

## PASSIVATION OF THE POSITIVE ELECTRODE OF THE LEAD/ACID BATTERY: A CONSEQUENCE OF SELF-DISCHARGE

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### Introduction

Self-discharge reactions in batteries take place during open-circuit periods. This phenomenon of self-discharge has been known since the development of the lead/acid battery. For example, Gladstone and Tribe [1] discussed the subject in 1882. Since then, many papers have been published on the problem, with most of these dealing with the influence of self-discharge on capacity loss.

It should be recognized, however, that self-discharge reactions not only cause a reduction in the discharge time,  $t$  (capacity loss  $\Delta C = \Delta t \cdot I$ ), during the following discharge, but also similarly affect the discharge voltage (see Fig. 1).

The difference ( $\Delta U$ ) between the discharge potential of an electrode before ( $U$ ), and after ( $U_{sd}$ ), self-discharge is called the passivation ( $\eta$ ), i.e.,

$$\eta = \Delta U = U - U_{sd} \quad (1)$$

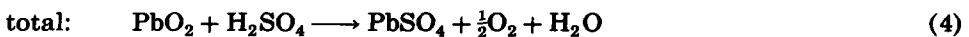
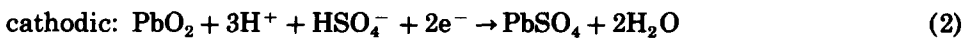
This paper discusses the influence of different self-discharge conditions on passivation.

### Theoretical background

Self-discharge reactions of the positive electrode in the lead/acid system are caused, from the thermodynamic point of view, by instabilities. These instabilities can be illustrated by a Pourbaix diagram (Fig. 2). It can be seen that reactions between (i)  $\text{PbO}_2$  and  $\text{H}_2\text{O}$ , (ii)  $\text{PbO}_2$  and  $\text{Pb}$ , and (iii)  $\text{PbO}_2$  and  $\text{H}_2$  rate are possible. The reaction, between  $\text{PbO}_2$  and  $\text{H}_2$  is, however, very low (i.e.,  $5 \times 10^{-5} - 10^{-6} \text{ A cm}^{-2}$ ) [2 - 4], and thus the important reactions are (i) and (ii).

#### (i) Active-material/electrolyte interaction

The reactions between  $\text{PbO}_2$  and  $\text{H}_2\text{O}$  are as follows:



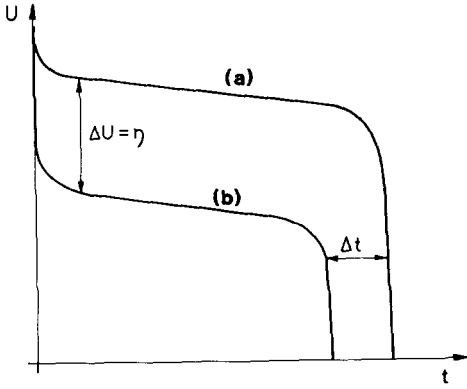


Fig. 1. Galvanostatic discharge curves of charged positive electrodes: (a) immediately after formation; (b) after self-discharge (storage).

As is obvious from the Pourbaix diagram, reaction (4) can take place only in an acid medium. The upper pH-limit is dependent on the sulphate-ion activity.

The rate-determining step is the anodic process (3). Thus, the rate of the overall reaction (4) is determined by the oxygen overpotential (which can be changed by introducing additives to the electrode or electrolyte), acid concentration, and temperature.

(ii) Active-material/grid interaction

The interaction between the active material and the grid is the same as the discharge reaction of the lead/acid system. In contrast to the above mentioned active-material/electrolyte interaction, the active-material/grid reaction takes place at all pH-values. Therefore, lead oxide and different

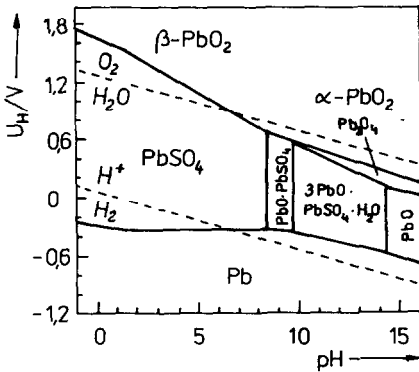


Fig. 2. Pourbaix diagram of Pb/H<sub>2</sub>O system ( $a_{\text{SO}_4^{2-}} = a_{\text{HSO}_4^-} = 1$ ).

basic lead sulphates can also be formed as reaction products. Such processes have been described by various authors, *e.g.*, refs. 4 - 12. The overall process is very complicated as the reaction pathway goes via the corrosion layer which is a multiphase system.

The components of the grid alloy (*e.g.*, antimony) can also take part in the anodic reaction [3]. Finally, the active-material/grid interaction can proceed not only in the presence of electrolyte, but also via solid-state reactions [11, 12].

### Self-discharge conditions

As mentioned earlier, the self-discharge of the positive electrode takes place during open-circuit periods. The latter occur during rest periods of operating accumulators, the storage of pre-charged accumulators, and the production of pre-charged accumulators (*e.g.*, during drying of positive electrodes). As already shown, self-discharge rates are mainly determined by the acid concentration, the temperature, and the grid material.

The acid concentration, and especially its change during self-discharge, is strongly dependent on the design of the battery system (see Fig. 3). Two types of system can be distinguished:

(i) acid-starved systems

- wet-charged accumulators (3 ml  $\text{H}_2\text{SO}_4$  (38%) per A h)
- dry-charged accumulators (residual humidity 0.05 - 2%, pH 3 - 5)
- positive electrode before drying (pH 4 - 6)
- accumulators with immobilized electrolyte (8 - 10 ml  $\text{H}_2\text{SO}_4$  (38%) per A h)

(ii) acid-flooded systems

- (10 - 15 ml  $\text{H}_2\text{SO}_4$  (38%) per A h)

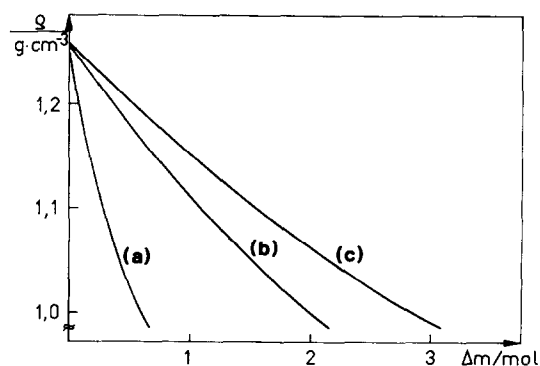


Fig. 3. Sulphuric acid density ( $\rho$ ) as a function of sulphuric acid consumption ( $\Delta m$ ) for: (a) wet battery; (b) starved (gel) battery; (c) flooded battery.

The temperature is usually determined by the temperature of the surrounding air. In the production process, however, the drying of electrodes for dry-charged accumulators gives rise to temperatures in excess of 100 °C.

## Results

### Self-discharge

Figure 4 shows the  $\text{PbO}_2$  consumption for different self-discharge reactions. Curve (a) was obtained by measuring the mass loss of the grid of pasted model electrodes. Curve (b) was determined by first measuring the total consumption of  $\text{PbO}_2$  in the active material and then subtracting the grid/active-material contribution (*i.e.*, curve (a)).

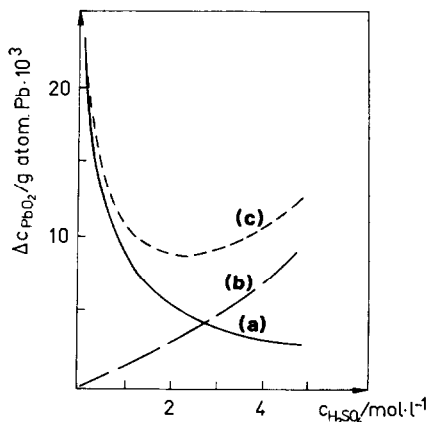


Fig. 4. Dependence of  $\text{PbO}_2$  consumption ( $\Delta c_{\text{PbO}_2}$ ) in a positive plate (Pb grid) on sulphuric acid concentration ( $c_{\text{H}_2\text{SO}_4}$ ) after 60 days storage at 40 °C. (a) grid/active-material reaction; (b) electrolyte/active-material reaction; (c) = (a) + (b).

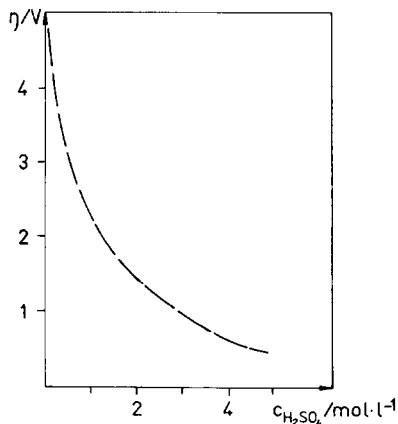


Fig. 5. Dependence of passivation ( $\eta$ ) of positive plate on sulphuric acid concentration. Storage: 60 days at 40 °C. Activation: 20 min in 1.28 g  $\text{cm}^{-3}$   $\text{H}_2\text{SO}_4$ .

TABLE 1

Dependence of passivation ( $\eta$ ) of thermally treated positive plate on grid material. Storage medium:  $1.01 \text{ g cm}^{-3} \text{ H}_2\text{SO}_4$ ; storage temperature:  $40^\circ \text{C}$ . Activation: 20 min in  $1.28 \text{ g cm}^{-3}$ .

	Grid			Pt
	Pb	Pb-2.5%Sb	Pb-2.5%Sb-1.5%Sn	
Storage time (weeks)	2.5	6	5	18
$\eta$ (mV)	2900	600	180	32

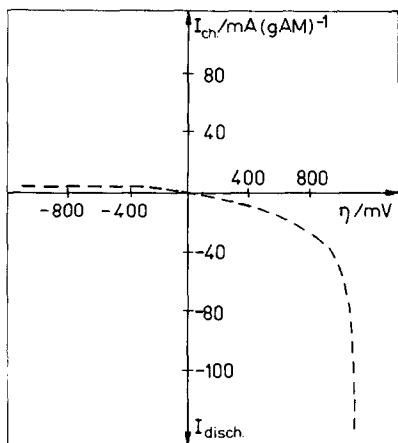


Fig. 6. Dependence of passivation ( $\eta$ ) of thermally treated positive plate on current. Activation: 20 min in  $1.28 \text{ g cm}^{-3} \text{ H}_2\text{SO}_4$ .

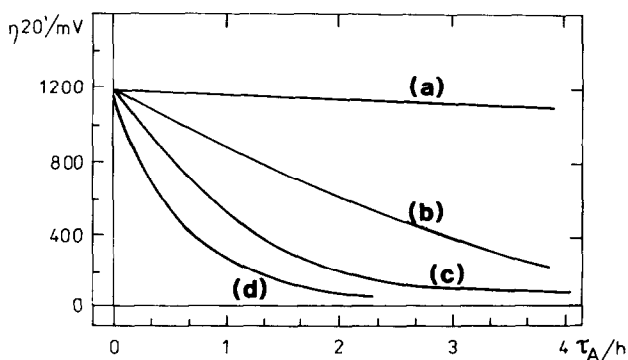


Fig. 7. Dependence of passivation ( $\eta$ ) of thermally treated positive plate on activation time ( $\tau_A$ ) and sulphuric acid concentration. (a)  $\text{H}_2\text{O}$ ; (b)  $1.4 \text{ g cm}^{-3} \text{ H}_2\text{SO}_4$ ; (c)  $1.28 \text{ g cm}^{-3} \text{ H}_2\text{SO}_4$ ; (d)  $1.05 \text{ g cm}^{-3} \text{ H}_2\text{SO}_4$ .

### Passivation

Figure 5 illustrates the influence of acid concentration. Table 1 shows the passivation ( $\eta$ ) of positive electrodes with different grids.

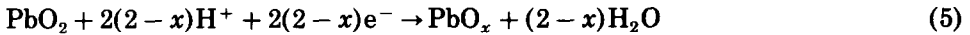
Finally, the dependence of the passivation of positive electrodes after thermal treatment (175 °C, 1 h) on current as well as on activation time and acid concentration is shown in Figs. 6 and 7, respectively.

Normally the passivation is determined by a discharge current of  $3 \times C_{20}$ .

### Discussion

The above results clearly show that the grid/active-material reaction is the main cause of the passivation phenomenon. This self-discharge reaction occurs at different parts of the electrode.

The *cathodic reaction* takes place in the  $\text{PbO}_2$  region of the corrosion layer and in the active mass. The first step is the electrochemical reduction of  $\text{PbO}_2$ , *i.e.*,



In simple terms, *i.e.*,  $x = 1$ , eqn. (5) becomes:



The second step in the cathodic reaction is purely chemical, *i.e.*,



If the pH of the electrolyte is relatively high, then the rate of the chemical stage, eqn. (7), is low. Under these conditions, therefore, a  $\text{PbO}$ -layer is formed in the corrosion-layer region. The cathodic reaction can also take place in the solid state, especially if the reaction temperature is relatively high, *i.e.*,  $>100$  °C. In this case, oxygen species are transported from the  $\text{PbO}_2$  region in the direction of the grid [11, 12].

The *anodic reaction* occurs at the phase boundary of the grid/corrosion layer, and results in the formation of  $\text{Pb}^{2+}$  ions:



The fate of such  $\text{Pb}^{2+}$  ions is determined by the electrolyte. If the solubility of corresponding lead compounds in the electrolyte is relatively high, then  $\text{Pb}^{2+}$  ions remain in the solution or are precipitated a good distance from the reaction site. On the other hand, if the solubility is low,  $\text{Pb}^{2+}$  ions are precipitated close to the anodic reaction site.

If lead sulphate is precipitated, then a semi-permeable  $\text{PbSO}_4$  membrane is built up; this is non-permeable to  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$  and  $\text{Pb}^{2+}$  ions [13-16]. Thus, there is a decrease in the concentration of sulphuric acid ( $C$ ) beneath the membrane. This phenomenon gives rise to a sulphuric acid concentration

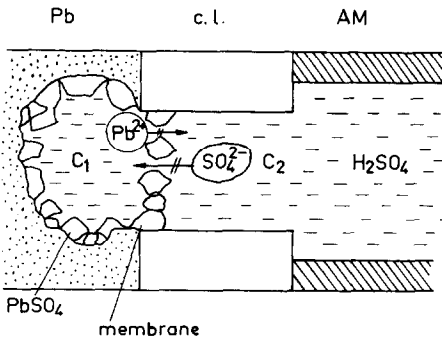


Fig. 8. Sulphuric acid concentration cell with a semi-permeable  $\text{PbSO}_4$  membrane.

cell with  $C_2 > C_1$  (Fig. 8). The following reactions take place:

(i) region with  $C_1$  concentration of  $\text{H}_2\text{SO}_4$ :



(ii) region with  $C_2$  concentration of  $\text{H}_2\text{SO}_4$ :



## Conclusions

In sulphuric acid of higher concentration ( $1.28 \text{ g cm}^{-3}$ ), where a semi-permeable  $\text{PbSO}_4$  membrane is built up,  $\text{PbO}_2$  is the main product of the corrosion layer at the grid/active-mass interface. Under these conditions, no passivation is observed. At lower acid concentrations (*i.e.*,  $1.01 \text{ g cm}^{-3}$ ) the main reaction products are  $\text{PbO}$  and basic lead sulphates of low conductivity. Thus, the resistivity of the corrosion layer increases and passivation occurs. Parallel with the liquid phase reaction, and independent of the acid concentration, a solid-state reaction takes place. The latter results in the formation of  $\text{PbO}$  in the corrosion layer and, as a consequence, passivation is observed [11, 12]. Therefore, the discharge behavior of a positive electrode is determined by the relative rates of the liquid-phase and the solid-state processes. In the case of the drying of electrodes, both processes are quasi separated.

The kinetics of the liquid phase process are mainly dependent on the anodic reaction area, that is, the porosity of the corrosion layer. This porosity is determined by the mechanical stress of the corrosion layer (which is greater for  $\text{Pb}$  than for  $\text{Pb-Sb}$  alloy substrates) and by the covering of the anodic area by reaction products (note,  $\text{PbSO}_4$  crystal size is smaller in the presence of  $\text{Sb}$  [17]). The kinetics of the solid-state process are determined by the temperature. The reaction rate is low at normal temperature.

The electrical behaviour of the passivation layer is mainly determined by the charge transfer through the phase boundaries. The electronic path

consists of a Schottky barrier (Pb/PbO) in series with a pn-junction (PbO/PbO<sub>2</sub>) [18]. Therefore, passivation is a semiconductor phenomenon.

In acid-flooded systems, the acid concentration decreases slowly (see Fig. 3) during storage. Thus, passivation is observed only after a long period of storage. In acid-starved systems, and especially in a wet accumulator, the decrease in acid concentration is relatively rapid (see Fig. 3) during storage. Therefore, passivation sets in after short storage times.

With the drying of electrodes, passivation is observed in all types of cell design at the end of the process. This is because no depassivation reaction is possible.

Passivation can be reversible and is dependent on the activation (depassivation) conditions. The extent of passivation can be reduced by the use of Pb-Sn alloys and by applying Sn coatings to the grid [18].

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