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THERMOPASSIVATION OF THE POSITIVE LEAD–ACID BATTERY ELECTRODE
PART II. INFLUENCE OF ACTIVATING CONDITIONS ON THE THERMOPASSIVATION OF DRY-CHARGED POSITIVE ELECTRODES OF THE LEAD–ACID ACCUMULATOR

A. N. ANASTASIJEVIĆ, J. GARCHE and K. WIESENER

Department of Chemistry, Dresden Technical University, Mommsenstrasse 13, 8027 Dresden (G.D.R.)

Zusammenfassung

Durch Umsetzung der die Thermopassivation (η_T) verursachenden PbO_n-Passivationsschicht ($1 \leq n < 1.5$) mit der Aktivierungsschwefelsäure kommt es zur Reduzierung von η_T gegenüber η_T^0 der Thermopassivation einer nichtaktivierten PbO_2-Elektrode. Diese Differenz wird Depassivation (δ_T) genannt. δ_T ist abhängig von den Aktivierungs- (Aktivierungszeit τ_A und -temperatur ν_A) sowie den Messbedingungen (Entladestromstärke I und Messtemperatur ν_M).

Mit wachsenden τ_A und ν_A kommt es zu einem Anstieg von δ_T. Bei $\nu_A = -25$ °C beträgt nach $\tau_A = 4$ h die Depassivation nur 200 mV. Bei $\nu_A = +35$ °C beträgt nach $\tau_A = 1$ h die Depassivation 1400 mV, d.h., die Elektrode ist völlig depassiviert.

Bei kleinem I ist δ_T grösser als bei höheren I. ν_M nimmt Einfluss auf den Widerstand der Passivationsschicht, dessen Temperaturkoeffizient bei geringer Aktivierung negativ ist.

Summary

On reaction of the PbO_n-passivation layer ($1 \leq n < 1.5$) causing thermopassivation (η_T), with activating sulphuric acid, a decrease of η_T to η_T^0 in the thermopassivation of a non-activated PbO_2 electrode occurs. This difference is defined as depassivation (δ_T).

δ_T depends on the activating conditions (activating time τ_A and activating temperature ν_A) as well as on the measuring conditions (discharge current, I and measuring temperature ν_M).

With increase in τ_A and ν_A an increase of δ_T is obtained. At $\nu_A = -25$ °C the depassivation after $\tau_A = 4$ h amounts to only 200 mV. At $\nu_A = +35$ °C the depassivation after $\tau_A = 1$ h amounts to 1400 mV, *i.e.*, the electrode is completely depassivated.

At low discharge currents, δ_T will be higher than at higher values of discharge current. ν_M influences the resistance of the passivation layer, the temperature coefficient of which is negative with little activation.

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1. Introduction

The production of dry-charged lead–acid accumulators has, in general, been successful because the battery can be stored for an extended period without being recharged. However, problems arise during the drying of electrodes. In the case of the positive electrode a decrease in discharge voltage on the first discharge after storage can occur.

This phenomenon has been described previously in the literature [1 - 7]. Pavlov and Ruevski were the first to refer to this voltage decrease, as related to the undried electrode, as thermopassivation [4].

Manoim and co-workers [3] suggested that thermopassivation was caused by the formation of poorly conducting PbO. Pavlov and Ruevski, and Anastasijević et al. [7, 8] proposed as the cause the formation of a non-stoichiometric PbO_n-layer with semiconducting properties. These authors suggested a model for the formation of this layer based on oxygen diffusion and on a solid state reaction [8].

The extent of thermopassivation, apart from other influences, depends mainly on the activating conditions of the accumulator and of the positive electrode.

Pavlov and Ruevski [4, 5] showed the influence of the activating medium and time on activation, Garche et al. [7, 8] showed the influence of temperature, and Lahme [9] demonstrated the influence of alkaline pre-treatment of the electrode on activation.

This paper discusses activation of the thermopassivated positive electrode of the lead–acid accumulator.

2. Experimental

Tests were carried out on pasted 0.144 A h circular electrodes (PbSb5-As0.1), as described in refs. 7 and 8. Normally, the electrodes were dried at 175 °C for one hour.

As formulated by Pavlov and Ruevski [5], thermopassivation (η_T) is the difference between the discharge voltages of an undried (U_D^{ud}) and a dried electrode (U_D^d) both being activated before discharge.

$$\eta_T = U_D^{ud} - U_D^d. \tag{1}$$

The depassivation of the thermopassivated PbO_2 electrode ($\delta_T^{\tau_A}$) is the difference between the discharge voltage of a dried electrode (U_D^{d,τ_A}) activated for τ_A minutes, and that of an unactivated electrode (U_D^{d0}).

$$\delta_T^{\tau A} = U_D^{d\tau A} - U_D^{d0} \tag{2}$$

As shown later, U_D^{d0} is obtained only by extrapolation.
Our normal measuring conditions are:
— activating time (τ_A):   20 min
— activating temperature (ν_A):   20 °C
— measuring temperature (ν_M):   20 °C
— electrolyte concentration: 4.93M H_2SO_4
                                 ($\rho_{25°C} = 1.28$ g cm^{-3})
— specific discharge current (I):
    galvanostatically: I $\hat{=}$ 3 × C_{20} (360 mA/g active mass)
                        (U_D measured 15 s after start of discharge)
    galvanodynamically: (7.5 mA/s)
                        (U_D measured at 360 mA/g active mass).

The activating temperature may be defined as the temperature of the activating electrolyte, as no quantitative information can be given on the temperature at the reaction site.

Divergences from the normal measuring conditions have been pointed out where necessary.

The measurements were carried out on at least three electrodes for all the points measured. The error in the thermopassivation values is ±100 mV.

3. Results

3.1. Dependence of thermopassivation on activating temperature

The PbO_2 electrode under our normal measuring conditions was activated at 20 °C by immersion in sulphuric acid ($\rho_{25°C} = 1.28$ g cm^{-3}) for 20 min and then tested at this temperature. In general, this meets the National and International Standard Specifications [10]. (There is also the "Cold-Activation Test", however, which specifies an activating and testing temperature of −1.1 ± 1.1 °C [11].)

In ref. 7 we gave values for an activating and testing temperature of −18 °C which showed that the thermopassivation of commercial 15 A h electrodes at that temperature is about 600 mV higher than at +20 °C.

As in ref. 8 we operated at different activating and testing temperatures and showed that each influenced thermopassivation. The influence of the activating temperature can be attributed to the temperature dependence of the depassivation velocity, and the influence of the testing temperature can be traced back to the temperature dependence of the resistance of the thermopassivated electrode. These points are considered quantitatively by the tests given in Table 1, using an example to show the influence of the activating and testing temperatures of the electrodes.

It was shown by a preliminary test using a thermocouple to determine the temperature equalization of the electrode, that when changing from elec-

TABLE 1

Thermopassivation as a function of measuring temperature (ν_M), of activating temperature (ν_A) and of activating time (τ_A)

Trial run	Activation				Test	
	$(\tau_A)_1$ (min)	$(\nu_A)_1$ (°C)	$(\tau_A)_2$ (min)	$(\nu_A)_2$ (°C)	ν_M (°C)	η_T (mV)
A	10	−25	10	+35	+35	780
B	7	+35	13	−25	−25	950
C	10	+35	—	—	+35	780
D	10	−25	—	—	−25	1570

trolyte 1 with ν_1 to electrolyte 2 with ν_2, both with $\nu_1 = -25$ °C and $\nu_2 = +35$ °C, and with $\nu_1 = +35$ °C and $\nu_2 = -25$ °C, the new temperature, ν_2, was reached after 3 min. The electrodes of run A and of run B were therefore activated in the same way (10 min at −25 °C, 3 min transition −25 °C ... +35 °C, 7 min at +35 °C) but in a different sequence. Assuming that the change in sequence has no influence on depassivation, the difference, $(\eta_T)_B - (\eta_T)_A = 170$ mV, shows the influence of the resistance change during transition of the testing temperature from +35 to −25 °C.

The temperature dependence of the depassivation velocity, 620 mV, and that of the resistance of 170 mV, are in the ratio 3.7:1 and result in the difference (Table 1) $(\eta_T)_D - (\eta_T)_C = 790$ mV.

3.2. Dependence of thermopassivation on activating time

In further investigations we varied the activating time in addition to the activating and testing temperatures.

It was important to determine how the activating times required to reach a stable rest potential value can falsify the thermopassivation values. The response time of the rest potential also depends on the resistance layer which determines the thermopassivation caused during drying, as shown in Fig. 1. For exact measurements of the rest potential, a minimum electronic
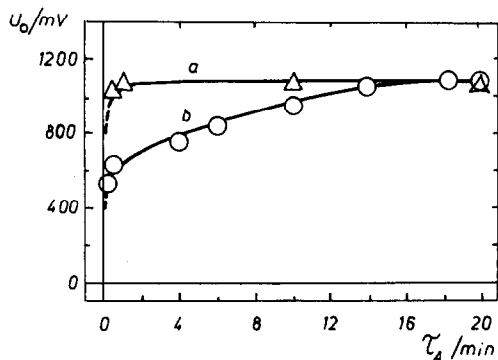

Fig. 1. Adjustment of the rest potential (U_0) at +20 °C for electrodes with different thermopassivations $(\eta_T^{20'})$. a: △, $\eta_T^{20'} = 0$ mV; b: ○, $\eta_T^{20'} = 1400$ mV.
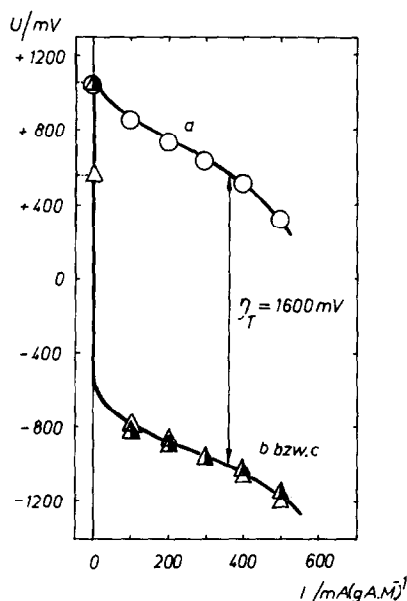
Fig. 2. Galvanodynamic discharge graphs of electrodes pretreated differently, at -25 °C. a: ○, undried PbO_2 electrode, b: △, dried PbO_2 electrode, τ_A = 10 min; c: ▲, dried PbO_2 electrode, τ_A = 30 min.

transition of the active material to the collecting electrodes, or *vice versa*, is necessary to obtain a stable potential. If this transition is impeded, as, for instance, by the passive layer on the grid, the rest potential adjustment of the thermopassivated PbO_2 electrode (plot b) will be retarded compared with an unpassivated electrode (plot a). To determine the influence of the rest potential on thermopassivation it was necessary to test in conditions allowing no, or minimum, depassivation at -25 °C. The results (Fig. 2) show that there is a difference of 460 mV in the rest potential between electrodes activated for 10 min and electrodes activated for 30 min, but there is no difference in the thermopassivation values. Apparently, the discharge current impulse produces conditions conducive to the adjustment of the rest potential.

Thermopassivation as a function of the activating time for different activating temperatures is shown in Fig. 3 where the electrode testing temperature corresponded to the activating temperature. It can be seen from this that the depassivation process depends strongly on temperature, and that thermopassivation may be completely eliminated. A maximum depassivation (δ_T) of 200 mV is observed at -25 °C after 4 h activation, whereas a complete depassivation has already occurred after 1 h at $+35$ °C.

Thermopassivation values extrapolated to the activating time τ_A = 0 min at different measuring temperatures are shown in Fig. 4. They are of special interest for further consideration, as this value is not influenced by depassivation.
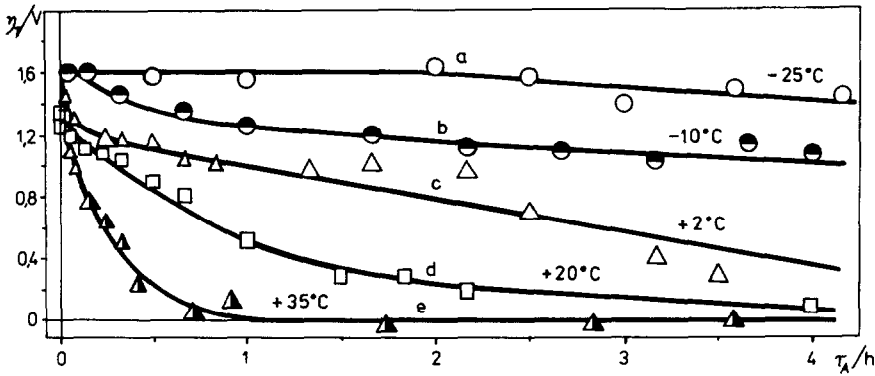
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Fig. 3. Thermopassivation (η_T) as a function of the activating time (τ_A) for different activating temperatures (ν_A): a: ○, $\nu_A = -25\ °C$; b: ●, $\nu_A = -10\ °C$; c: △, $\nu_A = +2\ °C$; d: □, $\nu_A = +20\ °C$; e: ▲, $\nu_A = +35\ °C$.
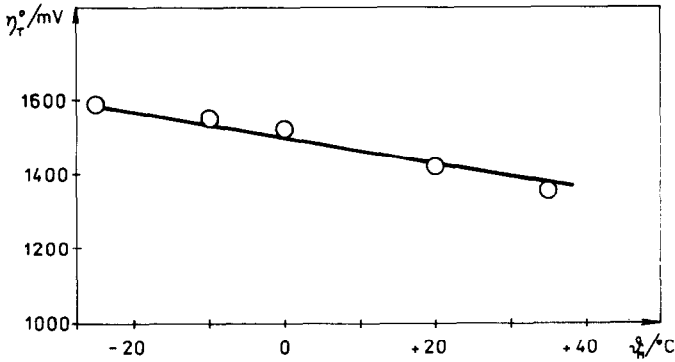

Fig. 4. Thermopassivation (η_T^0) of the non-activated PbO_2 electrode as a function of the measuring temperature (ν_M) ($\tau_A = 0$ min).

3.3. Thermopassivation as a function of discharge current

Normally, thermopassivation is calculated at a discharge current of $I \triangleq 3 \times C_{20}$ (360 mA/g A.M.). In diverging from this value, the $\eta_T^{20'}-I$ dependence shown in Fig. 5, plot c, is obtained, which may also be written as eqn. (3)

$$\eta_T^{20'} = 25 + 425 \log I. \tag{3}$$

Moreover, in varying the activating time, the results shown in Fig. 5 are obtained. The $I-\eta_T$ plots are a function of the activating time and it is noteworthy that a limiting thermopassivation value will be reached at very short activating times ($\tau_A \to 0$). It is characteristic of the resistance film that it gradually shows ohmic behavior due to depassivation and its effect will be greater at lower than at higher discharge currents, as is shown more clearly in Fig. 6.
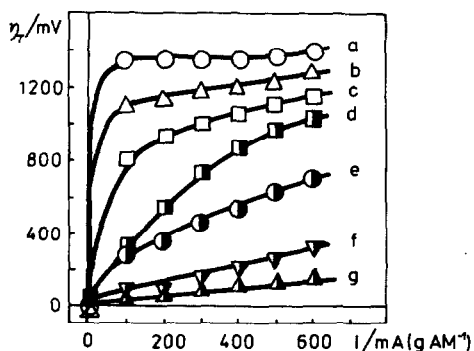
Fig. 5. Thermopassivation (η_T) as a function of the specific discharge current value (I) for different activating times (τ_A): a: $\circ$, $\tau_A = 0.5$ min; b: $\triangle$, $\tau_A = 4$ min; c: $\square$, $\tau_A = 20$ min; d: $\blacksquare$, $\tau_A = 40$ min; e: $\bullet$, $\tau_A = 60$ min; f: $\blacktriangledown$, $\tau_A = 130$ min; g: $\blacktriangle$, $\tau_A = 240$ min.
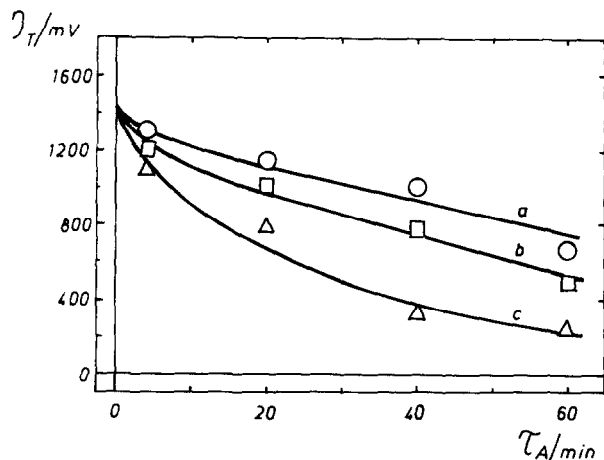

Fig. 6. Thermopassivation (η_T) as a function of the activating time (τ_A) for different specific discharge currents (I) ($\nu_A = +20$ °C): a: $\circ$, $I = 620$ mA/g A.M.; b: $\square$, $I = 360$ mA/g A.M.; c: $\triangle$, $I = 100$ mA/g A.M.

4. Discussion

On immersing dry-charged positive electrodes into electrolyte, the active mass is soaked by the electrolyte and consequently the PbO_2 electrode is ready for operation, *i.e.*, it is activated. On the other hand, because of the interaction with the electrolyte (H_2SO_4) the PbO_n layer ($1 \leq n < 1.5$) causing the thermopassivation will change, *i.e.*, the electrode will be depassivated. As shown in Fig. 3 and also by Pavlov and Ruevski [5], the electrode can be completely depassivated. This change can only be due to a conversion of the PbO_n layer ($1 \leq n < 1.5$) into a product showing electronic conductivity similar to that of the corrosion layer of the undried PbO_2 electrode. It appears that this is a PbO_n layer of $1.5 < n < 2$. Therefore it is not necessary

for the corrosion layer in its original state (undried electrode) to be completely reproduced, as the specific resistance of PbO_n is nearly constant in the range $1.5 < n < 2$ [8].

From the equations to define thermopassivation, (1), and depassivation, (2), the thermopassivation of a dried PbO_2 electrode activated for τ_A minutes is as follows:

$$\eta_T^{\tau_A} = \eta_T^0 - \delta_T^{\tau_A}. \tag{4}$$

From this equation it may be concluded that the thermopassivation value of all activated electrodes is a superposition of passivation (formation of a PbO_n layer) to be seen in η_T^0, and of depassivation (decomposition of a PbO_n layer) $(1 \le n < 1.5)$. Therefore, all results concerning the formation of the PbO_n layer [7, 8] must be examined and possibly investigated more precisely, as these results refer to an activating time of $\tau_A = 20$ min, i.e., to $\eta_T^{20'}$.

Samples showing great differences in the normal thermopassivation value $(\eta_T^{20'})$ as a function of the manufacturing conditions of the electrode can have a nearly identical original value (η_T^0) i.e., a very similar passive layer. The $\eta_T^{20'}$ differences can be traced back to different depassivation velocities. However, it is not only due to the conversion velocity of the PbO_n layer formed during the drying process and its influence on the depassivation velocity $d\delta_T/d\tau_A$. The resistance (R) of the PbO_n layer determines the additional voltage drop, i.e., the thermopassivation, as is postulated in ref. 8. This drop generally follows the equation:

$$\eta_T = IR = I\sigma \frac{l}{q}. \tag{5}$$

For the given measuring conditions only the discharge current (I) and the surface layer (q) are constant, but the specific resistance (σ) and thickness (l) of the layer are not.

The specific resistance is a function of the measuring temperature (ν_M) and, because of the semiconducting property of the PbO_n $(1 \le n < 1.5)$, of the value of the discharge current (I), and of the change in the composition of the layer during the transformation process, it is also a function of the activating conditions (ν_A, τ_A).

The layer's thickness (l) under constant drying conditions is only a function of the activating conditions.

Thus thermopassivation is a complex function:

$$\eta_T = \frac{I}{q}\sigma(I, \nu_A, \tau_A, \nu_M)l(\nu_A, \tau_A) \tag{6}$$

and according to eqn. (4) also of the depassivation (δ_T) and thus the depassivation rate.

In general, eqn. (6) may be solved analytically but only by a complicated mathematical process.
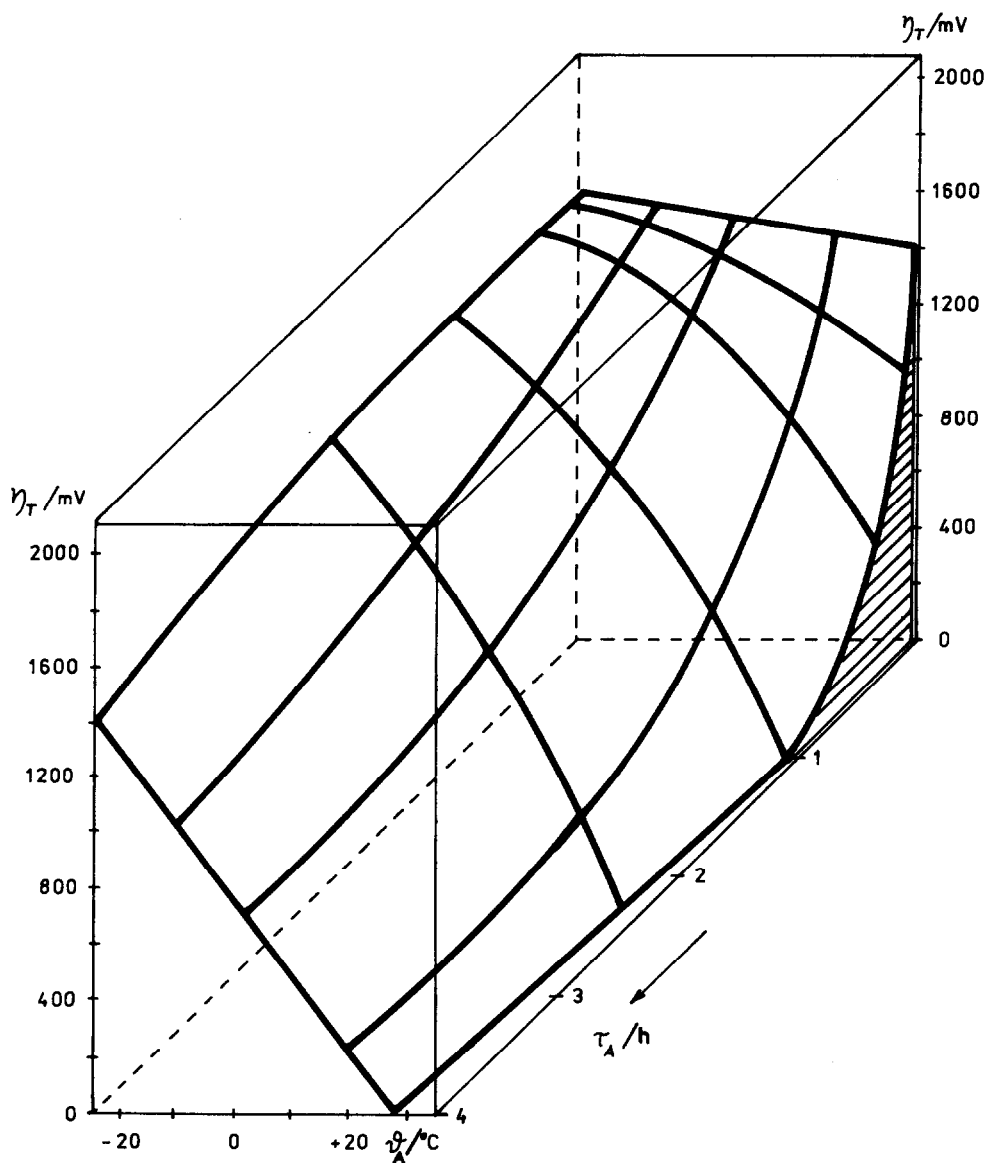
Fig. 7. Thermopassivation (η_T) as a function of the activating conditions: activating temperature (ν_A) and activating time (τ_A).

The effect of the different parameters on depassivation or thermopassivation can be examined by maintaining the other parameters constant.

For the influence of the activating conditions (ν_A, τ_A), Fig. 7 gives a partial solution of the case $\nu_M = \nu_A$ for $I = \text{const} \triangleq 3K_{20}$. To a first approximation the depassivation of the PbO_n layer is shown here. It increases with

increase in activating temperature, whereas the transformation velocity of the layer becomes smaller as the transformation proceeds (see also Fig. 3).

The influence of the measuring temperature (ν_M) on depassivation (δ_T) is superimposed on the influence of the depassivation (see Fig. 7) and therefore the above mentioned approximation is obtained.

The influence of the measuring temperature is shown in Fig. 4. The calculated temperature coefficient from this, *i.e.*, the temperature coefficient of the resistance of the non-activated electrode layer, is $dR/dT = -1.08 \times 10^{-2} \; \Omega \; K^{-1}$. With increasing depassivation, the reaction product of the transformation of the layer, *i.e.*, PbO_n $(1.5 < n < 2)$, the coefficient of which is $d\delta/dT > 0$, increasingly influences the temperature coefficient of the layer's resistance, so that with increasing decomposition of the layer a decrease of dR/dT takes place, and in the borderline case positive values may occur.

The superposition of the effect of the measuring temperature and of the effect of the depassivation temperature on the depassivation value (δ_T) depends on the relationship between the two effects; this relationship, as previously mentioned, is defined by the depassivation stage. So, for the run cited in Table 1 the relationship is 1:3.7. This, however, is only valid for the chosen test conditions.

Concerning the influence of the discharge current value (I) on depassivation (δ_T) the following points should be noted. With increasing transformation of the PbO_n layer with semiconductor properties $(1 \leq n < 1.5)$ into a layer with ohmic behaviour $(1.5 < n < 2)$ the I–η_T plot must also show ohmic behaviour with increasing depassivation. This is shown in Fig. 5. As the decrease in resistance arising from this becomes apparent, particularly in the range of lower currents, the depassivation (δ_T) must be more intensive at small current density values than at greater ones, as shown in Fig. 6.

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