A REVIEW OF OXYGEN RECOMBINATION IN THE SEALED LEAD-ACID CELL

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Summary

A brief review, with 25 references, of the 'state of the art' of oxygen recombination technology, which is an important developing area of lead-acid battery manufacture, is presented.

Introduction

The lead-acid secondary industry has historically provided batteries which require relatively little maintenance, some occasional "freshening" charges, and the addition, from time-to-time, of water in order to replace that removed from cells as a consequence of electrolytic action during charging. The magnitude of the electrolytic reaction is determined by the rates of conversion of lead sulphate to lead and lead dioxide, compared with the rates of the hydrogen evolution reaction and the oxygen evolution reaction at the negative and positive electrodes, respectively. At the lead negative electrode the hydrogen overvoltage is very high in the absence of metallic impurities such as Sb and Cu, and contemporary technology has achieved this by the use of Ca alloys so that the hydrogen reaction is no longer a problem. In the case of the PbO_2 positive electrode, however, the redox $PbO_2/PbSO_4$ reaction occurs totally in the oxygen evolution region and, since the reaction

$$PbSO_4 + 2H_2O \longrightarrow PbO_2 + H_2SO_4 + 2H^+ \tag{1}$$
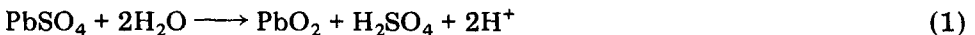
is relatively slow, the charging step for the positive electrode is relatively inefficient, generating significant amounts of oxygen early on in the recharge. Formerly this would have resulted in a water loss to the system but it has been found that if the evolved gas can diffuse to the negative electrode and be oxidised there to re-form water then the system can be conserved in a

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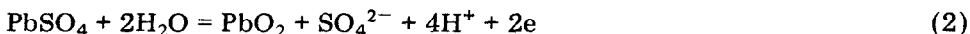*Author to whom correspondence should be addressed.

stable state. This transfer of oxygen gas to the lead electrode is difficult in a flooded system, but if the electrolyte is disposed in a thin film on a porous medium, then gas transport via the pores occurs in parallel with electrical transport in the continuous electrolyte film, and the desired stable state is preserved. This is the basis of oxygen recombination in the modern, fully sealed, maintenance-free battery.

Oxygen recombination reactions

There are many references in the literature to the performance and charge characteristics of sealed lead–acid batteries. Barak [1] has recently reviewed the topic and this important review constitutes a comprehensive overview of the manufacturing electrotechnology. Information is scarce, however, on the recombination mechanism and the actual reactions taking place in the cell.

The principle of a sealed electrochemical energy conversion device functioning during overcharge on an oxygen recombination cycle is reported to have been first advanced by Lange *et al.* [2]. A development from this was the sealed nickel–cadmium cell which employed an oxygen recombination cycle that was described in a patent specification by Levien and Thompson [3]. Jeannin, in his patent [4], defined the classical rules governing the manufacture of such sealed cells and defined the principles to be used in the extension of this conception to sealed lead–acid cells. Ruetschi and Okerman [5] described the mechanism of the recombination process which was expected to occur in such cells. It was sometime later, however, before the specific chemical reactions involved in sealed nickel–cadmium cells were described [6]. The same overall principles have been applied to the lead–acid system [1] and can be written as follows.
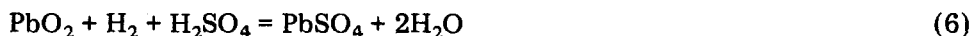
At the positive electrode:

$$PbSO_4 + 2H_2O = PbO_2 + SO_4^{2-} + 4H^+ + 2e \qquad (2)$$

$$PbO_2 + H_2SO_4 = PbSO_4 + H_2O + \tfrac{1}{2}O_2 \qquad (3)$$

and at the negative electrode:

$$PbSO_4 + 2e = Pb + SO_4^{2-} \qquad (4)$$

$$Pb + H_2SO_4 = PbSO_4 + H_2 \qquad (5)$$

Under charging conditions oxygen and hydrogen are evolved when the appropriate potentials are reached. At the positive electrode oxygen is evolved from PbO_2 already formed, while reaction (1) is occurring. At the negative electrode the hydrogen evolution reaction is a thermodynamic possibility at potentials more negative than ~ 0.0 V against the normal hydrogen electrode and, since the lead sulphate reduction of reaction (4) is fast, it follows that hydrogen evolution is insignificant until reaction (4) is

almost complete. Oxygen and hydrogen evolution generally occur under fully charged conditions. Therefore, in the absence of low overvoltage materials on the negative electrode (the positive electrode is less efficient for the charging process than the negative electrode), oxygen is always evolved at a lower state of charge and, indeed, all the reactions of PbO_2 in the Pb–acid cell occur in the O_2 region [7]. Hydrogen is only evolved from the negative electrode when the cell approaches the fully charged condition [8, 9].

For a perfect, sealed, lead–acid cell, the liberated oxygen and any evolved hydrogen must recombine to form H_2O. The recombination reactions are thermodynamically favourable but may be kinetically hindered. Whilst oxygen recombination can take place readily at the negative electrode, hydrogen recombination can take place only relatively slowly via

$$PbO_2 + H_2 + H_2SO_4 = PbSO_4 + 2H_2O \tag{6}$$

at the positive electrode.

This hydrogen recombination is reported to be insignificant [10 - 12] and it is generally agreed that the reaction is likely to be inhibited by sulphate ion adsorption [10 - 12].

Because of the highly active nature of fully charged microporous lead electrodes, oxygen is reduced at the very high specific surface of the negative electrode although there is some doubt about the exact nature of the reaction. Direct combination with O_2 to form PbO, which subsequently becomes $PbSO_4$ and is, thereafter, reduced to Pb is one alternative.

$$2Pb + O_2 \longrightarrow 2PbO \text{ (chemical)} \tag{7}$$

$$PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O \text{ (chemical)} \tag{8}$$

$$PbSO_4 + 2e \rightleftharpoons Pb + SO_4^{2-} \text{ (electrochemical)} \tag{9}$$

The other alternative involves the potential-dependent, direct reduction of the gas.

$$O_2 + 4H^+ + 4e \overset{Pb}{\rightleftharpoons} 2H_2O \text{ (electrochemical)} \tag{10}$$

There are, clearly, problems involved in deciding which of the reactions is the most likely. The major problem, which must be settled before any investigation can be made, is that all the reactions are occurring in the hydrogen evolution region. This requires that the "oxygen" current must be obtained by correcting the total current for the simultaneous hydrogen evolution

$$2H^+ + e \rightleftharpoons H_2 \tag{11}$$

An initial study of cathodic reduction of oxygen in a sealed lead–acid cell was reported by Hills and Chu [13], and brief reviews on this subject have also been reported recently [14, 15]. The first commercial, sealed

lead–acid cell functioning according to the above principles was described by McClelland and Devitt [16]. Descriptions of the behaviour and construction of a number of sealed lead–acid test cells, also functioning on the oxygen recombination cycle, have been published by Mohato et al. [11].

Atkin et al. [17] confirmed that the mechanism for O_2 recombination which occurs in sealed lead–acid cells, is similar to that observed in sealed Ni–Cd cells. They claimed that the reduction currents involved were a function of oxygen solubility. This was 5 times as high in 5 M H_2SO_4 as in 7 M KOH, in agreement with the difference in solubility of oxygen in the same solutions. Fleming et al. [18] established that diffusion was the main controlling factor concerned in the cathodic reduction of O_2 on lead and showed that it appeared to be a 4e process. They found that the oxygen reduction currents in 0.5 M H_2SO_4 were three times greater than those in 10 M H_2SO_4, in agreement with the difference in solubility of oxygen in the two aerated solutions.

Using a rotating disc lead electrode, Thompson and Warrell [19] calculated the maximum oxygen recombination rate as 2.15 mA cm^{-2} in 5 M H_2SO_4. In order to calculate this result they assumed the diffusion layer thickness (δ) to be 10^{-3} cm, as obtained by Dick et al. [20] for oxygen reduction at a Cd rotating disc electrode in KOH. They reported 0.16 mA cm^{-2} as the maximum recombination rate in such a system. In the opinion of these reviewers, the main criticism of this calculation is that the choice of a diffusion layer thickness of 10^{-3} cm is unrealistic: it is at least one order of magnitude smaller than it would be in practice.

Diffusion control of the reaction was confirmed by Armstrong and Bladen [21] using the rotating disc technique. In a more thorough investigation, Khomskaya et al. [22] separated the oxygen reduction currents from the total current passing across the electrode on rotating disc electrode lead in O_2-saturated H_2SO_4. These workers showed that the O_2 reduction currents are independent of potential. Khomskaya et al. also studied the temperature dependent nature of oxygen reduction and calculated an activation energy of 13.8 kJ mole^{-1} for the overall process.

Using prismatic electrodes and electrolyte disposed as a thin film on the porous separator structure, Mohato et al. [11] obtained recombination rates of about 15 mA cm^{-2} (taking the geometrical area of the electrode) for oxygen at atmospheric pressure. For a nominally similar system, obtained by draining a cell such that the electrode was just in contact with the surface of the electrolyte, Thompson and Warrell [19] obtained a value for the oxygen recombination rate in starved conditions of ~ 1.25 mA cm^{-2}, which compared with a value of 0.7 mA cm^{-2} in excess electrolyte. The work of Mahato et al. [11] had been carried out using a porous matrix (an addition of phosphoric acid to the basic sulphuric acid electrolyte in these experiments is considered to be of minor importance), and it can be concluded that the nature of the construction of the electrode–electrolyte system is crucial in determining the magnitude of the oxygen recombination. The currents observed by Mahato et al., however, are approximately two

orders of magnitude greater than the value calculated according to the equation of steady-state diffusion in a stationary electrolyte [23].

Such high rates can be accounted for as a result of a substantial reduction of the thickness of the diffusion layer [23, 24]. This can be best illustrated by the experimental work of Lyzolov and Aguf [23]. The method used by these authors involved cathodically polarized lead electrodes which were raised slowly from 5 M H_2SO_4 so that the electrolyte film carried a substantial current. The cathodic currents were recorded at a number of different electrode heights. It was found that the currents flowing were virtually constant until the electrode was raised to a height of 0.18 cm. Raising the electrode above 0.18 cm resulted in a greatly enhanced current. This was interpreted as being caused by a thin film of electrolyte on the surface. The sharp current increase is evidence of a substantial acceleration of the rate of reduction of oxygen arising from a decrease in the thickness of the reaction layer and providing evidence of the extent of the diffusive control.

Recently, Khomskaya *et al.* [24] studied the effect of separator materials on the reduction of oxygen on porous, pasted lead electrodes. When there was no separator the reduction currents were in the range 0.1 - 0.2 mA cm^{-2}, which were in good agreement with the calculated currents with natural convection. Under these conditions the observed fraction of O_2 removed was less than 5%. There was an order of magnitude increase in current when the electrodes were closely packed with separators and the currents were also significantly higher when the cell systems were sealed. Using different separator materials they concluded that soft materials adhere closely to the electrodes, providing a higher gas pressure in the space between the electrodes which results in an enhanced oxygen reduction rate. Certain combinations of separators with large pores (holes) and electrodes with fine pores lead to an excessive gas filling of the separator with little penetration of oxygen into the electrode. On the other hand, separator materials with fine pores, which adhere tightly to the electrodes, create a higher pressure in the space between the electrodes, and thereby enhance penetration of the oxygen into the pores of the negative electrode. They finally concluded that the oxygen absorption rates depend not only on the selection of the separator material in the space between the electrodes, but also on the ability of the oxygen to penetrate the electrode.

Requirements for efficient oxygen recombination

The present state-of-the-art allows some general rules for efficient oxygen recombination in sealed lead–acid cells to be delineated. These are set out below.

(i) Electrodes

To minimise the hydrogen evolution reaction the negative electrode must have a high hydrogen overvoltage. To achieve this and to maintain the

essential properties required for the satisfactory mass production of grids, and subsequently pasted plates, a Pb/Ca/Sn alloy is generally used. A concomitant requirement is that the total system must be free of impurities which may be transferred to the negative in the course of cycling and thereby reduce the overvoltage; an example is that Sb, and similar metallic impurities, must be absent from the positive plates.

A crucial requirement is that when oxygen is being evolved from the positive there must be "free lead" available at the negative in order to remove the gas. The positive/negative balance is thus of paramount importance.

The gas path between the electrodes must be as short as possible so that plates may be thin and the plate pitch small.

(ii) Separators

The basic requirements of the separators are to isolate the electrodes, while allowing a rapid transfer of oxygen between positive and negative electrodes and without making the ionic conductivity path excessive. These requirements are an antithesis and a compromise is needed to optimise cell performance. This is generally obtained with a glass wool media on which the electrolyte is disposed. The porous matrix provides continuous "holes" for the gas and continuous "films" for the electrolyte.

(iii) Electrolyte

The quantity of the electrolyte (separator–electrolyte ratio) must be sufficient to provide for the requirements inherent in (ii) above and also to satisfy the energy output requirements of the battery. This has resulted in a somewhat increased acid specific gravity becoming conventional. The optimum specific gravity for oxygen recombination may not necessarily be the optimum for cell electrical performance [25] and some caution should be exercised in increasing electrolyte concentrations.

Final comments

The effects described above have been utilised commercially and a number of patents describe aspects of the devices covered (ref. 16 is a major one in this connection). It is clear, however, that much work needs to be done to specify completely the rates of the fundamental reactions involved and the importance of certain component materials. The interplay between the pore and hole sizes and the construction of the porous separators is not well understood. The unique application of glass wool in this connection is of some importance, and the possibility of replacing or improving the constitution vis-a-vis the recombination performance have hardly been reported upon. The relative absorptive properties of the lead negative and the porous glass wool matrix are also still in some dispute.

As yet the potential of the recharging process (maximum cell voltage is generally limited at ~2.65 V) must be relatively strictly controlled. It remains to be seen whether cells can be developed for wider, more flexible operation.

A final question remains as to whether, or not, recombination can be applied to other processes and technologies and what advantages may be gained.

References

1 M. Barak, in M. Barak (ed.), *Electrochemical Power Sources: Primary and Secondary Batteries, I.E.E.E. Series 1*, Peter Peregrinus Ltd., U.K., 1980, p. 291.
2 A. E. Lange, E. Langguth, E. Breuning and A. Dassler, *U.S. Pat. 2 131 592* (1938).
3 A. Levin and W. S. Thompson, *Brit. Pat. 571 820* (1943).
4 R. Jeannin, *French Pat. 102 709* (1950).
5 P. Rüetschi and J. Ockerman, *Electrochem. Technol., 4* (1966) 383.
6 S. U. Falk and A. J. Salkind, *Alkaline Storage Batteries*, Wiley, New York, 1969, p. 192.
7 W. Sunu and B. W. Burrows, in J. Thompson (ed.), *Power Sources 8*, Academic Press, London, 1981, p. 601.
8 K. Peters, A. I. Harrison and W. H. Durant, in D. H. Collins (ed.), *Power Sources 2*, Pergamon Press, Oxford, 1968, p. 1.
9 A. I. Harrison, *Chem. Ind.*, 17 March (1986) 201.
10 P. Ruetschi and R. T. Angstadt, *J. Electrochem. Soc., 105* (1958) 555.
11 B. K. Mahato, E. Y. Weissman and E. C. Laird, *J. Electrochem. Soc., 121* (1974) 13.
12 I. A. Aguf and N. K. Grigalyuk, *Sov. Electrochem., 19* (1983) 965.
13 S. Hills and D. L. K. Chu, *J. Electrochem. Soc., 116* (1969) 1155.
14 M. Hayes and A. T. Kuhn, in A. T. Kuhn (ed.), *Electrochemistry of Lead*, Academic Press, London, 1979, p. 199.
15 D. J. Schiffrin, *Electrochemistry*, Vol. 8, The Royal Society of Chemistry, London, 1983, p. 135.
16 D. McClelland and J. Devitt, *U.S. Pat. 3 704 173* (1970).
17 J. Atkin, R. Bonnaterre and J. F. Laurent, in D. H. Collins (ed.), *Power Sources 6*, Academic Press, London, 1977, p. 91.
18 A. N. Fleming, J. A. Harrison and J. Thompson, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1974, p. 1.
19 J. Thompson and S. Warrell, in J. Thompson (ed.), *Power Sources 9*, Academic Press, London, 1983, p. 97.
20 K. L. Dich, T. Dickinson, R. J. Doren, S. E. A. Pomroy and J. Thompson, in J. Thompson (ed.), *Power Sources 7*, Academic Press, London, 1979, p. 195.
21 R. D. Armstrong and K. L. Bladen, *J. Appl. Electrochem., 7* (1977) 345.
22 E. A. Khomskaya, N. F. Gorbacheva and N. B. Tolochkov, *Sov. Electrochem., 16* (1980) 48.
23 P. Yu Lyzlov and I. A. Aguf, *Sov. Electrochem., 18* (1982) 807.
24 E. A. Khomskaya, N. F. Gorbacheva, T. V. Arkhipova and N. F. Burdanova, *Sov. Electrochem., 21* (1985) 331.
25 C. S. C. Bose and N. A. Hampson, in preparation.