IN SITU CONDUCTANCE MEASUREMENTS OF LEAD ACCUMULATOR NEGATIVE PLATES

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(Received September 3, 1982; in revised form February 3, 1983)

Summary

The electrical conductance of negative lead–acid battery plates was measured *in situ* by the d.c. method. By subtracting the conductance of the grid, the conductance of the active mass was obtained. With freshly charged plates this was appreciably lower and increased with time; this effect was attributed to adsorption of hydrogen on lead. During cycling, a decrease in the conductance was observed which is discussed in terms of recrystallization of the active mass. The conductance of dry plates was found to be appreciably lower than that of wet plates.

Introduction

In our previous work [1], we observed differences in the electrical conductance between dry and wet negative plates of the lead accumulator, measured by the four-point d.c. method, which is generally regarded as sufficiently accurate. We continued our investigations using specially designed, smaller electrodes, whose resistance was measured during cycling and in various stages of charge and discharge without removing the electrolyte from the pores. The advantage of our method is that the test electrodes need not be removed from the electrolyte and their structure is not in the least affected (*e.g.*, by oxidation). In the course of our work, unexpected phenomena were observed, such as irreversible conductance changes and time effects, whose study forms the subject of the present work.
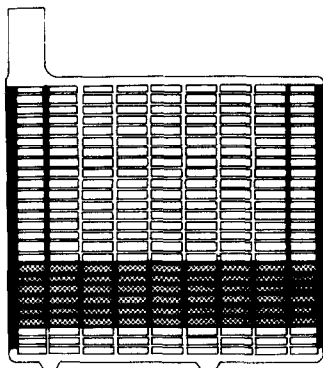
Fig. 1. Test electrode prepared from a pasted plate by removing certain parts (the final form indicated by thick lines).

Experimental

The electrical conductance of the negative electrode mass was measured in laboratory cells with test electrodes of dimensions 14.2 × 3.0 cm, prepared from about 4 mm thick pasted electrodes by removing substantial parts of the grid and active mass as shown in Fig. 1. The first and last vertical ribs of the grid served as d.c. current leads, and the second and penultimate ribs as contacts for the measurement of the d.c. voltage drop. The test electrodes were cycled with a current of 1 A, corresponding to a rather slow (about 5 h) discharge, so that the distribution of the current on their surfaces was practically uniform. The current used in the conductance measurements was 2 A, one measurement lasting for up to 10 s, which obviously could not have any measurable effect on the composition of the electrode even if this current passed through the lead/electrolyte interface. The potential drop during the conductance measurement was less than 10 mV. Some less accurate measurements were made with smaller electrodes of 2 mm thickness and dimensions of 14.2 × 1.0 cm; these were cycled at a current of 0.2 A (see Fig. 2) and the potential drop during the conductance measurements was up to 21 mV.

The grid, active mass, and electrolyte form a system which can be modelled by an equivalent diagram composed of the individual resistances connected in parallel, where the electrolyte resistance is combined with a series polarization resistance. The conductance of this system is equal to the sum of the individual conductances. That of the grid is considered constant during the measurement and can be measured either on a dry, unformed plate, or after removing the active mass at the end of the experiments. The electrolyte conductivity is about four orders of magnitude lower than that of lead and it can therefore be neglected (even more so if we take into account the polarization resistance). This is in accord with the purely ohmic voltage response to a current pulse.

The test cells consisted of one negative and four positive electrodes of the same shape, so that there was a large excess of the positive mass. One of
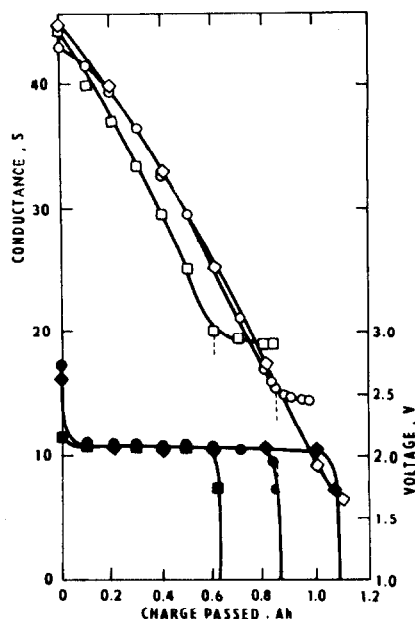
Fig. 2. Conductance changes of the negative electrode mass (open symbols) and voltage against the PbO$_2$ electrode (solid symbols) during discharge at 0.2 A in the 1st ($\Diamond$, $\blacklozenge$), 14th (O, ●), and 15th (□, ■) cycles.

the two current leads for the resistance measurement served also for cycling; to eliminate the resulting ohmic potential drop the cells were disconnected during the measurement of the resistance.

To measure the differences between the conductances in the dry and wet states, the test electrodes were dried as follows. First, the electrolyte was leached out with flowing water (13 °C, 2 h). The wet electrode was then dipped into hot xylene to remove water (105 °C, 0.5 h), and finally it was heated at 150 °C for 2 h to remove xylene. Its conductance was measured at 25 °C immediately afterwards, then after 50 h standing in air at room temperature, and finally after wetting once more with the electrolyte (25 °C, 0.5 h).

Results and discussion

The measured conductance changes of the negative active mass are shown in Fig. 2 (upper part), which refers to the 1st, 14th, and 15th discharges at a current of 0.2 A. The discharge curves are shown in the lower part for comparison. It is seen that the conductance decreases during discharge until the electrode potential breaks down. This decrease is roughly proportional to the electrode capacity, i.e., to the quantity of precipitated lead sulphate. (The capacity decreases because of deep discharging and interrupted cycling.) Analogous results were obtained when the capacity was
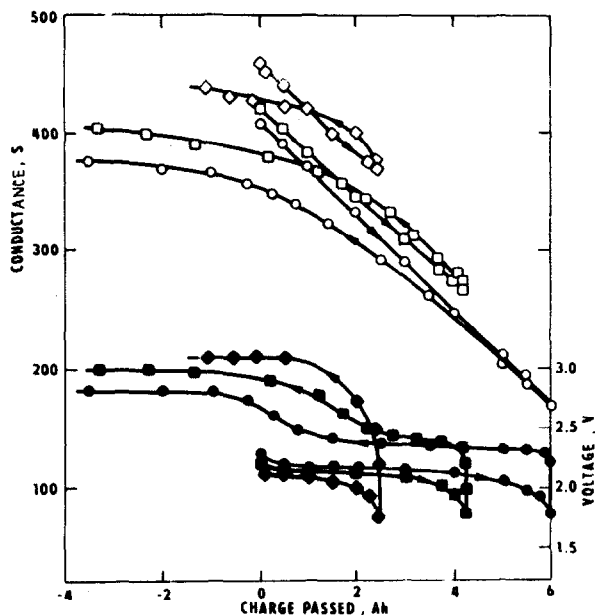
Fig. 3. Conductance changes of the negative electrode mass (open symbols) and voltage against the PbO_2 electrode (solid symbols) at -20 ($\lozenge$, $\blacklozenge$), $+2$ ($\square$, $\blacksquare$), and $+25$ °C ($\bigcirc$, $\bullet$) during discharge (arrows from left to right) and charge (arrows from right to left) at 1 A.

changed by changing the temperature or discharge rate. The dependences of the conductance on the charge passed, in three successive cycles at a 1 A rate at -20, $+2$, and 25 °C, are shown in Fig. 3. The electrodes in this case were only discharged to 1.75 V cell voltage. The discharge and charge curves are also shown for comparison. It is seen that the conductance of the electrode mass increases during charging as would be expected; this effect is small at lower temperatures. Also in this case, the decrease in conductance is roughly proportional to the discharge capacity, i.e., to the quantity of $PbSO_4$ formed in the electrode pores.

At the end of charging, however, the conductance does not attain the original value corresponding to the beginning of the preceding discharge, although the charge was obviously finished as evidenced, e.g., by the constant cell voltage (Fig. 3); and it increases further only very slowly.

It is surprising that the electrode conductance changes even during the currentless state after charging, as shown in Fig. 4. This process is very slow, reaching a limiting value after 4 - 5 days, usually equal to the original value prior to discharge. Sometimes, however, the recovery is not complete.

The decreased conductance of a freshly charged electrode (i.e., the electrode mass) could possibly be caused by the adsorption of hydrogen on the highly developed surface of the spongy lead and its subsequent penetration into the crystal lattice. It is known that adsorption of hydrogen on metal layers considerably decreases their electrical conductance [2, 3]. The conductance curves in Fig. 3 obtained during charging are also probably in-
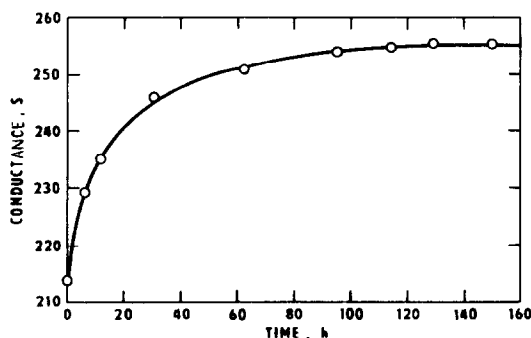
Fig. 4. Increase in conductance of the negative electrode mass with time after charging at 1 A corresponding to 125% of the capacity in the preceding (*i.e.*, 5th) cycle.

fluenced by this phenomenon. During idling of the electrode on open circuit, lead corrodes due to the dissolved oxygen and the adsorbed hydrogen is slowly desorbed, whereby the conductance of the metal phase slowly increases and eventually decreases again as a result of self discharge.

We attempted to test this hypothesis. Placing the cell with the test electrode under vacuum (produced by a water pump) had no effect on the conductance. However, when the electrolyte was replaced with a similar one but saturated with *p*-nitrophenol, the conductance of the test electrode increased over an hour by 10% (from 119 to 131 S), and then decayed slowly (resembling a first-order reaction rate) to 3 S after 100 h with a simultaneous breakdown of the electrode potential. Picric acid had an effect similar to *p*-nitrophenol. Thus, it seems that during the first hour the adsorbed hydrogen was oxidised, resulting in a conductance increase which was, however, overcompensated during the later stage by a drop in the conductance caused by oxidation of the lead with the nitro compound in the acid medium, giving $PbSO_4$.

Replacing the acid electrolyte with a solution of 2.8M KOH had a pronounced effect: the electrode conductance increased by 25% (from 182 to 228 S) in the course of 50 h. Since the standard potential of the reaction (from the data of Latimer [4])

$$Pb(OH)_2 + 2e^- = Pb + 2OH^-, E_o = -0.55 \text{ V}$$
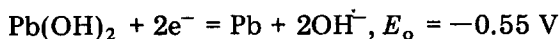
is more positive that that of the reaction

$$2H_2O + 2e^- = H_2 + 2OH^-, E_o = -0.828 \text{ V}$$

it is clear that if hydrogen is adsorbed on the lead electrode in acid solution, it is more or less rapidly oxidised to water after immersing in the alkaline electrolyte. The electrons set free in this reaction are consumed in the reduction of oxygen dissolved in the electrolyte (eventually, of $PbSO_4$ if the electrode is not fully charged). Thus, this experiment also supports our assumption that desorption of hydrogen is responsible for the observed increase in the conductance of the lead electrode.
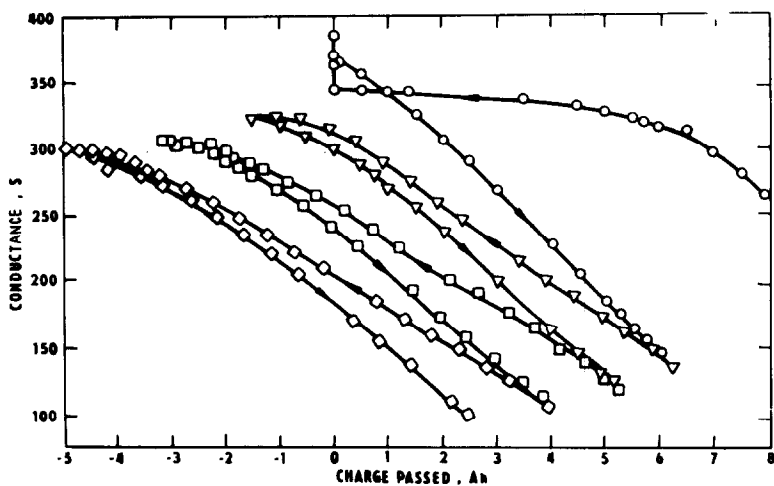
Fig. 5. Conductance changes during four subsequent cycles. ○, 24th; ▽, 25th; □, 26th; ◇, 27th cycle. Arrows from left to right denote discharge to final cell voltage of 1.75 V; from right to left charge (1 A, 25 °C).

The dependence of the conductance of the negative electrode mass on the charge passed during several cycles is shown in Fig. 5. The origin of the charge scale corresponds to the beginning of the 24th cycle. Prior to this, the electrode was charged to 187% of the capacity obtained in the 23rd cycle and it. was left on open circuit for 100 h while its conductance increased from 344 to a maximum of 380 S after 80 h and then decreased somewhat (apparently owing to self discharge). It is seen that overcharging with a subsequent idling period results in a conductance increase with a nearly linear dependence on the charge passed during subsequent discharge.

In three further cycles, discharging to 1.75 V end voltage commenced immediately following charging to 125% of the capacity obtained in the preceding cycle, which is generally considered sufficient. Here, the conductance values both at the beginning and at the end of discharge are decreased. The discharge capacity increases somewhat with decreasing conductance (in our case from 6.2 to 7.4 A h), probably owing to recrystallization of the active mass accompanied by an increase of its active surface area.

We studied this phenomenon in more detail and the results are shown in Fig. 6 beginning from the 19th cycle of uninterrupted cycling, where the conductance at the beginning and at the end of the discharge (to 1.75 V/cell) is plotted against the cycle number. The upper and lower curves correspond, respectively, to the charged and discharged states. It is seen that the conductance drop in the course of cycling is as great as during discharge. The electrode capacity increased during cycling (curve C) to a maximum at the 50th cycle, showing a roughly inverse behaviour with respect to the conductance, as stated above. Owing to the rather deep discharge, the structure of the negative plate changed profoundly, as was apparent from its two-fold increase
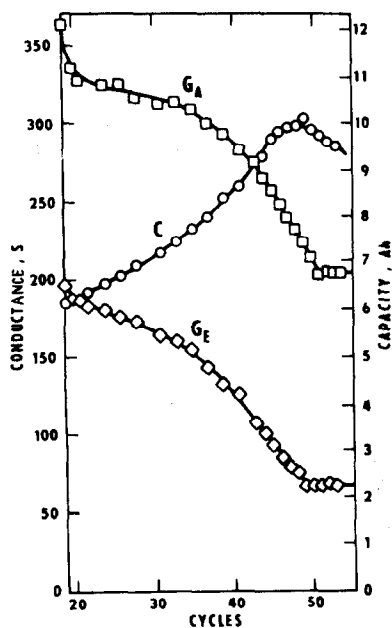
Fig. 6. Changes of initial, G_A, and final, G_E, conductances of the electrode mass and the electrode capacity, C, during uninterrupted cycling.

TABLE 1

Conductance changes of the negative electrode mass in the course of drying and after wetting with the electrolyte (at 25 °C)

Medium	Conductance	
	(Ω^{-1})	(%)
Electrolyte	142.0	100.0
Water	143.1	100.8
Xylene	116.7	82.2
Air	94.9	66.8
Air (after 50 h)	94.3	66.4
Electrolyte	146.2	103.0

in thickness. This is in accord with the substantial drop in conductance. The resulting more open structure of the plate with a higher porosity results in a higher discharge capacity, but, of course, only to a certain limit (Fig. 6).

The results of the measurements on the plate wetted with the electrolyte and during drying (see "Experimental") are given in Table 1. In this case, there was a decrease of about one-third in the conductance on drying. The conductances of the plate wetted with the electrolyte at the beginning and at the end of the experiment, and that of the plate wetted with water, were practically the same. The difference between dry and wet electrodes may

possibly be attributed to a difference in the quality of the contacts between the crystalline particles of lead. The lead grid without the active material did not show this effect. Differences between conductance values of dry and wet porous electrodes were also found by Euler and Müller [5], who proposed a similar explanation. It seems that the formation of an oxide film, soluble in the acid electrolyte, plays a rôle in our case. The clarification of these phenomena will form the subject of further work.

Conclusions

The measurement of the electrical conductance of porous lead electrodes can give an insight of the changes in their physicochemical structure during cycling. Our results suggest the influence of ageing, recrystallization, and adsorption of hydrogen. An in-depth study of these phenomena, some of which can, no doubt, play a rôle in the testing of batteries, seems desirable.

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