THEORY OF THE POSITIVE PLATE OF THE LEAD-ACID BATTERY*

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A theory of the positive plate of the lead-acid battery was elaborated under the assumption that a kinetic relationship between the local faradaic current density and potential applies. Exact transport equations for concentrated electrolytes were used and volume changes in the solid and liquid phases were taken into account. The solution of the resulting system of three partial differential equations depends on the initial porosity of the electrode and on two dimensionless criteria involving electrode thickness, current load, specific surface area and exchange current density. Numerical solutions for special cases are discussed.

The previous theoretical work on the lead-acid battery was based mostly on the assumption that the Nernst equation for the potential in the pores can be applied[1]. Although this is exactly true for zero current and approximately for small current loads usual in practical discharges except for automotive batteries, difficulties arise if the theory is to be extended to involve diffusion from the bulk of the electrolyte into the pores[2]. This, however, is of importance when the discharge capacity is calculated theoretically. Therefore, the kinetic approach appears inevitable and this even more so because the factors limiting the discharge capacity of the positive plate are still not well understood. The theories employing the Nernst equation come necessarily to the conclusion that the end of the discharge is determined mainly by exhaustion of sulphuric acid on the surface of the plate, whereby its potential is shifted towards negative values[3,4]. This concept was made use of even by authors who carried out discharge capacity measurements in a large excess of a stirred sulphuric acid solution[5]. However, as already shown by us, it is unrealistic to assume that the minimum of the acid concentration is just on the plate surface, and to remove this assumption means to replace the Nernst equation in the theory by a more general one[2]. Reliable numerical data concerning the kinetic current-overpotential relationship for lead dioxide electrodes in sulphuric acid solutions were lacking until Simonsson published the results of his measurements[6] and employed them in a simple theory of the current distribution in the pores. A similar theory, also disregarding the concentration changes in the electrolyte but supplemented with equations describing volume changes in the solid phase and not restricted to a special case was worked out by Gidaspow and Baker[7] who emphasized the role of choking the outer ends of pores in determining the end of the discharge. These authors considered erroneously the difference of the solution potential between the outer and inner ends of the pores to be equal to the "overpotential" of the electrode. Recently Simonsson[8] presented a more advanced theory of the positive plate involving diffusion of the electrolyte, volume changes in the solid phase

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and a parameter, X_{max}, equal to the "maximum fraction of the electrode material which can be utilized at the actual current density"; a rough agreement between the calculated and measured discharge $(E–t)$ curves was attained by a suitable choice of this parameter in the range $0.45—0.60$. The author assumes that exhaustion of sulphuric acid *in the pores* limits discharge capacity in accord with the original view supported by the Liebenow experiment[9]; however, the comparison of the calculated and measured $E–t$ curves remains open for discussion.

Our aim was to supplement the exact transport equations derived previously[1] by a kinetic current–potential relationship and by taking the diffusion of the external acid into the pores into account. An attempt will be made to elucidate the factors that control the end of the discharge and the coefficient of use of the active material.

Electrode Model and Basic Equations

The electrode model described previously[1] will be used except that the plate is dipped in a large reservoir filled with a stirred solution of sulphuric acid to eliminate transport restrictions in the bulk of the electrolyte. (This corresponds, *e.g.*, to the experiments of Gillibrand and Lomax[5].) The plate-shaped, porous lead dioxide electrode of thickness $2d$ and porosity V_p is polarized from both sides. For reasons of symmetry we shall consider only one half of this plate of thickness d. The discharge current, $I < 0$ (A/cm^2), may be considered either constant or a function of time; the present calculations are restricted to the case of constant current.

The basic equations $(1)–(14)$ from ref.[1] will be used with the alteration that the term $(\partial E/\partial c*) \nabla c*$ in (6) and (7) will be replaced by ∇E expressing the circumstance that the local polarization, E, will be considered as a function of the coordinate x similar to porosity V_p. We assume that the local faradaic current, J, depends on E according to the equation

$$J = i_0[\exp(2F(E - E_r)/RT) - \exp(-2F(E - E_r)/RT)], \qquad (1)$$

which for $2F(E_r - E)/RT \gg 1$ takes the form of the equation used by Simonsson[6]; E_r denotes equilibrium potential of the half-cell $Pt|H_2|H^+(a = 1)|H_2SO_4|PbSO_4|$. $PbO_2|Pt$. The local faradaic current flowing in 1 cm^3 of the active porous mass is equal to JS, where S means the electrochemically active surface area of PbO_2 in 1 cm^3 of electrode, and this product is equal to the divergence of the ionic current, ∇i_2 $(i_2$ in A/cm^2 of the cross section of the electrode). Hence, Eq. (1) can be directly combined with (3) in ref.[1] After some calculations we arrive at the following partial differential equations describing the transport of mass and electricity in the given porous system:

$$\frac{\partial V_p}{\partial \tau} = K \frac{\partial}{\partial \xi}\left[V_p \left(\psi_1(u) \frac{\partial u}{\partial \xi} + \psi_2(u) \frac{\partial \eta}{\partial \xi} \right) \right], \qquad (2)$$

$$V_\mathrm{p} \frac{\partial u}{\partial \tau} + u \frac{\partial V_\mathrm{p}}{\partial \tau} = \frac{\partial}{\partial \xi}\left[V_\mathrm{p}\left(\psi_3(u)\frac{\partial u}{\partial \xi} + \psi_4(u)\frac{\partial \eta}{\partial \xi}\right)\right], \tag{3}$$

$$\frac{\partial V_\mathrm{p}}{\partial \tau} = (KI_0/I_\mathrm{d})\left(e^{2(\eta-\eta_r)} - e^{-2(\eta-\eta_r)}\right). \tag{4}$$

The initial and boundary conditions are

$$\tau = 0, \quad \xi \geqq 0: \quad u = 1, \quad V_\mathrm{p} = V_\mathrm{p0}, \quad \eta = \eta_r, \tag{5}$$

$$\xi = 0, \quad \tau > 0: \quad \partial\eta/\partial\xi = \partial u/\partial\xi = 0, \tag{6}$$

$$\xi = 1, \quad \tau > 0: \quad u = 1, \quad V_\mathrm{p}\left[\psi_1(1)\frac{\partial u}{\partial \xi} + \psi_2(1)\frac{\partial \eta}{\partial \xi}\right] = I/I_\mathrm{d}. \tag{7}$$

We have introduced the dimensionless parameters

$$u = c^*/c_\mathrm{a}^*, \quad \eta = EF/RT, \quad \tau = t(D_{10} + D_{20})/2d^2 = t/t_\mathrm{G}, \quad \xi = x/d, \tag{8}$$

$$K = c_\mathrm{a}^*(V_4 - V_3), \quad I_0/I_\mathrm{d} = d^2 i_0 S/c_\mathrm{a}^*(D_{10} + D_{20})F, \quad I/I_\mathrm{d} =$$
$$= d I/c_\mathrm{a}^*(D_{10} + D_{20})F, \tag{9}$$

where c^* and c_a^* denote concentration of sulphuric acid (in mol/cm³) in the pores and in the bulk of the electrolyte, V_3 and V_4 (cm³/mol) molar volumes of PbO_2 and $PbSO_4$, respectively, t (s) time, D_{10} and D_{20} diffusion coefficients of H_3O^+ and HSO_4^- ions in the pores at infinite dilution[1]. The functions ψ_i are defined as follows:

$$\psi_1(u) \equiv (1-2t_1^0)(\partial \ln a_\pm/\partial u)\psi_2(u), \quad \psi_2(u) \equiv u(D_1 + D_2)/(D_{10} + D_{20}), \tag{10), (11}$$

$$\psi_3(u) \equiv u[(1-2t_1^0)f_1(u)(D_1 + D_2) + D_2 F_1 f_2(u)](\partial \ln a_\pm/\partial u)/(D_{10} + D_{20}), \tag{12}$$

$$\psi_4(u) \equiv u[(D_1 + D_2)f_1(u) + D_2 f_2(u)]/(D_{10} + D_{20}). \tag{13}$$

The mean molal activity of sulphuric acid, $a_\pm$, was corrected according to Wirth[2] on the assumption that H_2SO_4 behaves as a strong binary electrolyte. Expressions for the diffusion coefficients D_i, transference number of H_3O^+ ions t_1^0, auxiliary functions f_1 and f_2 were taken from our previous communication[1]. The auxiliary

function $F_1 = 1 + c^* D_{01}/c_0^* D_{12}$ was calculated on the basis of the corrected activity $a_\pm$ in our previous work[2]. Thus, the functions ψ_2 and ψ_4 could be expressed directly by polynomials, ψ_1 and ψ_3 were approximated by polynomials calculated by the least squares method for $0 < u \leqq 1$ as follows:

$$\psi_1(u) \equiv -0.61375 - 0.09536u - 1.44553u^2 + 1.82501u^3 +$$
$$+ 0.07611u^4 - 0.40633u^5 < 0 , \tag{14}$$

$$\psi_2(u) \equiv u - 0.81575u^2 + 0.15169u^3 > 0 , \tag{15}$$

$$\psi_3(u) \equiv -0.42825 - 0.10535u - 1.05842u^2 + 1.52431u^3 +$$
$$+ 0.05632u^4 - 0.36470u^5 < 0 , \tag{16}$$

$$\psi_4(u) \equiv 1.35186u - 0.98698u^2 + 0.10485u^3 + 0.01403u^4 +$$
$$0.00294u^5 > 0 . \tag{17}$$

It is assumed throughout that $c_a^* = 0.005 \text{ mol/cm}^3$, i.e., $u = c^*/0.005$. The reversible potential η_r was expressed previously[1] by a formula which can be simplified for $0.1 \leqq u \leqq 1$ as $\eta_r = 59.735 + 8.398u$, since acid concentrations below $u = 0.1$ are unlikely to be attained with respect to the boundary condition (7).

Values of Input Parameters

The quantity $I_0 = d i_0 S$ in Eqs (9) has the meaning of exchange current per 1 cm^2 of electrode; it is not constant since the specific surface area, S, of lead dioxide diminishes in the course of the discharge. We assume that S is directly proportional to the amount of PbO$_2$, m (mol/cm^3), present in 1 cm^3 of the plate:

$$S = S_0(m - m_1)/(m_0 - m_1) . \tag{18}$$

Here m_0 and S_0 denote initial values of m and S in a fully charged electrode, m_1 minimum (critical) value of m corresponding to a situation where all remaining particles of PbO$_2$ are isolated or encapsulated[10] by crystals of PbSO$_4$. The value of m is, of course, a function of coordinate and time; it can be expressed as

$$m = (1 - V_{p0})/V_3 + (1/2F) \int_0^t \nabla i_2 \, dt . \tag{19}$$

If we combine this equation with (3) in ref.[1] it turns out that m is a linear function

of porosity V_p:

$$m = (1 - V_{p0})/V_3 - (V_{p0} - V_p)/(V_4 - V_3), \tag{20}$$

hence Eq. (18) can be rewritten in the form

$$S = S_0(V_p - V_{p1})/(V_{p0} - V_{p1}), \tag{21}$$

where V_{p1} means the least possible value of the porosity (corresponding to m_1). In the absence of reliable data, m_1 can be estimated to obtain V_{p1} from Eq. (20). For example, for $V_{p0} = 0.5$ we have $m_0 = 0.01961 \text{ mol/cm}^3$; if about 1/8 of the initial content of PbO_2 remains after complete discharge then $V_{p1} = 0.1$. The BET surface area is of the order of several m^2/g (ref.[11,12]) representing the upper limit for S_0. The value of i_0 can be found from a Tafel line published by Simonsson[6] for a nonporous film of $\beta\text{-}PbO_2$ on platinum in $5\text{M-}H_2SO_4$ to be $1.2 \cdot 10^{-5} \text{ A/cm}^2$ along with $dE/d \log I = -0.03 \text{ V}$.

The parameters t_0 and I_d in Eqs (8) and (9) depend on D_{10} and D_{20} which are inversely proportional to the tortuosity factor of the electrode pores, l_p. This was set equal to 1.5 (ref.[1]) approximately in agreement with Euler[13] and theoretical considerations[14]. From the conductivity measurements of other authors[6,15] follow values of l_p in the range $2.5-5$. At the start, we shall use the values[1] $l_p = 1.5$, $c_a(D_{10} + D_{20}) F = 0.04012 \text{ A/cm}$. The remaining characteristics will be $d = 0.1 \text{ cm}$, I from -0.05 to -0.3 A/cm^2, $S_0 = 5 \cdot 10^4 \text{ cm}^{-1}$, $V_{p0} = 0.5$, $V_{p1} = 0.1$, $K = 0.117$, $c_a^* = 0.005 \text{ mol/cm}^3$.

Method of Solution

On eliminating $\partial V_p/\partial \tau$ from Eqs (3) and (4) we obtain an equation of the form

$$\partial u/\partial \tau = \varphi_1(u_{\xi\xi}, u_\xi, V_{p\xi}, V_p, \Theta_\xi, \Theta), \tag{22}$$

where $\Theta = \eta - \eta_r$ and the subscript ξ denotes differentiation. Eq. (4) has the form

$$\partial V_p/\partial \tau = \varphi_2(V_p, \Theta), \tag{23}$$

since I_0 depends on S and this in turn on V_p through Eq. (21). Similarly, Eqs (2) and (4) can be combined to give

$$\Theta_{\xi\xi} = \varphi_3(u_{\xi\xi}, u_\xi, V_{p\xi}, V_p, \Theta_\xi, \Theta). \tag{24}$$

The space derivatives in (22) and (24) were expressed by finite differences with $\Delta\xi = 0.05$; in this manner we obtained a system of 42 ordinary differential equations, which was solved for the first two steps in $\Delta\tau$ numerically by an explicit scheme and for further steps by using the always stable

Crank–Nicholson scheme enabling to shorten the computer time necessary for the calculation of the discharge characteristics by about two orders of magnitude. Eq. *(24)* was solved by iterations; after its linearization we obtained a system of linear equations with a tridiagonal matrix. The iterations were carried out after every step in $\Delta\tau$ with the aim to fulfil the boundary conditions *(6)* and *(7)*. However, owing to an insufficient number of steps in $\Delta\xi$ it was not possible to fulfil satisfactorily the condition *(7)* without changing the value of the integral of the faradaic current J. We therefore considered more appropriate to replace the "differential" boundary condition *(7)* by the faradaic current integral:

$$\int_0^1 S \sinh\,(2\Theta)\,\mathrm{d}\xi = I/2\mathrm{d}i_0 \tag{25}$$

obtained from *(1)*, the mentioned relation $JS = \nabla i_2$ and the conditions $\xi = 0$, $i_2 = 0$; $\xi = 1$, $i_2 = I$. The calculations were performed on a Tesla 200 type computer and the program was elaborated in Tesla-Fortran IV.

RESULTS AND DISCUSSION

The calculated dependences of concentration (u) and porosity (V_p) on coordinate (ξ) and time (τ) are shown in Figs 1–4 in the upper and lower halves, respectively. The calculations were in the majority of cases stopped after the porosity for $\xi = 1$ attained the value of 0·1 since this means practically blocking of the pore entrances and inactivation of the electrode surface. After this state has been reached, the electrode potential corresponds no longer to the outer surface of the plate but rather to a pla-
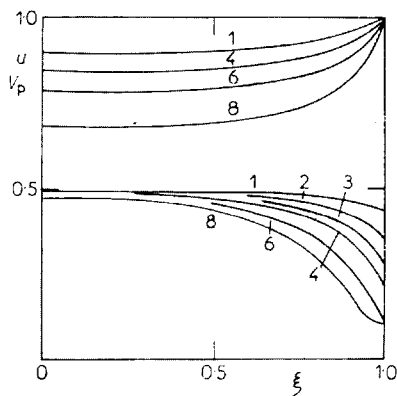
FIG. 1

Calculated Distributions of Concentration and Porosity for $I = -0.05$ A/cm^2

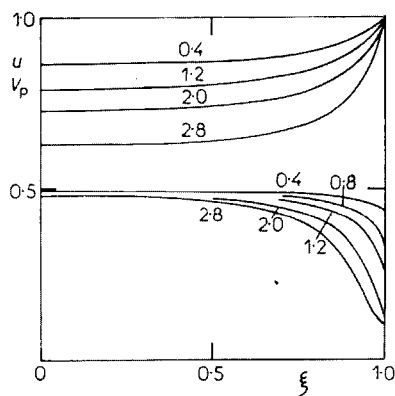Values of τ given in the diagram; $t_d = t_0\tau_d$ = 240·5 . 7·78 = 1 871 s.

FIG. 2

Calculated Distributions of Concentration and Porosity for $I = -0.1$ A/cm^2

Values of τ given in the diagram; $t_d = t_0\tau_d = 240·5 . 2·704 = 650$ s.

ne immediately under the inactivated layer. The electrode polarization is then increased by an amount corresponding to the ohmic potential drop in the inactivated layer of a small porosity and further by an amount corresponding to the decreased concentration of sulphuric acid under this layer. These effects could not be taken into account in the present theory; they are obviously responsible for the formation of the so-caled knee on the discharge curve. Therefore, the time after which the plate surface becomes inactive $(S = 0$ and $V_p = 0.1$ for $\xi = 1)$ will be regarded as the discharge time t_d; the corresponding capacity, K, and the coefficient of use of the active material, q, are as follows:

I, A/cm^2	-0.05	-0.1	-0.2	-0.3
t_d, s	1871	650	219	116
K, As/cm^2	93·6	65·0	43·8	34·8
q, %	24·8	17·2	11·6	9·2

The values of q are in the range reported in ref.[9], p. 211. The dependence of the discharge time on current can be expressed approximately as $t_d = 18.16|I|^{-1.547}$, which is identical in form with the well-known Peukert equation (ref.[9], p. 216). The calculated discharge data are compared with those measured by Gillibrand and Lomax[5] in Fig. 5 in bilogarithmic coordinates; the agreement is surprisingly good.

The porosity changes were calculated on the assumption that the apparent volume of the plate does not change during discharge, i.e., the expansion of the solid phase
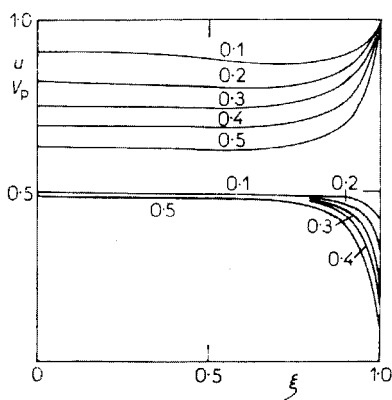

FIG. 3

Calculated Distributions of Concentration and Porosity for $I = -0.2$ A/cm^2

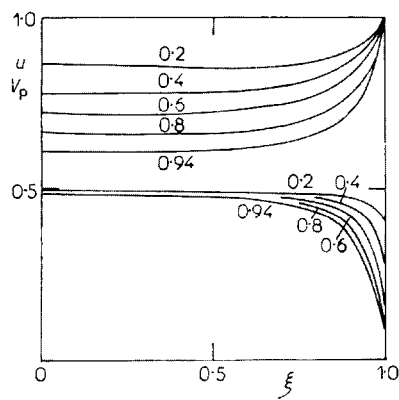Values of τ given in the diagram; $t_d =$ $= t_0\tau_d = 240.5 \cdot 0.912 = 219$ s.

FIG. 4

Calculated Distributions of Concentration and Porosity for $I = -0.3$ A/cm^2

Values of τ given in the diagram; $t_d =$ $= t_0\tau_d = 240.5 \cdot 0.484 = 116$ s.

takes place at the expense of the pores (ref.[9], p. 226.) In spite of the small plate thickness the distribution of the electrochemical process along the x axis is very unequal as can be seen from the lower curves in Figs 1 − 4. This fact is unexpected on the basis of the very good electrical conductivity of sulphuric acid solutions and must be attributed to the rather high exchange current density for the reduction of lead dioxide. With decreasing value of i_0 the depth of penetration of the electrode process into the pores would increase, *i.e.*, the distribution of the faradaic current and porosity would become more equal. Such effect could be achieved by adding suitable surface active substances into the electrolyte and it is probable that the presence of the so-called expanders in negative plates serves the same purpose.

For comparison, calculations were carried out for $I = -0.05$ and -0.1 A/cm² with the use of a higher tortuosity factor, $l_p = 4.8$, a value derived from Simonsson's work[8]. This means a higher diffusion resistance, which can be ascribed to the presence of oxygen bubbles in the pores of the positive plate[15]. As could be expected, the higher value of l_p results in a more rapid decrease of the acid concentration in the pores, more unequal distribution of the faradaic current and porosity, and lower discharge capacity. The calculated values of t_a, K and q are 910 s, 45.5 As/cm², 12.0% for I −0.05 A/cm² and 322 s, 32.2 As/cm², 8.5% for I −0.1A/cm². However, the values of K appear too low and are difficult to reconcile with the measurements[5].

Another interesting point is the effect of the plate thickness, $2d$. Comparative calculations were performed for $d = 0.2$ cm and $l_p = 1.5$, other parameters being the same as before. The calculated discharge data are as follows:

I, A/cm²	−0.05	−0.1	−0.2	−0.3	−0.35
t_d, s	2160	800	281	145	114
K, As/cm²	108	80	56.2	43.5	39.9
q, %	14.3	10.6	7.4	5.7	5.3

The values of K are naturally higher than for $d = 0.1$ cm, but their increments are rather small. The dependence of the discharge time on current can be expressed approximately as $t_d = 26.3|I|^{-1.471}$, which is of the same form as before. The largest relative increase of the capacity (in %) on doubling the plate thickness should be expected in the region of small current densities, however this is not substantiated by the theoretical values of K. The discrepancy is probably due to the approximate nature of our definition of the discharge time as the time after which the plate surface becomes inactivated ($V_p = 0.1$ and $S = 0$ for $\xi = 1$).

The calculated E–t curves in the region beyond t_d are not comparable with measurements for reasons mentioned above. The initial absolute values of the polarization, $|E - E_r|$, for $d = 0.1$ cm were calculated as 10, 19, 32.5 and 41 mV for $|I| = 0.05$, 0.1, 0.2 and 0.3 A/cm², respectively, while the final values at the theoretical

discharge time t_d are 64, 77, 91 and 99 mV. Practically the same results were obtained for $d = 0.2$ cm. By plotting the final values against $\log |I|$ we obtain a straight line with a slope $dE/d \log |I| = -0.045$ V. The initial values lie on a similar straight line except for the first one (10 mV), which is so small that the back reaction becomes appreciable. From the measurements of Gillibrand and Lomax[5] follows $dE/d \log |I| = = -0.04$ V in good agreement with our theory. (It is, of course, not possible to derive this value directly from Eq. (1)). This shows that at least the initial course of the E–t curves corresponds to reality. With a larger tortuosity factor, $l_p = 4.8$, the E–t curves are shifted by $8-9$ mV to more negative potentials indicating that the current load on the outer plate surface is somewhat higher as a result of decreased penetration of the current into the depth of the plate. However, the value of $dE/d \log$ . . $|I|$ is practically the same as in the former case. The further course of the E–t curves (after the time t_d is reached) was calculated in two cases up to a polarization of 200 mV without obtaining a "knee" which would indicate the end of the discharge. The reason for this was already discussed. The polarization values beyond $70-100$ mV are in our model conditioned by the fact that the criterion I_0/I_d in Eq. (4) is proportional to the value of S, which according to Eq. (21) approaches zero if V_p approaches V_{p1}. This occurs in our case for $\xi = 1$ $(x = d)$, $V_p \rightarrow 0.1$. The computer was unable to calculate larger polarizations than about 200 mV owing to a numerical overflow. It is remarkable in this respect that also Simonsson's E–t curves end at about 200 mV polarization[8]. The reason for this is obviously the same, and our conclusion that the course of the calculated E–t curves in the region beyond t_d or above 100 mV does not correspond to reality is applicable also to the cited work[8].

The current–overvoltage relationship (1) involves a term corresponding to the back reaction, i.e., oxidation of $PbSO_4$ to PbO_2. This term was added to fulfil the condition $J = 0$ for $E = E_r$; it should enable to calculate the course of the charging process after reversal of current. However, the back reaction term is not based on experimental data, which are lacking, and its form must be therefore regarded as a rough

FIG. 5

Comparison of Calculated and Measured Discharge Time

● Values from ref.[5] for 2 mm thick positive plates in an excess of stirred $6M$-H_2SO_4 solution at 21°C; plate surface area (both sides) 336 cm^2; ○ present theory; the total current was calculated as 336 I. Numbers on the ordinate give total current (A), those on the abscissa discharge time (min).
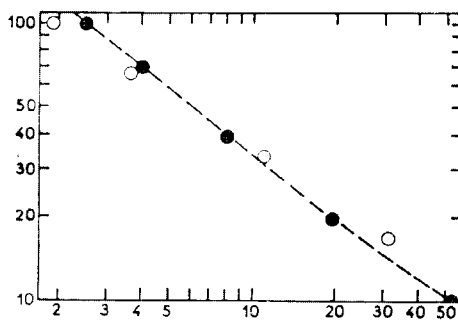
approximation. Furthermore, we assume that oxidation of $PbSO_4$ is the only reaction proceeding in the pores during charging, but this condition is fulfilled only during the first $50-60\%$ of the charging time and then a more or less appreciable evolution of oxygen commences[16]. Such a behaviour must be expected in view of the fact that a portion of the lead sulphate close to the plate surface is oxidized preferentially leaving a thin layer free of sulphate where the rise of the potential is most pronounced and the oxygen evolution favoured.

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