

ON THERMOPASSIVATION OF THE POSITIVE LEAD-ACID BATTERY ELECTRODE

PART 3: THERMOPASSIVATION OF SMOOTH PbO_2 ELECTRODES

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Summary

Smooth (unpasted) PbO_2 electrodes are passivated after thermal treatment, indicating that such passivation occurs in the region of the grid/corrosion layer phase boundary. Concurrent with the passivation process, however, a synproportionation reaction occurs between the Pb grid and the PbO_2 corrosion layer, which decreases the discharge capacity and accelerates depassivation. The influence of the synproportionation reaction on the discharge behaviour of pasted PbO_2 electrodes is discussed.

Zusammenfassung

Auch glatte (unpastierte) PbO_2 -Elektroden weisen nach starker thermischer Behandlung Passivation auf. Das zeigt, dass die Passivationsreaktion im Bereich der Phasengrenze Gitter/Korrosionsschicht verläuft. Der Passivationsprozess wird jedoch von einer Synproportionierungsreaktion zwischen Gitter-Pb und Korrosionsschicht- PbO_2 überlagert. Diese Reaktion führt zu einer Reduzierung der Entladekapazität und beschleunigt die Depassivierungsreaktion. Der Einfluss der Synproportionierung auf das Entladeverhalten pastierter PbO_2 -Elektroden wird diskutiert.

1. Introduction

An additional decrease in the discharge voltage is observed during the initial discharge of a pasted PbO_2 electrode dried under unfavourable conditions. This phenomenon, called thermopassivation by Pavlov and Ruevski [1], has been the subject of a series of papers cited in ref. 2.

Thermopassivation (η_T) is the difference between the discharge voltages of undried (U_D^{ud}) and dried (U_D^d) electrodes, which have been activated before discharge.

$$\eta_T = U_D^{ud} - U_D^d \quad (1)$$

We have shown that the thermopassivation voltage is dependent on the activation time (τ_A) and is divided into two terms

$$\eta_T^{\tau_A} = \eta_T^0 - \delta_T^{\tau_A} \quad (2)$$

The first term, η_T^0 , is the thermo-passivation value at zero activating time ($\tau_A = 0$) due to the formation of a PbO_n layer in a solid state reaction during drying.

The second term, $\delta_T^{\tau_A}$, is the depassivation at activating time τ_A , due to the decomposition of the PbO_n layer ($1 \leq n < 1.5$) in a liquid phase reaction as a consequence of the activation [2 - 5].

In our papers [2 - 5] it was postulated that the formation of the PbO_n layer occurs at the corrosion layer and its boundary with the grid material. The thermopassivation effect, therefore, should also occur with smooth PbO_2 electrodes obtained by anodic polarization of the grid lead.

The work reported in this paper was undertaken to study the influence of thermal treatment on the discharge behaviour of smooth PbO_2 electrodes

2. Experimental

Smooth PbO_2 electrodes were produced by galvanostatic polarization ($i = 3 \text{ mA/cm}^2$) on a sheet (2 cm^2) of the alloy $PbSb5AsO 1$ ($Pb-5 \text{ wt } \% \text{ Sb}-0.1 \text{ wt } \% \text{ As}$) in pure H_2SO_4 ($c = 0.8 \text{ mol/l}$). The polarization time (τ_f) is variable and is indicated in the results.

After being polarized the electrodes were washed for 20 s in distilled water up to neutrality of the PbO_2 and then predried for 20 s by hot air at $45 \text{ }^\circ\text{C}$. One set of these electrodes was then immediately immersed in electrolyte (not thermally-treated electrodes) and the other set was immersed after a thermal treatment (1 h at $175 \text{ }^\circ\text{C}$) in a drying cupboard (thermally-treated electrodes)

Both sets of electrodes were characterized by electrochemical reduction (discharge current density $i_d = 1.5 \text{ mA/cm}^2$, $c_{H_2SO_4} = 4.93 \text{ mol/l}$, activating time $\tau_A = 5 \text{ min}$ discharge and activating temperature $\vartheta_d = \vartheta_A = 0 \text{ }^\circ\text{C}$), by rest potential measurement, and by chemical analysis to give the $c_{Pb^{4+}}/c_{Pb^{2+}}$ ratio ($c_{Pb^{4+}}$ —titration of Pb^{4+} by thiosulfate, $c_{Pb^{2+}}$ —after the Pb^{4+} reduction)

All the potentials are relative to an Hg_2SO_4/Hg reference electrode in $4.93M H_2SO_4$

3. Results

Figure 1 shows the galvanostatic discharge curves of thermally treated and untreated, smooth PbO_2 electrodes. Figure 2 shows the same for pasted

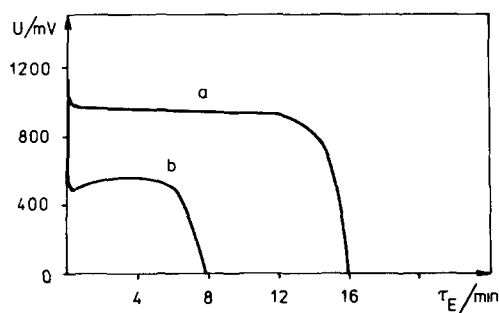


Fig 1 Galvanostatic discharge curves of smooth PbO_2 electrodes ($\tau_F = 50$ h) at 0°C a, Electrode not thermally treated, b, thermally treated electrode

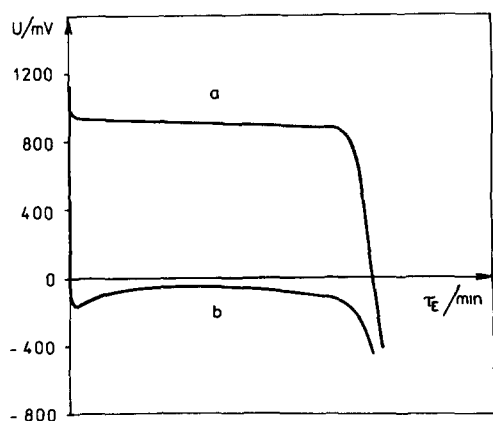


Fig 2 Galvanostatic discharge curves of pasted PbO_2 electrodes a, Electrode not thermally treated, b, thermally treated electrode $I = 1/3 \text{ h} \times C_{20}$, $\vartheta_d = \vartheta_A = 0^\circ\text{C}$, $\tau_A = 1$ h

PbO_2 electrodes In contrast to pasted electrodes the thermal treatment of smooth electrodes produced less thermopassivation and a considerable decrease in capacity, although the activating time of the smooth electrodes was much shorter. At lower activating temperatures ($\vartheta_A = -24^\circ\text{C}$) the thermopassivation of the smooth electrodes was similar to that of the pasted electrodes ($\eta_T = 1100$ mV).

The decrease in the discharge capacity (ΔC) will, to a first approximation, be independent of the PbO_2 layer thickness (formation charge q_F), as shown in Fig. 3 Experiments also show that when the formation charge is less than about 50 mA h/cm^2 the thermally treated smooth electrode no longer has any capacity.

This is also evident from plots of the steady state potential against activating time of different PbO_2 electrodes formed at $q_F = 12 \text{ mA h/cm}^2$ As Fig 4 shows, the thermally treated electrodes do not accept a $\text{PbO}_2/\text{PbSO}_4$ potential and the smooth electrode which has not been thermally treated no longer has any capacity below formation charges of about 15 mA h/cm^2 (Fig. 3)

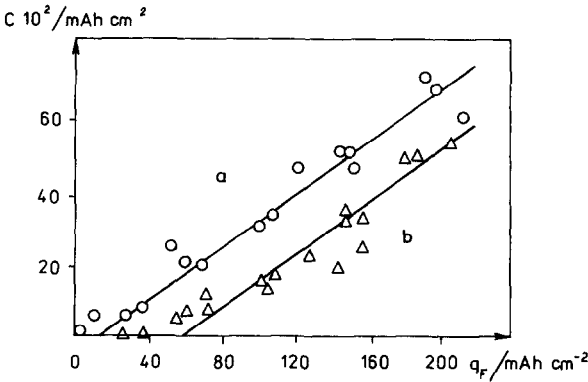


Fig 3 Discharge capacity (C) of smooth PbO_2 electrodes as a function of the amount of formation charge (q_F) a, Electrode not thermally treated, b, thermally treated electrode

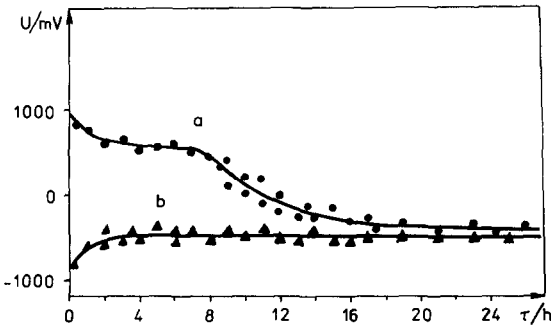


Fig 4 Open circuit potential-activating time curves of smooth PbO_2 electrodes ($\tau_F = 8 \text{ h} \cong q_F = 12 \text{ mA h/cm}^2$) a, Electrode not thermally treated, b, thermally treated electrode

TABLE 1

Degree of oxidation of the corrosion product, n , (error limit ± 0.05) of thermally untreated and thermally treated smooth PbO_2 electrodes formed with $q_F = 100 \text{ mA h/cm}^2$

	Thermally untreated electrodes	Thermally treated electrodes
n in PbO_n	1.88	1.72

An investigation of the effect of thermal treatment on the degree of oxidation of formed lead oxides showed that this treatment decreased the PbO_2 concentration. Table 1 shows this effect, although the absolute values depend on the formation charge (layer thickness) which for these data was $q_F = 100 \text{ mA h/cm}^2$

The effect the electrolyte remaining in the pores after predrying had on the capacity loss caused by the thermal treatment was also studied. Lead

TABLE 2

Discharge capacity (C) (error limit ± 0.04 mA h/cm²) of predried and vacuum (1 Pa, 35 °C, 16 h) dried smooth PbO₂ electrodes formed with $q_F = 140$ mA h/cm²

	Predried electrodes		Vacuum dried electrodes	
	Before thermal treatment	After thermal treatment	Before thermal treatment	After thermal treatment
C (mA h/cm ²)	0.47	0.29	0.42	0.41

dioxide electrodes were dried under vacuum (1 Pa at 35 °C for 16 h) before the high temperature treatment. The corresponding discharge capacities of the vacuum dried, and the normal predried, electrodes, before and after the high temperature treatment, are given in Table 2. To determine the influence of the collector material, electrodes made by anodically coating platinum with PbO₂ were examined. No thermopassivation and no capacity decrease were observed after the thermal treatment.

4. Discussion

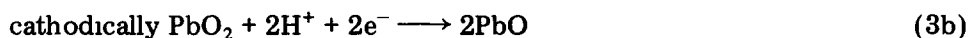
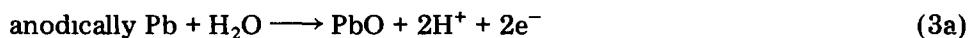
The results show that the PbO₂ electrodes are passivated by thermal treatment, even when there is no excessive PbO₂ active mass, as in the case of pasted electrodes. This substantiates our hypothesis that the passivation effect is based on reactions in the region of the Pb grid/corrosion layer phase boundary.

The decreases in the capacity (Figs. 1 and 3), and the degree of oxidation of the lead oxides (Table 1) indicate that reactions occur during the thermal treatment of the smooth electrodes which reduce the PbO₂ concentration. This is an electrochemical liquid phase reaction, because it may be prevented by removing the free water (Table 2). As far as the discharge of the PbO₂ in a neutral medium is concerned, only the interaction with the grid lead need be considered, as described by Feitknecht [7].

Equation (3) is the basic reaction*:

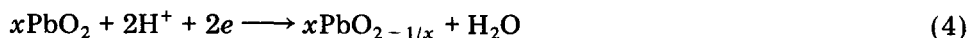


with the following individual reactions



The cathodic reaction proceeds by intermediate stages, as shown by curve "a" of Fig. 4, and may be written in the more general form

*In dependence on the pH and the $a_{\text{SO}_4^{2-}}$, basic sulfates could be present as reaction products



The constant difference in capacity, ΔC (about 0.17 mA h/cm²), between the thermally treated electrodes and those not thermally treated, as shown in Fig 3, is independent of the formation charge. It depends, instead, on the water content of the pores, which is determined by the predrying conditions. This is shown in Table 2.

When the water remaining in the pores is constant we can hypothesize that the area of the Pb/Electrolyte Interphase determines the rate of the synproportionation reaction (3), that is to say, the decrease in capacity. Since this area, to a first approximation, is independent of the formation charge, the difference in capacity must be constant. This is additional evidence for our hypothesis of a porous corrosion layer of the lead electrode in the rest period. Of course, not only does the capacity decrease during the thermal treatment, but it decreases also during pretreatment (washing and predrying) and activation. The decrease due to the pretreatment and activation, however, is much smaller in relation to the thermal treatment because both the temperature and the synproportionation reaction time are less.

The greater volume of the synproportionation reaction products causes mechanical stress which leads to disintegration of the corrosion layer and a consequent increase in porosity. Better conditions for the depassivation are thereby obtained. The depassivation reaction involves oxidation of the passivating PbO_n layer by PbO₂ *via* the electrolyte, so the greater the porosity of the layer the higher the reaction rate [5].

This depassivation reaction is, however, strongly suppressed by the precipitation of ice crystals in the pores [8] and the accelerating effect of the depassivation by the synproportionation reaction does not occur. This may, to a first approximation, explain the similar thermopassivation values of smooth and pasted electrodes.

The synproportionation reaction (3) not only influences the capacity but also the thermopassivation value (η_T^{TA}) by depassivation (δ_T^{TA}). Because this synproportionation reaction cannot take place with Pt as the collector material, thermal treatment did not change the discharge curve.

In the case of pasted electrodes, the influence of the synproportionation reaction on the capacity can be neglected because of the large excess of PbO₂ active mass in the electrode. This may also account for the lower influence on the depassivation of pasted electrodes compared with smooth electrodes. It is possible that the formation of a depassivating accelerating structure of the corrosion layer is limited, as the active mass of PbO₂ can also take part in the synproportionation reaction.

However, at long reaction times and high reaction temperatures the synproportionation reaction may influence depassivation. Because the synproportionation takes place only in the presence of water (see eqns. (3a) and (3b)) the reaction time is the same as the drying time. The reaction temperature is equal to the temperature of the electrode in the drying period. Figure 4 shows the influence of synproportionation on the depassivation of

pasted electrodes The thermal treatment time is 20 minutes in all cases. However at high temperatures ($T_T > 100$ °C) the reaction time (drying time) is shorter than 20 minutes (*i.e.* at 175 °C only 4 min [2]) and at temperatures between 75 °C and 100 °C the reaction time is determined by the thermal treatment time, that means 20 minutes

The reaction temperature is, to a first approximation, independent of the treatment temperature, because at $T_T > 100$ °C the electrode temperature does not rise over about 100 °C because of the isothermal evaporation of the water That means at lower treatment temperatures a greater loosening of the structure of the corrosion layer occurs and so a more rapid depassivation is observed

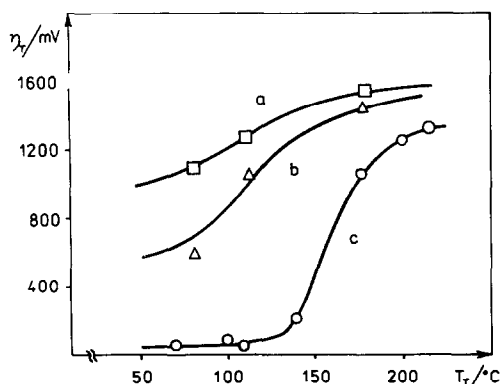


Fig 5 Thermopassivity of pasted PbO_2 electrodes as a function of the temperature of thermal treatment (T_T) at different activating times (τ_A), time of thermal treatment 20 min a, $\tau_A = 0.5$ min, b, $\tau_A = 3$ min, c, $\tau_A = 20$ min

List of symbols

c	Concentration
C	Discharge capacity density
i	Current density
i_d	Discharge current density
q_F	Formation charge density
T_T	Temperature of thermal treatment
U_d	Potential
U_D^d	Discharge potential of dried electrode
U_D^{nd}	Discharge potential of an undried electrode
ΔC	Capacity decrease
$\delta_T^{\tau_A}$	Depassivation after the activating time τ_A
ϑ_d	Discharge temperature
ϑ_A	Activating temperature

η_T	Thermopassivation
$\eta_T^{\tau_A}$	Thermopassivation after the activating time τ_A
η_T^0	Thermopassivation after the activating time $\tau_A = 0$
τ	Time
τ_A	Activating time
τ_E	Discharge time
τ_F	Formation time

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