

MEASURES FOR MINIMIZING HYDROGEN PRESSURE IN SEALED LEAD/ACID BATTERIES

H. DIETZ*, S. VOSS, H. DÖRING, J. GARCHE and K. WIESENER

Dresden University of Technology, Department of Chemistry, Dresden (G.D.R.)

Introduction

Control of the hydrogen pressure is an important feature of sealed lead/acid batteries. Whereas the reduction of oxygen can proceed at a sufficiently high rate, thus making an efficient oxygen cycle possible, hydrogen oxidation is kinetically hindered [1] so that accumulation of the gas in sealed lead/acid batteries is difficult to avoid [2]. Thus, special measures are required to: (a) minimize hydrogen evolution; (b) remove evolved hydrogen.

The principle of using auxiliary electrodes [3] for hydrogen recombination appears to be much too costly. Instead, catalysis of the hydrogen/oxygen recombination should be a more appropriate method, provided that an inexpensive catalyst with high activity and stability is available. Such a catalyst could be tungsten carbide on carbon [2].

Hydrogen evolution can be suppressed by various measures, such as decreasing the charging voltage, using materials of higher purity (*e.g.*, non-antimonial lead alloys), improving the oxygen recombination efficiency, etc. All these approaches influence the partial currents at the negative electrode during galvanostatic overcharging. This influence is examined in this paper.

Experimental

Sealed cells comprised a positive, 3 A h electrode and two negative, 3 A h electrodes that were separated by glass microfibre mats. The amount of sulphuric acid added is given as the degree of electrolyte filling the electrode-separator package (100% = maximum electrolyte absorptivity). Before commencing the measurements, the gas space of the cell (28 cm³) was purged with pure nitrogen. During galvanostatic overcharging, the cell overpressure, Δp , and the partial pressure of oxygen, $p(\text{O}_2)$, were measured using commercial sensors.

* Author to whom correspondence should be addressed.

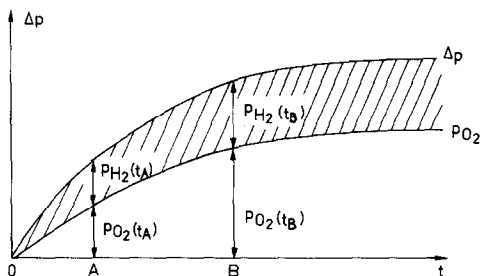
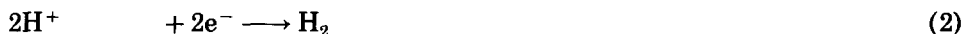
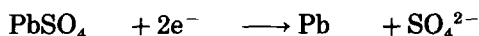
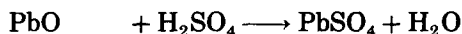
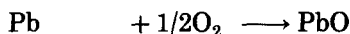


Fig. 1. Cell overpressure, Δp , and oxygen pressure, $p(\text{O}_2)$, during galvanostatic overcharging, in principle.

Background theory

Whereas evolution of oxygen is virtually the only anodic process during overcharging [4], three competing cathodic reactions may occur, as given by eqns. (1) - (3):



Assuming that hydrogen evolution and anodic reactions other than O_2 evolution can be neglected, for the galvanostatic overcharge, it follows

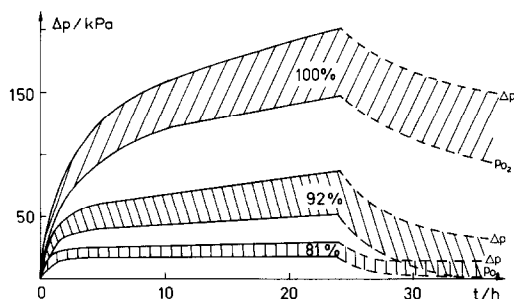
$$|I_{\text{OC}}| = I(\text{O}_2 \text{ ev.}) = I(\text{H}_2 \text{ ev.}) + I(\text{PbSO}_4 \text{ red.}) + I(\text{O}_2 \text{ red.}) \quad (4)$$

where the overcharging current, I_{OC} , is defined as a negative quantity. Figure 1 presents the idealized course of p (=cell overpressure) and $p(\text{O}_2)$ during galvanostatic overcharging, where the pressure difference ($\Delta p - p(\text{O}_2)$) corresponding to $p(\text{H}_2)$ is hatched.

The instantaneous values of the H_2 evolution current, $I(\text{H}_2 \text{ ev.})$, and the O_2 reduction current, $I(\text{O}_2 \text{ red.})$, or their fractions of I_{OC} , can be evaluated as an average current for any overcharge period, AB, from the differential increase in $p(\text{H}_2)$ or $p(\text{O}_2)$ according to eqns. (5) and (6).

$$I(\text{H}_2 \text{ ev.}) = \frac{(p(\text{H}_2, t_A) - p(\text{H}_2, t_B))}{(t_B - t_A)} \times \frac{2F}{RT/v} \quad (5)$$

$$I(\text{O}_2 \text{ red.}) = I_{\text{OC}} - \frac{(p(\text{O}_2, t_A) - p(\text{O}_2, t_B))}{(t_B - t_A)} \times \frac{4F}{RT/v} \quad (6)$$



Filling degree	Δt [h]	Δp_{H_2} [kPa]	I_{H_2-Ev} / I_{OC}	I_{PbSO_4-R} / I_{OC}	I_{O_2-Red} / I_{OC}
81%	0-2	7,3	0,7	2,6	96,7
	22-24	0,3	≈ 0	0	≈ 100
92%	0-2	12,8	1,3	5,5	93,2
	22-24	1,5	0,1	0,1	99,8
100%	0-2	18,1	1,8	10,9	87,3
	22-24	1,5	0,1	0,3	99,6

Fig. 2. Influence of degree of electrolyte filling of electrode-separator package (%) and $p(O_2)$ on cathodic current fractions of I_{OC} . I_{OC} : 300 mA; grid: Pb; dry-charged 3 A h electrodes; 100% fill = 37 ml H_2SO_4 ($\rho = 1.28 \text{ g cm}^{-3}$).

As may be seen from eqn. (6), $I(O_2 \text{red.})$ was calculated taking the cathodic total reaction, eqn. (1), as baseline. The current difference given by subtracting $I(O_2 \text{red.})$ and $I(H_2 \text{ev.})$ from I_{OC} can be explained as:

(i) an additional current $I(PbSO_4 \text{red.})$ that has been found [5] to increase the state-of-charge of the negative electrode;

(ii) being caused by hydrogen oxidation, following the gas-balance approach of Maja *et al.* [6];

(iii) corresponding both to $PbSO_4$ reduction and hydrogen oxidation.

Here, it is decided to attribute the current difference to $I(PbSO_4 \text{red.})$, *i.e.*,

$$I(PbSO_4 \text{red.}) = I_{OC} - I(O_2 \text{red.}) - I(H_2 \text{ev.}) \quad (7)$$

This approach has been taken because the hydrogen oxidation rate is supposed to increase with $p(H_2)$ [6], but the current difference decreases on increasing the overcharging time, *i.e.*, $p(O_2)$ (Fig. 2), and can increase if a hydrogen-evolution inhibitor is added (see Fig. 4, below).

Results and discussion

The rate of oxygen reduction is known to depend on the oxygen recombination conditions [6, 7] and is characterized by a constant and the oxygen pressure. The rate constant is mainly determined by the amount of H_2SO_4 added, *i.e.*, by the degree of electrolyte filling of the electrode-separator package.

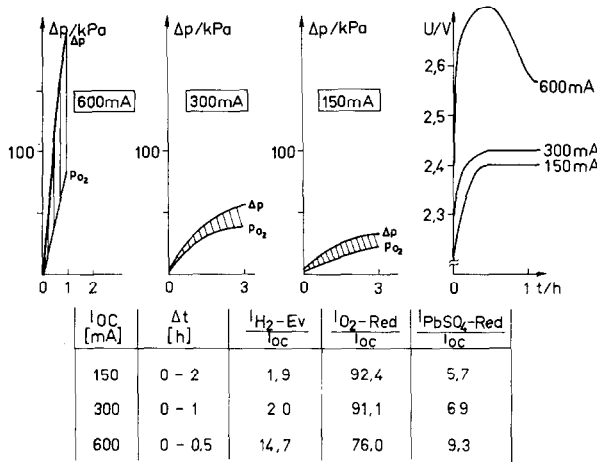


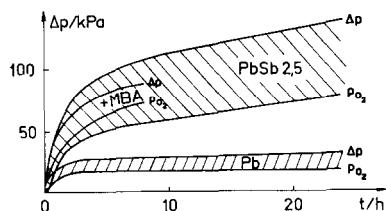
Fig. 3. Influence of overcharge current on cathodic current fractions of I_{OC} and cell voltage. (Grid: Pb; dry-charged 3 A h electrodes; filling degree: 92%.)

Figure 2 shows the influence of both $p(O_2)$ and the degree of electrolyte filling on the ratio of the cathodic current fractions during overcharging. It can be deduced that:

- (i) with decreasing amounts of H_2SO_4 and increasing $p(O_2)$ (i.e., increasing overcharging time), $I(O_2 \text{ red.})$ increases and thus depolarizes the negative electrode so that $I(H_2 \text{ ev.})$ and $I(PbSO_4 \text{ red.})$ decrease;
- (ii) $I(O_2 \text{ red.})$ increases with decrease in the degree of electrolyte filling; this is because within the separator matrix the number of continuous gas holes, required for rapid oxygen transfer between the electrodes, is increased;
- (iii) increase in the fraction $I(O_2 \text{ red.})/I_{OC}$ (O_2 recombination efficiency) is accompanied by a lowering of $p(O_2)$ as well as $p(H_2)$;
- (iv) at relatively low values of $I(O_2 \text{ red.})$, i.e., at the beginning of overcharging, especially with large amounts of H_2SO_4 , the $PbSO_4$ reduction reaction also assists in the suppression of hydrogen evolution;
- (v) with increasing overcharging time, all types of current fractions tend to become equal and $I(H_2 \text{ ev.})$ is reduced to zero, indicating that the quasi-steady-state is reached.

The influence of the overcharging current on the pressure, the ratio of the cathodic current fractions, and the cell voltage is shown in Fig. 3. It is evident that:

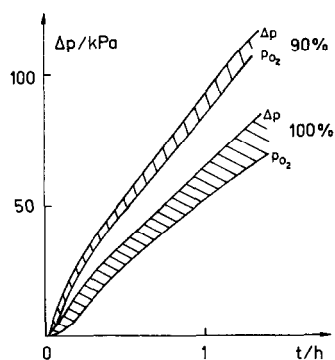
- (i) at low currents up to 300 mA, $I(O_2 \text{ red.})$ is very high and $I(H_2 \text{ ev.})$, as well as $I(PbSO_4 \text{ red.})$, is small, indicating an efficient oxygen cycle;
- (ii) on increasing I_{OC} , the overvoltage rises, so that $I(H_2 \text{ ev.})$ and $I(PbSO_4 \text{ red.})$ increase, thus decreasing $I(O_2 \text{ red.})$;
- (iii) increasing I_{OC} also increases the ratio $I(H_2 \text{ ev.})/I(PbSO_4 \text{ red.})$, because at higher overvoltage the hydrogen evolution reaction follows the Tafel equation [8];



Type	Δt [h]	Δp_{H_2} [kPa]	$\frac{i_{H_2-Ev}}{I_{OC}}$	$\frac{i_{O_2-Red}}{I_{OC}}$	$\frac{i_{PbSO_4-Red}}{I_{OC}}$
Pb	0-2	7,3	0,7	96,7	2,6
PbSb2,5	0-2	31,0	3,1	92,3	4,6
PbSb2,5 +MBA	0-2	18,0	1,9	90,8	7,3

MBA : o-Methoxy benzaldehyde (40mg/l)

Fig. 4. Influence of grid antimony and an H_2 -evolution inhibitor on partial current fractions of I_{OC} . ($I_{OC} = 300$ mA; dry-charged 3 A h electrodes; filling degree: 81%.)



Charge state [% C ₂₀]	Δt [min]	$\frac{i_{H_2-Ev}}{I_{OC}}$	$\frac{i_{O_2-Red}}{I_{OC}}$	$\frac{i_{PbSO_4-Red}}{I_{OC}}$
90	0-20	2,4	57,4	40,2
100	0-20	5,3	78,7	16,0

Fig. 5. Influence of state-of-charge of negative electrode on cathodic fractions of I_{OC} . ($I_{OC} = 300$ mA; grid: Pb; filling degree: 100%.)

(iv) at a current of 600 mA, only a high $p(O_2)$ enables the O_2 recombination to become so fast that the overvoltage is decreased and the hydrogen evolution becomes somewhat suppressed;

(v) at extremely high currents above 300 mA, the oxygen pressure achieved in practice is too low to ensure efficient oxygen recombination, and therefore no steady-state pressure is observed;

(vi) statement (v) confirms similar results reported previously [9].

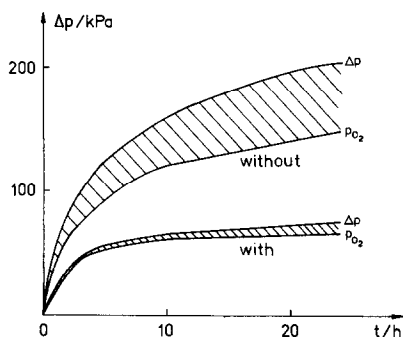


Fig. 6. Influence of a composite catalyst for hydrogen/oxygen recombination (WC on carbon) on cell overpressure and $p(\text{O}_2)$. ($I_{\text{OC}} = 300 \text{ mA}$; grid: Pb; dry-charged 3 A h electrodes.)

Figure 4 shows the effect of antimony on the pressure characteristics during overcharging. As antimony lowers the hydrogen overvoltage, $I(\text{H}_2 \text{ ev.})$ increases, thus decreasing $I(\text{O}_2 \text{ red.})$. On the other hand, when hydrogen-evolution inhibitors are used (*e.g.*, benzaldehyde derivatives [10]), the hydrogen evolution is considerably suppressed (Fig. 4). It is suggested [10] that this is due to adsorptive interaction between inhibitor species and the protons covering the antimony sites of the negative electrode.

Under the conditions pertaining to Fig. 4, the additive also appears to block the free-lead areas of the electrode, since oxygen reduction is similarly hindered. The extent to which this occurs may depend on the concentration, strength, and selectivity of the hydrogen-evolution inhibitor [11].

If hydrogen evolution is selectively inhibited, $I(\text{O}_2 \text{ red.})$ should increase, otherwise $I(\text{O}_2 \text{ red.})$ can even decrease (Fig. 4) in favour of PbSO_4 reduction, provided it is possible for the latter process to occur.

As demonstrated by the data in Fig. 5, a decrease in the state-of-charge of fully-charged negative electrodes to 90% favours the reduction of PbSO_4 . As a result, $p(\text{H}_2)$ decreases and $p(\text{O}_2)$ increases. The latter is due to a covering of the lead surface by discharge products, thus hindering oxygen reduction. At a 90% state-of-charge, however, the oxygen recombination is still sufficiently efficient to guarantee a decrease in hydrogen evolution.

Figure 6 illustrates the effect of a composite catalyst (WC on carbon) for hydrogen/oxygen recombination in sealed lead/acid batteries. Under favourable conditions, the catalyst is able to eliminate hydrogen almost completely by recombination. As oxygen is removed to a greater extent than is expected, there should also be an influence on the ratio of the cathodic partial currents.

Conclusions

The rate of hydrogen evolution is dependent on the characteristics of all cathodic reactions and can be decreased by:

(i) directly decreasing $I(\text{H}_2\text{ev.})$, *i.e.*, by increasing the hydrogen over-voltage using hydrogen-evolution inhibitors and decreasing the antimony content of the grid alloy, or by decreasing the (over) charging voltage;

(ii) indirectly increasing $I(\text{O}_2\text{red.})$, *i.e.*, by increasing $p(\text{O}_2)$ or improving the conditions of oxygen recombination, *e.g.*, by decreasing the amount of electrolyte in the electrode-separator package;

(iii) indirectly increasing $I(\text{PbSO}_4\text{red.})$, *i.e.*, by lowering the state-of-charge of the negative electrode.

Method (i) has practical relevance since neither $I(\text{O}_2\text{red.})$ or the A h capacity are decreased. Efficient removal of H_2 is also possible by catalyzing the hydrogen/oxygen recombination.

References

- 1 C. S. C. Bose and N. A. Hampson, *J. Power Sources*, 19 (1987) 261.
- 2 D. Ohms, H. Dietz, J. Garche and K. Wiesener, in preparation.
- 3 P. Ruetschi and J. B. Ockermann, *J. Electrochem. Soc.*, 4 (1966) 383.
- 4 J. S. Symanski, B. K. Mahato and K. R. Bullock, *J. Electrochem. Soc.*, 135 (1988) 548.
- 5 H. Ziolkowski, *Diploma Thesis*, TU Dresden, 1989; unpublished results.
- 6 M. Maja and N. Penazzi, *J. Power Sources*, 25 (1989) 99.
- 7 J. Garche, D. Ohms, H. Dietz, N. D. Hung, K. Wiesener and J. Mrha, *Electrochim. Acta*, 34 (1989) 1603.
- 8 H. Bode, *Lead-Acid Batteries*, Wiley, New York, 1977.
- 9 J. Thompson and S. Warrel, in J. Thompson (ed.), *Power Sources 9*, Academic Press, London, 1983, p. 97.
- 10 W. Boehnstedt, C. Radel and F. Scholten, *J. Power Sources*, 19 (1987) 301.
- 11 H. Doering, *J. Power Sources*, 28 (1989) 381.