

ANODIC OXIDATION OF LEAD IN SULPHURIC ACID SOLUTIONS. THE EFFECT OF DIFFERENT PERCHLORATE SALTS ON PLANTÉ FORMATION

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Summary

The oxidation of lead to PbO_2 in dilute sulphuric acid has been studied. Small amounts of perchlorate ions in the electrolyte increase the oxidation rate and probably influence the ratio between α - and β - PbO_2 .

The cation of the perchlorate salt is important for the discharge properties of the PbO_2 formed. The discharge capacity, the active surface area and the self discharge current all increase in the sequence $\text{K}^+ < \text{Na}^+ < \text{Li}^+ < \text{H}^+$.

Introduction

The lead/acid battery can be manufactured in several ways giving rise to different qualities of the product. The oldest manufacturing procedure is Planté formation [1], invented in the middle of the 19th century. However, it is still used for stationary battery applications where high corrosion resistance and reliability are of ultimate importance.

The aim of the Planté formation method is to produce PbO_2 electrodes by electrochemical oxidation of pure lead in sulphuric acid. To speed up the oxidation process aggressive ions are added to the electrolyte. The most frequently used aggressive ion is perchlorate, but nitrate, tetrafluoroborate and acetate are also usable [2, 3]. The role of the perchlorate ions has been the subject of several investigations [4 - 7], and it has been discussed in terms of 'pitting corrosion' [8, 9]. The ions become incorporated into the lead sulphate layer and thereby the strength of the passive film is decreased.

In previous work, the dissolution of lead in perchloric acid [10] and mixtures of perchloric acid and sulphuric acid [11] was studied. The idea behind these investigations was to examine the oxidation reactions before, and during, the lead sulphate passivation reaction. It was shown that for low

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sulphate concentrations (<10 mM in 0.5 M HClO_4), the lead oxidation process proceeds similarly to the oxidation in pure perchloric acid, although the active surface will become partially blocked due to lead sulphate precipitation. At higher sulphate concentrations, an initial passivation is readily observed. However, by changing the potential in the positive direction an indistinct peak occurs. This peak can be attributed to 'pitting corrosion' [11], moving in the anodic direction as the sulphate concentration is increased.

In the present work, PbO_2 formation in the Planté electrolyte has been studied. The effect of the perchlorate ion is evident, especially with regard to the oxidation rate. However, depending on which perchlorate salt was used, different discharge behaviours were observed for the PbO_2 electrode. This effect is discussed in terms of crystal structure defects caused by the salt cation.

Experimental

The cells and instrumentation have been described elsewhere [10].

Electrodes

An Hg/HgSO_4 reference electrode was used for measurements in pure sulphuric acid and in the Planté electrolyte (containing perchlorate). A sodium saturated calomel reference electrode (SCE) was used in mixtures with higher perchlorate content. A platinum counter electrode was used throughout the work. The potentials are, for convenience, converted into the normal hydrogen scale, NHE, by adding 640 or 236 mV to the experimental value, depending on the reference electrode used. Rotating disc electrodes, with a geometric surface area of 0.2 cm², were prepared from 99.9985%-pure lead rods (Johnson-Matthey Chemical Ltd). The electrodes were moulded in epoxy, exposing only the circular disc surface.

Oxygen was not removed from the solution, since the potentials at which the measurements were made were high enough to allow oxygen evolution also.

Preparation of the lead dioxide electrodes

The lead electrode was wet ground on 1000 and 4000 mesh carborundum paper, washed in doubly distilled water, and immediately transferred to the cell.

The first oxidation step was performed at a constant current density of 5 mA/cm² and a rotation velocity of 50 rps. The electrolyte consisted of 0.5 M H_2SO_4 with 0.05 M XCIO_4 , where X stands for H^+ , Li^+ , Na^+ or K^+ . For comparison, one electrode was oxidized in pure 0.5 M H_2SO_4 .

After the first oxidation step, the electrolyte was changed to pure 0.5 M H_2SO_4 and the electrode was washed in doubly distilled water. The reduction was performed for the same time and at the same current density as for the oxidation.

Before re-oxidation, the electrolyte was changed once again to pure 0.5 M H_2SO_4 and the electrode was washed once again. The current density was the same as before and was applied for the same time.

The electrode was hereafter transferred to a cell containing 3.5 M H_2SO_4 , and charged in this electrolyte for 5 min at 0.5 mA/cm².

Measurements

The potentiodynamic sweeps (see Fig. 1) were performed at a sweep rate of 2 mV/s and a rotation velocity of 50 rps. Different mixtures of HClO_4 and H_2SO_4 were used as electrolyte. If not otherwise noted, the anion strength was 0.5 M.

The discharge experiments were performed at a constant current density of 0.5 mA/cm² and were interrupted at a potential of 1640 mV *versus* NHE. To evaluate the self-discharge currents, the electrodes were left to rest in the electrolyte for 30 min, and were then discharged. The capacities were compared with results obtained without rest. The self-discharge currents were then calculated with the assumption that the self discharge also continued during active discharge.

The current step technique for determination of the double layer capacitance is described elsewhere [12], as well as the assumptions under which these capacitance values can be correlated to the active surface area [10]. The measurements were performed at zero steady state current and the amplitude of the current step was 50 mA/cm². It was applied for 10 ms and the measured points were collected at a rate of 0.2 μs /point.

Chemicals

Puriss, p.a. perchloric acid, HClO_4 (Fluka Chemicals AG) and sulphuric acid, H_2SO_4 (Merck Titrisol and May & Baker Ltd. proanalys*ar), diluted with doubly distilled water were used throughout the work.

Results and discussion

As mentioned in the 'Introduction', the effect of perchlorate ions in the electrolyte during Planté formation is assumed to be a breakdown of the passivating lead sulphate film on the surface, causing pitting corrosion [8, 9]. This effect can be seen as an indistinct peak in the potentiodynamic sweep for lead in mixtures of sulphuric acid and perchloric acid. The peak moves in the anodic direction as the sulphate ion concentration increases, Fig. 1. On examination of the surface by an optical microscope, the pitting attack was readily seen. In a certain concentration region, this effect occurs at potentials where the oxidation to PbO_2 is possible, but where the oxygen evolution is still negligible. Under such circumstances (e.g. 0.5 M H_2SO_4 , 0.05 M HClO_4) the formation can be performed with a current efficiency near 100%. This is illustrated in Fig. 2, where curve a represents the oxidation of lead in the electrolyte mentioned at a current density of 5 mA/cm²,

while curve b represents the reduction of the same electrode at the same current density. It can be seen that the hydrogen evolution (at around -1 V *versus* NHE) starts after an amount of time almost exactly corresponding to the time of oxidation in curve a. As a comparison the same experiment without perchloric acid is shown in Fig. 2 curves c and d. In this case, the

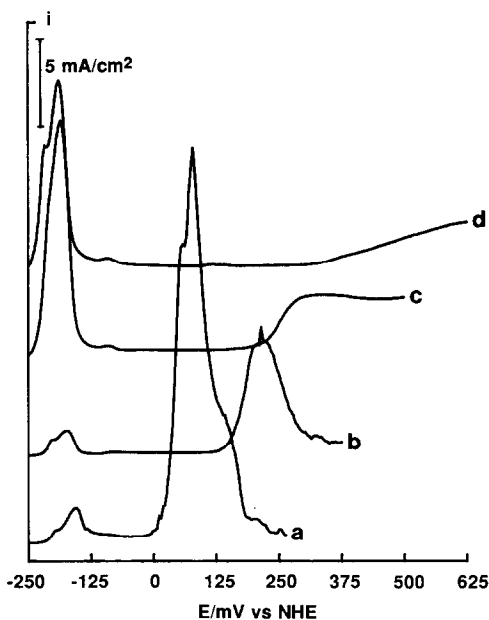


Fig. 1. Linear sweep voltammograms in $\text{HClO}_4/\text{H}_2\text{SO}_4$ mixtures. Sweep rate 2 mV/s, rotation velocity 50 rps. Anion strength 0.5 M. Sulphuric acid content: a, 100; b, 200; c, 300; d, 400 mM. Curves c and d are expanded 10 times (vertically).

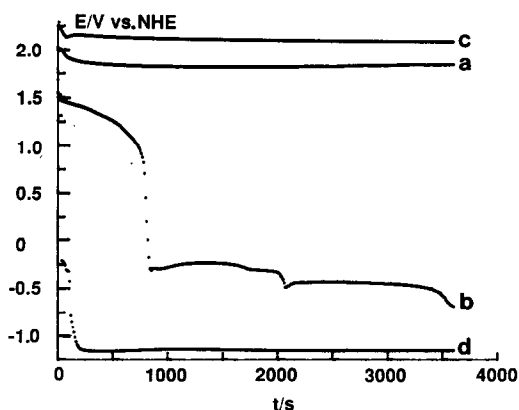


Fig. 2. Electrode potential as a function of time: a, oxidation; b, reduction in 0.5 M H_2SO_4 with 0.05 M HClO_4 ; c, oxidation; d, reduction in pure 0.5 M H_2SO_4 . Current 5 mA/cm^2 , rotation velocity 50 rps.

potential almost immediately drops to the value corresponding to the hydrogen evolution. Thus, the anodic charge is much larger than the corresponding cathodic charge for the reduction of PbO_2 to Pb. This indicates that less PbO_2 is formed, and that most of the anodic charge is consumed by the oxygen evolution.

The role of the perchlorate ions in the formation of PbO_2 from Pb has been discussed in the literature [4 - 7]. It was stated that perchloric acid affects the phase formation process [6, 7]. In sulphuric acid the reaction involves a two-dimensional instantaneous nucleation process. At low concentrations of perchloric acid in sulphuric acid, the growth of PbO_2 remains two-dimensional, but the nucleation becomes progressive [6, 7]. At higher perchlorate concentrations a three-dimensional growth of PbO_2 takes place, giving rise to a more porous PbO_2 layer. This favours the further oxidation of the underlying metal [4 - 7].

PbO_2 can be formed through both a solid state mechanism and a dissolution/precipitation mechanism [1]. By the solid state mechanism, $\alpha\text{-PbO}_2$ is formed from PbO , which in turn is formed through a solid state reaction from Pb, under the passivating PbSO_4 layer. In the dissolution/precipitation mechanism $\beta\text{-PbO}_2$ is formed [13]. There are reasons [1] to believe that $\beta\text{-PbO}_2$ is the more easily discharged oxide modification, while $\alpha\text{-PbO}_2$, normally, is discharged only to a small extent. When perchlorate ions are present, the dissolution/precipitation mechanism is dominating, yielding mainly $\beta\text{-PbO}_2$. Thus, in the absence of perchlorate ions, in Fig. 2 the rapid potential drop can be explained by the lower quantity of PbO_2 formed due to the overlapping oxygen evolution reaction, and probably by the formation of PbO_2 containing more $\alpha\text{-PbO}_2$, which is discharged only to a small extent.

The effect of the perchlorate ion has been discussed. However, there are other interesting phenomena related to the perchlorate assisted PbO_2 formation. Depending on which perchlorate salt is used, different discharge properties of PbO_2 can be observed. In Table 1 the discharge capacities for four identically formed PbO_2 electrodes are shown. The only difference is the perchlorate salt used. The discharge current is 0.5 mA/cm^2 . It can be seen that the capacities vary over a wide range and that the size of the cation seems to be important.

TABLE 1

Discharge capacity as a function of the perchlorate salt used during formation

Perchlorate salt	Discharge capacity (mA h/cm^2)
KClO_4	0.274
NaClO_4	0.299
LiClO_4	0.333
HClO_4	0.517

Since the PbO_2 layer is thin, porous, and formed on a solid lead electrode, there is a considerable self discharge. To calculate the real discharge capacities of Table 1, the self discharge had to be measured and a correction applied. In Fig. 3 the self-discharge currents are plotted *versus* the ionic radius of the cation. Since the cations seem to be built in the PbO_2 structure, the anhydrous ionic radii are used. The H^+ radius is set to zero as no new ion was introduced into the system. A linear relationship arises, indicating a decrease in the self discharge with an increase in the cation radius. The self discharge is probably dependent on the porosity of the structure. This is a remarkable effect, especially since the formation procedure (as described in 'Experimental') includes a reduction to Pb in pure sulphuric acid, reoxidation after a further change of electrolyte to pure sulphuric acid, and an electrode washing before each electrolyte change. This means that the structure of the PbO_2 remains almost unchanged despite the reduction and the re-oxidation step. This was further examined by measurements of the active surface area of the Pb electrode in the reduced stage. The measurements were carried out as current steps [12] from which the double layer capacitances were evaluated. Under conditions outlined in ref. 10, these capacitance values are proportional to the active surface area. In Fig. 4 the capacitance values are plotted as a function of the ionic radius of the cation, resulting in a straight line with almost the same slope as for the self-discharge plot. Thus, it is suggested that the reduction to Pb and the re-oxidation to PbO_2 , to a large extent, are both solid state processes in which the morphology of the original PbO_2 structure is retained. However, earlier studies [4] stressed the importance of soluble Pb(II) species in the formation of PbO_2 . It has also been shown by RRDE studies that soluble Pb(IV) species are formed during both formation and discharge of PbO_2 [14, 15]. Since the collection efficiency is not given, no conclusion is reached on the importance of the solution route compared with the solid state process. However, Hämeenoja *et al.* [16] showed that the amount of soluble Pb(IV) species did not exceed the values due to the chemical solubility of PbO_2 ,

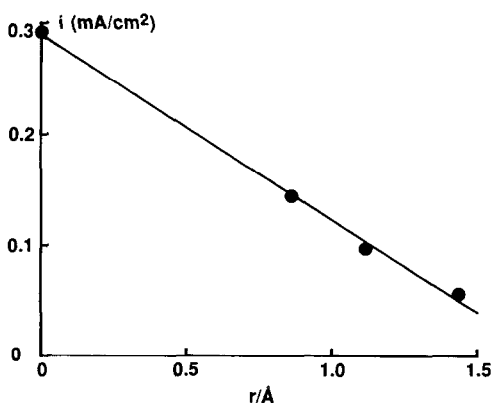


Fig. 3. Self-discharge current as a function of cation radius.

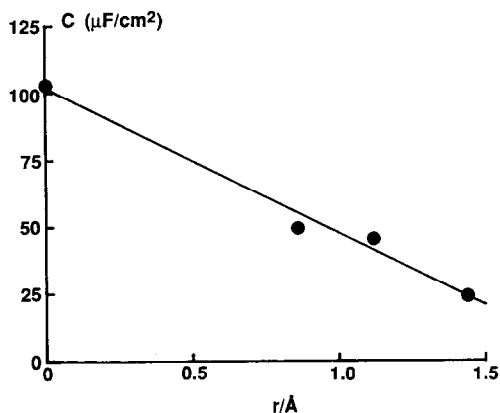


Fig. 4. Double layer capacitance as a function of cation radius.

and they claimed that Pb(IV), presumably, was not a reaction intermediate, but formed through chemical dissolution of PbO_2 . Soluble lead ion intermediates have also been reported for the Pb/PbSO_4 process [17]. In this case the amount of soluble Pb(II) species that can be detected at the ring is only 0.1% of the total reaction. Thus, even if a parallel reaction with soluble intermediates is possible, it will not change the macroscopic morphology of the original PbO_2 structure.

The role of the cation can be discussed in terms of a crystal structure defect. It is well known that electrochemically formed PbO_2 is non-stoichiometric [1, 13] and contains significant quantities of hydrogen [18, 19]. At least two different configurations of hydrogen have been suggested, one corresponding to the hydrogen orientation in the water molecule, and one interstitial. Since the experimental data show large differences in the discharge behaviour, depending on the cation used, it seems plausible that cations can be built in the structure and form different kinds of defects.

All formations with perchlorate in the electrolyte showed the same high current efficiency as discussed in relation to Fig. 2. However, it is well known that, in solid state chemistry, small amounts of impurities play a significant role in the crystal growth process, and that these impurities can determine which structure will be formed [20]. The size and charge of these impurity ions are extremely important, e.g. a small change in ionic radius can give rise to a change in the structure. Often, as in the present case, the different phases are semi-conductors [13], and the impurity ions, therefore, also have a charge stabilizing task. It is reasonable to assume that the cation has an impurity effect, and that the potassium ion stabilises the growth of the $\alpha\text{-PbO}_2$ structure more than the sodium and lithium ions, giving rise to the differences in discharge properties. Structural examinations of the layers formed will be presented in a forthcoming paper.

From a technical point of view, it is important to produce PbO_2 which not only has a high discharge capacity but also has good mechanical proper-

ties and the ability to collect current in the discharged stage. α - PbO_2 has a more compact structure and is less willing to be discharged [1]; it is probably important, therefore, to incorporate it in the electrode to maintain the mentioned properties. This was obviously the reason for the widespread use of potassium perchlorate in the industrial Planté formation processes.

Conclusions

- The addition of perchlorate to the Planté electrolyte causes pitting corrosion in a potential region where oxidation to PbO_2 is favoured compared with oxygen evolution. This effect is probably due to substitution of sulphate ions by perchlorate in the lead sulphate passive layer. When perchlorate is present, the oxidation can be performed with a current efficiency of almost 100%.

- Depending on which perchlorate salt is used, different discharge capacities of PbO_2 can be observed. The current efficiency for the oxidation is not influenced, but the ratio between α - and β - PbO_2 probably is. In the sequence $\text{K}^+ < \text{Na}^+ < \text{Li}^+ < \text{H}^+$ the discharge capacity increases, as does the self-discharge current and the active surface area. The effect is memorized in the structure and remains in the absence of the perchlorate salt after reduction to Pb, washing of the electrode, and reoxidation to PbO_2 . The effect is discussed in terms of crystal structure defects.

Acknowledgement

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References

- 1 H. Bode, *Lead-Acid Batteries*, Wiley, New York, 1977.
- 2 S. E. Afifi, W. H. Edwards and N. A. Hampson, *Surf. Technol.*, 4 (1976) 173.
- 3 W. H. Edwards and N. A. Hampson, *J. Appl. Electrochem.*, 9 (1979) 381.
- 4 A. Ragheb, W. Machu and W. H. Boctor, *Werkst. Korros.*, 23 (1972) 105.
- 5 C. Lazarides, N. A. Hampson and G. M. Bulman, *J. Power Sources*, 6 (1981) 83.
- 6 C. Lazarides, N. A. Hampson and M. Henderson, *J. Appl. Electrochem.*, 11 (1981) 605.
- 7 N. A. Hampson, C. Lazarides and M. Henderson, *J. Power Sources*, 7 (1981/1982) 181.
- 8 A. A. Abdul Azim, *Corros. Sci.*, 10 (1970) 421.
- 9 A. A. Abdul Azim and S. E. Afifi, *Corros. Sci.*, 12 (1972) 603.
- 10 E. Ahlberg and B. Berghult, *Electrochim. Acta*, in press.
- 11 E. Ahlberg and B. Berghult, *Electrochim. Acta*, in press.
- 12 E. Ahlberg and B. Berghult, *Electrochim. Acta*, submitted for publication.
- 13 D. Pavlov, *Electrochim. Acta*, 23 (1978) 845.
- 14 M. Skyllas-Kazacos, *J. Electrochem. Soc.*, 128 (1981) 817.

- 15 M. Skyllas-Kazacos, *J. Power Sources*, 13 (1984) 55.
- 16 E. Hämeenoja, T. Laitinen and G. Sundholm, *Electrochim. Acta*, 32 (1987) 187.
- 17 V. Daniel and V. Plichon, *Electrochim. Acta*, 28 (1983) 785.
- 18 R. J. Hill and M. R. Houchin, *Electrochim. Acta*, 30 (1985) 559.
- 19 R. J. Hill, *J. Power Sources*, 25 (1989) 313.
- 20 P. A. Cox, *The Electronic Structure and Chemistry of Solids*, Oxford Science Publications, Oxford, 1987.