Investigations into the electrochemistry of recombinant, sealed lead/acid batteries

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Abstract

In modern stationary and cycling operations of lead/acid batteries, gas-recombination technology is being used more and more frequently to eliminate battery maintenance. Research studies in the Central Laboratory of Batteries and Cells (CLAiO) are focused on the optimization of the gas-recombination process in lead/acid batteries, mainly in float duties. This work includes investigations of the kinetics of gas evolution on different types of alloy, and of the effect of paste composition and the method employed for electrolyte immobilization (i.e., gel or absorptive glass-mat). Tests have been performed on stationary cells of 4.5 A h capacity *(C/10)* and using grids of size 66.0 mm×96.5 mm. The grids were made from low-antimony alloy (1.7 wt.% Sb), lead–tin–calcium–aluminium alloy, or pure lead. Investigations of the gas-evolution kinetics has confirmed that during the initial phase of float operation, the lowest gassing is observed for nonantimonial and pure-lead grids in cells using absorptive glass-microfibre separators. Higher rates of gas evolution take place in cells with gelled electrolyte, but these decrease as the float operation is continued. Cells have been dismantled in order to investigate changes in the phase composition of the positive active material. Changes in phase composition of the active material during float operation have been monitored by X-ray diffraction phase analysis.

Introduction

During charging of a lead/acid battery, electrolytic decomposition of water takes place and involves evolution of oxygen on the positive electrode and hydrogen on the negative. In conventional batteries, these gases together with sulfuric acid mist are released and result in accelerated corrosion of battery components and the surrounding environment. The volumes of the evolved gases depend on the components of the lead alloy and, in particular, on the content of antimony in the battery grids. As a consequence, conventional batteries containing more than 3 wt.% Sb in the grids require periodic topping-up with either distilled or demineralized water. Decrease of the antimony content in the grids to ~1 wt.% diminishes considerably the rates of water decomposition and gas evolution.

The condition that is necessary for achieving a fully maintenance-free battery operation is an enforced gas-recombination. Optimization of various battery factors can promote an oxidation reaction between the spongy lead of the negative plate and the oxygen liberated from the electrolytic decomposition of water [1], i.e.:

$$Pb + 1/2 O_2 \longrightarrow PbO \tag{1}$$

$$PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O \tag{2}$$

In order to achieve this reaction, the following conditions must be fulfilled:
- diffusion of oxygen from the positive to the negative plates through a highly absorptive glass-microfibre separator or a gelled electrolyte
- choice of lead alloy for battery grids that increases the gas-evolution overvoltage
- correct proportion of active materials, adequate composition and quality of paste
- control of gas-evolution overpressure by means of a safety vent

Oxygen recombination takes place on the negative electrode and its diffusion is promoted by a special glass-microfibre separator of high absorptivity [2]. Besides the basic requirements for separators that are demanded by all types of lead/acid batteries, this separator should feature both high oxygen permeability and an ability to transport a sufficient amount of electrolyte to the entire plate surface [3]. The separator thickness should be adjusted to ensure an adequate volume of electrolyte to deliver the nominal battery capacity.

Battery grids in recombinant batteries are made from nonantimonial lead alloys such as lead–calcium, lead–calcium–tin, lead–calcium–tin–aluminium, as well as from pure lead [5]. The individual alloying elements are selected quantitatively so as to obtain optimum grain size for reduced corrosion and long battery life.

Batteries with electrolyte absorbed in either a glass-microfibre separator or a gelled electrolyte provide capacities that are 5 to 15% lower than those obtained from liquid-electrolyte counterparts [6]. For this reason, some authors recommend [7] the addition of graphite to the positive paste in order to improve the utilization of active material. Baker *et al.* [8] attribute the effect of graphite not only to an increase in active-material porosity and a concomitant facilitated diffusion of ions, but also to electro-osmotic transport of electrolyte.

Given the above reports, the Central Laboratory of Batteries and Cells (CLAiO) has developed a project for making and testing cells that use the following components:
- various grid alloys, i.e., Pb–Sb–1.7wt.%Se, Pb–Ca–Sn–Al, and pure Pb
- two types of electrolyte: (i) absorbed in glass-microfibre separator, and (ii) gelled with silica type Aerosil 200 from Degussa, Germany
- two types of positive paste: (i) standard, and (ii) with a small quantity of graphite FRL1 from Kropfmöhl, Germany

The testing schedule included:
- 10-h capacity test
- constant voltage charging at 2.23 V per cell and measurement of gas emission
- analysis of changes at the interphase of the grid and the positive active material
- analysis of changes in phase composition of positive material

Experimental

Lead/acid cells with a nominal $C/10$ capacity of 4.5 A h were composed of 1 positive plate and 2 negative plates. The electrode grids were 66.0 mm $\times 96.5$ mm in size and were fabricated from pure lead or the following two alloys:
- low-antimony alloy with 1.7 wt.% Sb made in Poland, termed 'PbSb1.7Se' alloy
- nonantimonial calcium alloy from RSR Corporation, USA, termed 'PbCaSnAl' alloy

The chemical composition of the lead alloys is given in Table 1. Pure lead grids were made from 99.99 wt.% Pb.

Battery pastes were produced from Harding leady oxide powder with a 62.4% oxidation level and a sieve residue at 0.15 mm mesh of 0.3%. The leady oxide was mainly composed of α-PbO and metallic lead particles. The series of cells used for

TABLE 1

Chemical composition of lead alloys

Component	Composition (wt.%)	
	'PbSb1.7Se'	'PbCaSnAl'
Antimony	1.7	
Arsenic	0.2	
Tin	0.15	0.550
Selenium	0.02	
Aluminium		0.0110
Calcium		0.066

TABLE 2

Physical and chemical properties of RFL1 graphite

Parameter	Content
Carbon content (wt.%)	99.0–99.98
Average grain size (μm)	520
Humidity content (wt.%)	0.08
Volatile substance content (wt.%)	0.09
Ash content (wt.%)	0.94
Copper content (wt.%)	0.00017
Iron content (wt.%)	0.06

testing were made with the same pastes to eliminate the influence of any accidental factors. One paste option contained 0.5 wt.% of RFL1 graphite from Kropfmöhl, Germany. The physical and chemical properties of this material are listed in Table 2.

Depending on the electrolyte type, the following separator materials were used:
• for absorbed electrolyte: glass-microfibre separator from Technical Fibre Products Ltd., UK
• for gelled electrolyte: polyethylene separator from Cookson-Entek Ltd., UK

After charging and three control 10 h discharge cycles, the cells were subjected to constant-voltage charging at 2.23 V. The gas evolved was collected in a burette and the volume of gas was measured daily.

Cells were dismantled periodically in order to investigate changes in the phase composition of the positive active material during cell operation. These changes were investigated by X-ray diffraction analysis.

For this purpose, test samples of active material were crushed and then powdered in a mortar to obtain a uniform consistency.

Results and discussion

Three 10-h discharge cycles to a cell cutoff voltage (U_f) of 1.80 V revealed that all cells achieved 100% of nominal capacity on the first cycle, except for those that contained gelled electrolyte. In the latter case, the cell capacity was only 95% of the nominal value but became 100% after the third cycle.

Cells with graphite addition to the active material exhibited capacities that were, on the average, 5 to 10% higher than those of other cells. This supports the observation of other workers [7] that graphite increases the porosity of the active material and hence improves plate efficiency.

Results from the daily measurements of the collected gas volume during 60 days of constant-voltage charging at 2.23 V are given in Figs. 1 to 3. In order to eliminate possible measurement errors, the plots refer to those cells in which maximum gassing was observed. It should be emphasized, however, that differences in the shape of integral curves for cells with similar designs and characteristics were negligible. It can therefore be assumed that these integral curves provide a good representation of each type of cell.
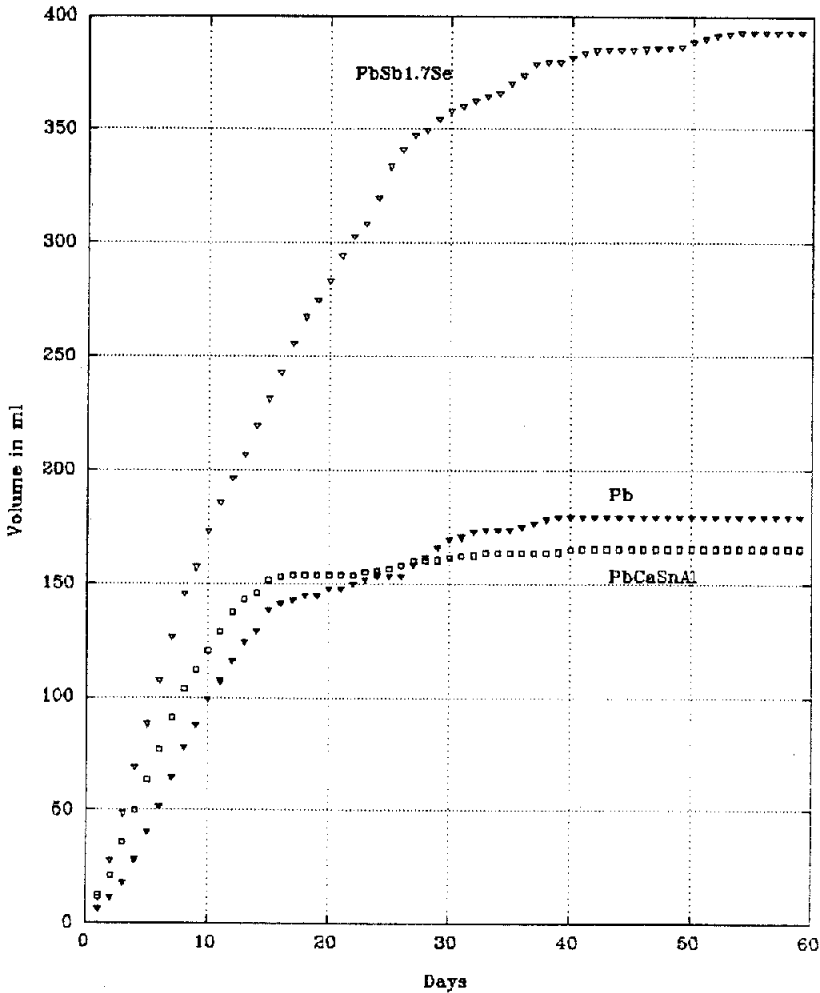

Fig. 1. Gas evolved from cells with different grid material. Glass-microfibre separator; float voltage 2.23 V.
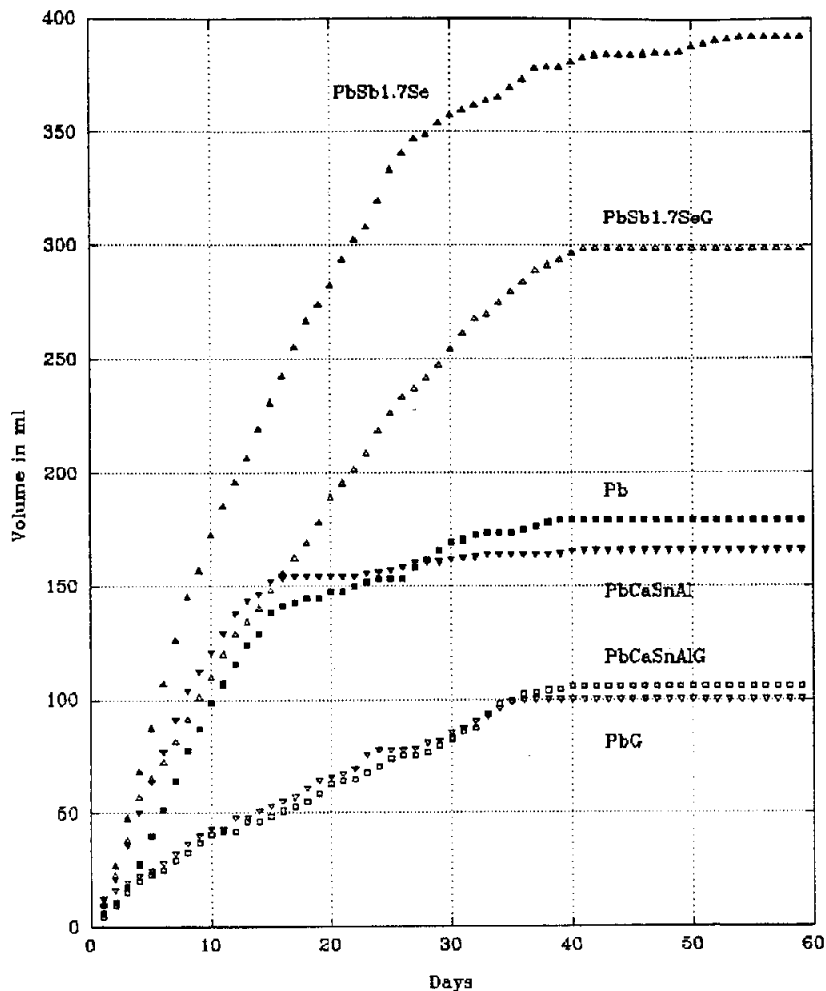
Fig. 2. Gas evolved from cells with different grid materials and with/without graphite (G) in the positive active material. Glass-microfibre separator; float voltage 2.23 V.

It was observed that gas emission is irregular. In the preliminary phase of cell operation, gassing is high and then decreases. The highest volume of gas occurred in cells using a gelled electrolyte and with a low-antimony alloy.

The gas volume decreased with time. After about 20 days, the daily gas evolution in cells with antimony-free alloys or pure lead was ~1 cm^3, or less. For cells with gelled electrolyte and low-antimony alloys, an apparent decrease in the gas volume was observed after 40 days of float operation.

The above observations can be explained in the following way. Oxygen diffusion to the negative plate and partial oxidation of spongy lead is the condition for gas recombination to occur. In order to achieve this, the electrolyte must have free pores or channels. Depending on the type of electrolyte used, these channels are formed after different times of cell operation. In the case of absorbed electrolyte, the condition
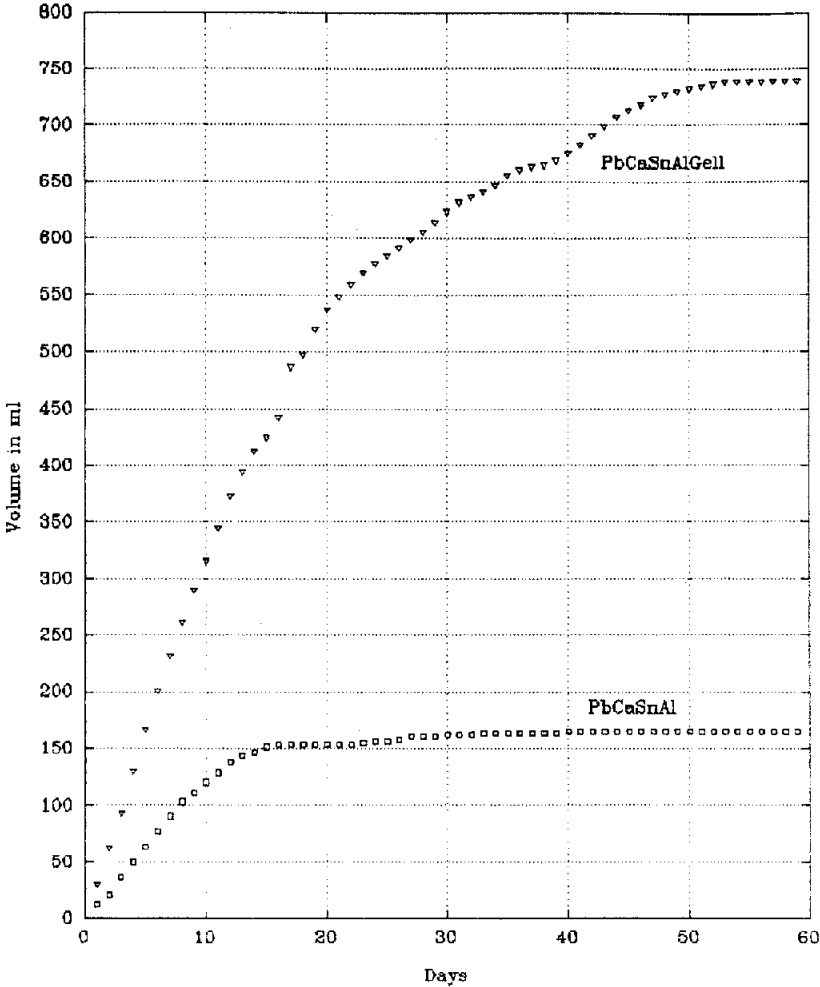
Fig. 3. Gas evolved from cells with 'PbCaSnAl' grids with gelled electrolyte or glass-microfibre separator; float voltage 2.23 V.

for recombination occurs much earlier than in gelled electrolyte. Therefore, in the initial stage of constant-voltage charging, the gassing is higher until some equilibrium state is reached when the volume of free space in the electrolyte is sufficient for oxygen diffusion. At this stage, the volume of evolved gas (mainly hydrogen) is minimum, i.e., 0.5 cm^3, or sometimes zero. Minimum gas volumes were observed in cells with grids made from antimony-free alloys or pure lead.

The above findings confirm recommendations of the Draft-IEC Publication 896-2 of January 1992. Paragraph 12.4 of this draft indicates that hydrogen emission from a single cell during float charging should not exceed 10 cm^3 (NPT)/cell A h C_{10} nominal capacity for 30 days.

When recording the changes of the charging current and trying to correlate them with recombination efficiency, it should be remembered that active material continues

to be formed in the initial stage of constant-voltage charging. In other words, a certain amount of the energy charged into the positive plate is consumed for oxidation of bivalent lead to tetravalent lead. This was confirmed by control tests made after 25 and 50 days of charging at $C/3$ to $U_f = 1.60$ V/cell. A systematic increase in capacity was observed.

Within 60 days of constant-voltage charging, irrespective of the alloy type, a marked effect of graphite in the active material was confirmed: the volume of evolved gas decreased immediately from the start of charging. The reduction in the gas volume within 60 days was ~20% for the 'PbSb1.7Se' alloy and 40% for 'PbCaSnAl' alloy. After 40 days of charging, the graphite exerted no effect on the daily rate of gas evolution.

With regard to chemical and phase composition, the following observations were made. Formed positive active materials contained the required amount of PbO_2, i.e., 80 wt.%. The presence of α- and β-PbO_2 phases was confirmed; the α-PbO_2 content was in the range 20 to 28 wt.% for different cells. Similar testing after 50 days of constant-voltage charging revealed the total PbO_2 content in the positive plates to be 88 to 93 wt.%; the α-PbO_2 content was 27 to 40 wt.%. This increase in the level of the α-PbO_2 phase occurred in all cells. This suggests that during oxidation of Pb^{2+} to Pb^{4+} under constant-voltage charging conditions, α-PbO_2 was preferentially formed.

The crystal sizes of α-PbO_2 and β-PbO_2 were in the ranges of 220 to 400 Å, and 520 to 850 Å, respectively. At this stage of testing, it has not been possible to define any clear trends in the changes of crystal size. The testing of structural parameters by X-ray diffraction and microscopic methods will be continued.

Conclusions

Investigations of the gassing kinetics in lead/acid cells under float operation show that the volume of evolved gas depends on the type of grid alloy used. The efficiency of gas recombination in cells with glass-microfibre separators becomes stable much earlier than that in cells with gelled electrolyte.

Taking into account advantageous initial parameters, it is considered worthwhile to continue testing of cells with positive active material containing graphite to determine the effect of this additive on cell life.

In order to obtain final results from an examination of the structural changes in plate active materials and the grid/active-material interphase, it is necessary to continue further investigations during prolonged periods of time.

References

1 J. S. Symański, B. K. Mahato and K. R. Bullock, *J. Electrochem. Soc.*, *135* (1988) 548–551.
2 J. W. Reitz, *J. Power Sources*, *23* (1988) 109–111.
3 H. Nicolle, *Proc. Lead Battery Power for 90s, Paris, 1988*, Lead Development Association, London, p. 24.
4 R. D. Prengaman, *2nd Int. Symp. Mechanization Automation, New Materials and Recycling in Battery Industry, MaBat 91, Sept. 17–19, 1991*, Warsaw, Poland.
5 M. Winter, in L. J. Pearce (ed.), *Power Sources, 11, Research and Development in Non-Mechanical Electrical Power Sources*, International Power Sources Symposium Committee, Leatherhead, UK, 1987, p. 536.
6 A. M. Hardman, *J. Power Sources*, *23* (1988) 127–134.
7 A. Tokunaga, M. Tsubota and K. Yonezu, *J. Electrochem. Soc.*, *136* (1989) 33–36.
8 S. V. Baker, P. T. Moseley and A. D. Turner, *J. Power Sources*, *27* (1989) 127–143.