

ON THERMOPASSIVATION OF POSITIVE LEAD-ACID BATTERY ELECTRODES.

PART I: THE INFLUENCE OF DRYING POSITIVE, DRY-CHARGED LEAD-ACID BATTERY ELECTRODES ON THERMOPASSIVATION AND ITS CAUSES

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Summary

The influence on thermopassivation (η_T) of the drying time (τ) and drying temperature (ϑ) of formed positive electrodes for dry-charged lead-acid batteries has been investigated. It has been shown that there is no thermopassivation in the case of $\tau \leq 4$ min up to approx. $\vartheta = 250$ °C, while drying temperature has a different influence on thermopassivation at $4 \text{ min} < \tau < 30$ min. Passivation is observed at $\tau > 30$ min even where $\vartheta < 100$ °C. The effect of thermopassivation increases with falling cell temperature. If drying conditions and cell temperatures are not extreme, thermopassivation has hardly any influence on the immediate ampere-hour capacity, but has a comparatively large influence on the immediate watt-hour energy content.

Physico-chemical and electrochemical investigations show that the PbO_2 electrode is thermally damaged during the drying process. This is apparent from changes in the primary structure of the active mass (destruction of preprotonized structure) and — especially at higher temperature — also in the secondary structure (reduction of BET surface) as well as in the composition of passivating layers. However, the contributions of primary and secondary structure variations to the overall amount of thermopassivation are comparatively low. The principal reason for this phenomenon is the generation of poorly conductive and, thus, passivating layers with semiconductor properties.

1. Introduction

Dry-charged lead-acid batteries are in general use nowadays. Drying of electrodes after formation is often accompanied by problems mainly in connection with oxidation of the lead sponge of the negative plate [1]. However, there are also changes to the positive plate, especially at drying temperatures

above 100 °C; these become apparent as a reduction of discharge potential [2 - 7]. This voltage drop relative to the undried plate was first called thermopassivation by Pavlov [5].

The process of drying formed positive electrodes — in tunnel furnaces, in drying chambers at normal pressure or under vacuum, and in drying cases — has an important influence on thermopassivation: the present paper is intended to investigate more precisely this influence during plate drying in a case, and to determine its causes.

2. Experimental

Tests were carried out on formed 15 A h, grid type, starter battery plates (grid alloy PbSb5As0.1) washed in running water for five hours prior to drying. Contact drying in a resistance-wire-heated drying case which permits stepless temperature setting up to 250 °C was employed. Due to the arrangement of the heating wires there were different temperature zones on the plate; they differed from the nominal value by about 8 per cent. in either direction. Inertia of regulation may result in a further deviation of $\pm 5\%$.

An investigation of the causes of thermopassivation (Section 4) was carried out with round (14 mm dia.) 0.12 A h electrodes dried in the drying oven.

For discharge, each positive electrode was combined with two undried negative electrodes.

Thermopassivation (η_T) is defined as the difference between the discharge voltage of an undried electrode (U_D^{ud}) and the discharge voltage of a dried electrode (U_D^d) when discharged at corresponding currents after activation in the working electrolyte for 20 min prior to discharge

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

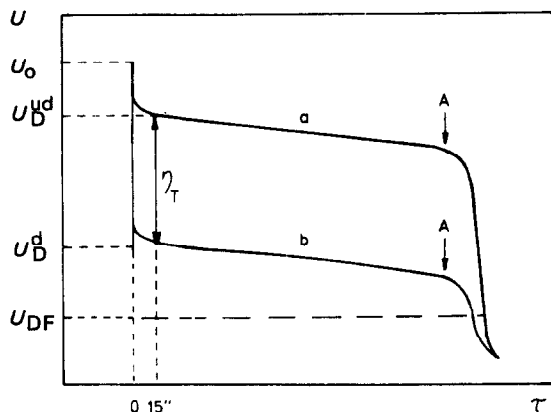


Fig. 1. Typical discharge characteristics for undried (a) and dried (b) positive lead-acid battery plates.

Unless otherwise stated, thermopassivation has been determined at 20 °C with a current, I , of $3 \times K_{20}$ (starting current) 15 s after the start of discharge in sulphuric acid ($\rho_{25\text{ }^\circ\text{C}} = 1.28\text{ g/cm}^3$). The discharge characteristics are shown in Fig. 1.

Twenty electrodes have been investigated for the determination of the reference value U_D^d , and at least two electrodes for U_D^d .

Resistive polarization was determined by means of an interrupter unit (type PU 1 made by the Research Institute of Meinsberg) with a 10 : 1 ratio of load to interrupt time and an interrupt time of 5×10^{-5} s.

The active mass was ground and classified (50...100 μm) for investigation with the suspension electrode. The collector was a cylindrical gold electrode (60 cm^2), with a platinum counter electrode separated by a diaphragm. 2.5N HClO_4 was used as the electrolyte because the reduction currents in H_2SO_4 were too low, obviously due to the high transition resistance caused by PbSO_4 . Measurements were carried out potentiodynamically ($dU/d\tau = 200\text{ mV/min}$). The ^1NMR wideband investigation was carried out using a device made by the Dresden College of Technology.

3. Results

3.1. Drying process

To minimize self-discharge of the positive electrode, a water content of no more than 0.5% (referred to the active mass) after drying is required. The water contents shown in Fig. 2 have been determined as functions of the drying conditions (temperature, time). In the case of the drying technology

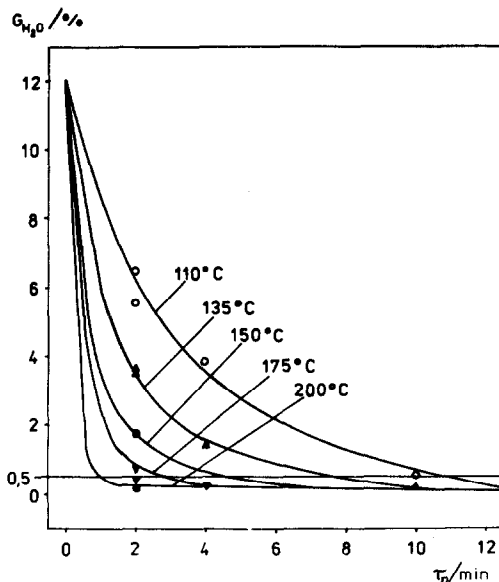


Fig. 2. Drying isothermal lines of positive lead-acid battery double plates.

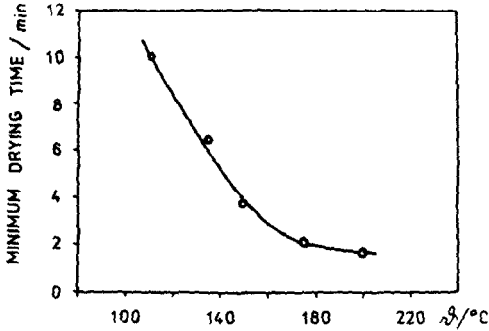


Fig. 3. Minimum drying time as a function of drying temperature.

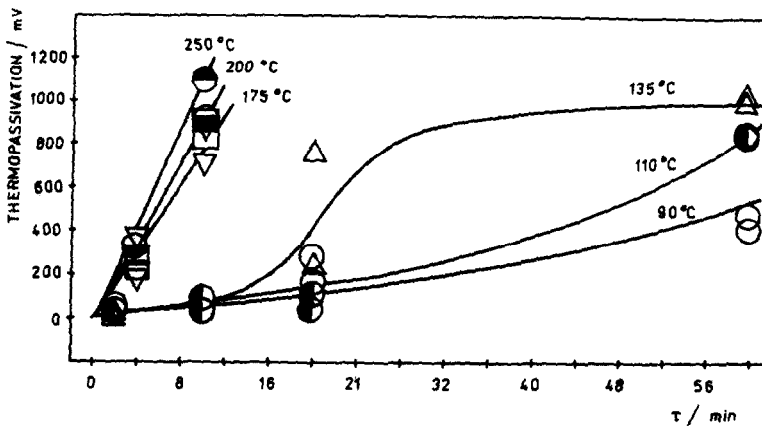


Fig. 4. Thermopassivation as a function of drying time at different drying temperatures.

applied, the minimum drying time, τ_{\min} (shortest time required to attain the necessary water content of 0.5% at a given temperature), is accompanied by the dependence shown in Fig. 3.

3.2. Thermopassivation as a function of drying temperature and time

The dependence of thermopassivation on drying time and drying temperature is represented in Fig. 4.

There are three principally different ranges which are best characterized by the drying time (τ).

$\tau < 4$ min

No, or only a very low thermopassivation is observed at all temperatures investigated. At high drying temperatures this is obviously due to the fact that the temperature of the active mass will hardly exceed the 100 °C limit up to complete vaporization of the water, in spite of the high case temperature. Thus, the high temperatures act on the plate for only a comparatively short time.

$4 \text{ min} < \tau < 30 \text{ min}$

Drying temperature has a different influence on thermopassivation.

A drying time of 10 min (Fig. 4) at about 140°C is not accompanied by thermopassivation. Above this it increases rapidly up to about 170°C and again has a lower temperature dependence at higher temperatures.

$\tau > 30 \text{ min}$

Thermopassivation occurs at all drying temperatures, even at $\vartheta < 100^\circ\text{C}$. Obviously the degree depends on the drying time.

It must be concluded that thermopassivation occurs at all the temperatures in question if the drying time is sufficiently long. For instance, a drying temperature of only 50°C , caused a thermopassivation of 250 mV after a drying time of 120 min.

If the maximum permissible water content of 0.5% in the active mass is obtained in accordance with the time-temperature function shown in Fig. 3, there will be no thermopassivation in the whole validity range of this function.

3.3. Thermopassivation as a function of cell temperature

As mentioned in the "Experimental" section, in general discharges have been carried out at 20°C . However, a cold activation test at -18°C results in the thermopassivation dependence shown in Fig. 5. It is apparent from this that reduction of cell temperature from 20°C to -18°C results in a thermopassivation increase by an average of 600 mV at all drying temperatures.

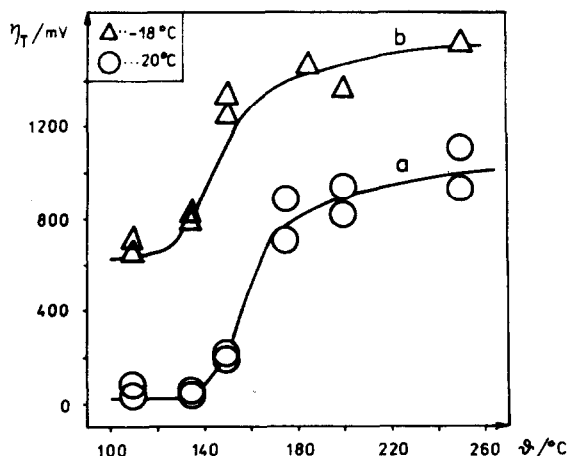


Fig. 5. Thermopassivation as a function of drying temperature at drying time of 10 min. Test temperature: (a) $+20^\circ\text{C}$; (b) -18°C .

Our results showed that thermopassivation decreases with increasing soak time in the electrolyte (see also ref. 6). Thus, this temperature effect can either be due to heavy depassivation reduction resulting from a soak time of only 20 minutes at lower temperature, or be due to a distinct temperature dependence of the mechanism on which thermopassivation is based.

3.4. Thermopassivation as a function of immediate activation properties

Changes resulting from the drying process are eliminated after a sufficiently long soak time in sulphuric acid, so that thermopassivation will affect no quality parameter other than the immediate activation properties found at a current of $I \hat{=} 3 \times K_{20}$ 20 minutes after filling with acid.

3.4.1. Immediate ampere hour capacity

As shown by the typical discharge characteristics in Fig. 1 for an undried and a dried electrode, the $U-\tau$ characteristic of the thermopassivated plate is just shifted along the potential axis relative to the non-passivated plate.

This results, to a first approximation, in the fact that, as long as capacity reduction is not considered, thermopassivation will be less than the difference between the starting voltage of the undried electrode (U_D^{ud}) and the final discharge voltage (U_{DF}).

$$\eta_T < U_D^{ud} - U_{DF}. \quad (2)$$

The difference ($U_D^{ud} - U_D^d$) is about 800 mV, and the discharge voltage of the electrode is reduced in the course of discharge relative to the starting voltage by approx. 200 mV at voltage collapse (point A in Fig. 1). Thus, considerable capacity reduction must be expected if thermopassivation is higher than 600 - 800 mV. Figure 6 represents the relative capacity K (the ratio between the cell capacity with a dried electrode and that of the cell with an undried positive electrode) as a function of drying time for different drying temperatures.

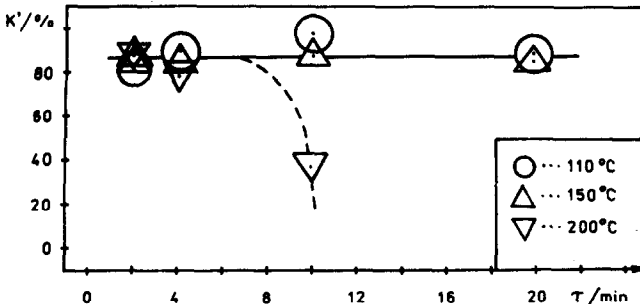


Fig. 6. Capacity as a function of drying time and drying temperature.

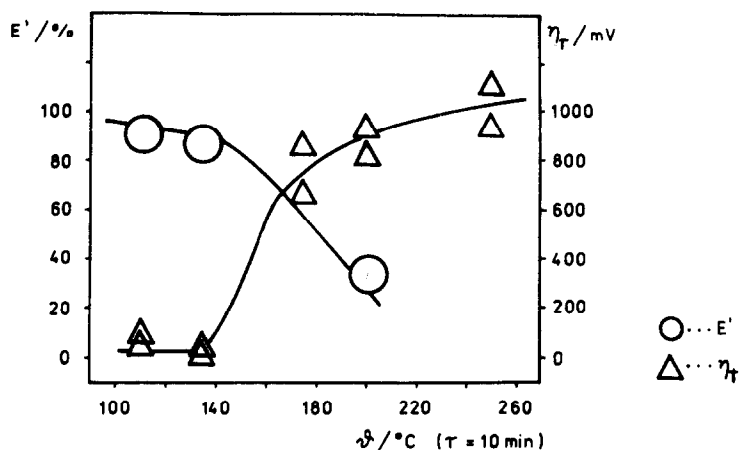


Fig. 7. Thermopassivation and energy as functions of drying temperature at drying time of 10 min.

There is no capacity reduction except at extreme drying conditions ($\tau > 4$ min, $\vartheta > 150$ °C or $\tau > 20$ min, $\vartheta > 110$ °C) or low cell temperatures (-18 °C).

3.4.2. Immediate watt hour energy content

The energy content is the product of the ampere hour capacity and the mean discharge voltage and, thus, is subject to heavier thermopassivation than the immediate ampere hour capacity.

Figure 7 shows the relative energy content E' (the ratio between the energy content of the cell with a dried positive electrode and that of the cell with an undried electrode) and the thermopassivation as a function of drying temperature.

4. Discussion

The causes of thermopassivation are specified by Badger [2] and Tiegel [3] as an increase of the internal resistance, while Manoim *et al.* [4], who were the first to describe these phenomena in detail, mention the formation of insulating PbO layers. At higher temperatures these are supposed to be generated faster at the boundary layer between the lead alloy and the active mass due to synproportionation according to eqn. (3):



Pavlov and Ruevski [5, 6] discuss the generation of a passivating, semiconducting, non-stoichiometric PbO_n layer ($n < 2$) at the phase boundary between the corrosion layer and the active mass.

Conversion of the entire PbO in the active mass into lower compounds need not be considered because rest potentials of the thermopassivated and the non-passivated electrodes are all equal within the limits of error. However, even thermal damage of the active mass must be taken into consideration so that the following items should be discussed:

- changes in active mass composition;
- changes in active mass structure;
- formation of passivating layers.

4.1. Changes in active mass composition

Drying at high temperature can effect the thermal dissociation of PbO₂ according to the formula



This is accompanied by generation of PbO_{2-n} with a lower conductivity which, in turn, could effect an increase in resistance of the active mass. Chemical and X-ray analyses, however, do not show changes in active mass composition as a function of drying conditions. This is in accordance with expectation because thermal dissociation should not begin below 290 °C [8].

4.2. Changes in active mass structure

These changes are possible in the primary and secondary structure ranges.

4.2.1. Primary structure

The real formula of lead dioxide in the electrodes is PbO_{2-y} (x H₂O). It is highly probable that the specified water is integrated into the lattice in such a way that the oxygen of the water is in the oxygen vacancies (y up to approx. 0.2) and the hydrogen of the water on interstitial sites [9]. This hypothesis is supported by our ¹H-NMR wideband investigations which show that decreasing temperature is not accompanied by an essential band widening (Table 1), and that hydrogen has a comparatively good mobility down to approx. -190 °C, which can only be explained by protons on interstitial sites, not by physically adsorbed water.

The hydrogen ions were then not allocated to a certain oxygen in a fixed location, but result in the generation of hydrogen bridges which are responsible for the mobility of the proton in lead dioxide (H⁺-diffusion coefficient in PbO_{2-y} x H₂O = 7 × 10⁻⁵ cm² s⁻¹ [10]). This allows essential preprotonation of oxygen in lead dioxide. These O-H groups make the Pb²⁺, in accordance with Lewis, still more acidic, and lead dioxide reduction (eqns. (5) and (6)) is favoured mainly in the first electrochemical step.



TABLE 1

$^1\text{H-NMR}$ bandwidth recorded at PbO_2 as a function of measuring temperature

ϑ ($^{\circ}\text{C}$)	^1H bandwidth (G)
+25	1.3
+15	1.2
-50	1.1
-68	1.4
-110	1.6
-183	1.5
-190	1.5

Thus, thermal treatment of the active mass could cause disintegration of water belonging to the lead dioxide and, consequently, of the O-H groups, which would effect concentration polarization.

Investigation of the active mass alone with the suspension electrode showed the dependence of potentiodynamically generated $I-U$ characteristics on the drying conditions (Fig. 8).

These results confirm that thermal damage of the active mass cannot be neglected. The voltage drop at a current of $I \hat{=} 3 \times K_{20} = 100$ mA (provided that no more than one third of the particles are in contact with the collector electrode per unit of time) amounts to no more than 25 mV, so that it is much lower than the thermopassivation value.

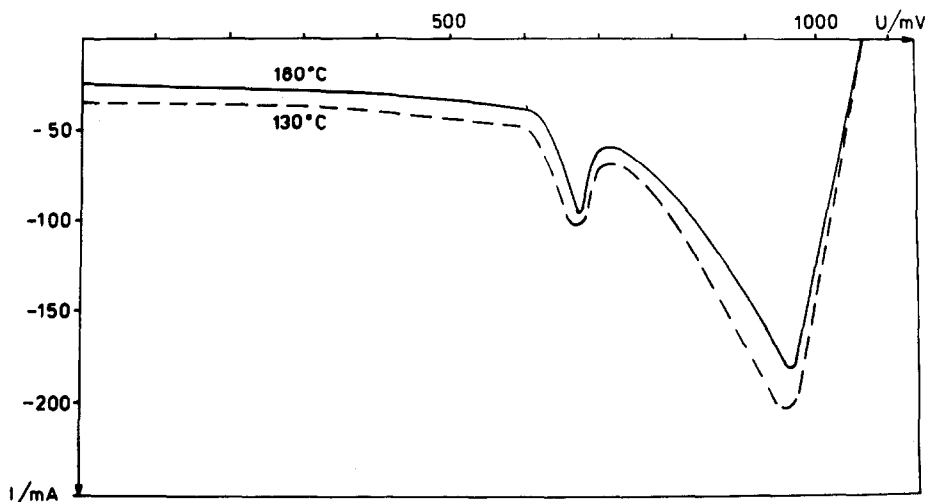


Fig. 8. $U-I$ curves of PbO_2 electrodes logged potentiodynamically with the suspension electrode as a function of drying temperature (drying time 10 min).

4.2.2. Secondary structure

A change in the secondary structure can result in deceleration of transport processes (diffusion and migration) by reduction of the pore volume or a shift of the maximum in the pore volume distribution, or in an increase of the local current density by reduction of the BET surface.

Structure analyses, however, did not show any dependence of pore volume and pore volume distribution on drying conditions. A slight, repeatable decrease of the BET surface only (Fig. 9) has been observed at high drying temperatures. Recordings taken by electron scan microscopy confirm these findings (Fig. 10). Sintering of the mass is distinctly visible in the samples dried at 200 and 250 °C. This decrease of the BET surface from approx. 4 m²/g to 3 m²/g increases the current density referred to the actual surface by 33%, whereby the overvoltage can thus be increased. Galvanodynamic characteristics of the undried sample, however, show that the amount does not exceed 80 mV which is insufficient to be the only reason for the much higher amount of thermopassivation. In addition, it is difficult to see why this surface change should be eliminated again after a short soak time in the electrolyte.

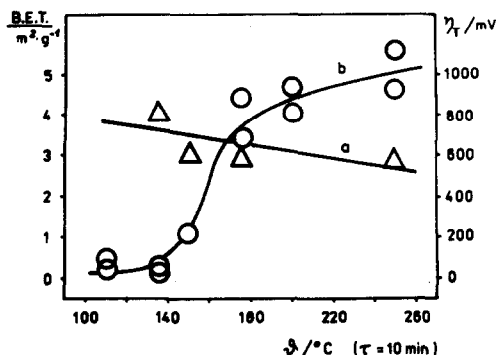
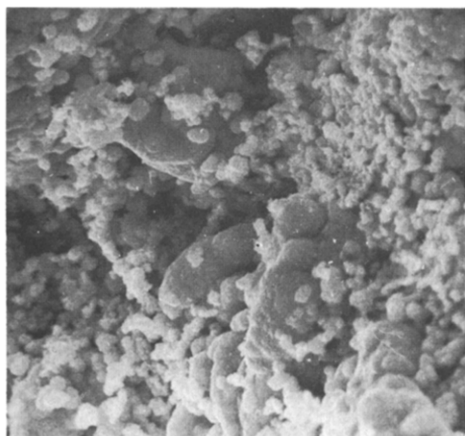


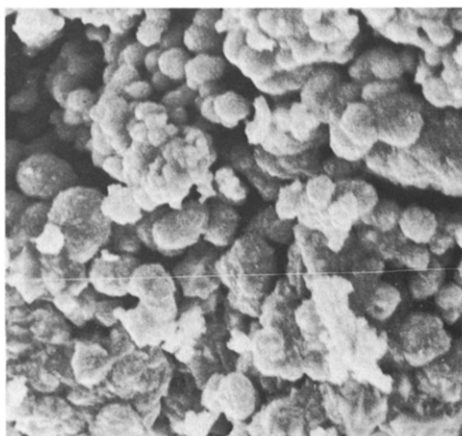
Fig. 9. BET surface (a) and thermopassivation (b) as functions of drying temperature at a drying time of 10 min.

4.2.3. Formation of passivating layers

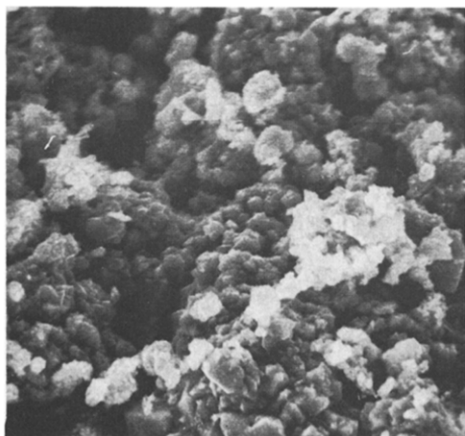
The current density–thermopassivation characteristic (Fig. 11) of our round electrodes are not of a pure ohmic type and in contrast to Pavlov and Ruevski [6] we found that the thermopassivation approximated to a limiting value at high current densities. This could be due to different geometric conditions of the mass carrier and has no ohmic character. The causes of this behaviour could be inhibition of the electrode reaction or the formation of resistive layers with semiconductor properties. The interrupter method has been applied for the elimination of the influence of electrode reactions. This confirmed that the undried electrode resistance is ohmic and that the dried



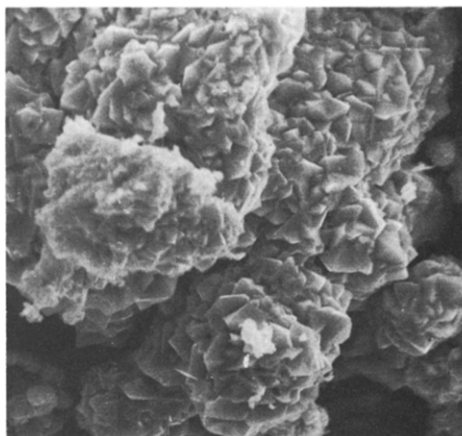
(a)



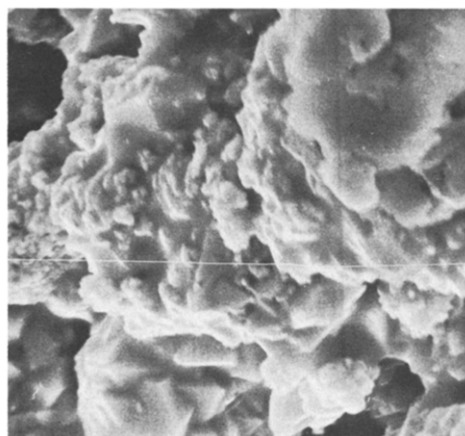
(b)



(c)



(d)



(e)

Fig. 10. Electron micrographs of PbO_2 active mass dried at different temperatures ($\times 3000$, $\tau = 10$ min). (a) 110°C , (b) 150°C , (c) 175°C , (d) 200°C , (e) 250°C .

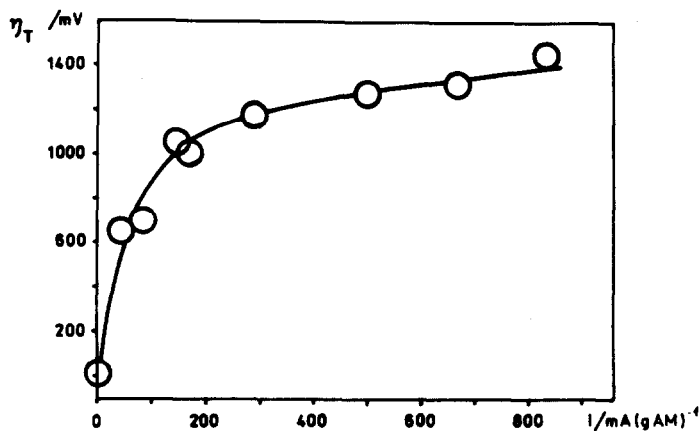


Fig. 11. Galvanostatic $I-\eta_T$ characteristic of the PbO_2 electrode.

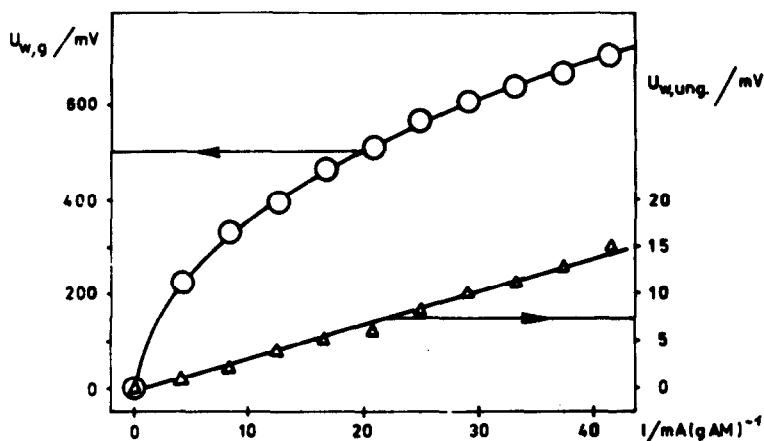


Fig. 12. Dependence of resistance polarization (U_w) on current density. (a) For the undried, round PbO_2 electrode ($U_{w,ung}$) Δ , (b) for the round PbO_2 electrode dried for 60 min at 175°C ($U_{w,g}$) \circ .

electrode does not show this phenomenon (see Fig. 12). This results in the conclusion that a resistance-increasing layer has been generated. The characteristic (Fig. 12) — resistance decrease at increasing current density — makes semiconductor properties obvious. Thus, the thermopassivation effect is mainly a resistance polarization.

Further investigations must be conducted to determine the formation mechanism and the composition of this layer.

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