Gas detection and minimization of gas and heat production at the end of fast charging

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Abstract

Fast charging of lead/acid batteries in electric vehicles has become a focal point of attention. Fast-charge algorithms depend on the accurate determination of the gassing point during any state-of-charge and are generally limited to providing 85% of the charge in a very short time. The remaining 15% requires much more time due to the low charge acceptance of the battery. This paper describes test results that indicate that with accurate determination of the gassing point and by pulse charging with a frequency and amplitude related to the state-of-charge of the battery, one can accelerate the final phase of charging. The test results show that there is a time lag between the onset of the charge reaction and the onset of the gassing reaction if a charge pulse is given to a lead/acid battery. This time lag depends on the state-of-charge and the battery charge current amplitude. The result has important implications for a fast-charge algorithm: if the current is pulsed such that it is reduced before full gassing sets in, then higher charging rates are possible during the gassing phase of the charge, at reduced gas development, by using pulse charging than would be possible with constant-current charging.

Background

It is well known that a lead/acid battery is capable of accepting high charge currents in a discharged state. High-current charging is limited throughout most of the charge schedule by the charge acceptance of the battery which is defined as the limit current at which gassing of the battery is negligible. At the beginning of charge, the current is often limited below charge acceptance because of excessive heat development due to the internal resistance of the battery. Excessive heat development is detrimental to battery life and we have evidence that substantial grid corrosion sets in above 54 °C and shortens battery life, as seen in Fig. 1.

The problem of fast charging is therefore to limit cell temperature and to determine the charge acceptance of the battery at any time during charging.

Limiting cell temperature during fast charging

The temperature can be controlled in two ways: (i) by improved heat transfer, and (ii) by reduction of the internal battery resistance to reduce the development of heat.

We have measured the time constant for cooling a 4×4 battery pack to be in excess of 20 h. The thermal mass of a battery is about half that of an equal volume of water and contrary to some suggestions most of the heat is not ablated through
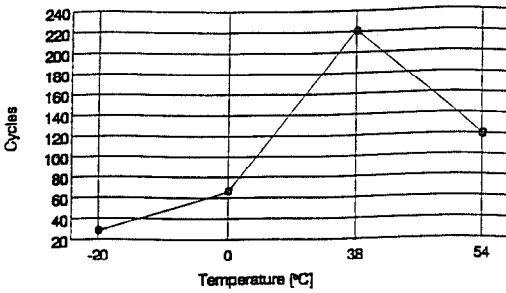
Fig. 1. Life cycles of a 96 V ALCO 2200 flooded lead/acid battery as a function of operating temperature (discharge to 20% state-of-charge).
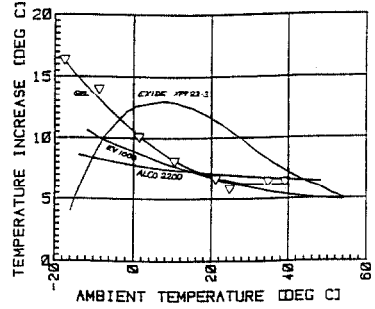
Fig. 2. Influence of cell design on cell temperature development during charging.

the battery post but through the walls of the battery case, in particular the top. The specific heat based on weight of a module is about equal to air, 0.24 kcal (kg °C).

The temperature rise in the battery during charging at the $C/5$ rate is typically of the order of 10 °C. Doubtless, heat-transfer-conscientious design might improve the heat transfer. For example, better designs of intercell connectors and the use of heat-conducting plastics, that are nonconducting electrically, could improve the heat-conduction characteristic of the battery casing.

How cell design can affect temperature is seen in Fig. 2, indicating the temperature rise in cells of different manufacture during cycling with identical duty-cycle schedules. The low temperature rise of the XPV23-3 is due to short charge time at low temperature, because of poor charge acceptance at these temperatures. It is clearly seen that differences in design give a battery different thermal qualities even though the fundamental concept is the same for all four battery models in Fig. 2. However, equally effective is a reduction in the internal resistance. The resistance of the battery to pass electric charge through the cells constitutes 97% of the total heat production. The heat production is a consequence of electrical losses as evidenced by the overvoltages of the battery. The overvoltage is defined as the actual battery voltage minus the equilibrium voltage of the electrochemical processes that are involved during charging. They are different for the charge reaction and the gassing reaction. Consequently, each of these processes contributes to a different extent to the total losses involved in the charging process.

Equations (1)–(5) indicate how the internal resistance of the battery can be defined on the basis of electrical losses which account for the heat production.

$$Q = (U - 0.97U_0)I + (0.97U_0 - U_{0E})I_{EL} \tag{1}$$

$$I_{EL} = C \frac{dV}{dt} \tag{2}$$

$$Q = R_i I^2 \tag{3}$$

$$I = I_{CR} + I_{EL} \tag{4}$$

$$R_i = \frac{U - U_0}{I} \frac{I_{CR}}{I} + \frac{U - U_{0E}}{I} \frac{C}{I} \frac{dV}{dt} \tag{5}$$

Where Q denotes the heat rate developed in the battery, U the battery voltage, U_0 the equilibrium voltage, I the total battery current, U_{OE} the equilibrium voltage of the gassing reaction, I_{EL} the current used up by the gassing reaction, C the proportionality constant between current I_{EL} and gas volume at constant pressure, R_i the battery internal resistance, I_{CR} the charging current, respectively.

Equation (1) is a simplified expression for the heat development in the battery due to the overvoltage for the charge reaction and the gassing reaction. The current that is used for electrolysis can be expressed in terms of gas volume development according to the Faraday relationship. This is indicated in eqn. (2). Equation (3) indicates that with total current I going through the battery the heat rate Q developed in the battery corresponds to a certain amount of electrical power which the battery needs to generate in order to produce the corresponding heat rate. This total battery current is of course the sum of the charge current and the current going into electrolysis as indicated in eqn. (4). By equating eqns. (1) and (3) a relationship between the battery resistance R_i and the overvoltages is established that, when solved for R_i, results in eqn. (5) as a simplified expression for the internal resistance of the battery responsible for the heat production.

If the internal resistance as defined by eqn. (5) is plotted versus time during constant-current/constant-voltage charging as seen in Fig. 3 a number of significant properties of the internal resistance can be seen. Except for at very low temperatures, the internal resistance at the beginning of charging, when the battery is not in the gassing status, is relatively low. As gassing sets in, however, the resistance increases to more than ten-fold for all but high temperatures. The reduction of the internal resistance in the later part of charging at 4 and -16 °C is due to the internal heating process that raises the temperature in the cells to more moderate values where the internal resistance is lower. However, quite generally, it can be seen that the resistance strongly depends on temperature and increases with decreasing temperature.

The graph clearly suggests that gassing not only contributes to an increase in maintenance due to the need for watering and to a low charge efficiency but also to considerable heat production. It can be concluded that a reduction in gassing not only would increase battery efficiency but would also reduce battery heating and therefore have an additional effect on extending battery life.

The following sections describe some recently-obtained results from tests at the Electrochemical Energy and Electric Propulsion Laboratory (EEPL) which indicate that a substantial gassing reduction might be possible by using pulse charging during the gassing phase of the charging process.
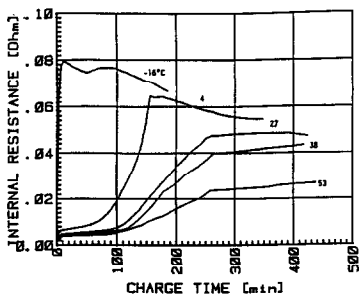

Fig. 3. Internal resistance development during charging at various operating temperatures.

Hysteresis effect between the charge and gassing reactions

Tests at the EEPL indicate that there is a time lag between the onset of the charge reaction and the onset of the gassing reaction if a charge pulse is given to a lead/acid battery. This time lag depends on the state-of-charge of the battery and on the current amplitude. The result has important implications for a fast-charge algorithm: if the current is pulsed such that it is reduced before full gassing sets in, then higher charging rates are possible during the gassing phase of the charge, with reduced gas development during the pulsing, than would be possible with constant-current charging.

Test set-up

This result was obtained from the following experiment in which two almost fully-charged cells, one being a flooded lead/acid cell the other being a lead/acid cell with gelled electrolyte, were involved. The test set-up is shown in Fig. 4. Both cells were carefully sealed and equipped with a glass tube, which reached into the gas space above the electrodes inside the cells. Using a thin plastic tube, the glass tube was connected to a very sensitive low-pressure meter (electronic digital micromanometer (EDM) by Neotronics). The cells were connected to a computer-programmable power supply and a current shunt was used to measure current. The shunt and the pressure meter were connected to a two-channel oscilloscope which monitored current and cell pressure.

Objective of the test

The objective of the test was to correlate current and pressure development in the cell to determine if the response of the charge reaction and the gassing reaction to a current pulse is simultaneous. The basic concept of the test is as follows: since the cells were sealed when connected to the pressure sensor, any gas development in the cells must result in a pressure increase. The pressure meter is very sensitive so that even slight pressure changes are detected by the meter. In addition, the meter is very fast, even for tiny pressure differences. Consequently, even small amounts of gas development in the cells results in an immediate indication of pressure increase on the oscilloscope. The scope used was a digital scope by Philips (PB 3365/50).

It can be shown that for small pressure changes and constant temperature in the cells for the duration of the current pulse the pressure increase is directly proportional
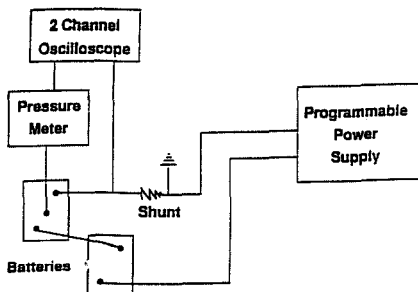

Fig. 4. Test set-up for hysteresis measurements.

to the gas volume increase at initial (atmospheric) pressure. Therefore, the pressure increase as indicated by the oscilloscope is a measure for the gas volume development at atmospheric pressure in the cell, differing only by a constant factor.

Any current passing through the battery during charging is consumed either in the charging reaction or in the gassing reaction, including gas recombination. If gassing is to start synchronomous with charging, then an immediate pressure increase must accompany the current step. If the ratio of the charge current to gassing current is assumed to be approximately constant for the short duration of a charge pulse, then the pressure development over current development is as indicated in Fig. 5(a), if the charge reaction and the gassing reaction to a current pulse are simultaneous.

Test conduction

The test consisted of imposing a step current on the cells and measuring and correlating the pressure responses. Before the test, the pressure in the cells was equalized with the outside air (atmospheric pressure) and a pretest measurement was made to insure that the cells were not gassing at open voltage.

Test results

The actual relationship between current and pressure is as indicated schematically in Fig. 5(b). Actual test results are seen in Figs. 6, 7 and 8. Clearly, the difference between Fig. 5(a) and Fig. 5(b) is that Fig. 5(b) implies a variable pressure gradient immediately after the current step. Tests were made to ensure that this phenomenon was not due to the inertia of the meter.

The gradually-increasing pressure after a current step indicates that gas development after the current step is not immediate but sets in gradually. Since the current throughout the pulse is constant, more of the current must be initially consumed by the charge reaction than by the gassing reaction until quasi-steady-state conditions have been reached and gassing developes at a constant rate commensurate with the state-of-charge. If the pulse lasted long enough a linear increase in pressure eventually developed. Consequently, high-current pulsing can be applied even to an almost fully charged battery provided the high current pulses are kept short enough. This is indicated by the three representative test results seen in Figs. 6–8.

The measured cells were almost fully charged. At 1 A constant-current charging the gas rate of the flooded lead/acid cells was approximately 8 ml/min. Charging with
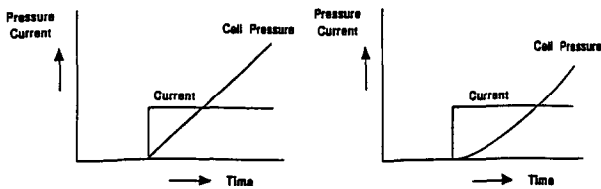

Fig. 5. Pressure and current development during step charging of battery at high state-of-charge (a) without hysteresis and (b) with hysteresis.
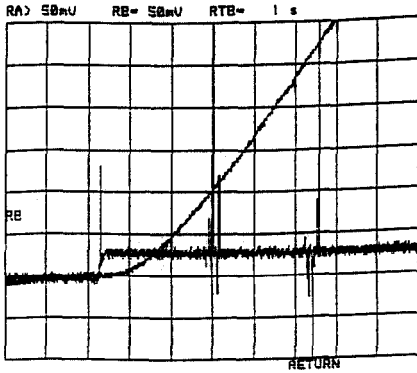
Fig. 6. Current and cell pressure development at 30 A charge current step.
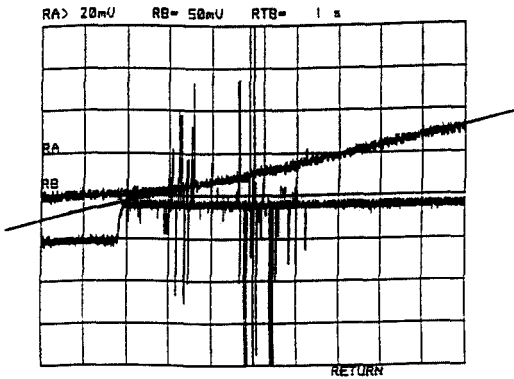

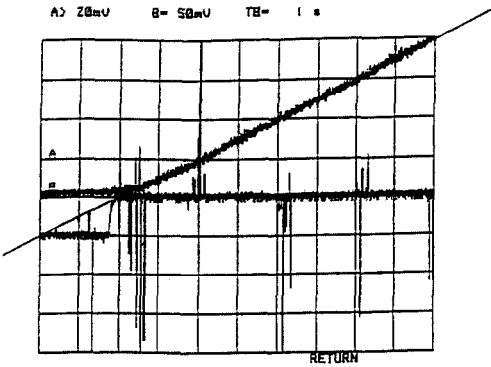Fig. 7. Current and cell pressure development at 40 A charge current step.

Fig. 8. Current and cell pressure development at 50 A charge current step.

30 A took more than 1 s for the gassing to reach terminal gassing rate. For 40 A current pulsing 0.5 s was needed and for 50 A current pulsing 0.3 s was needed. At 10 A pulsing 4 s were needed before the gas rate had stabilized. When the tests were

repeated at reduced state-of-charge, the time needed for the gassing gradient to stabilize increased.

Conclusions

The tests clearly show that a current step imposed on a lead/aid cell which is at an advanced state-of-charge causes the gassing reaction to set in with a time delay. This suggests that the gassing reaction sets in later than the charge reaction. The results further suggests that the time delay depends on the state-of-charge and on the amplitude of the current step. If a reduction of the current step to zero reinstates the conditions before the step, then this has important implications for the construction of a fast-charging algorithm that would allow high-current pulsing with variable frequency at an advanced state-of-charge, avoiding the high rate of gassing usually encountered during constant-current charging. The current reduction phase of charging which accounts for most of the charge time could be accelerated.

While known fast-charge algorithms are taking advantage of the high-charge acceptance during initial charging, when the battery is almost fully discharged, they need just as much time to fully charge the battery beyond the 85% state-of-charge as conventional charge algorithms. The phenomenon discussed in this paper could provide a significant cut in charge time that would supplement existing fast-charging algorithms during the particular charge phase where conventional charge algorithms can not accelerate charging.

Pulse charging has been investigated previously. However, it invariable is done with constant frequency not considering the need for adapting the frequency to the state-of-charge. Tests done at the EEPL indicate that, unless this condition is satisfied, pulsing can actually have a detrimental effect with respect to gassing.

This might be the reason why reports on the effect-of-charge pulsing offered different conclusions ranging from helpful to detrimental to battery life.

The success of the current-pulsing method depends on the restoration of the cell condition after the pulse. Therefore, a sufficiently long wait period or rest period is needed to allow equalization of the potential at the electrode surface/electrolyte interface. This is to ensure that the effect of the current pulse on the gassing reaction has ceased. The optimum length of the rest period, in terms of a fraction of the pulse lengths, has not been investigated. Initial tests have shown that a very short discharge pulse following immediately the charge pulse helps shorten the rest period.