

Processes involving gases in valve-regulated lead/acid batteries

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Abstract

The kinetics of O₂ and H₂ reactions with the active mass of the plates have been investigated by carrying out open-circuit and overcharge tests on cells and plates coming from commercial valve-regulated lead/acid batteries of different producers. The tests at open circuit showed that the rate of O₂ reduction at the negative plates is about four orders of magnitude higher than that of the other four reactions examined (evolution of O₂ at positive plates and of H₂ at freshly charged negatives, H₂ consumption at positive and partially discharged negative plates). H₂ leaking through the battery walls, which showed a permselective membrane behaviour, was also considered. Overcharge tests allowed the mathematical model proposed elsewhere to be verified and provided information on the cell behaviour when the overcharge current became equal or lower than the O₂-reduction limiting current. The experiments on single plates and on couples (1 positive and 1 negative) sealed in glass vessels showed that the cell construction has a strong influence on the rate of gas-recombination processes.

Keywords: Valve-regulated lead/acid batteries; Hydrogen; Oxygen

1. Introduction

The main feature of valve-regulated lead/acid batteries (VRLA), in which the acid is gelled or retained in a microfibre glass mat, is their capability of consuming the gases evolved during service, so that the container can be in principle completely sealed.

The literature reports a number of papers on this subject. Together with review articles [1–4], there are some more specific ones dealing with the behaviour of commercial systems [5,6], with the definition of a method for the recombination-efficiency evaluation [4,7–9] and with the kinetics of processes regarding O₂ [4,10,11] and H₂ [12–14].

Fundamental studies on H₂ and O₂ reactions in a gas-recombining system have already been carried out by our group [15–19]. An experimental method based on the monitoring of the cell internal pressure was developed in order to determine the kinetic constants of H₂- and O₂-consumption reactions [17].

Through preliminary investigation the reliability of the proposed model was verified, showing that the kinetic constant of O₂ reduction at the negative is much higher than that of H₂ oxidation.

The results of such preliminary tests clearly indicated that a correct analysis of gas-recombining cells must include, in addition to O₂ reduction, the following processes: (i) H₂ leakage through the plastic walls; (ii)

H₂ oxidation, and (iii) spontaneous O₂ evolution, both at the positive plates [18,19].

In this work we have extended the test duration to 500–1000 h and applied gas chromatographic analysis to establish the composition of the gaseous mixture during overcharge and hence obtain information on the occurring processes.

2. Basic theory

The developed model [17,18] describes the behaviour of gas-recombining lead/acid batteries submitted to a constant overcharge current I . It considers a fully charged cell in a sealed container at a given temperature T and a free volume V , initially filled with some gaseous species (air or O₂ or H₂ or N₂).

The processes involving the gaseous species present in the free volume are indicated in the scheme of Fig. 1. The gas reactions are coupled with PbO₂ or Pb sulfate.

The material balance of the various gases is described by the following simultaneous differential equations:

$$dN_{\text{O}}/dt = I_{\text{O}}/4F - K_{\text{O}}N_{\text{O}} + f_{\text{O}} \quad (1a)$$

$$dN_{\text{H}}/dt = I_{\text{H}}/2F - K_{\text{H}}N_{\text{H}} + f_{\text{H}} \quad (1b)$$

$$dN_{\text{N}}/dt = f_{\text{N}} \quad (1c)$$

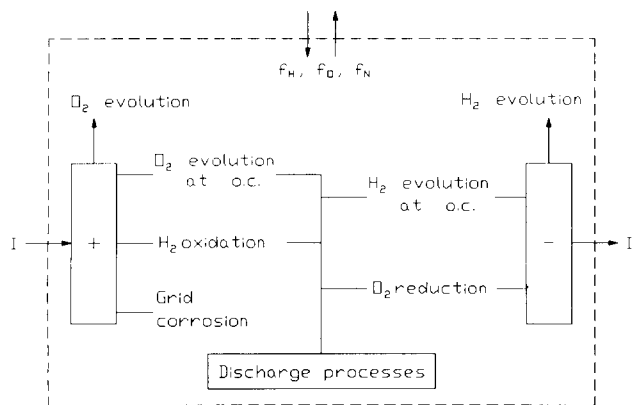


Fig. 1. Schematic representation of the processes regarding the O_2 and the H_2 cycles in a VRLA cell; o.c.=open circuit.

where N_O , N_H and N_N are the oxygen, hydrogen and nitrogen numbers of moles in the free volume V of a cell, K_O and K_H the kinetic constants of O_2 reduction and H_2 oxidation. f_i ($i=O, H, N$) is a parameter, accounting for the gas transfer into and out of the battery through leaks in the container, which depends on the internal pressure value. I_H and I_O are the rates, expressed as an electrical current, of H_2 and O_2 evolution. These current intensities are calculated [19] taking into account both the external current I , the rate of the plates discharge caused by gas reaction, and that of the positive grid corrosion.

If we take T and V constant and the gaseous species as ideal gases, their numbers of moles can be expressed as partial pressures. The kinetic constants can be determined from the internal pressure monitoring at open circuit or from the gas composition analysis in a cell maintained under galvanostatic conditions. In addition, K_O can be obtained from the measure of the limiting current of oxygen reduction at the negative plate which is equal to $4FK_O N_O$ [17,19].

The kinetic constants of the O_2 - and H_2 -consumption reactions can be used to evaluate the amount of the water lost by a cell during overcharge, by calculating the volume of gas escaped through the pressure vent.

If the gas-consumption reactions occur under limiting current conditions, [20–23], K_O and K_H are not dependent on the plate potential. Their values are affected by the extent of the total active surface of the plates and by the internal free volume of the cell, as the gas concentration at the reaction sites depends on the gas pressure, that is on the N_i/V ($i=O, H, N$) ratio. So, aiming to compare batteries having different geometry, we consider the specific kinetic constants K_{Os} and K_{Hs} defined by:

$$K_{Os} = K_O V / S_n \quad (2a)$$

$$K_{Hs} = K_H V / S_p \quad (2b)$$

In the case of O_2 reduction, it is of some interest to introduce the merit factor F_O defined as the ratio

between K_{Os} for a complete cell and K_{Os} for a couple of plates (one positive and one negative) coming from the same cell. The F_O value depends only on the fraction of the negative plate which is active to O_2 reduction.

3. Experimental

The four types of batteries used in the tests are commercial stationary VRLA batteries coming from different manufacturers (Yuasa Battery Company, Tudor, Chloride Ltd., and FIAMM SpA). All of them have the electrolyte supported by glass-fibre separator, the voltage ranges from 6 to 12 V, the capacity between 50 and 100 Ah.

The batteries, three for each type, were preliminary checked according to the procedure reported in Ref. [17]. The cells of each battery were equipped with an electronic pressure sensor and tests on the vent plugs carried out.

The cells were then prepared for the internal free volume measurement and the subsequent tests [17]. The pressure monitoring, at open-circuit or in galvanostatic conditions, was performed with the case free volume initially filled with a known gas (air or O_2 or H_2 or N_2), according to the procedure described in Ref. [18]. The tests lasted from 500 to 1000 h. When needed, gas chromatographic analysis of the internal gas mixture was performed.

Tests on single plates and on couples, consisting of one positive and one negative plate, were also run. The plates, coming from the disassembling of batteries of the same kind of those tested, were charged before the tests and left immersed in 1.28 g/cm³ sulfuric acid for 1 h. After 1 min dripping, they were finally sealed in a glass container having a total volume of 400 cm³ and equipped with a pressure sensor. The couples were assembled, just before introduction into the vessel, with the interposition of a polyethylene separator between the plates. In some cases plates were wetted again during the tests: they were taken out of the vessel, immersed in the H_2SO_4 solution for 1 h, left to drip for 1 min and then sealed again.

All the tests were carried out at room temperature (23–28 °C) and all reagents were of analytical grade.

Particular attention was paid in preventing and controlling gas leakage, especially H_2 , through the connections of the cells under test. The empty battery cases used for the determination of H_2 loss through the plastic container wall were previously tested by monitoring their internal pressure after filling with N_2 (see Fig. 7, curve (b)). The same Figure reports, curve (c), the behaviour of a glass container filled, after control of its connections, with H_2 only.

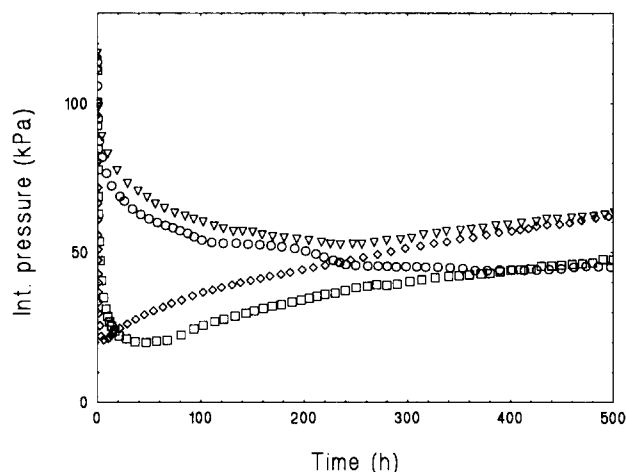


Fig. 2. Pressure vs. time plots for cells of the four battery types under test. All the cells, fully charged, were at open circuit and initially filled with pure O_2 .

Chemical analysis of the active mass was always performed on the negative plates coming from a just disassembled battery.

4. Results and discussion

4.1. Open-circuit tests

4.1.1. Oxygen reduction at the negative plate

The internal pressure of the four types of cell, fully charged, at open circuit and filled with pure O_2 , decreases with time as shown in Fig. 2. The initial rapid decay of pressure is related to the reduction of O_2 on the lead sponge of negative plates [15–17]. It is followed by a pressure increase due to H_2 evolution on lead. The curves show that, in some case, the two concurrent phenomena give origin to a well-defined minimum.

Under similar experimental conditions (open circuit and filling with O_2), the different couples of plates in sealed glass containers showed a very similar behaviour, an example is reported in Fig. 3. Analogous results were obtained by single negative plates in pure O_2 . The uniformity of these findings indicates that the differences in the curves of Fig. 2 must be ascribed to features of the battery other than the plates characteristics. The percentage of free pores in the separators, the plates compression, the amount of electrolyte, the amount of the free volume and the number of plates have a marked influence.

The values of the specific kinetic constant K_{O_s} range between the following values:

- (i) 0.9–1 cm/h for single negatives and positive/negative couples, and
- (ii) 0.02–0.1 cm/h for complete cells.

These values well agree with those obtained measuring the O_2 -limiting current, $I_{lim} = 4FK_{O_s}N_{O_s}S_N/V$.

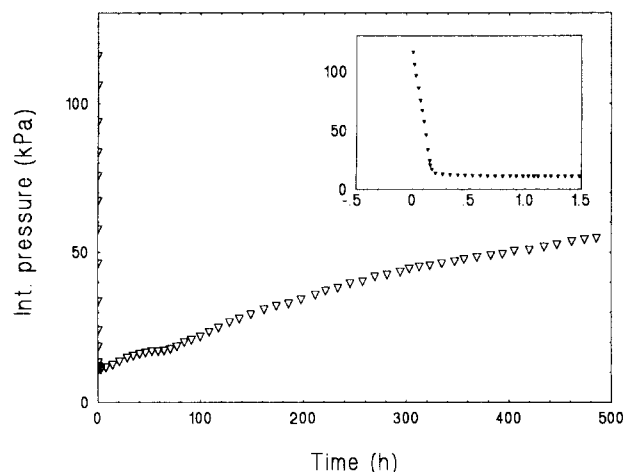


Fig. 3. Pressure vs. time plot for a couple of positive and negative plates, coming from the same battery, at open circuit in a sealed glass container filled with pure O_2 .

The merit factor Γ_O ranges between 0.022 and 0.11 showing that, in the cells, the extent of the plate active surface is greatly reduced.

Analysis of the experimental data indicates that the pressure–time curves follow an exponential law in the initial part of the decay only (up to 1 h in the case of cells), that is well before the attainment of the pressure minimum. This is verified for single negatives, couples of plates and complete cells. One can thus exclude the influence of diffusion phenomena in the gaseous phase or the effect of the amount of acid.

A possible explanation is that the pressure decay trend is influenced by the formation of a $PbSO_4$ barrier layer on the surface during O_2 reduction, partially blocking the sites where oxygen reacts [4]. To verify this hypothesis, the test concerning O_2 reduction on the negative plate has been repeated several times on the same sample, without wetting with acid at every new run. In the end, before the final test, the plate was wetted with acid and the test carried out. It can be seen, Fig. 4, that the first three pressure decays exhibit a standard trend while the fourth is markedly modified. The last one, with plate rewetting and O_2 refilling, is again similar to the first three decays, although the decay is here slower.

As the first three decays are practically identical, while the amount of $PbSO_4$ is progressively increasing, the K_O variation cannot be ascribed to the formation of a sulfate barrier layer. The lower rate at which the fourth decay takes place is probably due to a lack of sulfuric acid as suggested by the calculations of the quantity of acid consumed at each decay. In fact rewetting with acid restores the initial conditions.

The non-exponential part of the pressure decay, following the initial exponential one, could be due to water flow, produced by the O_2 -reduction reaction, from inside of the pores of the active mass towards the

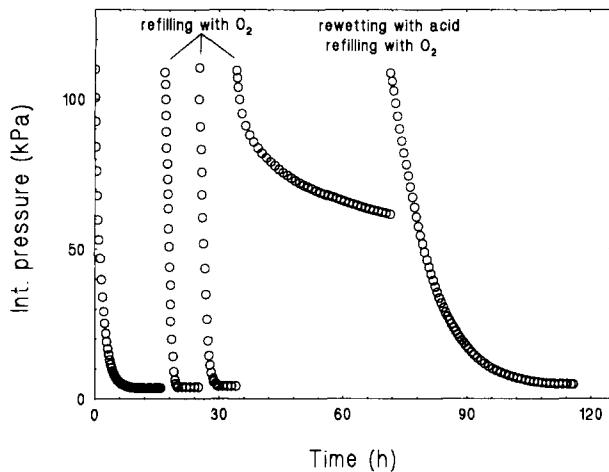


Fig. 4. Pressure decay vs. time for a negative at open circuit in a sealed glass container repeatedly filled with pure O_2 .

outside. Another reason could be the rapid increase of the surface temperature. Such a temperature rise reduces the O_2 solubility and causes water evaporation which visibly condenses on the glass walls. Finally, as a variation of the cell potential has been observed during oxygen reduction at open circuit, it is possible that, opposite to what is outlined in the literature [20–23], O_2 discharge does not take place in limiting-current conditions so being influenced by the potential variation.

4.1.2. Other gas-involving processes

The other processes that modify the internal pressure of a VRLA cell at open circuit proceed at a much lower rate. Investigations on single plates put in evidence four reactions at open circuit, three of them regarding H_2 and one O_2 .

The O_2 -evolution rate at the positive plate at open circuit can easily be detected from internal gas analysis and pressure monitoring in a vessel, containing a single positive, initially filled with pure N_2 or pure O_2 , Fig. 5 curves (a) and (b). The slope of the curves directly provides the reaction rate v_s whose value, referred to the unit of free volume and plate surface, is reported in Table 1.

Considering a positive plate in a sealed glass cell filled with pure H_2 , the pressure decrease, Fig. 5 curve (c), is due to the two processes of O_2 evolution and H_2 consumption. If the effect of O_2 evolution is eliminated from curve (c), the pressure decrease follows an exponential law from which it is possible to get the K_{H_2} value for H_2 consumption at the positive, Table 1.

As for the negative plate, the spontaneous H_2 evolution is the process which controls the internal pressure of a glass case containing a single negative filled with N_2 , Fig. 6 curve (a). If the vessel is initially filled with O_2 , Fig. 6 curve (b), H_2 evolution comes in evidence when all O_2 is exhausted. The H_2 -reaction rate, Table 1,

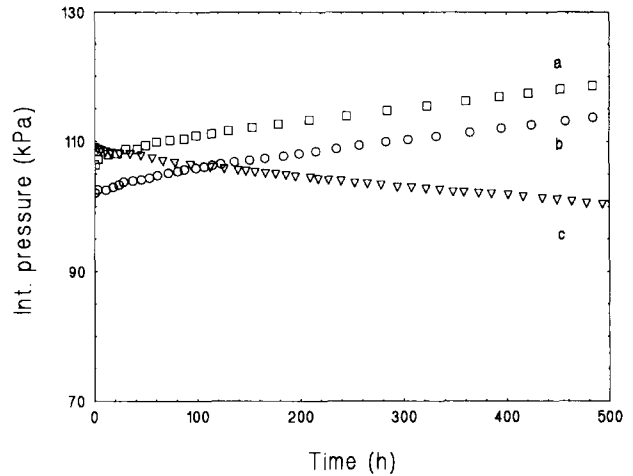


Fig. 5. Pressure vs. time plots for single positive plates, coming from the same kind of battery, sealed in glass containers filled with (a) pure O_2 , (b) N_2 , and (c) H_2 .

Table 1

Specific rates and kinetic constants of the slow reactions of gas evolution or consumption taking place in a VRLA system at open circuit

Process	v_s (kPa cm/h)	K_{H_2} (cm/h)
O_2 evolution at the positive	5×10^{-2}	
H_2 evolution at a freshly charged negative	7×10^{-2} ^a	
H_2 consumption at the positive		5×10^{-4}
H_2 consumption at a partially discharged negative		6×10^{-4}

^a Corresponding to about 0.04 mA/Ah.

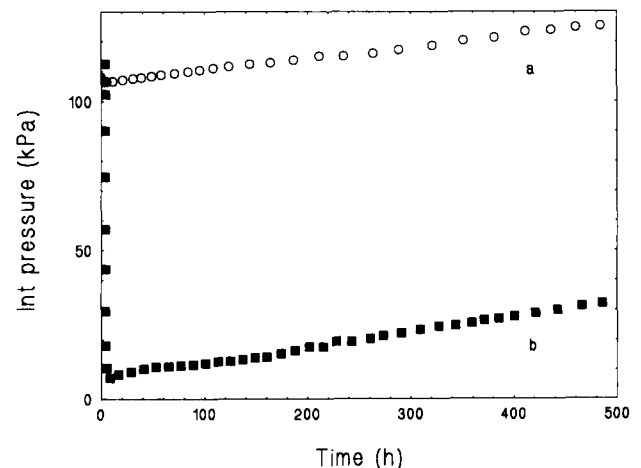


Fig. 6. Pressure vs. time plot for single negative plates, of the same kind, at open circuit in sealed glass containers filled with (a) pure N_2 and (b) pure O_2 .

appears constant within the first thousand of hours. In some exceptional cases, H_2 evolution became par-

ticularly marked showing a rate one order of magnitude higher than that reported in Table 1: in such cases analysis of the active material revealed the presence of a higher amount of antimony.

Carrying out the tests on single negatives at open circuit in pure O_2 , we found that at about a thousand of hours, pressure build-up slowed reaching a limit value of about 80 kPa. In those conditions all the initial O_2 had been totally consumed, causing a slight discharge of the plate, and the internal volume of the glass case contained only H_2 coming from the H_2 -evolution reaction. The existence of an H_2 -consuming process was therefore supposed.

Additional tests were carried out, in pure H_2 , on single negatives both freshly charged and partially discharged. The results, reported in Fig. 7 curves (a) and (e), respectively, indicate that only H_2 evolution is present in the case of the freshly charged plate while, in the case of the partially discharged one, H_2 consumption takes place also, leading, when the H_2 pressure reaches a sufficiently low value, to a steady-state situation. The curve for the empty glass case in H_2 , curve (c), shows that the pressure variations reported in curve (e) do depend on the presence of the slightly discharged negative plate.

These findings suggest that H_2 consumption is in some way related to the presence of $PbSO_4$ coming from the partial discharge of the plate. One can think to a possible reaction of H_2 oxidation via the formation of sulfide-type compounds. At present it can only be noted that similar pressure tests in H_2 , carried out on felt covered with sulfate and wetted with acid, showed the existence of an H_2 -consuming process.

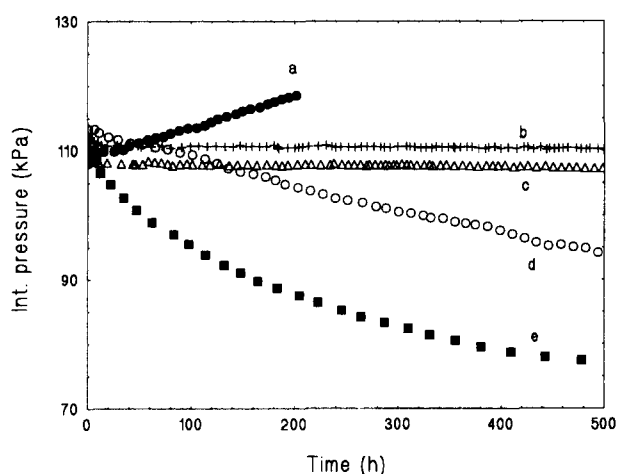


Fig. 7. Pressure vs. time plot for (a) a freshly charged negative in a sealed glass container initially filled with pure H_2 , and (b) an empty battery case initially filled with pure N_2 ; (c) an empty glass vessel initially filled with pure H_2 ; (d) an empty battery case of the same type as (b) initially filled with pure H_2 , and (e) a partially discharged negative of the same type and in the same conditions as (a).

Beyond these processes, we considered the passage of H_2 across the plastic case of the batteries. The results show that the walls of the container act as a permselective membrane since H_2 flows outwards even when the internal pressure is lower than the external, Fig. 7 curve (d). This phenomenon is typical of H_2 only, as can be seen by comparing curves (b) and (d) in Fig. 7, its rate being related to the extension of the case walls surface.

4.2. Overcharge tests

Overcharge tests at constant current have also been accomplished on complete cells, fully charged and initially filled with pure N_2 . The internal pressure increase during overcharge was limited by manually venting at 130 kPa until the pressure decreased to 100 kPa. The internal gas composition was periodically determined by gas chromatographic analysis of the vented gas.

An example of the results obtained is reported in Fig. 8 for an overcharge current of 2 A interrupted after 4 h for 2 h. At every opening of the vent plug the percentage of N_2 lowers as it flows out. On the contrary, the moles of H_2 and O_2 , which are evolving, increase as the process goes on, tending to the molar ratio 2 to 1. During the open-circuit stage, the most important process is O_2 consumption at the negatives. As a consequence, the O_2 molar fraction lowers and that of H_2 correspondingly increases.

In Fig. 8 are also reported the calculated values of the molar fractions obtained by applying the developed numerical method [17]. For all the batteries tested the fitting was at least as good as that reported in Fig. 8.

The time needed to reach the H_2/O_2 ratio of 2, starting from pure N_2 , depends on the rate of elimination of this gas, that is on the venting frequency which in

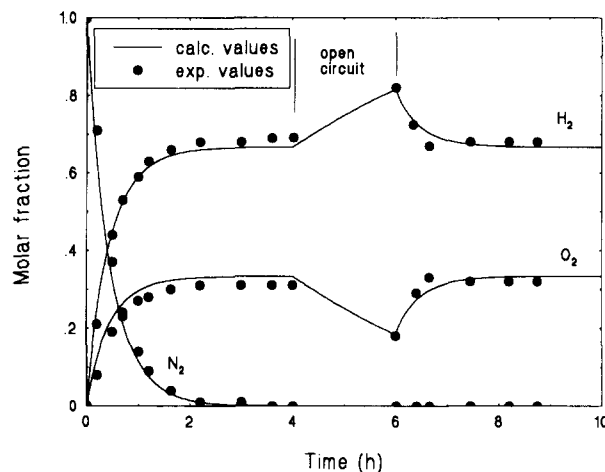


Fig. 8. Fitting of the experimental gas composition data for a cell (500 ml free volume, from a 12 V, 50 Ah battery) in overcharge at $I=2A$. Fitting parameters: $K_O=0.4 h^{-1}$; $K_H=1 \times 10^{-4} h^{-1}$; spontaneous H_2 -evolution current = 10 mA; $f_H=f_O=f_N=0$ mol/h.

turn is proportional to the value of the overcharge current.

The behaviour of the cells under overcharge is strictly dependent on the state-of-charge of the plates. In conditions of fully charged positives and partially discharged negatives, most of the current at the negative plates goes into reduction of PbSO_4 , so that the hydrogen/oxygen molar ratio is lower than 2 to 1.

Particularly interesting is the case in which a fully charged cell, initially filled with N_2 , is overcharged at a current intensity equal or lower than the O_2 -reduction limiting current [17,19]. At the beginning, Fig. 9(a), H_2 and O_2 evolution at the negative and positive plates occur. As the O_2 partial pressure builds up, the rate of O_2 recombination at the negative increases and, correspondingly, H_2 evolution decreases. The O_2 pressure attains in the end a value p_{lim} at which the O_2 -reduction limiting current becomes equal to the external current I , H_2 evolution ceases and the pressure becomes constant. After a new venting, the total pressure will again increase to a constant value, lower than before. In fact the starting value of O_2 partial pressure is, at every closing of the valve, higher, due to the progressive lowering of N_2 molar fraction, Fig. 9(c), so p_{lim} is reached at a lower value of the total pressure.

The transition from the O_2 -consumption to the H_2 -evolution stage at the negatives is shown, at constant current, by the variation of cell potential. This shift is most marked when the limiting current for O_2 reduction equals the external current, Fig. 10. Fig. 9(b) shows that at every venting, the cell potential rapidly moves to more positive values. This indicates the onset of H_2 evolution at the negatives. When the valve is closed again the O_2 moles number increases at a rate related

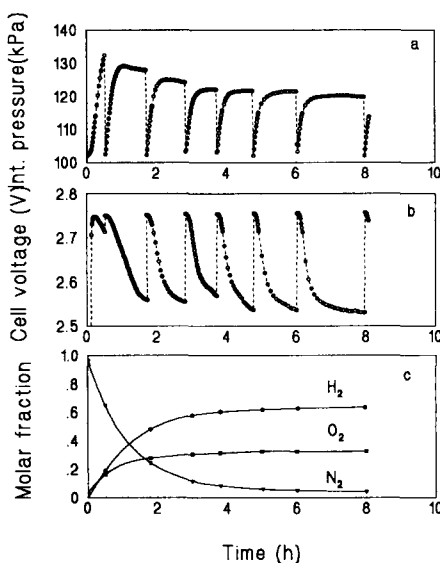


Fig. 9. Variation of (a) pressure, (b) cell potential, and (c) gaseous mixture composition for a cell (200 ml free volume, from a 12 V, 50 Ah battery) in overcharge at 0.5 A.

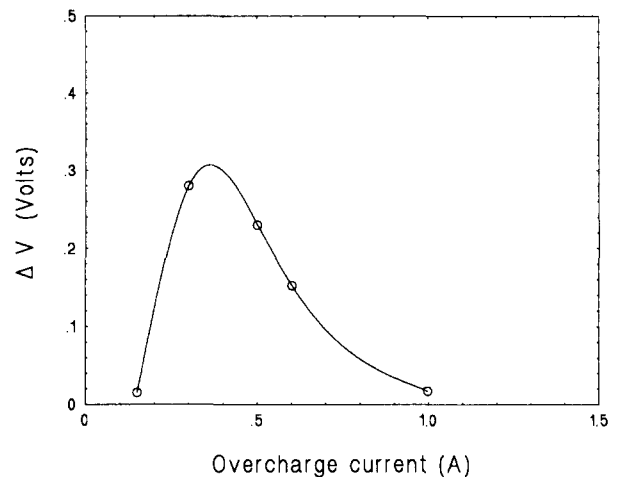


Fig. 10. Variation of the potential of a cell (200 ml free volume, from a 12 V, 50 Ah battery) at one of the valve openings during overcharge tests at various currents. The potential variation was measured when the gas composition inside the cell became constant, i.e. after about 8 h (see Fig. 9(a)).

to the external current I and the potential progressively lowers again.

4.3. Vent plugs

The experiments pointed out that the gas composition inside the cell is influenced not only by the current but also by the partial pressure of H_2 and O_2 as a consequence of periodic venting. We have therefore found it convenient from the technical viewpoint to investigate on the behaviour of the built-in vent valves of the cells considered.

The batteries were overcharged at constant current (from 1 to 5 A) for a time suitable to study the behaviour of the valves and then the circuit was opened while the internal pressure was being monitored. The plots in Fig. 11 refer to two of the cells under study in overcharge at 2 A. The opening pressure of the valve ranged in general between 110 and 130 kPa according to the type of cell and the overcharge current.

Curve (a) in Fig. 11 shows the behaviour of a correctly working vent plug. When, after the valve opening, the current is interrupted, the pressure decays very rapidly at the beginning, as long as the passage is still clear. After valve closing the internal pressure reaches values lower than atmospheric.

In the case of curve (b) in Fig. 11 it can be seen that, once opened, the valve does not close again completely, leaving the internal volume in communication with the outer ambient. This defect proved to be common to all the four types of accumulator, occurring in about 10% of the cells considered. The validity of these results is of course limited to the set of batteries used in the tests.

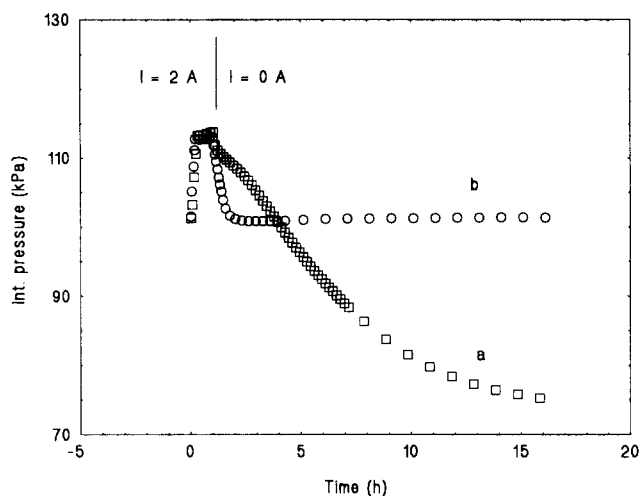


Fig. 11. Variation of the pressure in time for two different types of cell still equipped with the original vent plugs and in overcharge at 2 A.

5. Conclusions

All the batteries considered in this work, showed a similar behaviour with respect to O_2 recombination, with a K_{Os} value for the cells tested around 0.04 cm/h. Common is also the critical aspect regarding the limited reliability of the vent valves.

Comparison between the results of complete cells and couples of plates, giving a mean value of the merit factor of 0.06, has shown that the structural characteristics of the cells markedly limit the O_2 -recombination process.

Analysis of the pressure decay tests brought to conclude that O_2 reduction is: (i) scarcely influenced by the presence of small quantities of sulfate, and (ii) affected by local temperature variations and/or water flux.

Evidence was found for four slow rate processes, whose rate is of the order of 10^{-2} kPa/h. One of them is a reaction of H_2 consumption at a slightly discharged negative plate, which is apparently related to the lead sulfate presence at the plate surface.

Finally, it has been found that H_2 flows through the case walls at a rate comparable with that of the slow reactions considered and that the walls act as permeable membranes.

The overcharge tests with internal pressure, gas composition and cell potential monitoring provided a further verification of the suitability of the proposed mathematical model. The results indicate that the pressure variations due to venting exert their influence both on gas composition and on cell potential, particularly when the conditions are so that O_2 -limiting current equals the external one ($\Delta V_{max} = 300$ mV).

From the analysis of the whole set of overcharge tests we came to the conclusion that the H_2/O_2 molar

ratio in a battery submitted to a current can be lower than 2 when the negatives are not completely charged. It can be higher than 2 when: (i) low H_2 overpotential impurities are present; (ii) the corrosion process at the positive grids is not negligible, and (iii) the negatives do not behave uniformly.

6. List of symbols

F	Faraday's constant
f_H, f_N, f_O	gas leaks through the battery container (mol/h)
I	external current (A)
I_c	corrosion current at the positive plate (A)
I_H, I_O	H_2 -evolution current at the negative and O_2 -evolution current at the positive, due to the external current (A)
K_H, K_O	kinetic constants for the reactions of H_2 and O_2 consumption at the positive and negative plates (h^{-1})
K_{Hs}, K_{Os}	kinetic constants referred to the unit of free volume and geometric plate surface (cm/h)
N_H, N_O	number of H_2 and O_2 moles in the cell free volume at time t (mol)
p	cell internal pressure (kPa)
p_{lim}	value of the O_2 partial pressure at which, during the overcharge tests, the O_2 -limiting current becomes equal to the external current I (kPa)
S_n, S_p	total geometric area of the negative and the positive plates in a complete cell or in a couple of plates (cm^2)
t	time (h)
T	temperature (K)
v_s	specific reaction rate (kPa cm/h)
V	free volume of the cell (cm^3)
Γ_O	merit factor for O_2 reduction at the negative

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