

## PRELIMINARY RESULTS FROM AN IMPROVED THEORETICAL APPROACH TOWARDS CHARACTERIZING SEALED LEAD/ACID CELLS

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### Introduction

Following recent research [1] into reactions of the active material of the lead/acid battery with hydrogen and oxygen, a method has been developed, based on simple experimental tests, for the evaluation of the parameters controlling gas recombination in sealed cells. Tests conducted to date have demonstrated the feasibility of this approach towards the characterization of batteries from different manufacturers and the assessment of effects exerted by the presence of additives in the system [2, 3].

The proposed method [1] is based on the measurement of the internal pressure of a gas-recombination cell and does not take into account:

- positive grid corrosion;
- material exchange between the inside of the battery and the external surroundings;
- spontaneous oxygen development at the positive electrode.

From investigations into the long-term behaviour of various recombinant systems, it became clear that the internal pressure and gas composition inside the battery depend, in fact, upon these (ignored) parameters. For this reason, the theory is being extensively revised and the modified version will be discussed in a future publication.

The aim of the present work is the determination of the variability range of all the parameters influencing the behaviour of the sealed lead/acid cell.

### Experimental

The tests involved both standard production plates having Pb-Ca-Sn expanded grids (size 14.5 × 11.7 cm), and sealed 6 V 100 A h batteries assembled using plates of the same type. The cells, with supported electrolyte, contained 10 positive and 10 negative plates. After formation, plates and

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batteries were submitted to 20 charge–discharge cycles at a  $C/20$  rate and 25% depth-of-discharge.

The batteries were modified in a manner reported elsewhere [2] in order to eliminate the vent plugs, to allow the inlet or outlet of gas, and to provide connection to the pressure sensors. The free volume for each cell was also measured [2].

In a first series of tests, single plates saturated with sulphuric acid ( $1.28 \text{ g ml}^{-1}$ ) were sealed in a glass vessel and the internal pressure was monitored over time with an electronic sensor. All the plates were wrapped in an electrolyte-retaining separator, to ensure the presence of a sufficient quantity of electrolyte throughout the duration of the experiment.

A second group of tests consisted of monitoring the pressure inside the battery container, both under charge at constant current and on open circuit.

Both batteries and plates were completely charged before the commencement of testing and the free volume was filled with hydrogen, oxygen, nitrogen, or air according to the conditions chosen. The experiments, carried out at 25 and 40 °C, lasted from 100 to 200 h. The electrolyte was prepared from dilution of reagent grade, concentrated sulphuric acid.

## Results

The mathematical treatment of the experimental results is based on the solution of three simultaneous differential equations describing the mass balances for the various gases present inside a completely charged system. Each balance equation has the following general expression:

$$dP_i/dt = G_i(I) - K_i(P_i) + F_i(P_i) \quad (1)$$

where:  $P_i$  is the partial pressure of gas  $i$ ;  $I$  is the external current;  $G_i$  is the rate of the gas generating processes calculated from Faraday's law;  $K_i$  is the specific rate of gas consumption;  $F_i$  is a term that takes into account the exchange of gas molecules with the atmosphere via leaks in the container.

Evaluation of the rates of spontaneous hydrogen and oxygen evolution and consumption has been accomplished by considering single plates in a sealed vessel. For such a system, the pressure decay with time shows different trends according to the type of plate, positive or negative, and the gas filling the container.

The pressure *versus* time plot for a negative plate in air (Fig. 1(a)) shows, as discussed previously [4], an initial rapid decrease in pressure due to the spontaneous consumption of oxygen, followed by an increase due to hydrogen development. If the container is filled initially with hydrogen, the results demonstrate (Fig. 1(b)) that the pressure is affected by the process of hydrogen evolution only.

In the case of a positive plate in air, the pressure increases continuously with time at a slope depending only on the rate of oxygen development due to  $\text{PbO}_2$  decomposition, Fig. 2(a). If hydrogen is present in the internal volume, the pressure plot shows a less positive trend, as reported in Fig. 2(b).

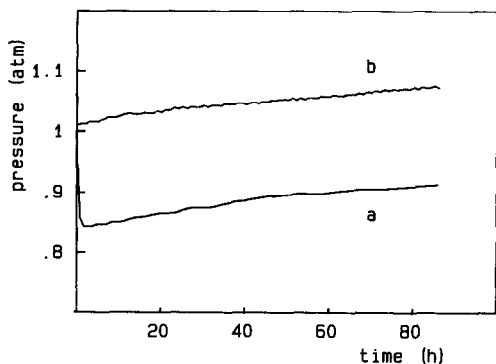


Fig. 1. Pressure vs. time plot for negative plate in (a) air, (b) hydrogen; temperature 25 °C.

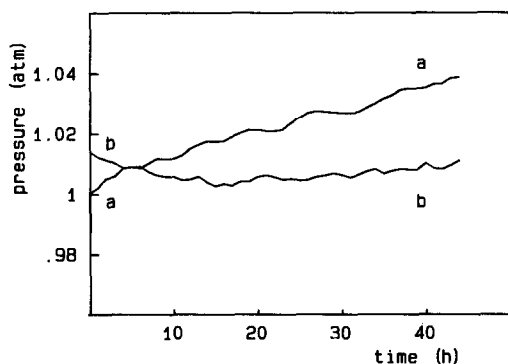


Fig. 2. Pressure vs. time plot for positive plate in (a) air, (b) hydrogen; temperature 25 °C.

The processes involved in this system are hydrogen consumption and oxygen evolution, and the relative values of the corresponding rates influence the variation of pressure with time.

From the experimental data regarding single plates, the following variability ranges for the kinetic parameters of hydrogen and oxygen consumption and evolution have been obtained:

Specific rate of  $H_2$  oxidation: from 0.001 to 0.01  $h^{-1}$

Specific rate of  $O_2$  reduction: from 0.1 to 1  $h^{-1}$

$H_2$  evolution current: from 0.1 to 1 mA

$O_2$  evolution current: from 2 to 4 mA.

The tests on the complete cells gave the internal pressure decay in the presence of air (Fig. 3(a)) and pure hydrogen (Fig. 3(b)). In the first case, the reduction of oxygen at the negatives prevails due to the relatively high oxygen concentration. Conversely, when only hydrogen is present, the initial pressure decrease is related mainly to hydrogen oxidation at the positives.

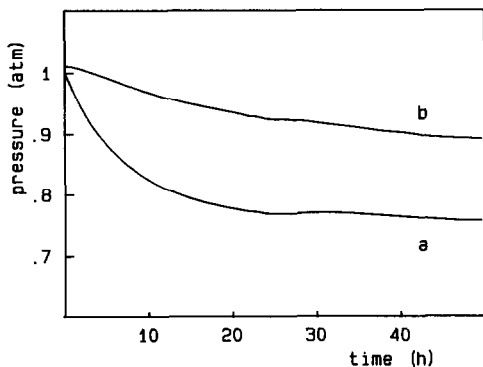


Fig. 3. Pressure decay with time for 100 A h cell filled with (a) air, (b) hydrogen; open-circuit condition; temperature 25 °C.

From analysis [1] of the experimental data, some of which are reported in Fig. 3, it has been found in the case of a 100 A h cell that the specific rate of hydrogen oxidation varies between 0.02 and 0.05 h<sup>-1</sup> and the specific rate of oxygen reduction varies between 0.5 and 1 h<sup>-1</sup>. It appears that these values do not correspond directly to those obtained from the single plates. This finding is probably related to the different conditions sensed by the plates in the two systems.

The value of the specific rate of O<sub>2</sub> reduction has also been calculated, from mass balance equations, in the case of a cell filled with air and charged at a current at which the internal pressure remains constant with time. This current value has been determined experimentally (Fig. 4), and for the system under consideration (100 A h cell) has been found to be 150 mA. The results obtained are in substantial agreement with those previously reported.

To test for leaks from the battery container, experiments have been carried out monitoring the internal pressure of cells filled with nitrogen at a

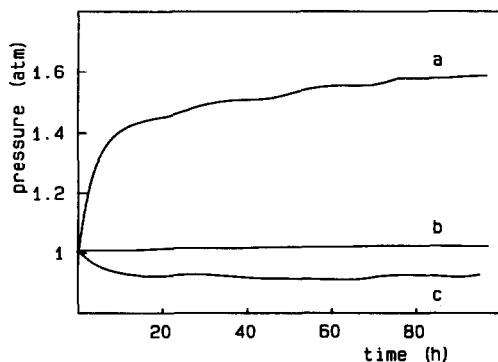


Fig. 4. Pressure decay with time for 100 A h cell filled with air under constant-current charge at: (a) 500 mA; (b) 150 mA; (c) 100 mA.

pressure slightly above atmospheric. Under these conditions, the gas evolution reactions are counterbalanced, in the long term, by the gas consuming processes, so that each pressure decrease can be related to leakage (if the internal pressure is higher than atmospheric). The results from tests conducted for over 200 h gave a value of  $2 \times 10^{-4}$  atm h<sup>-1</sup> for the leakage rate from the inside of the cell.

The determination of the corrosion current has been obtained from the results of studies performed previously [5] on the same type of plates used in the present work. Weight loss measurements for positive plates immersed in sulphuric acid (sp. gr. 1.28 g ml<sup>-1</sup>) gave an estimated corrosion current of about 0.06 to 0.1 mA per positive plate.

## Conclusions

The results obtained in this study have revealed the following information:

(i) there is a marked difference in the behaviour of the plate, particularly the negative, when in isolation in a sealed container or when in a cell; this is probably due to the different conditions of gas diffusion and to a variation in the extent of free surface;

(ii) PbO<sub>2</sub> spontaneous decomposition and grid corrosion at the positive cannot be neglected over long periods of time;

(iii) hydrogen is consumed at the positive at a specific rate that is one to two orders of magnitude lower than that of oxygen reduction at the negative.

## References

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