LEAD/ACID RECOMBINATION BATTERIES: PRINCIPLES AND APPLICATIONS

N. E. BAGSHAW

Consultant, 59 Clement Road, Marple Bridge, Stockport SK6 5AG (U.K.)

Principles

The 'oxygen cycle' in secondary cells has been known for many years. In 1933 Dassler *et al.* [1] showed that the oxygen evolving from the positive electrode of a nickel/cadmium cell could be easily reduced at the negative electrode. The hydrogen evolved from the negative electrode, however, was oxidized at the positive electrode only extremely slowly. By the 1940s, it had become recognized that the way to avoid hydrogen evolution in a nickel/cadmium cell was to have excess negative active material, so that the positive electrode was fully charged and began to evolve oxygen when the negative electrode was still only partially charged. If the evolved oxygen was then reduced at the negative electrode at the same rate that it was evolved at the positive electrode, the negative would remain only partially charged, hydrogen evolution would be suppressed and the cell could then be sealed. In this case, both electrodes would be working as gas electrodes with oxygen evolution at the positive and oxygen recombination at the negative. Neumann [2] then found that the rate at which oxygen could be recombined was increased if a limited amount of electrolyte was used in the cell. The first practical sealed cell using the principle of oxygen recombination was thus produced.

The application of the oxygen cycle to a lead/acid battery is, at first sight, much more difficult. The equilibrium voltage of the lead/acid couple is about 2 V but the decomposition of water (oxygen evolution at the positive and hydrogen evolution at the negative) is only 1.23 V (Fig. 1). Thermodynamically, the lead/acid cell should not, therefore, work at all and, on charge, oxygen and hydrogen should be evolved before the formation of lead dioxide and lead from lead sulphate takes place. The high oxygen and hydrogen overpotentials on the lead dioxide and lead surfaces enable the electrodes to be recharged before substantial amounts of oxygen and hydrogen are evolved.

The oxygen cycle can be made to operate with lead/acid cells provided that the principles (excess negative material, limited electrolyte) are followed. A simplified picture is shown in Fig. 2. On overcharge of the sealed recombining cell, the oxygen from the positive is recombined at the negative electrode, thus maintaining the negative in a partially charged condition and
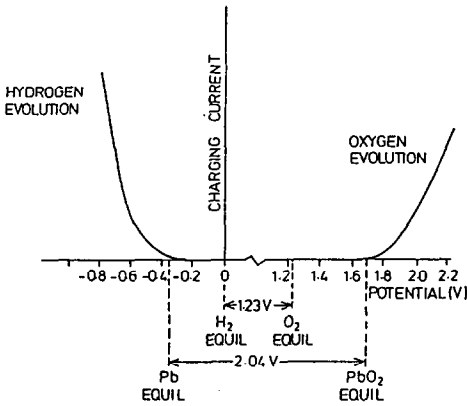
Fig. 1. Charging of lead/acid cell.

suppressing the evolution of hydrogen. The charge curves (at constant current) are also shown in Fig. 2. In the conventional flooded cell, after both electrodes have been fully charged, the voltage rises to the gassing voltage. In the sealed, recombining cell, the voltage profile is, at first, similar, but once the positive electrode is fully charged the evolved oxygen diffuses to the negative electrode where it reacts with the spongy lead on the surface, thus discharging it. This reduces its potential and causes a dip in the voltage curve. Fortunately, the charge acceptance of the negative is more efficient than that of the positive electrode and there is minimal hydrogen evolved from the negative electrode.

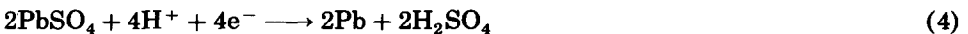The reactions occurring during the oxygen cycle are often stated to be:

(i) evolution of oxygen from the positive electrode;

(ii) reaction of oxygen with spongy lead to form lead monoxide;

(iii) reaction of lead monoxide with sulphuric acid to form lead sulphate and water.

Meanwhile, the negative electrode is being charged by conversion of lead sulphate to spongy lead. These reactions are:

Positive electrode

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \tag{1}$$

Negative electrode

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

$$2PbO + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O \tag{3}$$

$$2PbSO_4 + 4H^+ + 4e^- \longrightarrow 2Pb + 2H_2SO_4 \tag{4}$$

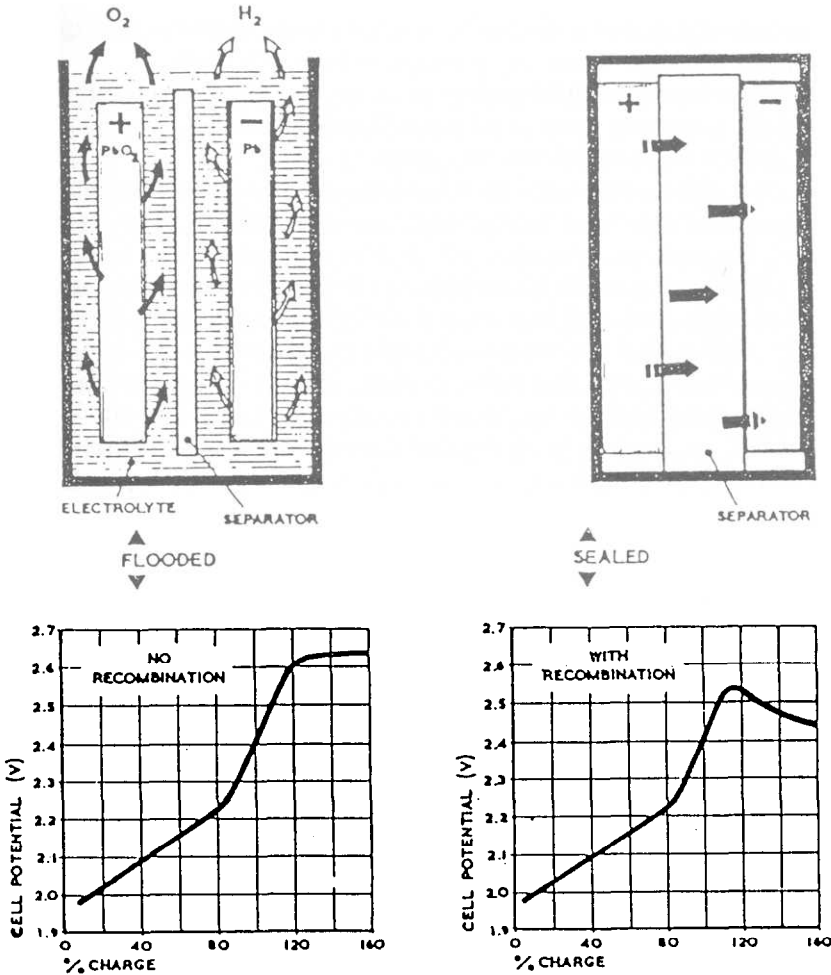$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \tag{5}$$

Fig. 2. Charging of (a) flooded, (b) gas-recombination ('sealed') lead/acid cells.

Whilst the positive electrode is evolving oxygen, a summation of the reactions at the negative electrode shows that it is consuming oxygen, eqn. (5). It is unlikely that the individual steps in the reaction at the negative electrode (eqns. (2) - (4)) actually take place. It is more probable that the oxygen is recombined directly to form water.

Some of the principles for successful application of the oxygen cycle were given by Hills *et al.* [3] and by Mahato *et al.* [4], but the first detailed descriptions of practical cells were presented by Desai [5] and McClelland and Devitt [6]. These covered small cells of both flat-plate and spirally-wound constructions. The critical design parameters are:

(i) the negative/positive material ratio must ensure that the negative is still only partially charged when the positive is fully charged;

(ii) the separator/electrolyte system must ensure that there is no free electrolyte and the separator must not be completely saturated, leaving paths for oxygen to diffuse to the negative electrode;

(iii) the grid alloys must have no additions (and no impurities must be present in the cell) that reduce the hydrogen overpotential on lead.

Pure lead is used in some designs, but it is more usual to employ lead–calcium alloys, often with the addition of tin. The separator is usually a microfibre glass material that can absorb the electrolyte. It has been found, however, that gelled electrolytes (sulphuric acid/silica gel) are capable of allowing oxygen diffusion after a short period of service because they partially dry out and form micropaths to the negative electrode. Since the acid is limited in volume, it is normal to use somewhat higher densities than in conventional cells.

The evolution of hydrogen from the negative electrode cannot be entirely suppressed (Fig. 1), and the 'sealed cell' must therefore have a non-return valve that allows the escape of gas if the pressure becomes too high. This also provides for safety of the cell in the event of abuse.

When designing and testing a recombination cell or battery, the usual principles for lead/acid systems must be followed. Special attention must be paid, however, to various additional aspects. For example, in maintenance-free applications, tests must be devised that simulate service conditions to show that water loss is very low. If the cell is to be installed in an office, tests must demonstrate that gas evolution is minimal. If the cell is to be used or transported at high altitude, it must be shown that it will operate efficiently and safely, without undue distortion of the container, as the external pressure varies. Finally, since in a recombination cell there is more heat evolution and less heat dissipation [7], the cell must be shown to be stable with no tendency for thermal runaway under the maximum charging voltage and ambient temperature conditions for the application. In the case of large-capacity cells, the design should allow for maximum dissipation of heat, even when floated at relatively low voltages (2.25 V).

Recombination lead/acid cells have been used in various duties where their characteristics have particular advantages. Clearly, a major benefit is that they do not require topping-up with water, and applications where this is difficult or costly are obvious areas of use, e.g., remote-area power supplies. Since recombination cells emit virtually no gas, with the associated danger of acid spray, they are suitable for office equipment. The low resistance of the separator results in a good performance at high-discharge currents and low temperatures and recombination batteries therefore find use in engine-starting applications. Since there is no free acid in the cell, there is no leakage of electrolyte if the container is cracked or damaged, and the cell will continue to operate for some time. This can be an advantage in certain duties.

Automotive batteries

Recombination batteries were first introduced into automobiles in Australia in the late 1970s. Since then, their use has been extended to South Africa, U.S.A., and finally to Europe.

In the late 1970s, the emphasis for automotive batteries was on good cranking performance, particularly at low temperatures. The low internal resistance of recombination batteries containing thin, antimony-free plates and microfibre-glass separators results in a good, high rate performance. Engine starting tests at $-20\,°C$ at various states of charge were reported by Peters [8], who showed that the peak power available from a recombination car battery was 15 - 20% better than that from a flooded battery equivalent. Jacq and Pompon [9] also showed that recombination car batteries gave a much improved initial voltage during high-rate discharge.

During the discharge reaction of the lead/acid battery, the acid is consumed, *i.e.*, it is an active material. At low rates, the discharge is limited by the acid and therefore a recombination battery has a lower capacity than the corresponding battery containing a larger volume of free electrolyte. Jacq and Pompon [9] reported a difference in capacity of 15%.

The typical discharge behaviour of recombination batteries compared with that of conventional automotive designs is summarised in Table 1, where catalogue figures for batteries of a similar size and reserve capacity are shown. The reserve capacity is the duration, in minutes, of a discharge at 25 A to an end voltage of 10.5 V, as defined by the British Standard [10]. The IEC 60 Second Test [11] is the current specified by the manufacturer when the battery is discharged at $-18\,°C$ for 60 s to 8.4 V.

It is clear that the recombination type has a superior cranking performance (IEC test) but an inferior low-rate performance (reserve capacity). Since the introduction of recombination batteries in cars, the emphasis in requirements has changed. When not in use, modern computer-controlled cars have a quiescent load on the battery that, over a period of time, can result in a significant degree of discharge. The low-rate capacity (and, on occasions, the ability to recover from a completely discharged state) assumes a greater importance and the recombination battery is at a disadvantage. Although recombination batteries are maintenance free, a free-electrolyte car battery with antimony-free grids and a sufficient reserve of acid can operate for extremely long periods without the need for topping-up. Recombination batteries, therefore, have little or no advantage in this respect.

The remaining advantages of recombination batteries are:

(i) absence of gas evolution with the attendant danger of acid spray;

(ii) no spillage of acid if the case is damaged or cracked.

This gives an opportunity for automobile designers to consider moving the battery out of the engine compartment. This additional design freedom may be used in future car designs but, meanwhile, the recombination battery has little advantage in present-day models.

TABLE 1

Performance of gas recombination (RE) and flooded-electrolyte (FE) batteries

Type	Weight (kg)	Volume (l)	IEC 60 s (A)	Reserve capacity (min)	20 h capacity (A h)
RE	11.5	6.5	325	56	35
FE	12.5	6.7	195	55	40
RE	16.0	8.8	480	110	54
FE	16.0	7.4	330	110	60

Aircraft batteries

In an aircraft, the battery has two prime functions to fulfil. First, it has to start the engine in small aircraft or the auxiliary power unit in larger aircraft. Its high-rate performance is therefore critical and, since weight is at a premium in an aircraft, it must have a high gravimetric power density. Second, the battery serves in an emergency role and, in the event of generator failure, must be capable of powering all the essential navigational equipment to bring the aircraft to safety. This usually corresponds to a current of about the $C/1$ rate. In the aircraft application, there is no low-rate requirement.

Batteries are usually removed from the aircraft every three months or so for maintenance, topping-up and testing. This is an inconvenient and costly procedure and the use of recombination lead/acid batteries, requiring no topping-up, overcomes the need for removal.

Recombination batteries were first used in aircraft applications in the late 1970s in the U.S.A., where individual cylindrical cells (with a $C/1$ capacity of 18 A h) were assembled in a rectangular outer case to give a 24 V battery. Although this had the maintenance-free advantage, there was a considerable waste of space and, in the early 1980s, recombination batteries were developed in the U.K. based on the traditional flat-plate construction. These consisted of two, sealed 12 V monoblocs connected in series in a glass-reinforced-polyester, non-sealed, outer container. The 6-cell monoblocs contained thin, pasted plates based on antimony-free grids, and microfibre-glass separators to absorb the electrolyte. Resealing valves were used to prevent excessive pressure build-up in case of abuse. Batteries of 24 V with $C/1$ capacities of 18 and 25 A h are already in production and a larger capacity battery (36 - 40 A h) is in the prototype stage of development.

The thin-plate construction, together with the low-resistance separator, results in a very low internal resistance. For a 24 V, 25 A h ($C/1$) battery, Scott [12] quotes typical resistance values of 9.7 mΩ at 23 °C and 17 mΩ at −26 °C. A recombination battery is capable of giving 8 - 8.5 min at a discharge current of 150 A (6 $C/1$) at ambient temperature. The operating voltage of a recombination battery is always higher than an equivalent battery with flooded electrolyte, and this difference is accentuated at high rates and low temperatures. The good, high-rate performance is demonstrated

TABLE 2

Power rating current for 24 V, 25 A h aircraft battery

Temperature (°C)	15 s Current at 12 V constant voltage (A)	
	RE battery[a]	FE battery[b]
+25	1000	700
−18	550	385
−30	350	245

[a]RE, recombination.
[b]FE, flooded electrolyte.

in Table 2, where results are given from the Power Rating Current Test of the IEC International Standard [13]. This requires a constant voltage test at half the nominal voltage of the battery. The current after 15 s is recorded.

Unlike nickel/cadmium aircraft batteries that have their own dedicated charger on board the aircraft, most lead/acid batteries are charged by being permanently connected to the d.c. voltage busbars on the aircraft (normally at 28 - 28.5 V). It is important to demonstrate that recombination batteries will operate without topping-up. This can be done simply by a continuous constant-voltage charge. For example, a bench test showed that after 5000 h at 28.5 V, a recombination 25 A h battery still gave 100% capacity with, of course, no topping-up during test. A conventional battery with free electrolyte and Pb–6wt.%Sb grids on the same test required an addition of 1200 ml of water.

For aircraft application, it is important to demonstrate that a battery is stable and not prone to thermal runaway. This is particularly important in the case of a recombination battery where the recombination process itself creates some heat. Tests on recombination batteries (24 V, 25 A h) on a constant voltage of 29 V at 40 °C have shown that they are stable and reach a constant internal temperature of about 55 °C. Batteries have also been tested after 100 cycles to 80% depth-of-discharge and they exhibit a similar internal temperature profile.

Since recombination batteries usually operate at a slight positive internal pressure, it would be expected that, at a high altitude, the reduction in external pressure would cause the pressure valves to open. The British Standard [14] therefore includes a test to simulate the effects of altitude. After 100 simulated flights, recombination batteries have been shown to have negligible loss of weight and to give 100% capacity.

Recombination lead/acid batteries have thus been shown to have good characteristics for aircraft applications and there will be an increase in their use, replacing both conventional lead/acid and also some nickel/cadmium batteries.

TABLE 3

Comparison of 6 V standby batteries

Battery type	Weight (kg)		Volume (l)	
	C/3 rate	C/1 rate	C/3 rate	C/1 rate
Recombination	22.0	22.0	9.8	9.8
Flat plate	36.6	40.8	13.8	16.7
Tubular	28.7	35.6	15.8	19.0
Planté	55.8	55.8	35.5	35.5

Standby batteries

Standby batteries (used to deliver power in the event of an interruption in the mains supply) are normally continuously floated at a constant voltage of about 2.25 V per cell until an emergency occurs. The main requirements are therefore long life under constant-charge conditions, and reliability in meeting the demand when the mains supply fails. Traditionally, the requirement has been met by large batteries, usually centrally located. Relatively-thick plates have been used for long life and a large reserve of electrolyte has been used to make the intervals between maintenance as long as possible. The discharge requirements normally vary from the 15 min to the 3 h rate.

The development of the 'sealed', recombination battery gave an opportunity for a maintenance-free battery for standby duties. Furthermore, since the recombination battery was office compatible (virtually no gases evolved with no associated acid spray), it enabled the whole philosophy of standby batteries in telecommunications equipment to be revised. In particular, British Telecom in the U.K. required a rack-mounted power system for their system X, and the first recombination battery of medium capacity (24 cells with a constant power of 2 kW for 1 h to an end voltage of 46 V) was developed for this purpose [15]. The battery was assembled from 3-cell monoblocs and the characteristics of the monobloc, compared with those of traditional Planté, flat-plate and tubular standby batteries [16] were given in 1983. For example, the advantage of the recombination battery is demonstrated in Table 3, which shows the weight and volume of 6 V batteries of the various types to give the same capacities at the C/3 and C/1 rates to an end voltage of 5.25 V. As would be expected, the advantage of recombination over conventional flat-plate and tubular batteries becomes greater at higher rates.

The batteries were designed with antimony-free grids and microfibre-glass separators not completely saturated with acid. It is interesting to note that, since that time, alloys containing antimony have been used in recombination standby batteries. Berndt [17] reported the use of an alloy containing 1 wt.% Sb, and Szymborski [18] an alloy containing an unspecified amount of

antimony. The long-term effects of a small amount of antimony in the battery under service conditions have yet to be seen.

It is impossible to suppress completely the evolution of hydrogen from the battery (Fig. 1) and it is therefore important to determine the amount of gas evolved. The British Standard [19] calls for a 300 day constant-voltage charge (with intermittent discharges) during which the gas is collected. The ampere-hour equivalent must be less than 5% of the total ampere hours passed through the battery. Gas evolution results have been reported [20] for the 3-cell monobloc used by British Telecom, and gas-recombination efficiencies better than 96% have been achieved.

Attempts to demonstrate the ten-year design life of the recombination monobloc by high-temperature accelerated tests [21] have proved inconclusive, resulting in predictions varying from 1.75 to 42 years, although the best fit curve corresponded to 9.9 years. Life predictions [22] based on degree-of-corrosion and gas-evolution measurements indicated that the life would be at least 10 years. O'Connor [23] has reported that both corrosion and growth in the cells are less than expected and that the intermittent hydrogen evolution is low; a life of over 10 years is predicted. O'Connor also reported that, of the 14 000 recombination batteries put into service by British Telecom between 1981 and 1988, only one internal short-circuit had been experienced. User experience in cells of medium capacity is therefore very good.

In more recent years, recombination cells of higher capacity have been designed. In 1986 Sasaki *et al.* [24] gave details of cells with capacities of 200 - 1000 A h and, in 1988, Sasabe *et al.* [25] reported that the range had been extended to 3000 A h. All the cells gave an increase of 15% capacity at the $C/1$ rate compared with the equivalent conventional free-electrolyte batteries. The recombination rate was close to 100% so that a maintenance-free life of over 10 years could be projected.

Special care has to be taken with higher capacity batteries to ensure that the heat evolved does not result in excessive increases in temperature. In one design [25], this involved reinforcing walls in the container, effectively dividing the element into four groups of smaller plates, with the aim of equalizing the heat-radiating area of the groups. Vertical ribs were also added to the external wall of the container to ensure heat dissipation when cells were installed in close proximity to one another.

Recombination batteries have now become firmly established and are replacing conventional flooded-electrolyte batteries in most standby applications. The major advantages of recombination technology in this field will ensure that the trend will continue.

Traction batteries

Traction cells for industrial truck operation are usually rated at the $C/5$ rate, although higher rates are used during acceleration and fast lifting of fork-lift trucks. At the $C/5$ rate, recombination cells have little or no

advantage in performance over conventional cells. Their maintenance-free capability, however, gives a benefit to the truck fleet operator who can make significant savings in maintenance costs. Traction cells are normally expected to have a life of five years, or 1500 deep discharge/charge cycles.

The design of a recombination cell for traction purposes is more difficult than for other applications. It is well known that antimony-free alloys have a much lower creep resistance than traditional lead–antimony alloys and, therefore, arduous deep cycling duties can result in considerable growth of the positive plates. The loss of capacity on cycling for cells containing antimony-free grids is also well known, although this effect is less marked with retained-electrolyte systems. The possibility of overdischarging is greater in deep-cycling applications and this can result in shorts by dendrite growths through the microfibre-glass separator. Finally, with traction charging regimes, it may be possible that high currents near the end of charge will exceed the recombination rate and result in drying-out. Nevertheless, cells have been developed and used for cycling purposes. Over 1.5 million batteries have been produced for deep-cycling, miner's cap lamp applications [8] since 1982 and a recombination efficiency of 98% over 1000 cycles has been achieved.

As already indicated, gelled-electrolyte batteries begin to operate as recombination batteries after a short time in service, as micropaths develop in the gel. Tubular batteries with gelled electrolyte have been produced for traction applications [26] and it is claimed that a cycle life equivalent to a flooded-electrolyte battery is obtained, although the batteries have to be charged with a controlled-voltage charger [27].

Traction cells using glassfibre separators have also been produced recently, although they are being supplied to carefully chosen customers where the cycling duty is not particularly arduous. It is too early to predict the service life, but it would be surprising at this stage if they had the long life and reliability of flooded-electrolyte batteries. Over the next few years, further improvements will no doubt be made and, perhaps, eventually, the cycling capability and abuse-resistance of conventional rugged traction batteries will be matched.

References

1 A. Dassler, *Ger. Pat. 674,829* (1933).
2 G. Neumann, *U.S. Pat. 2,571,927* (1951).
3 S. Hills and D. K. L. Chu, *J. Electrochem. Soc.*, *116* (1969) 1155.
4 B. K. Mahato, E. Y. Weissman and E. C. Laird, *J. Electrochem. Soc.*, *121* (1974) 13.
5 R. R. Desai, *U.S. Pat. 3,846,175* (1974).
6 D. H. McClelland and J. L. Devitt, *U.S. Pat. 3,862,861* (1975).
7 D. Berndt, *10th INTELEC Conf., San Diego, 1988*, IEEE.
8 K. Peters, *Lead Battery Power for the 90s, Apr. 28 - 29, 1988*, Lead Development Association, London, U.K., pp. 45 - 50.
9 B. Jacq and J. P. Pompon, *Lead Battery Power for the 90s, Apr. 28 - 29, 1988*, Lead Development Association, London, U.K., pp. 39 - 44.
10 *British Standard 3911: Part 1: 1982.*

11 *IEC Standard 95-1: Part 1: 1980.*

12 I. D. Scott, *Aerosp. Des. Components*, (Oct.) (1986) 32.

13 *IEC Publ. 952-1, 1988.*

14 *British Standard 4G205: Part 1: 1987.*

15 A. I. Harrison, N. E. Bagshaw and E. Thompson, *4th INTELEC Conf., Piscataway, 1982*, IEEE, p. 291.

16 N. E. Bagshaw, R. P. Bullough and T. M. Wolstenholme, *5th INTELEC Conf., Tokyo, 1983*, IEEE, p. 465.

17 D. Berndt, *9th INTELEC Conf., Stockholm, 1987*, IEEE.

18 J. Szymborski, J. L. Mulcahy and A. R. Abbott, *10th INTELEC Conf., San Diego, 1988*, IEEE, p. 83.

19 *British Standard 6290: Part 4: 1987.*

20 A. I. Harrison and B. A. Wittey, in L. Pearce (ed.), *Power Sources 10*, Paul Press Ltd., London, 1985, p. 447.

21 R. P. Bullough, W. H. Edwards and A. I. Harrison, *9th INTELEC Conf., Stockholm, 1987*, IEEE, p. 123.

22 R. P. Bullough and A. I. Harrison, *10th INTELEC Conf., San Diego, 1988*, IEEE, p. 25.

23 J. A. O'Connor, *Chem. Ind.*, Feb. (1988) 82.

24 M. Sasaki, S. Sasabe and Y. Kasai, *8th INTELEC Conf., Hamburg, 1986*, IEEE, p. 61.

25 S. Sasabe, M. Sasaki, M. Kishimoto, Y. Kasai and K. Fuchida, *Lead Battery Power for the 90s, Apr. 28 - 29, 1988*, Lead Development Association, London, U.K., pp. 101 - 108.

26 H. Tuphorn, *Lead Battery Power for the 90s, Apr. 28 - 29, 1988*, Lead Development Association, London, U.K., pp. 51 - 59.

27 H. Tuphorn, *J. Power Sources*, *23* (1988) 143.