

TIME EFFECTS IN CONDUCTIVITY MEASUREMENTS OF LEAD/ACID BATTERY ELECTRODES

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Introduction

The conductance of the active mass of lead/acid batteries changes as a result of electrochemical conversions, not only during discharging and charging, but also during standing on open circuit. Immediately after the termination of charging, the conductance of the active mass increases and then slowly decreases. With negative electrodes, the conductance increase is related to desorption of hydrogen from the crystal lattice of the spongy lead [1, 2], while the subsequent drop is closely related to self-discharge [2]. With positive electrodes, the conductance increase after charging is relatively rapid and is associated with deviations from stoichiometry of PbO_2 in the active mass [2]. The long-term changes in the conductance of positive and negative plates form the subject of the present paper.

Experimental

Test electrodes were prepared by pasting 100 g of wet, positive or negative active material onto a current collector consisting of parallel, equi-distant lead ribs [2, 3]. The electrodes were assembled in cells together with counter electrodes of opposite sign containing a large excess of active mass; the assembly was subject to formation and charge/discharge cycling before the conductance measurements. The electrolyte comprised 1 l of 4.9 M H_2SO_4 . The dimensions of the active zone of the test electrodes were $13.2 \times 3.1 \times 0.45$ cm. The four-probe d.c. method was used to measure the resistance between two ribs 12 cm apart. The applied current was 5 - 25 mA for the positive electrodes and 400 mA for the negative, the voltage response was mostly 1 - 5 mV; this ensured that the current passed only through the solid phase and not through the electrolyte. The cells were placed in a thermostatically controlled water bath at 25 °C.

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Results and discussion

Negative electrodes

When the conductance of a negative electrode is measured in the charged state (after five charge/discharge cycles) in the pure electrolyte, no change is observed over 300 h, except for an initial moderate increase, as demonstrated by curve 5 in Fig. 1. A decrease is only observable after a longer time. If, however, charging after the five formation cycles takes place in 4.9 M H_2SO_4 containing a small quantity of Sb_2O_3 , then the dependence of the conductance on the rest period changes very markedly. This is clearly illustrated by curves 1-4 in Fig. 1 that are representative of electrolyte containing 400, 300, 200, and 100 mg l^{-1} of Sb_2O_3 , respectively. For convenience, the conductance is expressed as a percentage of the value, G_o , corresponding to the state immediately following the last charging stage in the pure electrolyte. The final cell voltage during charging is given in Table 1, reflecting the effect of antimony on the overvoltage of hydrogen.

The residual discharge capacity, Q , of six test electrodes was determined as a function of their conductance. An approximately linear dependence was found; the regression line is given by the equation:

$$Q/Q_o = 0.933G/G_o + 9.18 \quad (1)$$

(coefficient of determination $r^2 = 0.971$).

Differentiation gives:

$$\frac{dQ}{dt} = 0.933 \frac{Q_o}{G_o} \frac{dG}{dt} \quad (2)$$

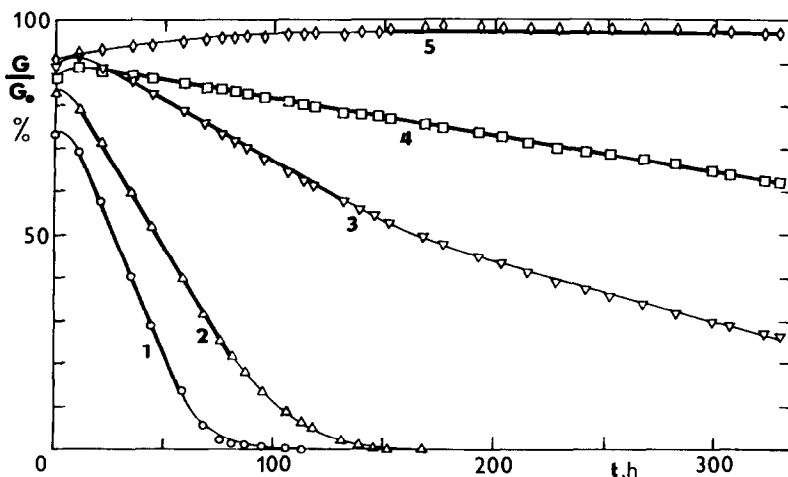


Fig. 1. Dependence of conductance of negative active mass on time after charging. Electrolyte: 4.9 M H_2SO_4 ; content of Sb_2O_3 (mg l^{-1}): 1, 400; 2, 300; 3, 200; 4, 100; 5, 0.

TABLE 1

Properties of electrodes with various additions of Sb_2O_3

Electrode no.	5	4	3	2	1
Sb_2O_3 (mg l^{-1})	0	100	200	300	400
Sb_2O_3 (mg per g active material)	0	1	2	3	4
End charging voltage (V)	2.86	2.58	2.54	2.49	2.48
$-(1/G_0) dG/dt$ (% per day)	0	2.0	6.0	19.9	29.0

Hence, the slopes of the curves in Fig. 1 are proportional to the rate of self-discharge, dQ/dt . The values of $-(1/G_0) dG/dt$ (in % per day), calculated from the linear portions of the curves, are given in Table 1.

It should be noted that Garche *et al.* [4] measured the rate of self-discharge of negative lead electrodes in 4.9 M H_2SO_4 containing 0.334 mg l^{-1} Sb_2O_3 , and the plots obtained of the rising capacity loss against time are similar to those of Fig. 1 (in the notation here, the capacity loss would be equal to $1 - Q/Q_0$, which is an increasing function of the time).

Positive electrodes

The following sequence of operations was carried out with the test electrode:

- (i) charging after formation and the first charge-discharge cycle;
- (ii) stand for t hours on open circuit;
- (iii) measure conductance, G_{ch} ;
- (iv) discharge and measure conductance, G_{d} (cycle number $n = 2$);
- (v) charge ($n = 3$);
- (vi) continued repetition of steps (ii) - (v).

TABLE 2

Experimental test procedure

n	Q_{ch} (A h)	t (h)	G_{ch} (S)	Q_{d} (A h)	G_{d} (S)
2	7.2	12	8.36	5.10	3.01
3	7.0	65	6.62	5.12	2.53
4	7.8	13	7.35	5.30	2.36
5	7.2	210	5.10	5.82	1.42
6	8.7	122	5.52	6.88	1.02
7	10.3	1500	2.28	6.97	0.60
8	9.0	3566	0.88	7.17	0.14
9	12.3	11	7.30	8.40	0.30
10	12.3	-	-	-	-

n = Cycle number; Q_{ch} = charge passed during charging at 1.2 - 1.5 A; t = rest period of electrode in the charged state; G_{ch} = conductance in the charged state after standing; Q_{d} = discharge capacity to 1.75 V at 1.5 - 2 A; G_{d} = conductance after discharge.

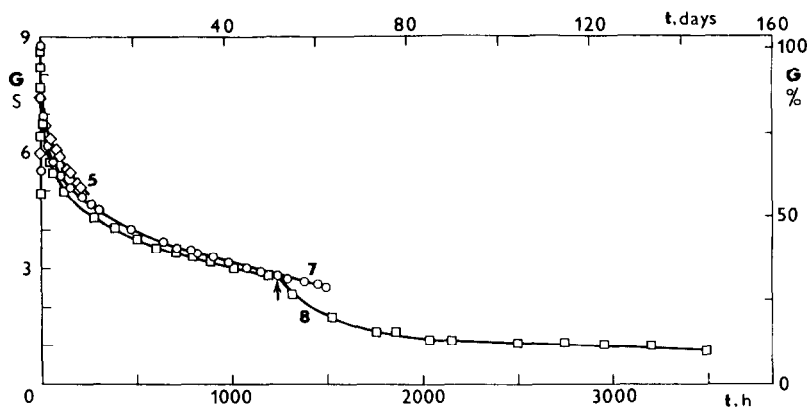


Fig. 2. Dependence of conductance of positive active mass on stand time on open circuit in 4.9 M H_2SO_4 . Numbers denote cycle number, n (cf., Table 2).

All these steps are summarized in Table 2 in the proper sequence. It is apparent that the conductance in the charged state decreases markedly with stand time, t , whereas the discharge capacity measured after standing increases with the cycle number, as is usually found during the first several 'formation' cycles. Hence, it follows that self-discharge of the positive electrode is negligible in the present case.

The dependence of the conductance on the stand time is shown graphically in Fig. 2 for three different cycle numbers, $n = 5, 7$, and 8 (corresponding to Table 2). The arrow denotes the instant at which the cell temperature during the 8th cycle was increased from 25 to 45°C. The rate of the conductance decrease obviously increases with the temperature, suggesting that some (electrochemical) corrosion process comes into play.

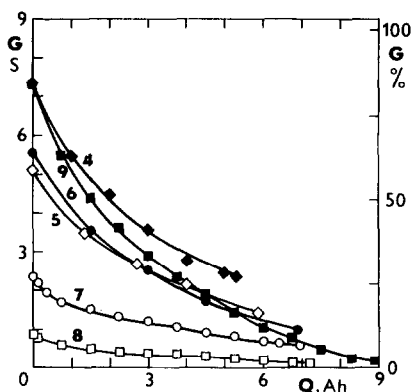


Fig. 3. Dependence of conductance of positive active mass on charge passed during discharging after standing on open circuit. Numbers denote cycle number, n (cf., Table 2).

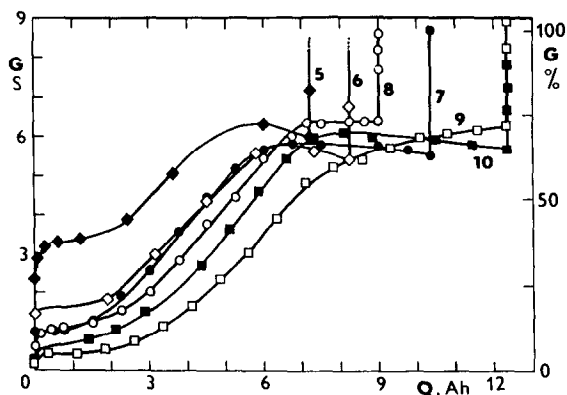


Fig. 4. Dependence of conductance of positive active mass on charge passed during charging (continuation of Fig. 3). Numbers denote cycle number, n (cf., Table 2).

When the electrode was discharged, its conductance decreased in the manner shown in Fig. 3. The preceding stand period obviously influences the course of the conductance, but there appears to be no correlation with the discharge capacity. During subsequent charging, the conductance rises to a certain limit, which is sometimes preceded by a moderate maximum (Fig. 4). As soon as the current is switched off, the conductance rises to a final value. This phenomenon, which takes place during the first 30 min after the end of charging, is also seen in Fig. 2; it was explained in earlier work [2] in terms of the changing concentration of oxygen defects in the crystal lattice of lead dioxide.

To explain the slow decrease in conductance during prolonged standing of the electrode (Fig. 2), it is assumed that a corrosion process takes place leading to the formation of a thin layer of PbSO_4 on the PbO_2 particles and thus to deterioration of the contacts between them. This is caused by the well-known instability of the PbO_2 electrode in acid solutions [5, 6]. Braun *et al.* [7] found that the conductivity of compressed, powdered material from charged positive plates was about one-fiftieth that of compact PbO_2 ; the difference was attributed to the existence of an insulating surface layer, presumably of PbSO_4 , on the PbO_2 grains.

According to measurements reported here, the BET surface area of a charged PbO_2 electrode is $5.7 \text{ m}^2 \text{ g}^{-1}$. The crystallographic radius of the SO_4^{2-} anion (*i.e.*, the length of the S-O bond) is 0.15 nm. A monolayer of PbSO_4 or SO_4^{2-} anions could thus contain 1.11×10^{19} molecules or 1.85×10^{-6} mol PbSO_4 per m^2 , or the electrode could contain 1.05×10^{-4} mol PbSO_4 per g or 3.2% PbSO_4 . This quantity could not be detected by measuring the electrode capacity, since the capacity increments from cycle to cycle (Table 2) interfere.

Electron microphotographs did not reveal any changes in the positive active mass during standing in the electrolyte for up to 1330 h. The BET

surface area did not change either, its mean value being $5.56 \pm 0.26 \text{ m}^2 \text{ g}^{-1}$ (from six measurements). X-ray diffraction phase analysis indicated that the ratio of $\alpha\text{-PbO}_2$ to $\beta\text{-PbO}_2$ increased somewhat during standing of the electrode in the electrolyte (from 0.23 initially to 0.31 after 1330 h); this suggests that some $\beta\text{-PbO}_2$ is lost.

Chemical analyses revealed that a conversion of PbO_2 to PbSO_4 indeed took place: the content of PbSO_4 in the active mass rose from 2.7% just after charging to 13% after being set aside for 1330 h. The increment would correspond, according to the above considerations, to three monolayers of PbSO_4 . This result does not mean, however, that a non-porous passivating layer is formed, since both the discharge curves and the discharge capacity were found to be quite normal.

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