Journal of Power Sources, *17* (1986) 369 - 377

AN EXAMINATION OF CORRODED POSITIVE GRIDS FROM A LEAD–ACID BATTERY

P. GRUBER*, E. FASCHINGBAUER and J. McGOLDRICK

Banner Batterien, Linz (Austria)

(Received March 1, 1985; in revised form January 29, 1986)

Summary

This paper is concerned with the problem of grid-corrosion caused by solid-state reactions on overcharging. With transmitted-light-polarisation-microscopy and X-ray diffraction it can be shown that solid-state grid-corrosion takes place in four stages:

(i) Metallic lead → an amorphous intermediate product;
(ii) The amorphous intermediate product → tetragonal PbO;
(iii) The tetragonal PbO → α-PbO_2;
(iv) α-PbO_2 → "black-PbO_2".

"Black-PbO_2" is the end product of the corrosion process but its existence cannot be shown using X-ray-diffractometry because it has the same lines as α-PbO_2. It can, however, be shown to exist using optical microscopy.

α-PbO_2 can be penetrated by polarised light and has an intense blood-red interference colour whereas "black-PbO_2" absorbs the polarised light and appears black. The physical properties of the lattice structure also change during the conversion; the "black-PbO_2" being hard and brittle.

"Black-PbO_2", which seems to be the natural aging product of the active positive mass, not only exists as a grid corrosion product, but also forms in the active mass. α-PbO_2 is very sensitive to overcharging and can yield plates having a loose and dusty surface after the formation process.

The present work further illustrates the reactivity of the solid-state, which is still underestimated when evaluating the chemical reactions in the lead–acid accumulator.

1. Introduction

The function of the grids in the electrodes of a lead–acid battery is to support the active mass and to conduct the electric current. They consist of lead and it's alloys and have to fulfill these functions as long as possible in

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*Author to whom correspondence should be addressed.

0378-7753/86/$3.50

spite of the extremely corrosive environment. Various alloy systems have been developed for this purpose, the most common being based on the lead–antimony or lead–calcium system. The object is to produce a corrosion-resistant grid of good mechanical strength. In spite of the high quality of present day grids, corrosion remains a common cause of battery failure.

2. Mechanisms of corrosion

Grid corrosion which primarily limits the life of the positive grid results from two fundamentally different types of reaction.

2.1. Electrolyte corrosion

The reaction of the lead grid with sulphuric acid to form lead sulphate has long been regarded as the most important corrosion reaction mechanism.

2.2. Oxygen corrosion via solid-state reactions

Mindt [1], Burbank [2], and especially Pavlov [3] and coworkers found that grid corrosion was primarily a solid-state reaction, initiated by penetrating oxygen and promoted by overcharging. At potentials of greater than +1300 mV an intense evolution of oxygen takes place at the interface of the positive grid whereon the lead is oxidised to PbO which is further oxidised to PbO_2. We found that the end product of this corrosion process is not α-PbO_2, but "black-PbO_2" which looks black in transmitted polarized light. "Black-PbO_2" has similar X-ray lines to those of α-PbO_2 but it has very contrasting optical and mechanical properties.

The reactions are facilitated by similarities in the crystal lattice structures of lead, lead monoxide and lead dioxide, demonstrated by Bode and Voss [4]. Mindt [1] examined various lead oxides and discovered that oxygen has a great degree of mobility in them. Burbank [2] and Ruetschi and Cahan [5] mentioned the existence of a lead oxide other than the α- and β-forms but did not pursue the matter further.

3. Examination of corroded grids

The object was to determine the exact cause of the failure of such grids. Several "Carefree"* batteries, with 0.7 mm thick Pb/Ca/Sn grids, failed after approximately three years due to "grid-growth" of the positive electrode. "Grid growth" is the increase in volume as the grid is converted into its corrosion products. The pressure caused by the phase changes from Pb to PbO_2 deforms the grid, sometimes to the extent of complete destruction of the grid frames and grid bars. Corroded grids break very easily and are extremely brittle.

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*3.1. Examination with transmitted polarized light**

3.1.1. Sample preparation

The dried positive plate is embedded in epoxy resin under vacuum, so that the pores of the plate are filled with the resin.

Pieces of the plate are then removed using a diamond saw and then polished using SiC paper until they are suitable for mounting.

After a period of hardening the sample on the mount is reduced to 0.2 mm using the diamond saw.

This is further reduced to 0.01 - 0.02 mm using SiC paper. A cover glass is then put over the specimen using Canada balsam. It is then ready to be viewed in transmitted polarized light.

3.1.2. Transmitted-light polarisation-microscopy

The various solid phases which occur in a lead–acid battery can be determined due to their various and characteristic interference colours.

The following phases and their appearance, given a sample of the correct thickness, are:

tetragonal PbO	yellow, orange,
α-PbO_2	blood-red,
β-PbO_2	brown-red,
"Black-PbO_2"	black,
metallic lead	black, but with reflected light,
$PbSO_4$	white crystals.

These interference colours are a property of the crystal and appear when a section, thin enough to allow light to be transmitted, is viewed between crossed polarising filters.

The observed colours therefore show differences in the basic structure and lattice-energies of the crystals and provide an additional method to X-ray diffractometry for identifying the phases in lead–acid accumulator electrodes. No other procedure can distinguish the phases, which occur in both the formed and the unformed mass, more distinctly.

3.2. Results of the microscopic examination of corroded grids

The corrosion mechanism, in its various stages from surface attack to complete destruction of the grid, can be identified in the Figures described below.

Corrosion at the grid surface. The corrosion in Fig. 1 is limited to the grid surface. The thickness of the corroded layer is approximately 0.1 mm. Tetragonal PbO appears as the first corrosion product — coloured yellow/orange in the Figure. At the edge of the PbO corrosion layer α- and β-PbO_2 are found with the beta form on the outside due to the influence of the electrolyte.

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*Initially described by R. G. Actor, Oldham & Son Ltd., Manchester, U.K. A Note, written about 1960 - 65, for which the author has no reference.

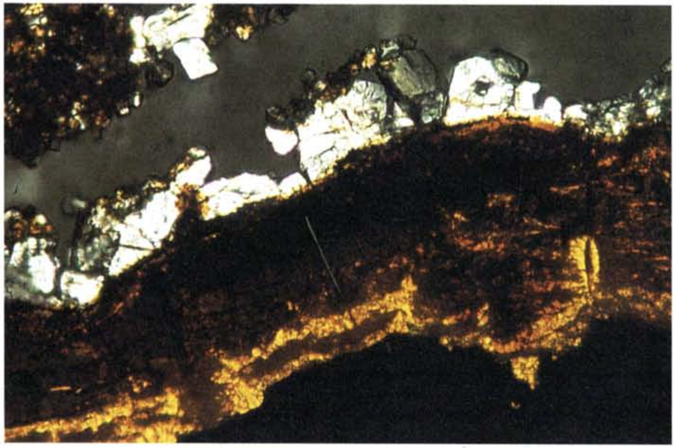

Fig. 1.

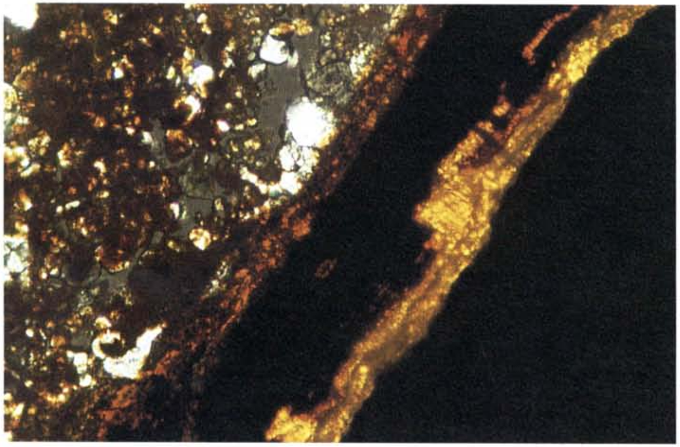

Fig. 2.

Fig. 3.

Fig. 4.

Progressing grid-corrosion. In Fig. 2 the grid is already enclosed in a 0.2 mm thick corrosion layer with a distinct 0.03 mm layer of tetragonal PbO present (orange/yellow). Between the lead grid and the crystallized tetragonal PbO an ochre-brown transition zone is also often visible. This intermediate stage could not, however, be determined.

Tetragonal PbO is then directly converted to α-PbO_2 (blood-red), of which only a very thin layer, about 0.01 mm remains, the rest having been quickly converted via a solid-state reaction to an opaque, black, end product we call "black-PbO_2".

Deep penetrating corrosion. This corrosion mechanism, shown in Figs. 3 and 4, occurs both on the surface of, and inside, the grid with identical results. Solid state reaction products appear clearly here, because they are not subject to any changing influences from the electrolyte. A thick, external crust of corrosion products protects this reaction site where metallic Pb (black) is converted to tetragonal PbO (yellow/orange) with an amorphous intermediate stage (ochre brown). Noticeably well developed is the 0.15 mm thick PbO layer which in turn, is converted to a thin (0.02 mm) zone of α-PbO_2 (blood red). Due to further oxygen migration this α-PbO_2 is directly converted to "black-PbO_2", the main and final component of the corrosion, and not α-PbO_2.

3.3. Characterisation of the "black-PbO_2" using X-ray diffraction

After removing the divalent lead compounds, consisting of tetragonal PbO and $PbSO_4$, using ammonium acetate solution, the only remaining products were mainly "black-PbO_2" with small quantities of α- and β-PbO_2. X-ray charts of the "black-PbO_2" show the typical lines corresponding to the standard values of α-PbO_2 (see Table 1).

4. Conclusion and interpretation of the results

The oxidation of the lead alloy in the grids to "black-PbO_2" takes place in four stages:

Fig. 1. Microscopic enlargement ×130. Corrosion at the grid surface. $PbSO_4$, white crystals; mixed α- and β-PbO_2, brown/red crystals; tetragonal PbO, yellow crystals.

Fig. 2. Microscopic enlargement ×130. Advanced corrosion. Metallic lead, black (bottom); tetragonal PbO, orange/yellow; α-PbO_2, blood red; "Black-PbO_2", black corrosion layer.

Fig. 3. Microscopic enlargement ×35. Deep penetrating corrosion. Metallic lead, black (grid centre); amorphous intermediate layer, ochre brown; tetragonal PbO, orange/yellow; α-PbO_2, blood red; "Black-PbO_2", black end product of corrosion reactions. Small islands of metallic lead which are coated in layers of PbO and α-PbO_2.

Fig. 4. Microscopic enlargement ×130. This is an enlargement of part of Fig. 3.

TABLE 1

X-ray data on "black-PbO_2" by comparison with the well known α-PbO_2

"Black-PbO_2"			α-PbO_2		
2θ	*d*-spacing (Å)	Rel. int. (%)	*d*-spacing (Å)	Rel. int. (%)	Indices
23.25	3.82	18	3.82	17	110
28.55	3.12	100	3.12	100	111
30.10	2.96	5	2.96	6	020
32.85	2.72	28	2.72	18	002
34.40	2.61	3	2.61	15	021
36.0	2.49	7	2.49	12	200
40.6	2.22	15	2.22	6	112
—	—	—	2.0	4	022
—	—	—	1.91	6	220
49.4	1.84	34	1.84	29	202/130
50.5	1.80	13	1.80	18	221
56.1	1.64	13	1.64	14	113
59.5	1.56	9	1.56	3	222
—	—	—	1.55	6	023
60.5	1.53	6	1.53	10	311
—	—	—	1.52	13	132

(i) Metallic Pb → amorphous intermediate product;
(ii) amorphous intermediate product → tetragonal PbO;
(iii) tetragonal PbO → α-PbO_2;
(iv) α-PbO_2 → "black-PbO_2".

Conversion of the lead grid to an amorphous intermediate product. The identification of this product was not possible. The compound is not only at the interface of the metallic lead, but it can quite often be observed between crystallites of tetragonal PbO.

Tetragonal PbO. The PbO layer is produced from the intermediate layer by reaction with penetrating oxygen. It appears as an orange/yellow colour in polarized light and is the most striking product. According to Pavlov and Iordanov [6] tetragonal PbO is the product of solid-state reactions of lead with penetrating oxygen, especially O^{2-} ions. PbO occurs at potentials as low as +200 mV over a wide non-stoichiometric range: O/Pb between 1.0 and 1.5. Thus, the newly formed PbO appears to be able to accept oxygen over a broad stoichiometric spectrum as may be concluded from the fact that the PbO layer becomes very thick without being changed, despite the fact that diffusing oxygen is added to it continually. For this reason the older, outer edge of the PbO layer is first converted to α-PbO_2, seemingly adapting itself to the oxygen excess.

As the O/Pb ratio reaches about 1.5 a new crystal symmetry becomes more stable and α-PbO_2 develops.

α-PbO_2. We have shown that α-PbO_2 is characterized by its blood-red interference colour. In the corrosion product layer, however, α-PbO_2 appears only as a thin band, and is therefore merely an intermediate product in the corrosion process. One may also conclude that this α-PbO_2 has only a limited capacity for absorbing oxygen, which corresponds very well to the O/Pb ratio of 1.51 - 1.60, which is now generally accepted.

"Black-PbO_2". In our case "black-PbO_2" arises due to grid corrosion caused by the influence of oxygen on the α-PbO_2. Due to further integration of oxygen into the lattice structure of α-PbO_2, the energy circumstances are changed to such an extent that all of the (normally) transmitted light is absorbed and therefore appears black. The structure of the starting product, α-PbO_2, is so minimally changed, however, that this cannot be shown by using X-ray diffraction. The lattice conversion, in spite of the fundamental change in the energy conditions, appears to be so restricted that no differences in the X-ray diagrams are noticeable (see Table 1). During this reaction, however, stresses and strains occur in the material. To date, no substantial scientific examination of "black-PbO_2" has taken place despite the fact that it can lead to problems in batteries.

4.1. *Experience with "black-PbO_2"*

In addition to their behaviour in polarized light, which suggest differences between α-PbO_2 and "black-PbO_2", they also exhibit different mechanical characteristics. "Black-PbO_2" is hard and brittle and remains sandy and powdery in the mortar. α-PbO_2, by contrast, tends to have almost lubricating characteristics. This difference in mechanical behaviour suggests differences in lattice-energies.

"Dusty" positive plates. In battery practice it is known that α-PbO_2 is sensitive to overformation. In α-PbO_2-rich, black-looking and dusty plates, we found that α-PbO_2 had been converted to "black-PbO_2". The earliest-formed α-PbO_2, a 0.1 mm layer at the plate surface, was converted, especially when the plate-forming process was too fast. Due to the stresses and strains in the material which occur during the conversion to "black-PbO_2" the cohesion between the PbO_2 particles was lost. Also, at a potential above 1500 mV, Pavlov [6] observed structural changes and internal tensions in the anodic oxidation layer which cause it to break up and to fall off.

X-ray diffractometry. The material which we refer to as "black-PbO_2" cannot be distinguished from α-PbO_2 using X-ray diffractometry. Faber [7] also reported a black form of PbO_2 which crystallized as β-PbO_2. We already know from earlier findings that β-PbO_2, after long exposure to oxygen through overloading, can also appear in a microscopic, opaque, black form.

Simon and Caulder [8] also established the presence of a black form of α-PbO_2 in the cycled positive mass which does not take part in the discharge, and is therefore not electrochemically active.

Life of the positive mass. We suppose that the positive mass is slowly converted to "black-PbO_2", which appears to be the most stable of all the PbO_2 forms. It is probably the "equilibrium oxide" — the most stable and only equilibrium oxide which Vetter [9] presumes every metal to have. The electrochemically active but thermodynamically unstable α- and β-PbO_2 modifications can be converted to the more stable form. We also expect decreased oxygen-overvoltage on the "black-PbO_2" form which would help to explain why older batteries gas more than new ones.

5. Grid corrosion and performance output

As soon as a PbO corrosion film exists on the surface of the lead grid the anodic current is limited. PbO acts as an insulator with a specific resistance of 10^{13} - 10^{14} ohm m [4]. Pavlov [10] claims that current can only be transported through the PbO film by means of ions such as Pb^{2+} or O^{2-} and not electrons. This mechanism limits the anodic current. It is therefore to be expected that grid corrosion can reduce the performance of a battery long before any damage to the grid is evident. This may also be the reason for unexpectedly low voltages in fully charged batteries. The PbO layer at the grid surface reacts with the sulphuric acid and forms a thick layer of $PbSO_4$:

$$PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O$$

on the positive grid. The battery acid does not react with metallic lead to such an extent.

6. Corrosion and grid alloy

The micrographs of the corroded grids show isolated islands of metallic lead with a PbO coating in a sea of the black oxide end product. These islands of metallic lead must be small areas in the grid alloy with a somewhat different composition and illustrate how small differences in the alloy composition can have a great effect on the corrosion resistance. Corrosion studies [11, 12] have confirmed that the antimony content in lead alloys retards the growth of the PbO corrosion film at the anode. In lead–calcium alloys even a few tenths of one percent. of tin can greatly improve the corrosion resistance of the alloys.

Due to the importance of the grid alloy and its resistance to corrosion, which is critical to its life, more attention must be paid to the grid alloys, especially their resistance to oxidation.

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