MEASUREMENT OF THE CONTACT RESISTANCE BETWEEN THE ACTIVE MASS AND THE CURRENT COLLECTOR IN LEAD/ACID BATTERY ELECTRODES

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Introduction

The contact resistance between the active mass and the current collector in lead/acid batteries can sometimes be a problem, *e.g.*, when antimony-free lead grids are used [1] or when charged electrodes are dried at an elevated temperature and thermopassivation occurs [1 - 4]. Thus, the contact resistance is an important parameter and is closely associated with battery performance. Although some evidence of the presence of a contact resistance can be obtained by comparing the discharge curves for batteries with normal and passivated electrodes, a reliable method for measuring contact resistance appears, hitherto, to have been lacking. This situation has now been improved by the development of a method using pasted electrodes with a specially designed lead grid. The new technique is described here and is somewhat similar to that proposed by Hampl [5] for measurement of the resistance of transition layers between a metal and a semiconductor.

Principle of the method

Laboratory electrodes were prepared by pasting the active material onto a current collector consisting of parallel, equi-distant ribs (Fig. 1) (note, this was also used in previous work [6] on conductance measurements). The equivalent diagram of such a laboratory electrode is shown in Fig. 2, where R_m denotes the resistance of the active material between two neighbouring ribs, R_{ki} ($i = 0, 1, \ldots n$) is the contact resistance between the i-th rib and the active mass, and R_{pi} is the effective resistance of the i-th rib. This can roughly be defined as the resistance between the potential probe at point C (Fig. 1) and a point at which the current passing through the interface is equal to its

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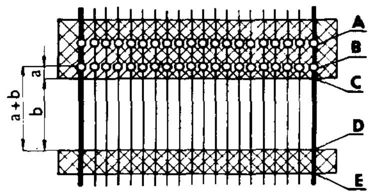

Fig. 1. Current collector with parallel, equi-distant ribs. Shaded areas correspond to epoxy resin frame, the area of width b serves for pasting. Current leads are connected at A, potential probes at B.

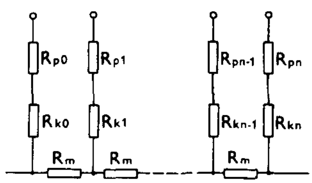

Fig. 2. Equivalent circuit of test electrode.

mean value. A theoretical calculation, which will be published later, revealed that approximately 1/3 of the rib section b is responsible for the effective resistance.

The measurement proceeds in two stages, denoted as (i) and (ii).

(i) Determination of contact resistance of first and last ribs

The measuring current, I, is taken to the outermost ribs of the electrode section considered (the voltage response being preferably kept within 5 mV) by current leads at A (Fig. 1). With voltage probes at B, the potential differences between the first (from the left) and the second, third, etc., rib are measured in turn.

For a mathematical formulation, the potential of the first ('reference') rib at point A will be denoted as φ_0, that of the second φ_1, and so on. The following system of equations can be established:

$$\varphi_i - \varphi_0 \equiv U_i = I(R_{p0} + R_{k0} + iR_m), \quad i = 1, 2, \ldots n-1 \tag{1}$$

$$\varphi_n - \varphi_0 \equiv U_n = I(R_{p0} + R_{k0} + R_{kn} + R_{pn} + nR_m) \tag{2}$$

Except for the last one, these equations represent an arithmetic progression with the difference equal to IR_m. By linear regression (which practically eliminates the influence of any variations in R_m), the parameters A and B of the regression line can be calculated:

$$U_i = A + B_i, \quad i = 1, 2, \ldots n-1 \tag{3}$$

The mean resistance, $\bar{R}_m$, of the active material between two neighbouring ribs can be expressed as:

$$\bar{R}_m = B/I \qquad (4)$$

and the contact resistance between the first rib and the active mass as

$$R_{k0} = A/I - R_{p0} \qquad (5)$$

If the values of $\bar{R}_m$ and R_{k0} are introduced into eqn. (2), then R_{kn} can be calculated (the values of R_{p0} and R_{pn} are considered to be known).

(ii) Determination of contact resistances of other ribs

The measuring current, I, is fed to the first rib (with $i = 0$), while the other current lead is connected in turn to the second rib, third, and so on. The potential probes are connected to the same ribs as the current leads. Thus, the measured potential differences are now given by:

$$\varphi_i - \varphi_0 \equiv U_i = I(R_{p0} + R_{pi} + R_{k0} + R_{ki} + i\bar{R}_m) \qquad (6)$$

and the contact resistances are given by:

$$R_{ki} = U_i/I - R_{p0} - R_{pi} - R_{k0} - i\bar{R}_m, \quad i = 1, 2, \ldots n \qquad (7)$$

For reasons of symmetry, the same results must be obtained if the test plate electrode is reversed from right to left and the measurements are repeated in the order indicated. To check the results, it is also possible to measure the resistances, R_m, independently by the four-probe d.c. method.

Experimental

For experimental verification of the method, positive electrodes were made by pasting an industrial active mass on to a current collector with parallel, equi-distant ribs (Fig. 1). After drying, the electrodes were formed in an excess of electrolyte. During measurement, they were taken out from the electrolyte.

The current collectors were made from industrial lead grids by removing the unnecessary parts [6]. Two types of grids were used: one consisting of 28 ribs of a Pb–5.5wt.%Sb alloy (type I); the other consisting of 20 ribs of a Pb–2.5wt.%Sb alloy (type II). The rib resistances of the latter were measured by the four-probe d.c. method. Constant current was supplied by a galvanostat with a range 0.1 mA - 4 A and the voltage response was measured with a digital d.c. voltmeter. The current was measured as a voltage drop on a calibrated resistance with a digital d.c. voltmeter.

Thermopassivation was effected by heating the electrode for 90 min at 150 °C in a laboratory oven. The temperature of measurement was 25 °C.

Results and discussion

The resistances of the ribs showed unexpected variations: the ribs with even numbers (*i.e.*, the 2nd, 4th, . . .) had a somewhat higher resistance than the others, and there was also a scatter that suggested slight variations in the thickness of the ribs as well as other irregularities. On average, for grid type II the resistance of section a (Fig. 1) was 3.1 mΩ for even ribs and 2.5 mΩ for odd ones (the thick frame excluded), while the corresponding resistances of section b were 11.2 and 8.4 mΩ. Thus, it was necessary to measure the resistance of each rib to obtain reliable values of the contact resistances.

The mean contact resistance $\bar{R}_k$ and the value of $\bar{R}_m$ for a test electrode with a type I grid are given in Table 1 as a function of the time elapsed after charging. It can be seen that both resistances increase with increase in standing period, and can be returned to approximately the original values after charging with a current of 0.1 C_{20} for 15 h. It is probable that the increase in the contact resistance is caused by the same solid-state reaction as thermopassivation, which proceeds very slowly at room temperature. The changes of $\bar{R}_m$ are in accord with those found in previous studies [7].

Changes in R_k and R_m values by various treatments of the electrode were followed by using a test electrode with a type II grid (active zone dimensions: 111 × 30 × 4 mm). Measurements were carried out at the following successive stages of electrode treatment:

(A) initial state, *i.e.*, after formation, four starting cycles (C_5 = 5.33 A h), and 48 h stand;

(B) after washing in running water at 40 °C for 1 h;

(C) after drying in air at laboratory temperature (26 °C) for 16 h;

(D) after heating at 150 °C in an oven for 1.5 h, immersion in the electrolyte, 4 h stand, and subsequent charging at 0.5 A for 12 h;

(E) after subsequent stand for 76 h;

(F) after discharge and recharge.

The results of the first stage of measurement are shown graphically in Fig. 3 (the thick outermost ribs originating from the grid frame were omitted in the measurements). It can be seen that the experimental points lie on straight

TABLE 1

Mean contact resistance, $\bar{R}_k$, and mean active mass resistance, $\bar{R}_m$, as functions of the stand time of the positive electrode (type I grid, 25 °C)

Stand time (h)	$\bar{R}_k$ (mΩ)	$\bar{R}_m$ (mΩ)
72	5.9	6.5
432	5.2	8.0
2832	15.5	16.5
2952	17.7	16.6
after charging	4.2	7.0

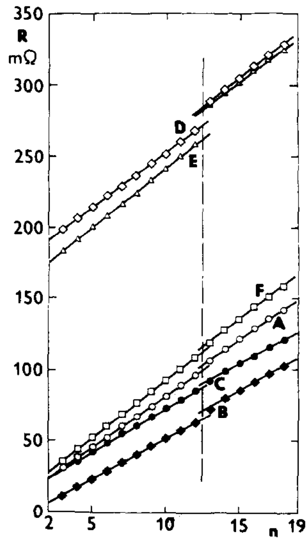

Fig. 3. Results of the first stage of resistance measurements.

lines. The discontinuity close to the 13th rib is due to a crack in the active mass running parallel to the ribs; this was visible with the naked eye and was formed during the curing process. Nevertheless, the determination of R_{k0} (corresponding here to the second rib) by extrapolation is accurate enough, since the crack was well separated from the second rib.

The second stage of measurement yielded the values of R_k for the particular ribs. Since these values were self-consistent, the values of R_{k0} are restricted to those that can be obtained from the diagram (Fig. 3) as the intersections of the straight lines with the ordinate. The standard deviations

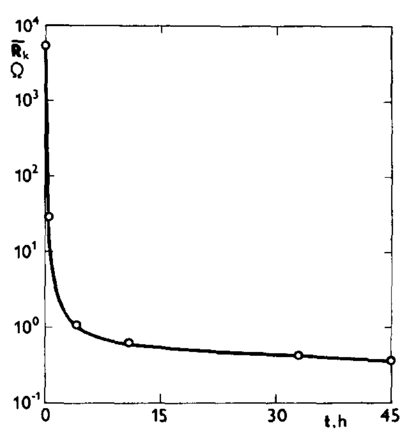

Fig. 4. Dependence of mean contact resistance $\bar{R}_k$ of thermopassivated electrode on time of immersion in electrolyte (4.9 M H_2SO_4).

of the R_k values for the individual ribs were about $\pm 10\%$. The scatter is probably caused by variations in the surface macrostructure of the ribs.

Variations in the mean resistance of the active mass, $\bar{R}_m$, due to the electrode pretreatment were small, as witnessed by the small variation in the slopes of the straight lines in Fig. 3; the values were in the range 5.6 - 8.3 mΩ (in the states A - F).

Pavlov and Ruevski [2] found that thermopassivation of positive plates decreases with the time of immersion in the electrolyte on open circuit. An analogous effect has been found for the contact resistance, as illustrated in Fig. 4. This supports the claims of Garche *et al.* [3, 4] that the thermopassivation is caused by a resistive film between the lead grid and the active mass. Hence, the contact resistance should be regarded as the resistance of a transition layer between the two phases.

The contact resistance appears to depend on the antimony content of the grid: for the type I grid (5.5% Sb) the resistance was 5.9 mΩ in the charged state (Table 1), whereas for the type II grid (2.5% Sb) the value was 24 mΩ (from Fig. 3, line A), *i.e.*, four times higher. More experiments are necessary to investigate this phenomenon.

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