

# Factors that accelerate the wetting of auxiliary electrodes in sealed lead/acid batteries

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Received 17 May 1996; accepted 30 July 1996

## Abstract

An auxiliary electrode is a useful means to operate successfully a sealed lead/acid battery for a long cycle life by absorbing any excessive amounts of gas. When the auxiliary electrode becomes wet with electrolyte, its capability for gas absorption deteriorates and, as a result, the service life of the battery is shortened. Consequently, it is very important to identify the main factors that accelerate the wetting of auxiliary electrodes. An auxiliary electrode in a sealed lead/acid battery is partly immersed in electrolyte and partly exposed to a mixed-gas atmosphere. The gas pressure in the battery can change over a wide range with time. The potential of the auxiliary electrode is regulated to a specific value through the use of a non-linear type resistor. Both electrochemical and chemical reactions occur simultaneously on the auxiliary electrode. In this study, various factors that accelerate the wetting of auxiliary electrodes have been identified and the degree of their individual effects have been determined. As a result, it has been found that the electrochemical reaction exerts the strongest effect.

**Keywords:** Lead/acid batteries; Auxiliary electrodes; Electrode wetness; Hydrogen absorption

## 1. Introduction

The principles and construction of a sealed lead/acid battery with an auxiliary electrode have been reported previously [1-3]. Such a battery is mainly used in large-size stationary applications. The service life of the battery is dependent largely on the wetness of the auxiliary electrode. Nevertheless, the relevant importance of factors that promote such wetting has not been elucidated in detail. Accordingly, in this work, an identification has been made of several factors that accelerate the wetness of auxiliary electrodes in sealed lead/acid batteries during actual operation.

In general, the auxiliary electrode is partially immersed in the electrolyte and a non-linear resistor, such as a diode [4] or varistor [5], is connected to it [6]. In many cases, the gas atmosphere in sealed batteries tends to hydrogen-rich due to corrosion of the positive grid [7,8]. Consequently, the auxiliary electrode is connected to the positive electrode via a non-linear resistor so that the hydrogen gas is absorbed in the auxiliary electrode.

The auxiliary electrode is subjected to very complicated conditions during actual operation of the battery. The following factors are assumed to accelerate the wetness of the auxiliary electrode:

1. change of gas pressure over a wide range;
2. regulation of the potential of the auxiliary electrode;

3. the electrochemical reaction (ECR) and the gas-phase reaction (GPR) that occur concurrently on the auxiliary electrode.

The hydrogen (oxidation) reaction at partially-immersed, platinum plate electrodes has been studied in detail [9-11]. By contrast, little attention has been directed towards understanding how the wetting of a partially-immersed porous electrode in a sealed lead/acid battery proceeds in a mixed-gas atmosphere.

In this work, an attempt has been made to measure the degree of auxiliary-electrode wetness that is imposed by each acceleration factor, as well as to study the water-repellent properties of porous electrodes that are prepared from various materials.

## 2. Experimental

Several sealed lead/acid batteries (40 Ah capacity) with auxiliary electrodes were constructed for test purposes. The batteries were overcharged to identify the degree of wetness of the auxiliary electrodes and the change in operation conditions during use. The factors that accelerated the wetness, together with the extent of wetness caused by each factor, were determined from the test results.

### 2.1. Preparation of sample electrodes

Resin-bonded porous electrodes were prepared [8] as test samples. They were made from amorphous graphite mixed with 25 wt.% of fluororesin co-polymer powder. For purposes of comparison, some samples were made with activated charcoal instead of amorphous graphite. The water-repellent properties of the auxiliary electrodes were evaluated by comparison of the following features.

Water-repellent property of auxiliary electrode without catalyst, but prepared by the same procedure as that employed for electrodes with catalyst addition.

The powders were mixed, press-moulded at  $127 \text{ kg cm}^{-2}$ , and then sintered at 330, 350 or 370 °C for 1 or 0.5 h. The dimensions of each sample were  $30 \text{ mm} \times 16 \text{ mm} \times 4.3 \text{ mm}$  and the weight was about 3.2 g.

### 2.2. Test cell

A schematic of the test cell used for the evaluation of the degree of wetness is shown in Fig. 1. The cell is provided with two circuits: (A) and (B). Circuit (A) consists of a power source, an auxiliary electrode, and a counter electrode. Circuit (B) comprises a power source, a pair of electrodes for gas generation, a pressure gauge, a safety valve, and two stop-cocks.

### 2.3. Expression for degree of wetness

The degree of wetness of the auxiliary electrode is defined as

$$\text{Wetness degree} = (W_1 - W_2) / W_2 \quad (1)$$

where  $W_1$  is the weight of the wet sample electrode;  $W_2$  is the weight of the wet sample electrode after washing and drying.

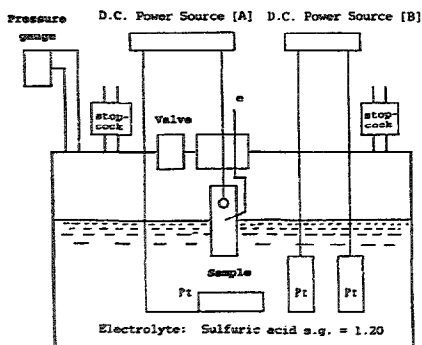


Fig. 1. Test cell.

### 2.4. Evaluation of water-repellent property (natural wetting)

Sample electrodes, without and with catalyst, were prepared from amorphous graphite and activated charcoal under various sintering conditions. For evaluation of the degree of wetness under normal conditions, sample electrodes were partially immersed in electrolyte in a nitrogen atmosphere. The electrodes were maintained at open-circuit.

### 2.5. Study of factors that accelerate the wetness of the auxiliary electrode

#### 2.5.1. Change of gas pressure

Sample electrodes were partially immersed in electrolyte under a nitrogen atmosphere and at open-circuit conditions. The pressure change was programmed as follows:

1. - 150 mm Hg versus atmospheric pressure for 1 day;
2. + 150 mm Hg versus atmospheric pressure for 13 days.

The test results under these conditions were compared with those for natural wetting (see Section 2.4) and with those for cases where the sample electrodes were fully immersed in the electrolyte.

#### 2.5.2. Regulation of the potential of the sample electrode

In order to regulate the potential of the sample electrode at a value half-way between that of the positive electrode and the negative electrode of the battery, the electric circuit shown in Fig. 2 was used, together with a nitrogen gas atmosphere.

When an electrochemical oxidation reaction occurs, the potential shifts towards the negative direction. Cyclic voltammetry of the sample electrodes without catalyst was conducted in a nitrogen atmosphere.

#### 2.5.3. Gas-phase reaction

Tests were performed on a sample electrode that contained 5 wt.% Pt. The sintering condition was 370 °C for 1 h, for which previous tests showed the sample to display the best water-repellent property. Sample electrodes were partially immersed in electrolyte. A mixed gas of 80%  $\text{N}_2$  and 20%  $\text{H}_2$  was introduced and the stop-cocks were closed.

The speed of the gas-phase reaction was controlled by adjusting the current of circuit (B) at 20, 40 or 60 mA. When the gas pressure reached a constant value, the speed of the

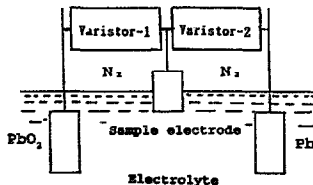


Fig. 2. Electric circuit to regulate the potential of a test electrode at a value intermediate between those of the positive and negative electrodes.

gas-phase reaction (GPR) was equal to that of gas generation in circuit B. In practice, the equilibrium pressure was found to be below 10 mm Hg versus ambient under the test conditions.

### 2.5.4. Electrochemical reaction

Tests were conducted on the same sample used to study the GPR. The electrode was partially immersed in the test cell (Fig. 1). The latter was filled with a mixed gas of 80% N<sub>2</sub> and 20% H<sub>2</sub>. The speed of the electrochemical reaction (ECR) was controlled by adjusting the current of circuit (A) to zero, 20 or 40 mA. The amount of gas consumed was found to be the same as that generated at the counter electrode.

### 2.6. Gas recombination reaction on wet electrode

Wet samples were taken from batteries with auxiliary electrodes at several intervals during an 18-month test. Each sample electrode was partially immersed in the test cell shown in Fig. 2. In order to evaluate the speed of the electrochemical reaction (ECR), a mixed gas of N<sub>2</sub>:H<sub>2</sub> = 80:20 was introduced and the electrode was maintained at open-circuit. The stable current was taken as a measure of the ECR.

In order to determine the speed of the chemical reaction in the gas phase (GPR), a mixed gas of N<sub>2</sub>:H<sub>2</sub>:O<sub>2</sub> = 9:2:1 was introduced under open-circuit conditions. The speed of pressure reduction was determined in a closed cell and then converted into a gas-phase reaction speed for which 10.2 ml per min = 1 A.

After these tests, the degree of wetness of the sample was measured and a study was made of the extent of degradation of the recombination reaction that was caused by the wetting.

## 3. Results and discussion

### 3.1. Behaviour of model cell

The electrochemical behaviour of the sealed lead/acid battery with an auxiliary electrode is shown in Fig. 3 in terms of the change in pressure, the hydrogen oxidation current, and the change in wetness of the sample electrode. At first, the pressure rapidly decreased to -120 mm Hg, but then increased to +300 mm Hg versus ambient, which is the opening pressure of the valve. The hydrogen oxidation current remained constant (zero) in the initial stages, but then suddenly increased when the pressure reached its minimum value. Finally, the degree of wetness increased gradually and displayed no dependence on either the change of pressure and/or current.

As noted above, the sudden change in pressure coincided with a sudden increase in current. Gas analysis confirmed that this behaviour is due to a change in gas composition from a surplus of oxygen to a surplus of hydrogen. A significant change in pressure was often observed when a battery was charged after discharge [3,7]. Thus, it is concluded that such

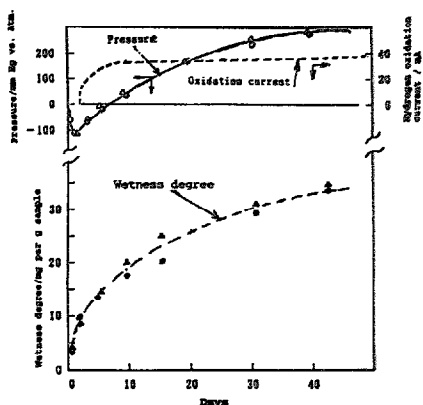


Fig. 3. Performance of sealed lead/acid test cell with auxiliary electrode. Auxiliary electrode: resin-bonded graphite electrode; 5 wt.% Pt; 25 wt.% fluororesin; sintering temperature 370 °C; capacity 40 Ah; overcharge current 40 mA.

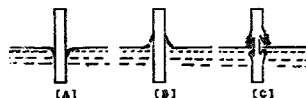


Fig. 4. Degradation of the auxiliary electrode.

a pressure change is one of the factors that accelerate electrode wetness. The degree of wetness of two sample electrodes was almost identical in these tests. This indicates that the above test has good reproducibility for the evaluation of the degree of wetness of auxiliary electrodes.

The shape of the meniscus changed during the test, i.e. from condition (A) to condition (B) in Fig. 4. This suggests that the water-repellent property of the sample electrode has degraded. Shape (C) was often observed when the sample electrode was subjected to constant current for over 12 months in a hydrogen atmosphere. It was not observed, however, in the present study.

### 3.2. Water-repellent property of porous electrode under natural wetting conditions

The changes, over 14 days, in the degree of wetness of sample electrodes which were prepared via various processes are presented in Fig. 5. In all tests, the degree of wetness reaches an almost constant value within 14 days. The extent of the wetness is influenced significantly by the sintering temperature. There is also a difference in behaviour between using activated charcoal or graphite as the catalyst carrier. This difference is not so marked, however, as that induced by a change in sintering temperature. There is also a difference in performance between sample electrodes with a cata-

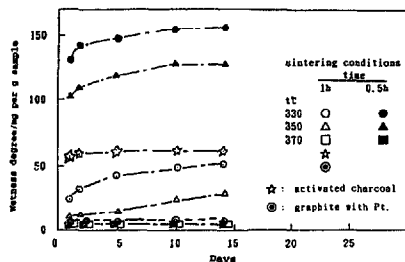


Fig. 5. Degree of wetness of a resin-bonded, porous carbon plate that is partially immersed in a nitrogen gas atmosphere without an electric circuit.

lyst and those without a catalyst. Again, the effect is less than that imposed by the sintering temperature.

### 3.3. Influence of different acceleration factors on the degree of wetness

#### 3.3.1. Pressure change

With a partially-immersed electrode, the degree of wetness was 3.3 and 3.1 mg per g of sample under pressure and natural wetting conditions, respectively. With a fully-immersed electrode under pressure, the degree of wetness was 100 mg per g of sample. These results show that the gas pressure and the electrolyte pressure are in equilibrium in the so-called 'three-phase' zone of a partially-immersed electrode.

#### 3.3.2. Potential of sample electrode

A comparison of the degree of wetness when a sample electrode is potential-free and when its potential is regulated at the value intermediate between that of the positive and negative electrodes is shown in Fig. 6. It can be seen that the different sintering temperatures exert an influence. The effect of potential is higher for sample electrodes with low water-repellent properties than for those with higher water-repellent properties. The degree of wetness of an electrode with the highest water-repellent property (which was sintered at 370

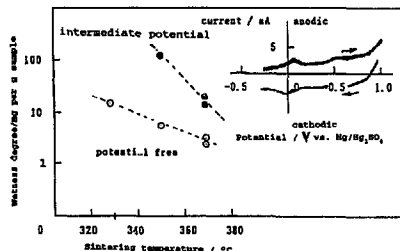


Fig. 6. Effect of regulated potential on the degree of wetness. Test sample: resin-bonded, amorphous graphite electrode without catalyst. Test condition: nitrogen gas atmosphere.

°C) is about 10 times greater at a regulated potential than under potential-free conditions.

A voltammogram obtained in a nitrogen atmosphere is also shown in Fig. 6. A small oxidation peak is observed during the potential scan in the positive direction. This peak is assumed to correspond to the reduction peak that is observed during the potential scan in the negative direction. This region is generally known as the 'oxygen absorption reaction zone' and the potential is close to that at which the auxiliary electrode is regulated. It was not possible to determine if such oxidation is related to the degradation of the water-repellent properties of the sample electrodes.

During operation of sealed lead/acid batteries, the gaseous composition has an excess of hydrogen. Thus, the hydrogen oxidation current is much larger than that reported above. Consequently, the regulation potential shifts about 200 to 300 mV towards the negative direction from the above value. When the diffusion of hydrogen is limited due to the wet sample electrode, and thus the partial pressure of hydrogen on the auxiliary electrode decreases, the hydrogen oxidation current will naturally decrease and, as a result, the potential will shift again in a positive direction. In this case, the regulation potential may become an important factor in accelerating the degree of wetness of the sample electrode.

#### 3.3.3. Gas recombination reaction

The relationship between the current of the gas-phase reaction (GPR) and the degree of wetness is given in Fig. 7. Similarly, the relationship between the current of the electrochemical reaction (ECR) and the degree of wetness is shown in Fig. 8. The wettability is influenced significantly by the ECR. By contrast, the effect of the GPR is very complicated. Whilst the degree of wetness is high for a high ECR current, it becomes lower when the GPR current is increased. Although the degree of wetness is low with a low ECR current, it increases slightly. It is assumed that an exothermic reaction occurs to some extent on the wet electrode and, accordingly, the electrode dries out rather than becoming wetter by the GPR.

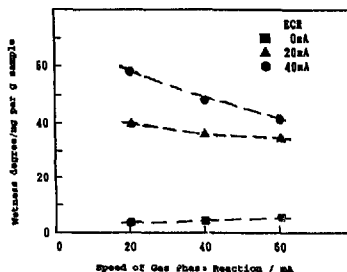


Fig. 7. Relationship between degree of wetness and speed of gas-phase reaction.

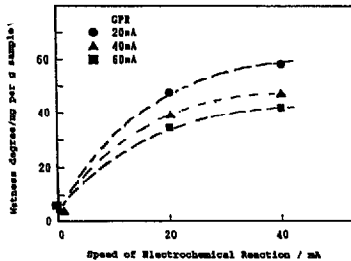


Fig. 8. Relationship between degree of wetness and speed of electrochemical reaction.

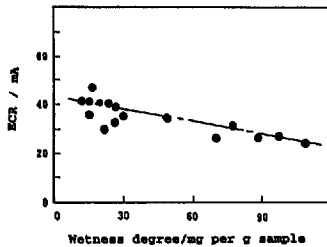


Fig. 9. Influence of the degree of wetness on the electrochemical reaction.

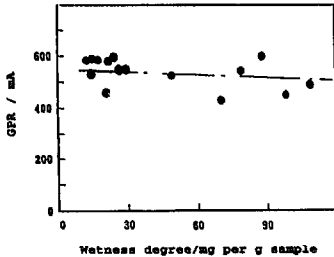


Fig. 10. Influence of the degree of wetness on the gas-phase reaction.

### 3.4. Gas-recombination reaction on wet electrode

The relationship between the degree of wetness and the ECR is presented in Fig. 9. At first, the ECR was negligibly small but then gradually increased over several days as the electrode wetness increased. The ECR then decreased to about 50% of the peak value.

The relationship between the degree of wetness and the GPR is given in Fig. 10. The GPR is little influenced by the electrode wetness.

It was not possible to determine which degree of wetness corresponds to the end of service life of an auxiliary electrode. As explained above, the ECR exerts the greatest effect on the wetness, and the wetness itself also influences the ECR. Consequently, the service life of an auxiliary electrode, as well as that of a sealed lead/acid battery, can possibly be improved when the wetness of the auxiliary electrode is properly controlled. Based on the above results, it is important that the proportion of the ECR is limited to below a certain degree and that the proportion of the GPR is increased.

## 4. Conclusions

Several factors have been identified as accelerators of the wetness of auxiliary electrodes in sealed lead/acid batteries during actual operation. In this respect, the following conclusions can be drawn:

1. The water-repellent properties of a resin-bonded auxiliary electrode are strongly dependent on the sintering temperature.
2. The wetness of an auxiliary electrode is accelerated by potential regulation in a nitrogen atmosphere.
3. The electrochemical reaction exerts the greatest influence on the wetness. The gas-phase reaction does not accelerate the wetness.
4. The wetness influences the electrochemical reaction.
5. The service life of an auxiliary electrode, as well as that of the sealed lead/acid battery, can be improved when the electrochemical reaction is limited below a certain degree and the gas-phase reaction is increased as much as possible.

## Acknowledgements

The author thanks Professor Dr Iwahara of Nagoya University for his useful advice.

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