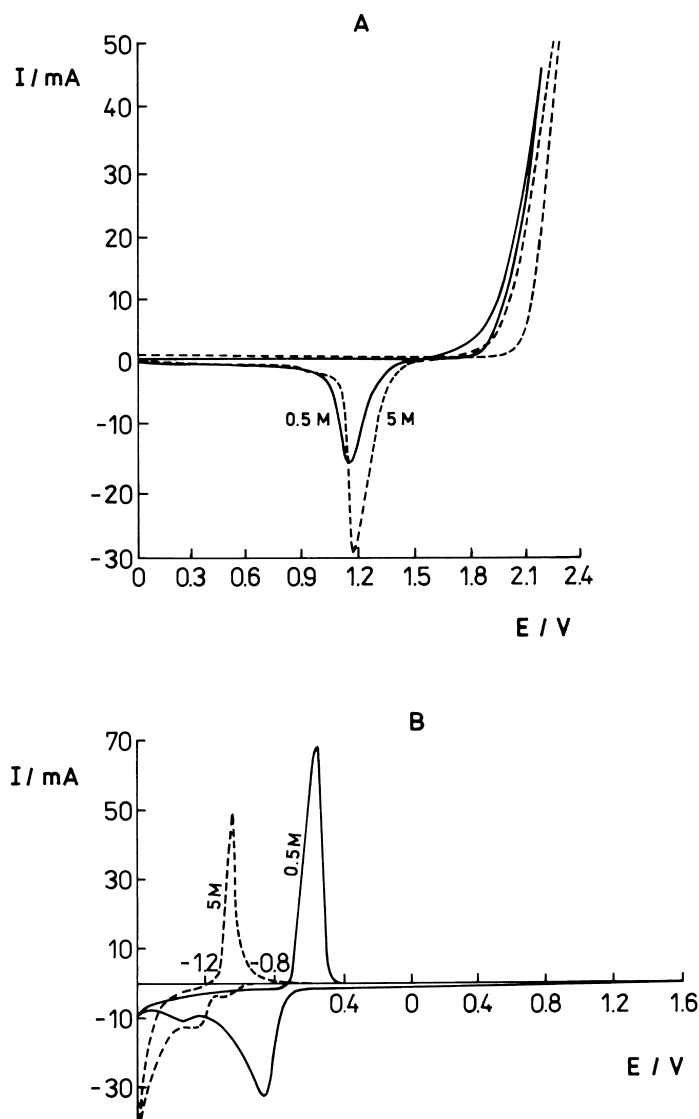


Fig. 4. Cyclic voltammograms, at $v = 10 \text{ mV s}^{-1}$, of the Pb electrode in H_2SO_4 solutions. (A) Polarization range: $0.0\text{--}2.2 \text{ V}$, $0.5 \text{ M H}_2\text{SO}_4$ (solid line), $5.0 \text{ M H}_2\text{SO}_4$ (dashed line). (B) Polarization range: $-1.6\text{--}1.6 \text{ V}$, $0.5 \text{ M H}_2\text{SO}_4$ (solid line), $5.0 \text{ M H}_2\text{SO}_4$ (dashed line).

the appearance and the position of the CV peaks. This behavior could be expected, since the change of a sweep rate also had no effect on the $d_2 \rightleftharpoons d_3$ transition in highly acidic solutions.

3.4. CV in a limited potential range

Fig. 4A and B show that the “anodic excursion” peaks, and the d_1 peak are not observed if the potential range in the CV experiments is restricted either at the cathodic limit (0.0–2.4 V, Fig. 4A) or at the anodic limit (–1.6–1.6 V) Fig. 4B). If the positive potential limit is not lower than 0.0 V, i.e., lead oxides and/or sulfates are not reduced to metallic lead and are also not further oxidized, only the c_1 peak is seen both at low (0.5 M) and high (5 M) sulfuric acid concentration. (A small shoulder at the tail of the c_1 peak is seen, though, suggesting that this shoulder is not related to the reaction scheme that involved the “anodic excursion” peaks as well as the d_1 peak.) Similarly, when the potential of the CV sweep is limited to 1.6 V, i.e., the lead dioxide is not formed, the peaks d_1 , d_2 and d_3 are not formed either.

The above experiments suggest that to obtain the effect of “anodic excursion”, the potential in the CV experiment should be changed continuously between the region of PbO_2 formation/reduction and $Pb(II)$ reduction/oxidation. Apparently, the reduction to the metallic lead, which occurs at high negative potentials, is required for the appearance of the “anodic excursion” peaks. It is possible that the energetically uneven metal surface is created, which, in turn, leads to various potentials of reduction (peaks c_1 and d_1) of the lead oxides and subsequent oxidation in “anodic excursion” peaks (peaks d_2 and d_3). This also means that when the lead dioxide electrode is used in batteries as a positive electrode, i.e., its potential is limited to positive potentials, the effects related to the “anodic excursion” processes, namely the cracking of the sulfate layer and the subsequent exposure of the bare metal, are not likely to occur.

4. Conclusions

The results of the cyclic voltammetric study of the reactions occurring on the lead electrode, the “anodic excursion” reactions in particular, have led to the following conclusions regarding the nature of these redox processes.

(1) The reduction of a small part of the lead dioxide occurs in the d_1 peak under the conditions of the continuous potential cycling of the lead electrode from highly anodic to highly cathodic potentials, i.e., when the continuous formation of lead oxides and their subsequent reduction to the metal occurs on the electrode. The d_1 peak is always accompanied by the d_2 peak. At certain sulfuric acid concentrations, certain sweep rates and/or certain

temperatures, the d_1 peak merges with the c_1 peak and the transformation $d_2 \rightleftharpoons d_3$ occurs, but it might as well be that these processes are independent.

(2) The oxidation reactions following the reduction in the c_1 and d_1 peaks occur in the d_2 and d_3 peaks. Also, the d_3 peak does not accompany the d_1 peak. The d_1 peak does not always precede the d_3 peak, but it is possible that the d_1 peak merges with the c_1 peak and is then not observable.

(3) The d_1 process is due to the reduction of a certain part of the lead dioxide, formed at high positive potentials in a continuous potential cycling within a full potential range. This reduction process ($PbO_2 + H_2SO_4 + 2H^+ + 2e \rightarrow PbSO_4 + 2H_2O$) is accompanied by a large increase of the molar volume and, as a result, the sulfate layer cracks, exposing the bare metal.

(4) The d_2 and d_3 oxidation processes occur on a freshly exposed lead surface ($Pb + H_2SO_4 \rightarrow PbSO_4 + 2H^+ + 2e$)

(5) The reduction of the main part of the lead dioxide occurs in the c_1 peak and it is independent of the range of the potential cycling. Some parts of the lead oxide are reduced in the d_1 peak at high negative potentials if the oxide has previously been reduced to the metallic lead, thus forming the energetically uneven surface.

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