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Summary

A detailed study of electrolyte concentration gradients within a commercial lead-acid battery showed that performance could be improved by disturbing the stratification which builds up during discharge-charge cycles. A simple, low-cost pumping device, which operates on pulsed air, without any moving parts was developed. A 96 V lead-acid traction battery was modified and tested at various temperatures. The performances of agitated and unagitated batteries are compared.

1. Introduction

In 1897, Liebenow [1] demonstrated that the poor utilization of active materials in lead-acid batteries during high current discharges is related to a sulfuric acid deficiency in the pore system of the electrodes. By passing electrolyte through a negative plate, he was able to triple the available capacity. Haebler et al. [2] studied the $PbSO_4$ distribution within partially discharged PbO₂ plates using a scanning X-ray microprobe technique and reported that a very small flow of sulfuric acid through the porous plate caused intense deformation of the PbSO₄ distribution, especially under high current load. Later, investigations of acid stratification in lead-acid traction batteries during charge-discharge cycles explained the flow of high density acid to the bottom of the cell [3] during charging. Premature battery failure was avoided by overcharging the batteries at elevated potential or using electrolyte mixing systems. Varta [4] and Globe Union [5] demonstrated that active material utilization, available discharge energy, and life time could be improved by maintaining an electrolyte flow in traction battery cells using inserted air lift pumps.

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In this work, flow visualization tests on a model battery were used to investigate flow patterns of a commercially available lead-acid battery and to design an effective pump system. After checking the techniques on a single 6 V battery module, a 96 V electric vehicle battery was modified to include a central air feed system and air lift pumps on 16 battery modules. Similar tests were performed on the unagitated and agitated 96 V battery. A performance comparison shows the advantages and the disadvantages of the two operating modes.

2. Characterization of the unagitated battery

A commercially available, 3 cell, 6 V ALCO 2200 battery (a golf cart battery commonly used by electric vehicles operators) was chosen as the testbed. Figure 1 shows a sectional diagram of the battery. The specific gravity of the electrolyte was measured simultaneously at the top and bottom of the electrolyte compartment while the test battery was cycled. These numbers were correlated with voltage and current. Figure 2 shows the data obtained during a 75 A galvanostatic discharge of the battery to 1.75 V/cell at 20 °C. It can be seen that the electrolyte concentration decreases faster in the top of the cell than in the bottom. After termination of the discharge, the concentration drops even further. This suggests that the rate determining step is the diffusion of sulfuric acid within the pores of the electrodes and through the tightly packed plate assembly.

Other investigations showed that the acid concentration in the pores drops to 3 mol/kg (1.16 g/ml, 25 °C) during discharge, whereas the electrolyte in the bottom of the cell maintains 5 mol/kg (1.24 g/ml, 25 °C) [6].

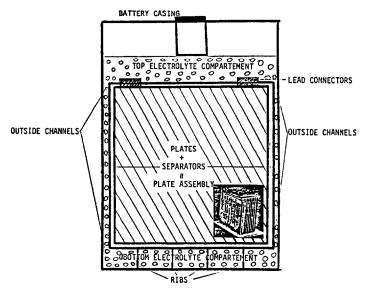


Fig. 1. Cutview of the lead-acid battery cell.

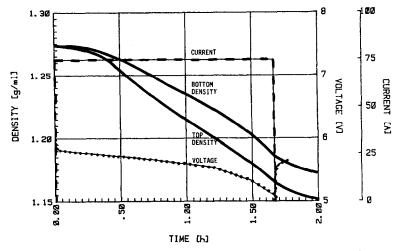


Fig. 2. Current, voltage and density curves of the unagitated test battery during discharge.

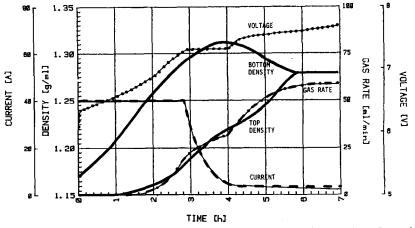


Fig. 3. Current, voltage, gas rate and density curves of the unagitated test battery during charge.

The non-uniformity in electrolyte concentration was more pronounced during charging (Fig. 3). Charging was done in three stages. The charge cycle began galvanostatically, at 40 A, until a temperature corrected cross-over voltage was reached. At this point, the charging became voltage-limited and continued in this mode until the current dropped to 6 A. The third and final phase involved charging at 6 A for a period of 3 h. The final phase is important in terms of disturbing the stratification that develops during charging (see Fig. 3).

Acid stratification causes a non-uniform current distribution [7] in the electrodes. The upper portions of plates in a stratified cell suffer from high current densities; the active material near the bottom suffers from concentrated acid. In an unagitated battery only gassing on overcharge removes the acid stratification with the penalty of low energy efficiency and reduced cycle life.

3. Methods of electrolyte destratification

3.1. Flow characteristics of the lead-acid test battery

The 19 plate test battery was modelled using acrylic plastic to visually determine the flow characteristics of the lead-acid battery and to investigate different pumping mechanisms. No separators were used for the optical tests and the electrodes were simulated by Plexiglass plates.

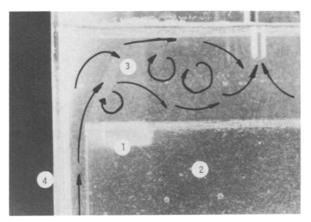


Fig. 4. Electrolyte is forced from bottom to top in a flow test. Flow lines indicate that the electrolyte moves upwards in the outside channels leaving the plate assembly unaffected [8]. 1, Lead connectors; 2, plate assembly; 3, top electrolyte compartment; 4, battery casing.

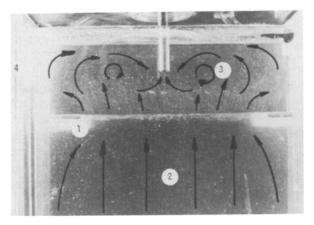
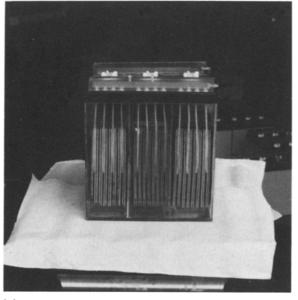
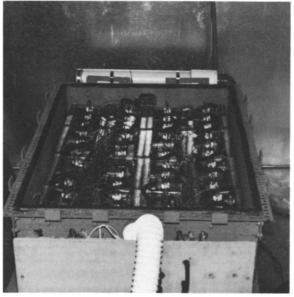


Fig. 5. Electrolyte is forced from bottom to top in a flow test. After clogging the outside channels, the electrolyte moves through the plate assembly [8]. 1, 2, and 3, as for Fig. 4.



(a)



(b)

Fig. 6. (a) Photograph of the air-lift pump installed into the outside channels of a test cell; (b) 96 V ALCO 2200 Retrofit battery in the test tray (air feed lines not shown).

Ink or special powder particles were used as tracers while an electrolyte flow was maintained from the top of the cell to the bottom or *vice versa*. The results of those tests were as follows [8, 9]:

(a) The ribs in the bottom of each cell (see Fig. 1) prevent efficient electrolyte mixing and should be perforated.

(b) The use of a pump to maintain an upward electrolyte flow in a cell with modified bottom ribs results in a uniform electrolyte concentration. Figure 4 shows that the main flow, however, travels in a channel created by the plate assembly and the battery casing (outside channels, see Fig. 1). Electrolyte circulation around the plate assembly removes any stratification in the cell but has little effect on the electrolyte concentration in the plate assembly and, as a consequence, does not improve the discharge performance significantly. Blocking the outside channels creates a flow through the plate assembly mixing the electrolyte in the porous electrode with the bulk electrolyte (Fig. 5).

3.2. Engineering design of the electrolyte mixing system

Analysis showed that an air lift pump system is the most inexpensive means to achieve electrolyte agitation [10]. It turned out, however, that it is not necessary to use thin plastic integrated air lift pumps like Varta [4] or Globe Union [5].

The air-lift pump described here is designed to make use of the channels at the small ends of the battery and simply pulse air into them (Fig. 6) [8, 10]. As shown in Fig. 7, air enters two acrylic manifolds that are mounted on the long sides of the battery cover. Twelve Teflon tubes are attached to

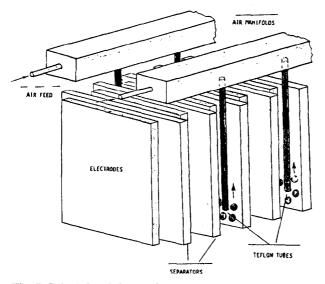


Fig. 7. Principle of the used air-lift pump (battery casing not shown).

each manifold. Each cell has eight air feed channels, four on each side, which are equidistantly spaced. The pump uses low pressure air pulses at 0.5 Hz. The air enters the pump channels through the tubes and rises to the electrolyte surface. The rising bubbles create an upward flow of the

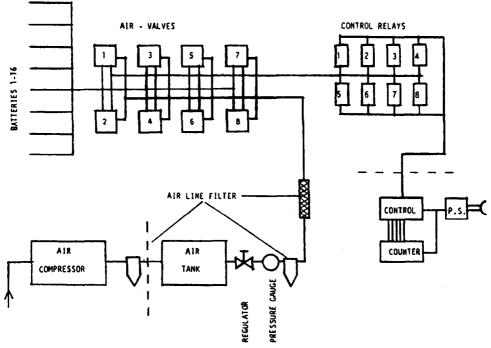


Fig. 8. The central air feed system design for the 96 V ALCO 2200 Retrofit battery.

electrolyte. Since two pumps are used for each cell (one at each end of the cell), the electrolyte rises at the cell ends and the back flow is forced down through the plate system. Sixteen test batteries were equipped with the pumps and will be referred to as ALCO 2200 Retrofit batteries. The bottom ribs of the batteries were not modified.

The central air feed system is shown schematically in Fig. 8. An air compressor supplies pressurized air to a tank. The air is distributed to the battery modules by eight solenoid valves which are connected in parallel to the main air feed line. The operation of the valves is electronically controlled so that the air supply feeds two modules at the same time. The air feed was 2.5 l/min per 6 V-module during the 120 A discharge and 1.5 l/min per 6 V-module during charging.

4. Test results and test analysis

The ALCO 2200 and the ALCO 2200 Retrofit battery were placed in an environmental chamber and charge-discharge cycles were obtained at different temperatures. The 120 A constant current was terminated whenever the first module voltage dropped below 5.08 V (1.69 V/cell). The charge schedule consisted of an initial 40 A constant current phase until a temperature corrected cross-over voltage was reached [11, 12]. The

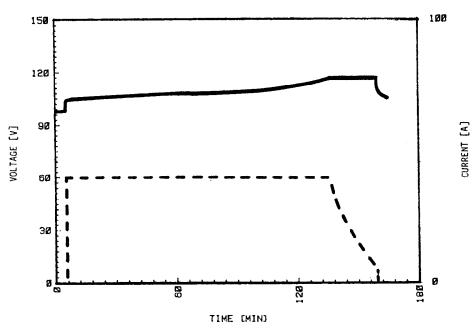


Fig. 9. Charge schedule for the ALCO 2200 Retrofit battery.

unpumped battery was then charged at constant potential until the current tapered down to 6 A, and charging was terminated after a gassing phase (3 h constant 6 A current) (see Fig. 3). The retrofit battery was charged with 40 A constant current and the cross-over voltage was maintained until the current tapered down to 5 A, where charging was terminated (Fig. 9).

4.1. Discharge capacity and energy performance comparison between the ALCO 2200 and the ALCO 2200 Retrofit battery

Figure 10 shows the discharge energy for the agitated and unagitated batteries at various operating temperatures. At temperatures below 20 °C, the ALCO 2200 battery performs better without electrolyte mixing. The reduced capacity of the ALCO 2200 Retrofit (when compared with the standard ALCO 2200 at low temperatures) is thought to be due to the fact that the forced flow moves the warm electrolyte away from the electrode surface where the chemical reaction takes place [12]. The warmer electrolyte from the plate assembly is mixed with substantial quantities of cold electrolyte from the bottom and top electrolyte which cools the electrodes. Evidence for this behavior can be found in Fig. 11 where the temperature increase during discharge is shown for both batteries. The graph shows that, at low temperatures, the top electrolyte compartment of the ALCO 2200 Retrofit battery is about 1 °C warmer than the ALCO 2200.

Figure 10 shows that, at temperatures above 20 °C, the discharge performance of the agitated ALCO 2200 Retrofit is superior to the performance

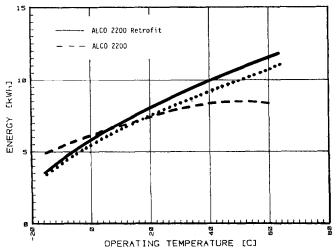


Fig. 10. Discharge energies for the ALCO 2200 and the ALCO 2200 Retrofit battery. (..... ALCO 2200 Retrofit including pump energy.)

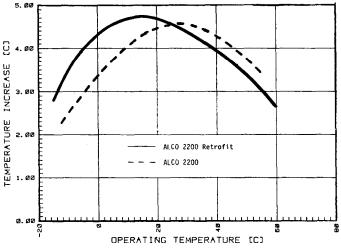


Fig. 11. Temperature increase during the 120 A discharge of a 96 V ALCO 2200 and an ALCO 2200 Retrofit battery.

of the unagitated battery. The discharge energy gain increases linearly with the temperature and, at 60 °C, the energy gain of the agitated battery was found to be 38% (Fig. 12). Taking into account the energy which was used to operate the pump system, the overall discharge energy gain at 60 °C was 25%.

Constant current discharge tests of the test battery were performed in the laboratory and in a moving van in stop and go traffic [10] to determine the necessity of electrolyte agitation during discharge. It turned out that acceleration and deceleration created a sloshing motion which appeared as a 15% discharge energy increase at 35 °C (75 A discharge to 1.75 V/cell).

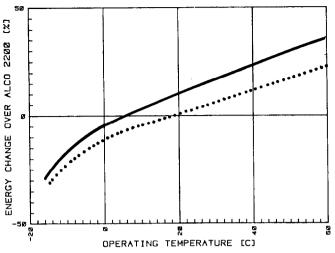


Fig. 12. Change in discharge energy of the ALCO 2200 Retrofit battery over the ALCO 2200 battery. (...... Energy change including the pump energy.)

These tests suggest that vibration of the batteries in an electric vehicle raises the available battery energy above the level found in the vibration free conditions of the laboratory. Driving an electric vehicle in stop and go traffic enhances electrolyte destratification by diffusion and convection. The use of the air pump system during the discharge of the batteries in an electric vehicle would not have a significant effect on the available discharge energy.

4.2. Comparison of the charge behaviour and efficiencies of the ALCO 2200 Retrofit and the ALCO 2200 battery

Comparing the charge schedule for the ALCO 2200 Retrofit battery (Fig. 9) with the charge schedule for the ALCO 2200 battery (Fig. 3), it can be seen that no trickle charging is needed at temperatures above 0 $^{\circ}$ C for the agitated battery. This cuts the charge time in half (Fig. 13). As a consequence, the water loss in the ALCO 2200 Retrofit battery is far smaller than in the ALCO 2200, and battery maintenance is reduced.

In consequence of the improved performance of the agitated battery during charging, energy losses due to heat (Fig. 14) and gassing are reduced. Therefore, the overall energy efficiency of the agitated battery is higher than that of the unagitated battery [13]. Figure 15 also shows the efficiency of the agitated battery when the air compressor energy consumption is incorporated. This system has not, however, been optimized in terms of auxiliary power consumption.

Other investigators [4] showed that reduced gassing has an impact on battery life, and acid circulation extended the cycle life of lead-acid batteries (Fig. 16). Investigations of the effect of cycling on the microstructure of ALCO-2200 batteries with, and without assisted electrolyte circulation

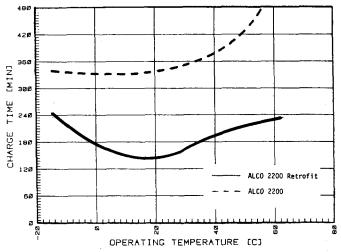


Fig. 13. Charging times for the ALCO 2200 and the ALCO 2200 Retrofit battery at various operating temperatures.

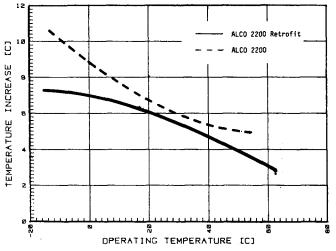


Fig. 14. Temperature increase during charge of a 96 V ALCO and a 96 V ALCO 2200 Retrofit battery.

proved that pumping increases the cycle life of the ALCO 2200 Retrofit over the ALCO 2200 battery [14]. The capacity of the ALCO 2200 battery dropped from 110 A h to 100 A h at 40 °C within 180 cycles. The ALCO 2200 Retrofit capacity increased to 120 A h at 40 °C in early cycles; after 300 cycles the capacity remained around 100 A h. Even after over 400 cycles, the ALCO 2200 Retrofit battery maintained a capacity of 95 A h. These tests indicate that the installation of an electrolyte agitation device will double the life time of the ALCO 2200 battery.

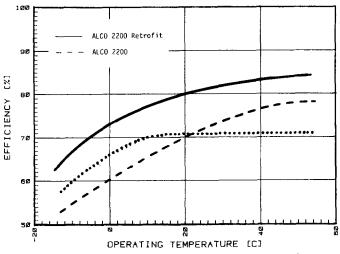


Fig. 15. Energy efficiencies for the ALCO 2200 and the ALCO 2200 Retrofit battery. (..... Pump energy included.)

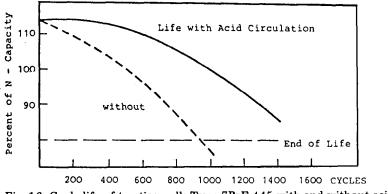


Fig. 16. Cycle life of traction cells Type 7PzF 445 with and without acid circulation [4].

5. Conclusions

The removal of acid stratification in lead-acid batteries by the use of an air lift pump system was demonstrated successfully.

The agitated ALCO 2200 Retrofit battery showed an improved discharge performance at temperatures above 20 °C. At temperatures below 20 °C, the electrolyte flow removes the heat developed at the electrode surface and causes a decrease in discharge energy over the unagitated battery version. Investigations of the effect of vibrations in a moving vehicle on the discharge performance of lead-acid batteries also showed an increase in available discharge energy. Therefore, the use of the air lift pumps during electric vehicle operation would not extend the range of the electric vehicle significantly. The benefits of the electrolyte mixing system are: a reduction of water loss during charging, the reduced charge time, and the increased energy efficiency. Taking into account the energy which is needed to operate the pump system, the efficiency is still comparable with that obtained with the unagitated battery. The agitated battery shows a significant increase in life cycles and should be considered for application in recharging of deep cycle lead-acid batteries.

Acknowledgements

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