

# Study of transport of oxygen and water vapour between cells in valve regulated lead–acid batteries

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## Abstract

Valve-regulated lead–acid batteries are maintenance free, safer, office compatible, and have higher volume efficiency than conventional designs. They are universally used in telecommunications and uninterruptible power supply systems. With the electrolyte immobilized in the separator or as a gel, it is feasible for a monobloc battery to have cells that are not fully sealed from one another, that is to have a common gas space, with certain attendant benefits. This study demonstrates that small differences in the saturation level, acid strength or operating temperature of the cells in such designs can initiate a cycle that may subsequently result in failure if the movement of oxygen and water vapour between cells is unrestricted. Cells that are initially out-of-balance will go further out-of-balance at an ever-increasing rate. This situation can also arise in monobloc designs with sealed cells if the intercell seal is inadequate or incomplete. Battery failure is associated with a re-distribution of water between the cells with some drying out and having high impedance. The preferential oxygen absorption in those cells produces heavily sulfated negative plates. Results on batteries tested under a range of overcharge conditions and temperatures are presented to illustrate these effects. The rate at which the cycle occurs depends on the initial relative density of the acid, the temperature or saturation imbalance between the cells, and the size of the interconnecting gas space. Batteries operating under a continuous cycling regime, particularly those with high overcharge currents and voltages that generate large volumes of oxygen, are more prone to this type of failure mode than batteries operating under low overcharge, intermittent cycling, or float conditions.

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## 1. Introduction

The development and commercialization of valve-regulated lead–acid (VRLA) batteries over the last 30 years has resulted in products with much improved performance features that meet the requirements of many new applications. Their maintenance-free characteristics, improved safety, office compatibility and high volume efficiency compared with the more conventional lead–acid batteries has ensured the continuing world-wide use of this battery chemistry in telecommunications and uninterruptible power supply (UPS) systems. With higher power capability, they are also a serious contender for use in advanced hybrid electric cars.

Whilst the development of VRLA batteries is a further step in the continuing evolution of lead–acid batteries, their operation and control is more critical than flooded designs. Oxygen evolution at the positive plate and subsequent recombination and reduction at the negative plate should be a closed cycle of operations with the reactions at the positive and negative plate proceeding at the same rate for satisfactory and long-lasting service. Secondary reactions such as corrosion and self-discharge at either the positive or negative electrode interfere with this balance and there has been much research into acceptable impurity levels and corrosion rates of grid alloys and into ways to minimize their effects. [1,2].

The equilibrium between charge rate and recombination is also affected if cells in a monobloc design are not adequately sealed so that oxygen and water vapour transfer between them. This is a situation that may occur due to poor intercell seals or when cell partitions to cover seals are broken. It may also take

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place in designs where single vents are used and are connected to individual cells via a manifold arrangement.

The risk associated with the transfer of gases between cells has not been quantified [3] but if the affect on service or performance is small, or can be controlled to an acceptable level, designs in which the gas space above each cell is interconnected, otherwise known as a ‘common gas space’, may be possible. There are potential benefits of such designs such as ease of manufacture, lower material costs and improved electrical characteristics such as specific power and energy. Misra et al. [4] described similar designs but with catalysts to aid recombination. Batteries were charged at 49 °C for extended periods and it was concluded that any imbalance between cells, due to the oxygen generated in one cell being recombined in another, would lead to different acid gravities but this would be corrected and the equilibrium restored by water vapour transport between the cells. The investigators found no evidence of the common gas space causing early failure.

This study is directed towards a better understanding of the reaction processes that take place when oxygen and water vapour can move between cells in a VRLA battery. The influence of design and external parameters, such as acid strength, saturation level and temperature, are examined.

## 2. Mechanism of mass transport between cells

The interchange of oxygen and water vapour between cells creates a progressive cycle of change, as described below. Two cells connected together with an open gas space shared by each cell are shown schematically in Fig. 1. The cells contain different amounts of acid so that their components have different levels of saturation. Whilst this is an artificially created situation to

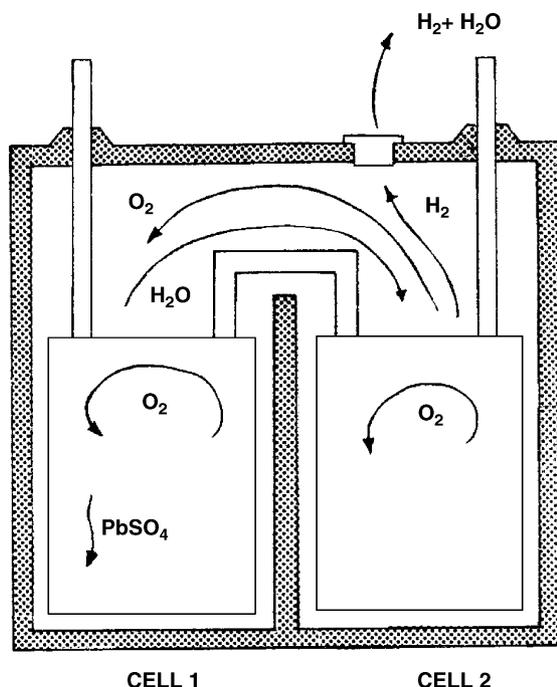


Fig. 1. Mechanism of mass transport in the gas phase.

explain the mechanism, the normal distribution of manufacturing parameters such as active material weights, plate porosity and acid fill volumes could create a similar situation in production cells. If cell 1 has the lower saturation, the following reactions can proceed during charge.

- (i) The passage of oxygen to the negative plate in cell 2 is impeded due to the higher saturation of the separator and oxygen can transfer to cell 1 via the headspace and react with the negative plates in cell 1.
- (ii) The charge current is only sufficient to recombine oxygen liberated in each cell and the additional oxygen in cell 1 results in the formation of lead sulfate at the negative plate.
- (iii) The sulfate formation in cell 1 reduces the acid strength via the reaction:



- (iv) The vapour pressure above each cell will now be different and water will be transferred from cell 1 to cell 2 to maintain cell 2 at a higher saturation level.
- (v) The saturation difference between the two cells increases and the process continues as in step (a).

This cycle will continue with cells becoming further out of step. Cell 1 will eventually dry out completely and result in fully-sulfated negative plates whilst cell 2 will be flooded. The positive feedback nature of this cycle is illustrated in Fig. 2.

Other imbalances between cells, such as acid strength, can lead to a similar result. As the rate at which the cycle continues is governed by the difference in vapour pressure between the two cells, temperature will accelerate the process. This is illustrated in Table 1 where a difference of 5% in acid concentration gives a vapour pressure difference of only 2 mmHg (270 Pa) at 20 °C but a difference of 20 mmHg (2.7 kPa) at 60 °C.

Consequently, VRLA batteries in which gas and vapour can transfer between cells are inherently unstable with the above mechanism likely to occur unless the process cycle can be restricted or prevented. To verify these effects and to understand the rate at which they may affect battery service, a programme

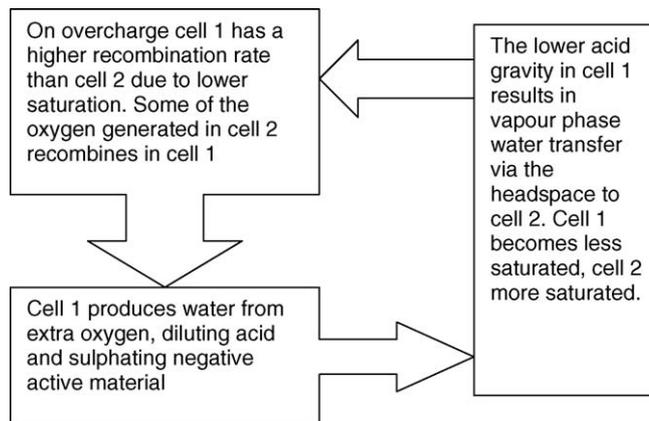


Fig. 2. Positive feedback mechanism operating in common head space.

Table 1  
Vapour pressure of sulfuric acid solutions

Temperature (°C)	Vapour pressure of 40% H <sub>2</sub> SO <sub>4</sub>	Vapour pressure of 35% H <sub>2</sub> SO <sub>4</sub>	$\Delta p$
20	10	12	2
40	33	40	7
60	93	113	20

Vapour pressure in mmHg (1 mmHg = 130 Pa).

of experiments was carried out with VRLA batteries in containers that were designed specifically to allow the transport of gas and water vapour between cells. The cells were arranged to be out-of-balance, in terms of varying saturation or electrolyte strength. The experiments were performed at elevated temperatures to accelerate the cycle and to obtain meaningful results in a reasonable period.

### 3. Experimental

Two experimental designs were used to measure the effect of acid strength and electrolyte volume on the rate of transport of water vapour.

#### 3.1. Batteries A, B, C and D

These were two-cell batteries that were designed and assembled so that they could be separated and examined individually. Each cell contained 11 plates (5 positives and 6 negatives) with a commercial grade of glass micro-fibre separator compressed by 15% during assembly. The plates were pre-formed and charged. An upper portion of the wall of the container was cut away and provided with a gasket so that gas and vapour could transfer between the two cells when they were placed together. The gasket maintained an atmospheric seal. The cells had a one-way valve venting to atmosphere at 2 psi (14 kPa). The design is shown in Fig. 3.

Four experimental variants were studied. In battery A, both cells were normal production design and made to standard manufacturing tolerances. Each contained 240 cm<sup>3</sup> of sulfuric acid, 1.300 relative density and were filled under vacuum. This volume had been pre-determined to give 100% saturation, i.e., there was no surplus electrolyte in the cell when fully charged. The cell capacity was 25 Ah at the C<sub>20</sub> rate. In batteries B, C and D, each pair of cells contained different volumes and strengths of acid, as shown in Table 2. The cells were weighed individually then strapped together to form a leak-tight seal and then charged

Table 2  
Battery design variables-type 1 design

Battery type	Replicates	Acid relative density		Acid volume (cm <sup>3</sup> )	
		Cell 1	Cell 2	Cell 1	Cell 2
A	3	1.300	1.300	240	240
B	4	1.300	1.266	240	240
C	2	1.300	1.300	240	216
D	2	1.300	1.300	240	192

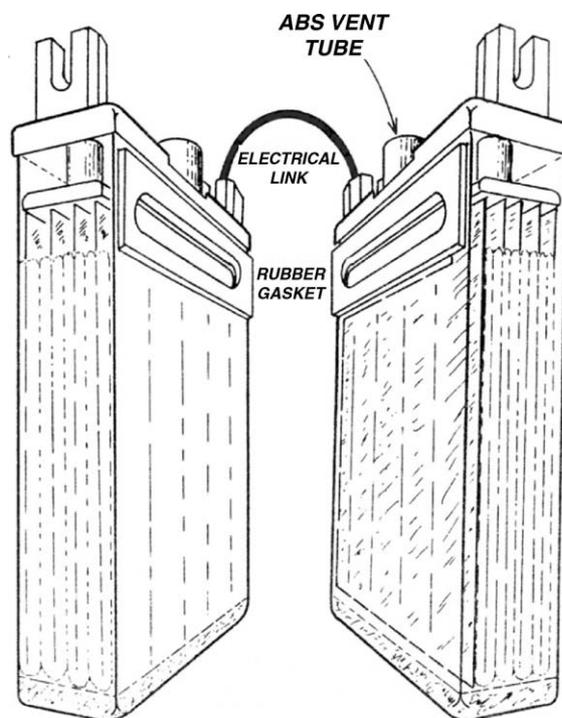


Fig. 3. Schematic experimental battery design.

at a constant current of 0.125 A with the temperature maintained at 60 °C. The on-charge voltage, open-circuit voltage, cell impedance and weight were recorded at regular intervals throughout the test.

The change in weight that results from the transfer of water from a donor cell to an acceptor cell during 6 weeks of over-charge at constant current is shown in Fig. 4. (Note that the batteries lost some weight during the test due to venting of water vapour to the atmosphere; all were equally affected and the amount was small and constant at 3.8 g per week). The change in impedance of the donor cells is displayed in Fig. 5. The impedance of the acceptor cells remained constant throughout the tests at 1 m $\Omega$  and is not shown.

The data in Figs. 4 and 5 confirm the mass transport mechanism postulated in Section 2. Type B batteries (cell 2 relative density < cell 1 relative density) experienced a mass transfer of water from cell 2 to cell 1. This exchange accelerated as the test proceeded and thereby increased the imbalance. Type C batteries (cell 2 acid volume < cell 1 acid volume) showed simi-

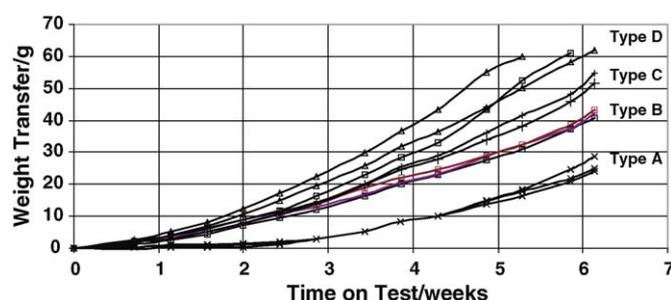


Fig. 4. Weight changes of batteries charged at constant current.

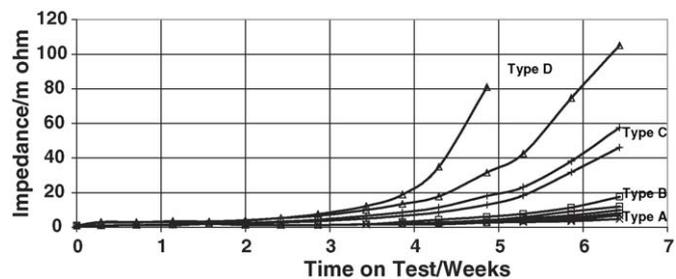


Fig. 5. Impedance of batteries charged at constant current.

Table 3

Battery variables				
Battery type	Voltage (V)	Current (mA)	Temperature (°C)	Cell imbalance
E	2.25		60	None
F	2.20		75	None
G		250	60	None
H	2.25		60	Relative density (1.236/1.285)

lar behaviour with the transfer of water increasing the imbalance between cells as the test continued. After 6 weeks on overcharge at constant current, the water transferred in type D batteries, which had the greatest difference in acid volume, was sufficient to flood the acceptor cell (cell 1). Type A batteries that were nominally in balance, but like all products were subject to manufacturing tolerances, remained stable for 3 weeks but thereafter became progressively out-of-balance.

The impedance results in Fig. 5 show a similar pattern and followed the weight changes in Fig. 4 with the impedance of the donor cells increasing as they progressively dried out. Based on the initial acid volume and the amount of water transferred, it is possible to estimate the change in saturation during the experiment. The saturation/impedance relationship of the donor cells is presented in Fig. 6. The shape of this curve is identical to that obtained in previous work [5] using a different technique, but it has a steeper increase in impedance as the saturation decreases. This is to be expected since the change in impedance in this study is due to both the decrease in saturation and the dilution of the sulfuric acid, whereas in the earlier work the change in impedance was caused only by a change in saturation. This relationship further demonstrates that impedance measurement is an acceptable and non-invasive technique for following the drying-out process.

under vacuum and the excess acid was poured off. Three batteries designs (E, F and G) had similar construction. The electrolyte in the two cells in battery H was adjusted to 1.236 relative density (cell 1) and 1.285 relative density (cell 2). They were placed on overcharge at different rates and temperatures for 6 weeks. The experimental variables are shown in Table 3. The impedance and voltage of each cell on test was measured daily.

The cells in this design could not be separated for weighing individually and impedance measurements were recorded in order to follow changes during overcharge. The impedance of the donor cells over a test period of 7 weeks is shown in Fig. 7. The values are based on the mean of two trials carried out for each set of experimental conditions given in Table 3. The impedance of the acceptor cells was constant at 1.8 mΩ throughout the test and is not shown.

Each pair of cells in batteries E, F and G had the same design; any variation was the result of manufacturing variances. The two cells in battery H contained different strengths of electrolyte, as shown in Table 3. The cells in battery type E, charged at 4.5 V (2.25 V per cell) at 60 °C, were still in balance and stable after 35 days (Fig. 7). By contrast, the cells in battery F started to go out-of-balance after 20 days due to the increased water vapour pressure at the higher temperature. This demonstrates the effect of temperature in accelerating the out-of-balance condition, as predicted in the original hypothesis for the mechanism. Battery G, charged at 250 mA and 60 °C, showed the greatest instability with cells starting to go out-of-balance at 10 days. This demonstrated the influence of constant current on the reaction rates compared with constant potential charging, where the cell voltage limits the reaction. As shown with batteries F and H, however, even batteries charged at constant voltage can still go out-of-balance. Type H batteries experienced this behaviour

3.2. Batteries E, F, G and H

These were also two-cell batteries, but were permanently attached. The top of the inter-cell partition was cut-away to provide an open pathway for gas and vapour between cells. Each cell contained six plates with glass microfibre separators compressed to 10%. The cell capacity was 16 Ah at the C<sub>10</sub> rate. The cells were filled with sulfuric acid (1.280 relative density)

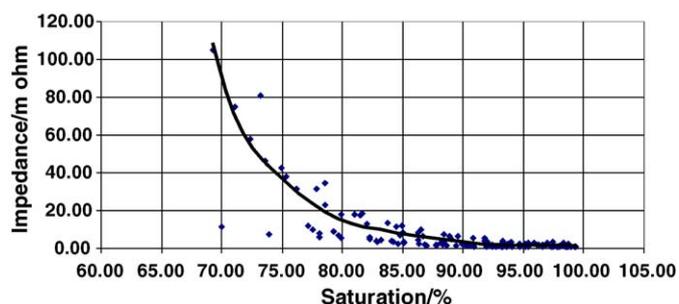


Fig. 6. Impedance/saturation relationship.

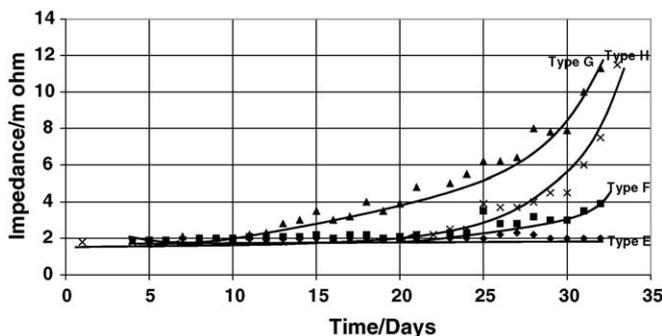


Fig. 7. Impedance of donor cells.

before type F, as expected due to the initial difference in acid strength in the two cells. Although type E batteries remained stable during the test, it must be expected that as the system is inherently unstable, cells will eventually deviate and show similar behaviour to the other types.

### 3.3. Measurement of the rate of transfer of water vapour

The continuing cycle of gas and vapour movement between cells depends on the positive feed back from the counter movement of water vapour and oxygen. Inhibition of either process, i.e., prevention or reduction of the rate at which it occurs, will reduce the cycle, possibly to such a rate that service life is not affected, even under extreme operating conditions.

Oxygen evolution depends on the external factors of charge rate and time with movement between cells dependent on pressure and diffusion rate, whereas water transport proceeds through three stages, namely: evaporation, diffusion and condensation. Evaporation and condensation are slow relative to gas-diffusion rates. Since the slowest process governs the overall reaction rate, the most productive method for moderating the cycle would appear to be to reduce the transfer of water.

To investigate the rate of water transport, two open-top containers, each with the same volume of sulfuric acid but of different strength (solution 1, 1.200 relative density; solution 2, 1.300 relative density) were placed inside a larger box (see Fig. 8). In three of the series of experiments, a roll of absorbent glass microfibre separator was placed in the acid so that the top 5 mm were exposed. This was to mimic a practical lead–acid cell in which the separator normally extends 5 mm above the plates. The roll of separator was of a size such that it covered 50% of the surface area of the acid. This was to investigate the possibility that acid absorbed into a separator of high surface-area would evaporate more quickly. In fact, the experimental results showed this not to be the case. After filling the inner boxes, the unit was hermetically sealed and placed in a stable temperature environment. Every 24 h, the individual boxes were removed and weighed to determine the amount of water that had transferred between the boxes. The experimental conditions are shown in Table 4. Each experiment was carried out in duplicate.

Confirmation that water transport between cells followed first-order kinetics was established by plotting the change in water concentration in the box that contained the weaker acid (1.2 relative density) from the water loss and water gain data. A straight line fit with a negative slope and a correlation coefficient

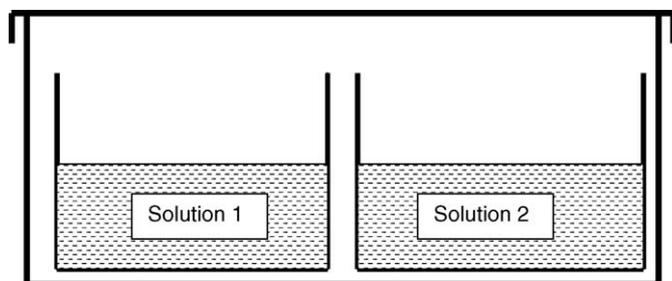


Fig. 8. Experimental design for measuring the kinetics of water vapour transfer.

Table 4  
Experiments in water vapour transport kinetics

Experiment number	Temperature (°C)	Acid volume (box cm <sup>-2</sup> )	Separator in box?
1,2	60	100	Yes
4,5	75	100	Yes
7,8	90	100	Yes
19,20	60	100	No
22,23	75	100	No
25,26	90	100	No

Inner box area 26 cm<sup>2</sup>.

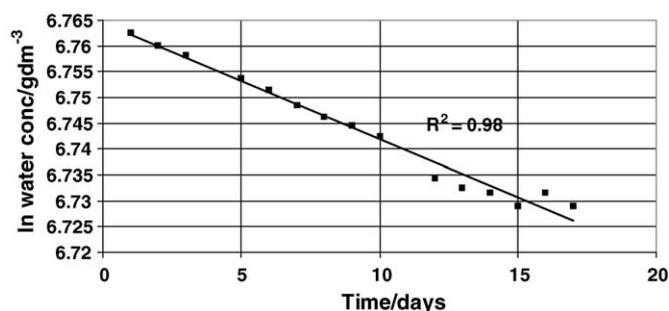


Fig. 9. First-order kinetics plot for experiment 1 (Table 4).

of 0.98 was obtained, as shown in Fig. 9. Whilst the increasing water concentration in the 1.3 relative density box was not calculated, it can be anticipated that it would produce a similar graph but with a positive slope.

The half-life of the water-transfer reaction for each of the experimental variables is shown in Table 5 and is plotted as an Arrhenius relationship in Fig. 10. The half-life decrease from 13 to 2 days as the temperature is increased from 60 to 90 °C. The rate constant is not affected by the presence of separator material in the acid.

## 4. Discussion

The experimental results illustrate that even small differences in the saturation level and operating temperature of cells in a VRLA battery can initiate a cycle that may subsequently result

Table 5  
Half-life calculations from water transfer data

Experiment number	Separator?	Temperature (°C)	Half life (days)
1	Yes	60	12.26
2	Yes	60	13.05
4	Yes	75	5.68
5	Yes	75	6.65
7	Yes	90	2.38
8	Yes	90	2.67
19	No	60	13.6
20	No	60	10.74
22	No	75	4.29
23	No	75	4.76
25	No	90	2.7
26	No	90	2.28

Inner box area 26 cm<sup>2</sup>.

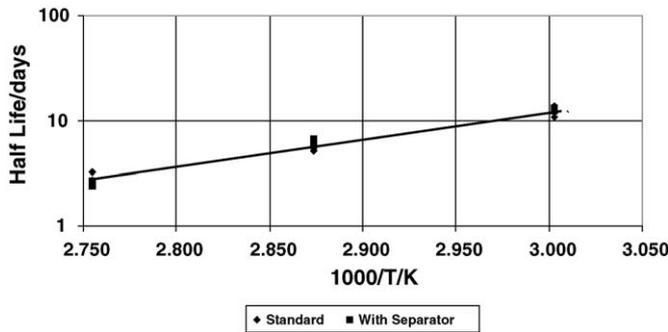


Fig. 10. Arrhenius plot of water transport data.

in failure if the movement of oxygen and water vapour between cells is unrestricted. Cells that are initially out-of-balance, for example in strength or volume of electrolyte (saturation), or operate at different temperatures, will go further out-of-balance at an ever-increasing rate. Battery failure is associated with a redistribution of water between the cells with some cells drying out and acquiring a high impedance. Due to the preferential oxygen absorption in these cells, the negative plates become heavily sulfated.

Since the mechanism of the cycle is based on positive feedback, small differences in the initial state will increase as the process continues. If cells are uniform in all respects, this cycle will not exist. This is unlikely, however, because of the unavoidable variation in manufacturing processes and cell temperature differences during service. The rate at which this instability manifests itself is governed by the rate of oxygen evolution and the imbalance between the recombination rates of the different cells in a battery. Thus, batteries that see high overcharge voltages and currents will suffer more from this cycle than those in which the current is limited or the float voltage is low. This aspect is demonstrated by the results in Section 3.2. Without the driving force of oxygen evolution, the cycle of gas and water transport would not occur. Consequently, the problems described previously do not arise (or occur minimally) with batteries on open-circuit for long periods or on float service at low voltage levels. This may explain why the results obtained by Misra [4] with common gas space designs did not show the progressive out-of-balance behaviour described in this work. Nevertheless, batteries subjected to a regular duty of that results in high overcharge currents or voltages might experience this cycle as a failure mode.

The results shown in Figs. 9 and 10 demonstrate that the transfer of water is under kinetic control. If oxygen or water vapour transfer is restricted by limiting or reducing the size of the interconnecting area that is open for gas transfer, the rate-determining step will change to diffusion control at some point. The cross-sectional area where the changeover occurs can be calculated from Fick's laws of diffusion.

Consider the specific example of battery type B (Table 2), the experimental parameters of which are summarised in Table 6. Using Fick's first law, viz.,

$$J = D dc/dx \quad (1)$$

where  $J$  is the water transfer flux,  $D$  the diffusion coefficient and  $dc/dx$  the concentration gradient, the estimated initial rate

Table 6  
Parameters for battery B

Interconnecting cross-sectional area	12.9 cm <sup>2</sup>
Interconnecting slot length	1 cm
Relative density, cell 1	1.266
Relative density, cell 2	1.300
Temperature	60 °C
Diffusion coefficient of water vapour in air	0.2 cm <sup>2</sup> s <sup>-1</sup>

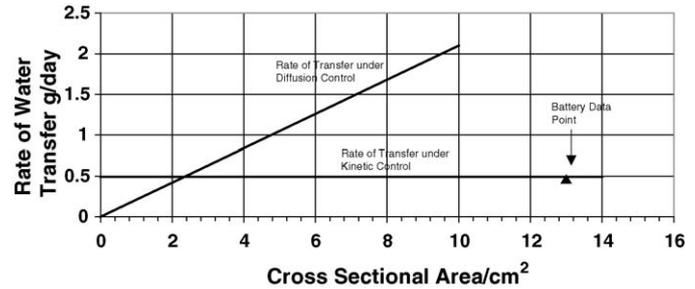


Fig. 11. Water transport rates as a function of inter-connecting hole cross-sectional area.

of water transfer between the cells is 0.21 g cm<sup>-2</sup> per day. By contrast, the observed rate under kinetic control is 0.49 g per day measured over the first 4 days. The latter is independent of the interconnecting area. This situation is illustrated in Fig. 11. When the open interconnecting area is less than 2.4 cm<sup>2</sup>, the transfer rate is diffusion controlled. The actual rate is dependant on the length and cross-sectional area of the gas path between cells.

The situation is shown in more detail in Fig. 12, in which are presented the results of two further experimental batteries with interconnecting areas of 3 mm<sup>2</sup> and 1 cm<sup>2</sup>. In all other ways, these batteries were similar to battery B and tested with the same procedure. The original data point for battery B at 12.9 cm<sup>2</sup> is also shown. It can be seen that the rate of water transfer for these cells falls on the predicted curve. The design with the 3 mm<sup>2</sup> connecting hole was on test for 90 days at 60 °C with no significant increase in impedance or water transfer over that period.

The length if the diffusion path in battery B, i.e., the space between the cells, was 10 mm and the relative density of the electrolyte in the two cells differed by 0.04. A more typical situation in a practical battery would be an intercell wall thickness of ~1 mm and an electrolyte strength that varies in relative density

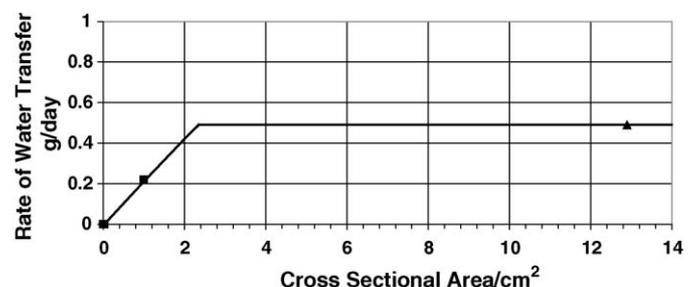


Fig. 12. Details of kinetic/diffusion control transition.

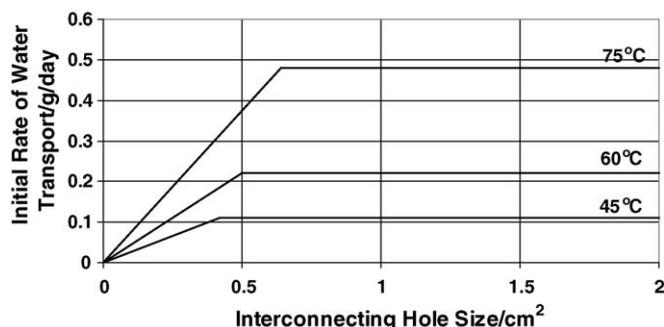


Fig. 13. Effect of temperature on kinetic/diffusion transition. Difference in relative density between cells = 0.015.

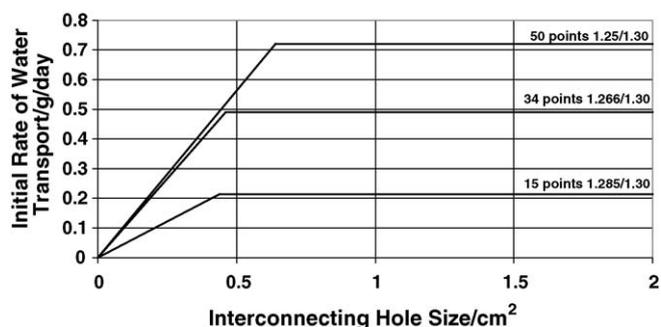


Fig. 14. Effect of difference in relative density on kinetic/diffusion transition.

terms by about 0.010. Using the previously determined transport data and the diffusion constants, similar graphs to Fig. 12 can be constructed using Fick's laws.

Examples of overcharge on a design similar to that of battery B, but with the electrolyte strength between cells differing by 0.015 and a diffusion path of 1 mm between interconnecting cells, are shown in Fig. 13. The rate of water transport (in g per day) was calculated for three ambient temperatures. The effect of greater differences in electrolyte strength in adjacent cells is shown in Fig. 14. It can be seen that the critical interconnecting area in both examples is much smaller than that calculated under the conditions in Fig. 12. This is accounted for by the difference in the length of the diffusion path between cells, i.e., approximately 1 mm. in Figs. 13 and 14, and 10 mm in Fig. 12.

## 5. Conclusions

Small differences in the saturation level, acid strength and operating temperature of cells in a VRLA battery can initiate a cycle that may subsequently result in failure if the movement of oxygen and water vapour between cells is unrestricted. Cells that are initially out-of-balance will go further out-of-balance at an ever-increasing rate. Battery failure is associated

with a re-distribution of water between the cells, with some cells drying out and having high impedance. Preferential oxygen absorption in these cells produces heavily sulfated negative plates.

The run-down process can be followed by weighing individual cells, or more conveniently by measuring cell impedance. The latter measurements offer a practical way of assessing the tendency for this process to occur in batteries that are operating in the field where it is impossible to weigh individual cells.

The instability only applies to batteries that are cycled and overcharged on a regular basis. It is only when the battery sees relatively high overcharge currents or voltages that the driving force of oxygen evolution causes the cycle of gas and water transport to occur at a significant rate. Consequently, problems associated with this behaviour do not occur, or may occur only minimally, with batteries that are on open-circuit for long periods or on float service.

A study of the slower of the two processes, i.e., the transfer of water, has shown that the process can be under either kinetic or diffusion control depending on the size of the interconnecting gap between cells. The critical dimensions of this gap, below which the transfer rate is diffusion controlled and the run-down rate limited, can be calculated and are given for typical battery sizes.

For VRLA monobloc batteries that see float duty at relatively low ambient temperatures or are infrequently cycled, appropriate design of the interconnecting gas space facilitates the use of common gas space designs without incurring the detrimental problems associated with the transfer of oxygen and water vapour between cells.

For batteries that are regularly cycled, this study demonstrates the need for intercell seals of quality. With inadequate seals that do not restrict gas and vapour transport between cells, the weakest cell in the battery i.e., (the cell with the lowest saturation or the highest ref. dens.) will act as a donor to the remaining cells in the battery and will sulfate and dry out, with other cells accepting excess water.

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