

Evaluation of criteria for design of current collectors of the lead–acid battery

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Abstract

The effect of the main structural parameters of the current collectors on efficiency of operation of the positive electrode of the lead–acid battery was investigated. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Efficiency of operation of the positive electrode of the lead–acid battery in many aspects depends on the design of the current collector, which to a greater extent predetermines both the electrical characteristics of the batteries and their service life. The proper selection of the design of the current collector allows optimization of the current distribution, achievement of the maximum value of active mass utilization factor (UF) and security of positive retention of active mass in the electrode over a lengthy service life. However, the process of selection of the design of the current collector is extremely difficult due to the fact that compliance with one set of requirements often contradicts the conditions for optimization of another set of requirements.

The most rational approach in a solution to the problem of optimization of the designs is connected with experimental determination of a number of criteria the implementation of which in the course of development should secure efficient operation of the structure as a whole.

As such criteria in design of the current collectors, one can suggest the following:

- weight fraction of the current collector in the make-up of the electrode $\beta = P_c/P_e$, where P_c and P_e are weights of the current collector and electrode, respectively;
- ratio of weight of the active mass (P_{am}) to the magnitude of the contact surface of the current collector (S_c): $\gamma = P_{am}/S_c$; the γ -coefficient was introduced for first time by Pavlov [1];

- ratio of linear size of the holes within of the current collector (a) to half-thickness of the bar (δ): $\eta = a/\delta$; the η -coefficient was introduced by Aguf [2];
- maximum current density (i_{max}).

It is evident that the electrical and service life characteristics of the electrode are extremely dependent on the first three parameters, which makes it possible to determine their optimum values. So, for example, with rise of β or drop in α the capacity of the electrode first increases due to increase in UF, but then starts to drop due to a decrease in the quantity of the active material. The optimum value (γ_{opt}) should be also true for the parameter γ . If $\gamma > \gamma_{opt}$, then part of the active mass will not be utilized and the capacity of the electrode will be below the maximum possible value, and the service life of the electrode will not reach the maximum. If $\gamma < \gamma_{opt}$, then the material of the current collector will be involved in the process of oxidation, which will result in a shorter service life of the electrode. The maximum current density is also an important parameter of the current collector. The increase of the current density results in undesirable heating of the current collector and a rise in resistance of the interface corrosion layer (ICL) due to formation of cracks in the current collector causing the value of the contact surface to decrease [1,3].

2. Experimental part and discussions

To determine the relationship between the capacity of the electrode and parameters η , β , γ , we prepared the current collectors measuring 143 mm × 134 mm × 2 mm with hole sizes of 16 mm × 3.1 mm; 16 mm × 7.1 mm; 16 mm × 11.5 mm; 16 mm × 15.8 mm; 16 mm × 20.5 mm

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Table 1
Parameters of the current collectors and electrodes

Item	Weight of electrode (g)	Weight of active mass (g)	η	β	γ
1	177.6	86.0	3.18	0.516	0.62
2	164.24	96.14	8.35	0.415	1.21
3	166.21	102.11	13.50	0.386	1.56
4	162.39	100.79	18.70	0.379	1.75
5	156.44	98.34	22.70	0.371	1.93
6	155.96	99.86	28.20	0.360	2.07

and 16 mm × 24.1 mm out of alloy Pb–4.5% Sb. The grids were pasted and enveloped in polypropylene separator 0.6 mm thick to secure a positive retention of the active mass. After pasting and formation of the electrodes the batteries were built, which were later tested by the cycling method. Discharge of the batteries was carried out at constant current at the 1, 5, 10 and 50 h discharge rates. Table 1 shows the parameters of the current collectors and electrodes.

Fig. 1 shows the relationship between the specific capacity of the electrodes (C_e) and value of the parameter β . As assumed earlier, the relationship $C_e = f(\beta)$ is of a non-linear nature. The maximum of the capacity lies in the range 0.40–0.45. The calculations showed that at $\beta > 0.40$ –0.45 UF has a constant value. For 50 h discharge mode it equals 0.56. Thus, the observed increase in the capacity of the electrodes is associated with an increase of active mass in the electrodes as a result of a reduction of the fraction of current collector in

the makeup of the electrode. With $\beta < 0.40$ –0.45, a drop in capacity of the electrodes takes place with a simultaneous decrease in UF, which indicates the lower efficiency of operation of the active mass with a lower weight fraction of the current collector. Figs. 2 and 3 show the relationships $C_e = f(\gamma)$ and $C_e = f(\eta)$. The figures indicate that a significant drop in the capacity of the electrodes occurs with values $\gamma > 1.2$ –1.4 and $\eta > 8.5$ –9.0. A decrease in UF also corresponds to the same values. One should note that with larger discharge currents the parameters of the current collector will exert a stronger effect on the specific capacity of the electrodes, which will manifest itself in a change of slope of the curves $C_e = f(\eta)$, $C_e = f(\beta)$, $C_e = f(\gamma)$. The effect of the geometry of the current collectors and discharge mode could be explained based on the general principles of the recovery process of the positive active masses (PAM). In the course of a discharge of PAM there follows a drop in oxidation level in accordance with the system $\text{PbO}_2 \rightarrow \text{PbO}_{II} \rightarrow \text{PbO} \rightarrow \text{PbSO}_4$. The process follows a solid phase mechanism due to transfer of electrons from the current collector to the reaction zone. The drop in oxidation level is simultaneously followed by a decrease in conductivity of the active material. The extent of oxidation is a maximum at the initial point of discharge and is practically uniform over the entire thickness of the active material between the bars of the current collector. As the discharge continues, the profile of the degree of oxidation changes as shown on the schematic. It is evident that the higher the

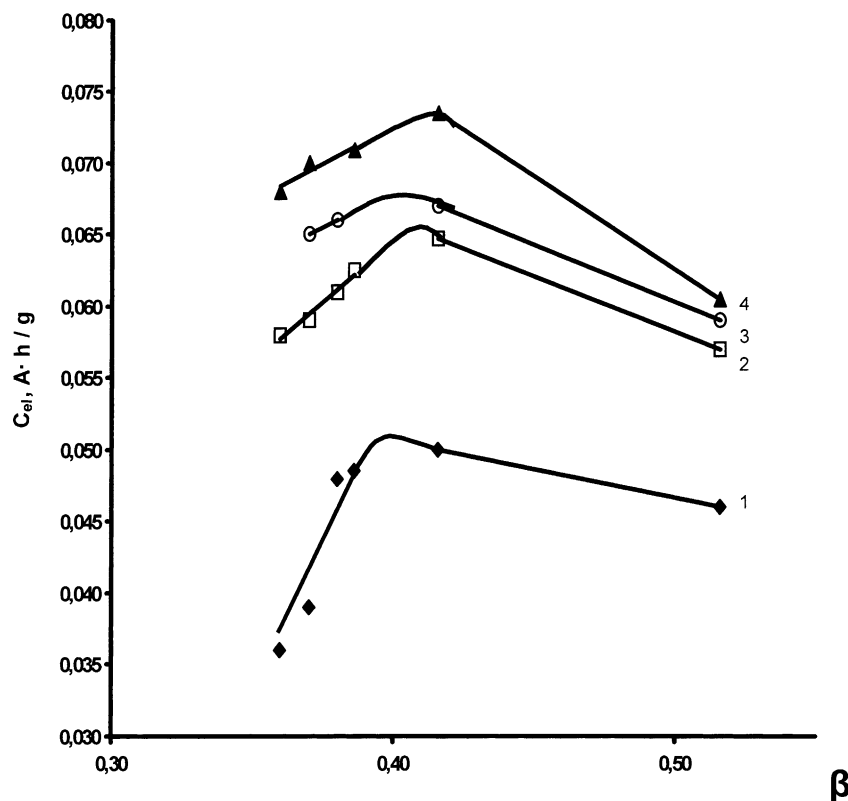


Fig. 1. Dependence of electrode specific capacity upon parameter β for 1 h (1); 5 h (2); 10 h (3); 50 h (4) rates of discharge.

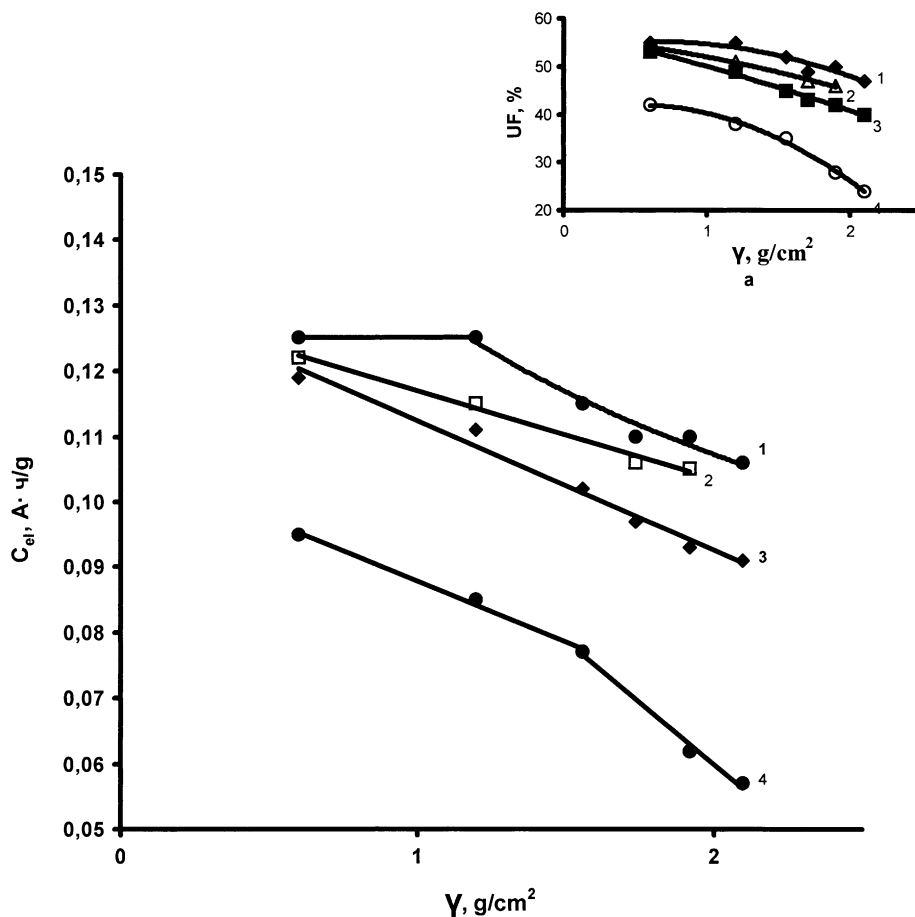


Fig. 2. Dependence of electrode specific capacity upon parameter γ for 50 h (1); 10 h (2); 5 h (3); 1 h (4) rates of discharge. α -Dependence of active mass utilization factor upon parameter γ (designations are the same).

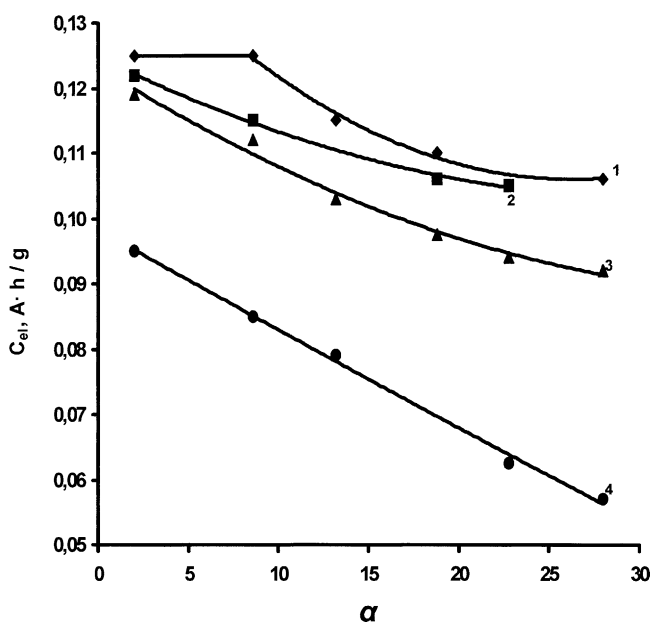


Fig. 3. Dependence of electrode specific capacity upon parameter η for 50 h (1); 10 h (2); 5 h (3); 1 h (4) rates of discharge.

parameters of the current collector and more intense the discharge mode, the more is the non-uniformity of the extent of oxidation in the direction normal to the current collector. The discharge process ends when the extent of oxidation of the layer directly adjoining the surface of the current collector reaches a critical value and its conductivity sharply drops. In this point the internal layers of the active mass may still have a high degree of oxidation, which, along with the known phenomena of the reduction in porosity of the active mass in the course of the discharge, results in a lowering of UF. It is clear that the higher the rate of discharge, the shorter is the time required for the PAM at the interface with the current collector to be reduced to low-conducting material, and the greater the quantity of highly oxidized material remains in the core of the cell. In the same way the increase in the size of the cell will lead to a drop in UF.

Thus, the tests performed showed that the maximum value of UF corresponds to the following parameters of the current collector: $\eta = 8.5-9.0$; $\beta = 0.40-0.45$; $\gamma = 1.2-1.4$. However, the values of the coefficients should not be regarded as absolute values, but rather as a variable that differs for the different plate designs. For example, the value $\gamma = 1.2-1.4$ is suitable for flat plate construction and $\gamma = 0.8$ [1]—for tubular electrodes.

Table 2
Results of calculation of dependence $i = f(\Delta T)$

Cooling medium	α , cal cm ² h	Current density securing heating by ΔT with $\tau = 1$, A/mm ²				
		10°	20°	30°	40°	50°
Vacuum	0	0.136	0.192	0.236	0.272	0.303
Air	2.2–2.5	0.373–0.400	0.530–0.560	0.640–0.690	0.750–0.800	0.830–0.890
Active mass + acid	8.0–11.0	0.702–0.806	0.983–1.112	1.204–1.376	1.392–1.584	1.567–1.723
Acid (1.1 g/cm ³)	40–55	1.481–1.732	2.108–2.463	2.574–3.00	2.971–3.475	3.321–3.892

It is known that passage of current through the current collector may cause its undesirable heating, resulting in the cracking of the interfacial corrosion layer and rise in its resistance [3]. The determination of current density at which the specified level of temperatures is achieved is of interest. It is evident that in conditions of absence of heat exchange when all heat associated with passage of current (Q_i) is used for an increase in temperature of the current collector (Q_T) there is balance

$$dQ_i = dQ_c. \quad (1)$$

By substituting in (1) $dQ_i = 0.24I^2R d\tau$, $dQ_c = C_p m dT$, $I = iS$, $R = \rho l S^{-1}$ and $m = nSl$, where I is the current passing through the current collector, R the resistance of the bar, τ the time of current passage, C_p , ρ , n the heat capacity, resistivity and density of material of the bar, respectively, l , S the length and cross-section of the bar, respectively, i the current density, one may derive the equation relating the current density and temperature of the bar in conditions of absence of heat exchange:

$$i = \sqrt{\frac{C_p n (T - T_0)}{0.24 \tau \rho}} = K_1 \Delta T^{1/2} \quad (2)$$

where T_0 and T are temperatures of the bar at the time 0 and τ . Having inserted into the Eq. (2) the known reference values for lead and $\tau = 1$ h we determine that the ΔT of the bar 10, 30, 50 °C could be reached with current density 0.136, 0.236 and 0.304 A/mm², respectively.

However, it is evident that in real conditions the heating will be significantly lower due to loss of heat to the environment (Q_0). Given the above statement, one could write:

$$dQ_i = dQ_c + dQ_0 \quad (3)$$

and derive the equation relating i and ΔT :

$$i = \sqrt{\frac{(C_p n l + \alpha \tau)(T - T_0)}{0.24 \rho \tau l}} = K_2 \Delta T^{1/2} \quad (4)$$

It is seen from the equation that taking the heat dissipation into account results in an increase of current density required for heating the current collector to the critical temperature. The heat dissipation factor α in Eq. (4) remains unknown and hard to determine from the published data. However, it can be determined on the basis of experimentally derived

cooling curves of the material tested in the respective medium. For the cooling process one can write:

$$dQ_c = dQ_0 \quad (5)$$

$$C_p m dT = \alpha S (T - T_0) d\tau \quad (6)$$

By integrating (6) while considering the initial conditions $\tau = 0$, $T = T_{st}$, where T_{st} is the heating temperature of the material, we will derive:

$$T = T_0 + (T_{st} - T_0) \exp\left(-\frac{\alpha \tau S}{m C_p}\right) \quad (7)$$

whence:

$$\alpha = -\frac{m C_p}{S \tau} \ln \frac{T - T_0}{T_{st} - T_0} \quad (8)$$

Having derived the experimental cooling curves $T = f(\tau)$, one can determine the values of the heat dissipation factor for the specific material and cooling conditions. Having inserted into Eq. (4) the earlier derived value α one can calculate the critical current density for a given degree of heating degree of the current collector bar.

We derived the cooling curves for the alloy Pb–3.0% Sb–0.5% Sn in air, in H₂SO₄ acid and in the acid impregnated active mass. The values of the factor α and results of calculation of dependence $i = f(\Delta T)$ are shown in Table 2.

The results presented in Table 2 provide a quantitative evaluation of the fact that with higher rate of heat dissipation the critical current density (causing undesirable heating), increases. The closest to real conditions of operation of the current collector is when in contact with the acid impregnated active mass. For such conditions the current density resulting the heating of the bars to a temperature 50–60 °C in 1 h is current density equal to 1.2–1.3 A/mm².

3. Conclusions

The effect of the main structural parameters of the current collectors on the efficiency of operation of the electrode was investigated.

It was shown that the maximum UF may be achieved under the following values of the tested parameters:

- ratio of current collector weight to electrode weight, 0.40–0.45;

- ratio of active mass weight to the magnitude of contact surface of the current collector, 1.2–1.4;
- ratio of size of the cell to half-thickness of the bar, 8.5–9.0.

The relationship between the heating of the bar of the current collector and the current density passing through the latter was established.

References

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