

COMMENTS ON SAMPLE TREATMENT IN THE X-RAY DIFFRACTION ANALYSIS OF THE OXIDATION PRODUCTS OF LEAD

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Summary

The influence of different sample pretreatment methods in the period between switching off the potential control and the actual X-ray scan on the results of *ex situ* X-ray powder diffraction analysis of thin corrosion films of Pb anodized in H_2SO_4 has been studied. Washing the sample with a water (or acetone or ethanol) spurt and drying it rapidly with compressed air or nitrogen immediately after switching off the potential and removing the electrode from the solution, gave the most reliable and reproducible results. The washing was essential to prevent the discharge of PbO_2 to $PbSO_4$ on the electrode surface. The moisture remaining in the corrosion layer was found to render a self-discharge reaction inside the film possible, thus changing the original composition of the layer. It is concluded that more discussion is needed in the literature on sample pretreatment before *ex situ* analysis.

Introduction

The identification of the oxidation products of positive grid materials is necessary to understand the corrosion mechanism and the passivation phenomena of the positive plate in the lead-acid battery. According to Bullock [1] the techniques most often applied to the study of corrosion layers formed on lead and its alloys in sulphuric acid solutions are electrochemical methods including photoelectrochemistry, X-ray diffraction, electron microscopy, micrography and laser Raman spectroscopy. Hill [2] has presented a resumé of the applicability and contributions of different diffraction techniques, including neutron diffraction, to lead-acid battery research.

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In practice *ex situ* powder XRD is the method most easily available that, in principle, is able to determine, qualitatively and partially quantitatively, all crystalline phases present in the corrosion layer of Pb and Pb alloys. (Neutron diffraction is unfortunately of limited availability.) A good example of the use of *ex situ* powder XRD is the work done by Pavlov in characterizing, in different potential regions, the composition of the corrosion layer of lead in 0.5 M H₂SO₄ [3].

Bullock [1], Hill [2] and Dasoyan and Aguf [4] have mentioned the limitations and difficulties connected with *ex situ* XRD analysis of anodic corrosion products of Pb and Pb alloys: poor spatial and peak resolution, the superimposition of the diffraction peaks of different oxidation products, etc. One serious difficulty is appropriately to take into account the effects of recrystallization and the interaction of the products with the substrate and with the electrolyte in the period between switching off the potential control and measuring the X-ray diffractogram of the electrode surface [4].

We were confronted with the effects of electrode sample preparation while studying the kinetics of oxide growth on lead (see for example ref. 5). Although a PbO layer beneath PbO₂ has been identified by Bullock and Butler [6] using laser Raman spectroscopy, our observations indicated that at least part of the divalent products detected in corrosion layers must be due to certain self-discharge processes on and inside the layer.

The thermodynamic instability of PbO₂ in electrolyte solutions is evident [7]. However, because no study of the effect of sample treatment on the amount and prevention of self-discharge of PbO₂, as well as no study of other effects of sample treatment on the results of powder XRD analysis of anodized Pb samples was found in the literature, we decided to study the subject. Because it is evident that the effects of self-discharge become more pronounced as the corrosion layers studied become thinner, and because the early stages of oxidation are important, considering especially the effect of alloying agents on the oxidation behaviour, we concentrated on very thin layers. This paper is a review of our results giving practical advice on how to prepare anodized Pb and Pb alloy samples for XRD studies. The main goal of the paper is, however, to be a stimulus for further publications concerning this topic, which is of great importance to each combination of electrochemical and *ex situ* analytical method.

Experimental

Samples were anodized potentiostatically in a three electrode cell using an EG&G model 273 potentiostat.

4.5 M H₂SO₄ was used as cell electrolyte. Potentials were measured *versus* an Hg₂SO₄/Hg reference electrode filled with the cell electrolyte. All potentials in this paper are given *versus* this electrode unless otherwise stated. A Pt plate served as a counter electrode.

Pb foils (Merck 99.97% Pb; thickness 0.25 mm, surface area 1 cm²) inserted into a Teflon holder were used as working electrodes. No Pb alloy samples were used in this study, because the effects of sample treatment were considered to be the same for pure Pb and for the different alloys. Before the experiment, the electrode surface was polished with ethanol and soft tissue paper. The electrode was then immersed into the solution and held at a potential (−1100 mV) below the equilibrium potential of Pb for 15 min to reduce the lead oxide formed on the surface due to contact with air. After that, a potential step to the PbO/PbSO₄ potential region (+500 mV) or to the PbO₂ potential region (+1337 mV = +200 mV *versus* PbO₂/Pb²⁺) was made, and the electrode was oxidized at a constant potential for 2.5 h. In some experiments a β-PbO₂ electrode, deposited on Pt according to the procedure reported by Mindt [8], was used as a working electrode. After the anodization the potential was switched off and the electrode was removed rapidly from the cell. In principle it is possible to switch off the potential after removing the electrode from the cell, but there is no fundamental difference: in each case the electrode will be exposed to a small amount of sulphuric acid for a short time without polarization.

The different methods of sample treatment used in this work are described below in the content of the results. The X-ray analyses were performed with a Siemens Diffrac 500 diffractometer mainly in the 2θ range 20° - 60° in 65 min. The interpretation of the diffractograms was performed with the help of JCPDS reference data. Because of the thinness of the oxidized layer X-rays penetrated it. So the whole corrosion layer was subjected to analysis, and the most intense diffraction peaks in all the diffractograms were those of metallic lead. Integrated diffraction intensities were used when comparing different diffractograms.

Results and discussion

A short qualitative summary of the XRD results that led us to study the effect of sample treatment is given in Table 1. In all cases PbO(tetr.) was detected. The amount of α-PbO₂ was astonishingly low compared to that of PbO(tetr.), even after anodization at very high potentials. The results were similar after anodization preceded by a high positive prepulse (see ref. 5) as well as after anodization for a markedly longer time (*e.g.*, for one week). The PbSO₄ content of the layer varied in a seemingly illogical manner in similar experiments. These variations were most obvious when thin corrosion layers were studied.

The current–time curves of a pure Pb electrode after a potential step from −1100 to +1337 mV and to +500 mV are shown in Fig. 1. In Fig. 1(a) the initial high current due to the dissolution of Pb in the divalent state, and the successive decrease in the current due to the passivating effect of PbO and PbSO₄, are clearly observable. An increase in current after the

TABLE 1

A qualitative X-ray diffraction analysis of Pb samples anodized at various potentials (vs. $\text{Hg}_2\text{SO}_4/\text{Hg}$) in 4.5 M H_2SO_4 for 1 h^a

E (mV)	Product				
	Pb	PbSO ₄	PbO(tetr.)	α-PbO ₂	β-PbO ₂
1237	+++	+++	+++	—	—
1337	+++	+++	+++	+	—
1437	+++	+	+++	+	—
1537	+++	+++	+++	+	+
2337	+++	—	+++	++	—

^a— = not detected; + = probably present in a small amount; ++ = present in a small amount; +++ = present in an amount that can easily be detected/present as one of the main products.

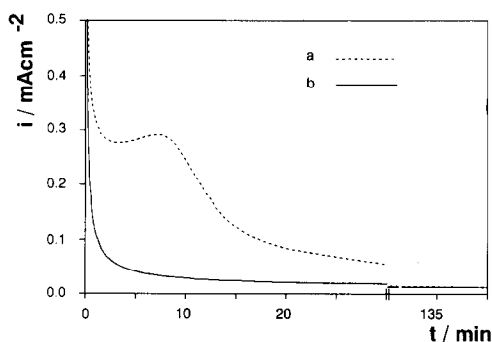


Fig. 1. The current-time curve of a pure Pb electrode after a potential step from -1100 mV (a) to $+1337$ mV and (b) $+500$ mV (vs. $\text{Hg}_2\text{SO}_4/\text{Hg}$) in 4.5 M H_2SO_4 .

initial passivation of the electrode is also observed. According to Pavlov [3] this increase is caused by the formation of non-stoichiometric PbO_x and by the nucleation and formation of $\alpha\text{-PbO}_2$ and $\beta\text{-PbO}_2$. The increase is followed by a maximum and a slowly decreasing current due to the thickening of the oxide layer. According to this interpretation one should find different lead oxides and probably traces of PbSO_4 in the corrosion product after 2.5 h oxidation. The presence of PbO_2 in the oxidation product after an anodization time of this order of magnitude has been verified, for example, by potential decay measurements [9].

In Fig. 1(b) no current increase due to the nucleation of new phases after the initial passivation can be seen. In the X-ray analysis PbO and PbSO_4 should be detected [3].

Figure 2(a) - (c) shows the diffractograms of three samples of six after oxidation for 2.5 h at 1337 mV. The first sample (Fig. 2(a)) was left wet with H_2SO_4 after oxidation, and the second (Fig. 2(b)) was rinsed rapidly with a water spurt and dried with compressed air. Compressed nitrogen was also used for drying, but although it is more inert than air, no difference

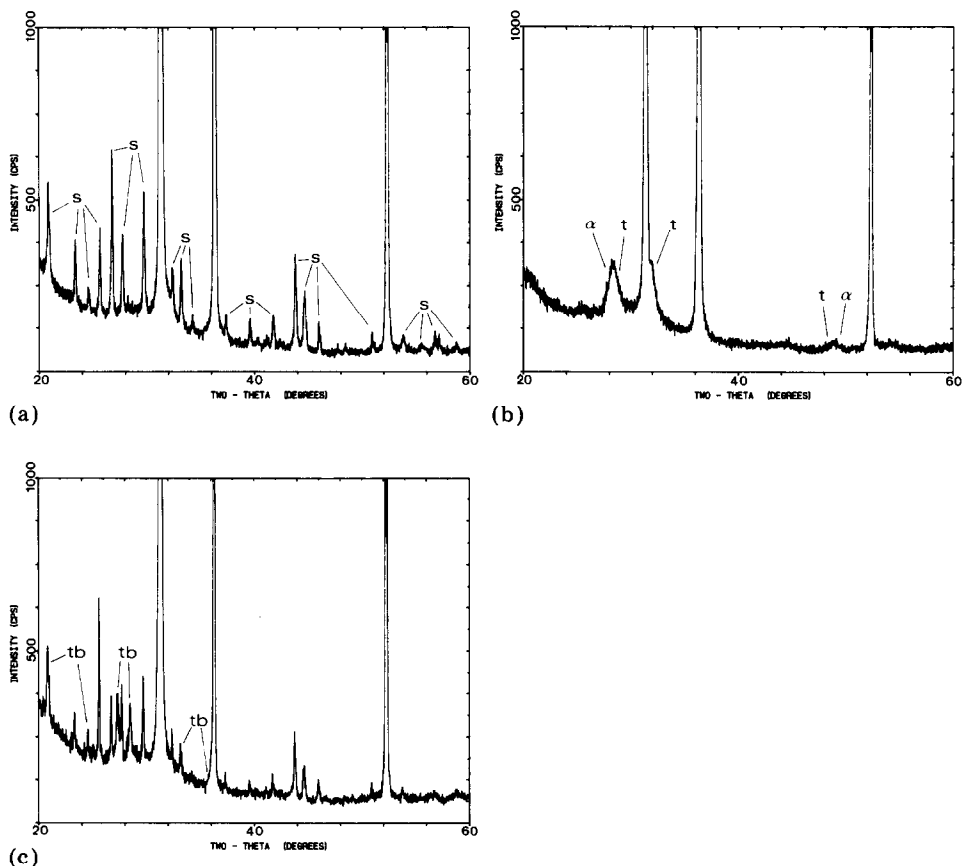


Fig. 2. X-ray diffractograms of Pb anodized at +1337 mV (*vs.* $\text{Hg}_2\text{SO}_4/\text{Hg}$) in 4.5 M H_2SO_4 for 2.5 h (the identification of the diffraction peaks based on JCPDS reference data; the most intense peaks are those of metallic lead). (a) Sample left wet with H_2SO_4 ; peaks due to PbSO_4 marked with s. (b) Sample rinsed with a water spurt and dried with compressed air; peaks due to $\alpha\text{-PbO}_2$ and $\text{PbO}(\text{tetr.})$ marked with α and t, respectively. (c) Sample rinsed with a water spurt, immersed and shaken in excessive water and dried with compressed air; in addition to PbSO_4 the presence of tribasic lead sulphate (tb) is evident (note: some of the diffraction peaks of the latter coincide with the peaks of PbSO_4 which have not been marked).

was observed between these two drying media. The third sample (Fig. 2(c)) was rinsed with water, and then immersed and shaken in water for 1.5 min before drying with compressed air. The fourth sample was rinsed with water in the same way as the second, but the drying was done in an oven at 80°C for 2 h. The fifth and sixth samples were treated in the same way as the second, but acetone and ethanol were used instead of water. The diffractograms of the fourth, fifth and sixth samples were almost identical with that of the second sample.

According to Fig. 2(a), PbSO_4 is the main product in the oxidized layer (due to the thinness of the layer the diffraction peaks of Pb are the most intense ones). Figure 2(b) (and also the diffractograms of the fourth, fifth and the sixth samples, which are not presented here) shows the presence of $\alpha\text{-PbO}_2$ and $\text{PbO}(\text{tetr.})$ in small amounts. Measurements on a more sensitive scale show some traces of $\beta\text{-PbO}_2$, as well as the possible presence of non-stoichiometric lead oxides, PbO_x ($x = 1 \dots 2$). However, no signs of PbSO_4 can be observed, although the oxidation procedure was the same as in Fig. 2(a). This can be explained in two ways. It is possible that PbO_2 formed during polarization is self-discharged into PbSO_4 and that PbO formed during polarization is chemically turned into PbSO_4 in the presence of H_2SO_4 . The discharge reaction can be written as



This explanation is in agreement with the fact that the peaks due to $\text{PbO}(\text{tetr.})$ and PbO_2 in Fig. 2(b) are not present in Fig. 2(a). So the oxides of lead have been consumed to generate the PbSO_4 observed in the diffractogram of Fig. 2(a).

An alternative explanation of the difference between the diffractograms of Fig. 2(a) and (b) is that rinsing with water, acetone or ethanol dissolves PbSO_4 formed during polarization, thus leaving only the oxide phases on the surface.

In order to see if the absence of PbSO_4 in the samples that had been washed after the oxidation was due to the dissolution effect of the washing medium, three samples were oxidized in the PbO/PbSO_4 potential region (at +500 mV) for 2.5 h. After the oxidation one of these samples was left wet, one washed rapidly with a water spurt and dried with compressed air, and one was washed rapidly with acetone and dried with compressed air. In all cases the diffractograms were identical showing no evidence of a

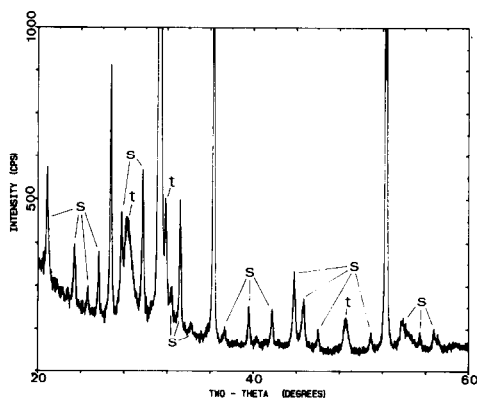


Fig. 3. X-ray diffractogram of Pb anodized at +500 mV (vs. $\text{Hg}_2\text{SO}_4/\text{Hg}$) in 4.5 M H_2SO_4 for 2.5 h; sample rinsed with a water spurt and dried with compressed air; peaks due to PbSO_4 and $\text{PbO}(\text{tetr.})$ marked with s and t, respectively.

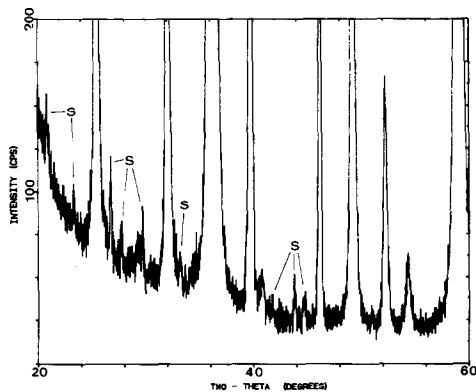


Fig. 4. X-ray diffractogram of β - PbO_2 on Pt anodized at +1337 mV (*vs.* $\text{Hg}_2\text{SO}_4/\text{Hg}$) in 4.5 M H_2SO_4 for 45 min and left wet with H_2SO_4 ; the most intense peaks belong to metallic Pt and β - PbO_2 ; peaks due to PbSO_4 marked with s.

dissolution effect by the washing medium. As an example, the diffractogram of the sample that had been washed with a water spurt and dried with compressed air is shown in Fig. 3.

The self-discharge of PbO_2 to PbSO_4 to such an extent that PbSO_4 can be detected with X-ray diffraction, was proven to be true by an experiment performed with a β - PbO_2 electrode deposited on Pt. This electrode was anodized for 45 min at 1337 mV and after that it was brought, wet with H_2SO_4 , to X-ray diffraction analysis. The diffractogram is shown in Fig. 4. The presence of PbSO_4 is evident, and the sharp shape of the PbSO_4 peaks indicates a slow nucleation rate and the rapid crystal growth of PbSO_4 during self-discharge. The results show that to avoid self-discharge of PbO_2 , H_2SO_4 has to be washed away as soon as possible after switching off the potential.

The abnormal results of Fig. 2(c) (lead sulphate and tribasic lead sulphate as main products) can be explained by a washing procedure of too long duration. When washing too long in water there is sufficient time for diffusion to take place due to steep concentration gradients in the layer, and also sparingly soluble products are slowly dissolved. Thus the surface composition is changed. The change was also seen during washing: the yellowish-brown surface turned to grey. This observation suggests that, even when only a small amount of water is used, the most reliable results are obtained if the sample is dried after washing.

Figure 5(a) - (c) shows the results of the experiment done to clarify the effect of storage time on the oxidized layer on Pb. The sample was prepared in the same way as the sample of Fig. 2(b) and analyzed in the 2θ range, $25^\circ - 38^\circ$, with a quick scan. For a period of two weeks the sample was stored in a desiccator under nitrogen atmosphere except for the time of further analysis and exposure to X-rays. Every third day the quick XRD analysis was repeated and additionally the sample was exposed to extra

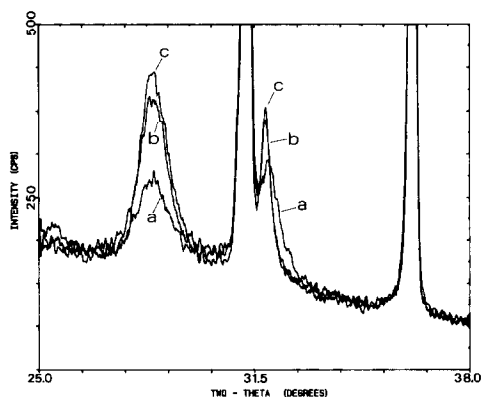


Fig. 5. Effect of storage time (and radiation) on the X-ray diffractograms of Pb anodized at +1337 mV (*vs.* $\text{Hg}_2\text{SO}_4/\text{Hg}$) in 4.5 M H_2SO_4 for 2.5 h. (a) Sample rinsed with a water spurt and dried with compressed air; diffractogram determined immediately after anodization. (b) After the first analysis sample stored in a desiccator for six days and exposed to radiation for 5 h (the time of analysis included). (c) After the first analysis sample stored in a desiccator for two weeks and exposed to radiation at regular intervals (see text).

radiation for 2 h each time. Another sample was prepared in exactly the same way and analyzed after the preparation. However, the analysis of the second sample was repeated only once, *i.e.*, after it had been stored for two weeks in a desiccator. The diffractograms of both samples immediately after the oxidation were identical. In both cases the XRD intensities of the broad diffraction peak at about $2\theta = 28.5^\circ$ (due to $\text{PbO}(\text{tetr.})$ and $\alpha\text{-PbO}_2$) and of the peak at 31.7° (due to $\text{PbO}(\text{tetr.})$; note also possible overlap of $\beta\text{-PbO}_2$) increased with time. This was not only an effect due to recrystallization, because simultaneously the integrated intensities of the lead peaks decreased. This shows that the amount of PbO and the thickness of the layer increased. The most dramatic difference was observed in the early stage of the two week period (see Fig. 5(a) and (b)). The total increase was slightly more pronounced in the case of the sample that had been exposed to excessive X-ray radiation. This observation, however, may be due to longer exposure to atmospheric moisture during repeated analyses. The results indicate that due to traces of moisture one or several self-discharge reactions proceed inside the oxidized layer. In a simplified way the self-discharge can be written as



but the actual reaction may involve gradual removal of oxygen from the PbO_2 lattice. Obviously, due to the drying of the corrosion layer the increase in the oxide peak intensities became slower with time.

The exact mechanism of the possible influence of X-rays on the corrosion layer of lead requires further investigations, which may also further elucidate the structure and properties of the layer.

In order to evaluate the possible influence of sample orientation on the results a pure and a corroded lead electrode were subjected to successive XRD analyses at short intervals. Between every XRD run the sample was turned around its vertical axis 10° at a time. The integrated intensities of the diffraction peaks of Pb in the pure metal sample remained constant, but they varied in the corroded sample. The integrated intensity of the lead oxide diffraction peak ($2\theta = 28.5^\circ$) in the corroded sample remained almost constant, although the relative intensity varied due to changes in the absolute intensities of the lead peaks. This shows that even thin corrosion layers are not of uniform thickness and that the path length of X-rays may change due to rotation of the sample. These observations support the idea that interpreting the diffractograms by using integrated intensities is a more reliable method in the case of thin corrosion layers.

Conclusions

First it should be pointed out that, considering Pb samples, these results are applicable only to the treatment of thin corrosion layers on solid Pb and Pb alloy electrodes. In the presence of active mass, and in the case of long oxidation times, the situation is more complicated, and also the amounts of different oxidation products are greater, so that a relatively small degree of self-discharge will not play a significant role.

The results clearly show that whenever PbO_2 is formed, H_2SO_4 has to be washed away in order to avoid the formation of extra PbSO_4 due to the self-discharge reaction (1). Distilled water, acetone, and ethanol are equally good washing media. With water the washing has to be performed quickly and the sample dried, because the use of excess water (in this case 1.5 min in a water bath was too much) may lead to the dissolution of some of the oxidation products.

Because of the remaining moisture in the corrosion layer the time delay between the oxidation and the actual analysis may render self-discharge inside the layer possible. The analysis has to be performed as soon as possible after the oxidation, and preferably by using a position-sensitive detector.

Because of the limitations of the *ex situ* method, X-ray powder diffraction during electrochemical polarization [10 - 12] seems to be an attractive tool. The applicability of *in situ* X-ray diffraction to the studies of corrosion layers on lead will be examined in more detail in the near future.

The treatment described above can also be recommended for use in sample preparation for other *ex situ* techniques — and probably also for the preparation of samples from other materials. However, the facts that the results of *ex situ* XRD are relatively sensitive to the preparation method and that a variety of different preparation methods are used in different laboratories dealing with the anodic behaviour of Pb and Pb alloys, show that there is a great need for open discussion in this area. We hope that

further comments and papers will appear showing which methods are used and what the advantages and drawbacks of them are.

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