

Short Communication

Continuous monitoring of acid stratification during charge/discharge by holographic laser interferometry

C.W. Chao^a, S.P. Lin^a, Y.Y. Wang^a, C.C. Wan^a, J.T. Yang^b

^a Department of Chemical Engineering, Tsing-Hua University, Hsin-chu, Taiwan, ROC

^b Department of Power Mechanical Engineering, Tsing-Hua University, Hsin-chu, Taiwan, ROC

Received 10 November 1994; accepted 16 December 1994

Abstract

The change in the acid concentration in the vertical direction in a lead/acid battery is monitored continuously during charge/discharge cycling by means of a holographic laser interferometry method. It is found that there is a difference in the acid distribution in the upper and lower parts of the electrolyte due to uneven reaction speeds and acid movement by natural convection. This causes an interesting re-emergence of an uneven distribution during the interval between charge and discharge.

Keywords: Lead/acid batteries; Acid stratification

1. Introduction

Uneven distribution of electrolyte in the vertical direction is very common in lead/acid batteries. It is particularly serious with large batteries and is usually referred to as 'acid stratification'. The acid concentration in the lower region is found to be significantly higher than that in the upper region [1,2]. It has also been shown that the concentration difference increases as charge/discharge cycles proceed [3].

Early determinations of electrolyte stratification [4,5] involved taking electrolyte samples from different vertical locations in the cell and then measuring the acid concentration. This method, however, unavoidably disturbs the fluid pattern and thus affects accuracy. It is difficult to conduct in situ monitoring. Nevertheless, Eklund and co-workers [6–8] successfully developed a new method to measure the changes in acid concentration. This made use of holographic laser interferometry (HLI). Most of the work reported was focused on a single charge or discharge process, and obviously this is quite different from the continuous cycling process that is commonly encountered in practice. The objective of the studies reported here is to employ the HLI technique to measure the variation in acid stratification during repeated charging and discharging duty.

2. Experimental

2.1. Cell preparation

In order to ensure that the electrodes were of uniform quality, industrially manufactured plates were used as test samples (Pailo Co., Taiwan). The dimensions of the plates were: 12.4 cm × 2.8 cm and 0.2 cm. One positive was positioned between two negatives with no separator in between. The inter-electrode distance was controlled at 0.3 cm. De-ionized water and reagent-grade sulfuric acid were used to prepare the electrolyte. The cell container was made of glass.

The electrodes were first electroformed in 10 wt.% sulfuric acid for 48 h. Then, the initial electrolyte was replaced by a 30 wt.% acid. After waiting for 48 h to allow the acid to penetrate into the porous electrodes, the cell was charged at 5 mA cm⁻² for 8 h. The cell was then switched to discharge. The discharge current was controlled at 4.6 mA cm⁻².

2.2. Concentration measurement

The basic principle of the HLI approach to measuring the acid concentration is to calculate the concentration difference between two consecutive fringes from the photograph [9] as given by the following equation:

$$k\lambda = (n_{k+1} - n_1)d \quad (1)$$

where d is the path length (in metres) of light; λ is the wavelength (in metres); n_1 is the acid refractive index at the first interference fringe; n_{k+1} is the refractive index as the $(k+1)$ fringe. The refractive index is directly related to the acid concentration. In the system used here, a He–Ne laser was used as the light source and the concentration difference between two adjacent fringes was ~ 2.6 mM. The experimental arrangement of the HLI system was similar to that reported by Ekund and co-workers [7].

2.3. PbO_2 measurement

The PbO_2 content in the positive was determined by the iodine titration method. The change of PbO_2 content served as a measure of the effect of acid stratification.

3. Results and discussion

The change in the acid concentration was determined continuously. The monitoring region is around the central position of the cell which, theoretically, should provide an average pattern of the overall acid distribution. In this work, the process is divided into five stages.

(i) First half of charging period

In this period, the charging efficiency is generally fairly high with little gas evolution. The results are shown in Fig. 1 (a) to (c). It can be seen that the stratification becomes more obvious and serious as charging proceeds. The upper part of the positive electrode is more favoured to undergo reaction than the lower part. This is due to the lower ohmic resistance in the upper region. In turn, this uneven reaction distribution results in uneven acid generation that makes the concentration change more apparent. The large amount of acid generated in the upper region tends to sink to the bottom until the concentration difference reaches a critical point and induces a seemingly steady state.

Table 1 shows the change of PbO_2 content at the top and bottom parts of the electrode during charging. It is clear that after charging for 1 h, the amount of PbO_2 formed at the top of the plate is significantly larger than that at the bottom. This is consistent with previous result and explanations.

Table 1
Change in PbO_2 content (wt.%)

Location	Before charging	After charging for 1 h
Top	21.7	40.1
Bottom	18.7	30.9

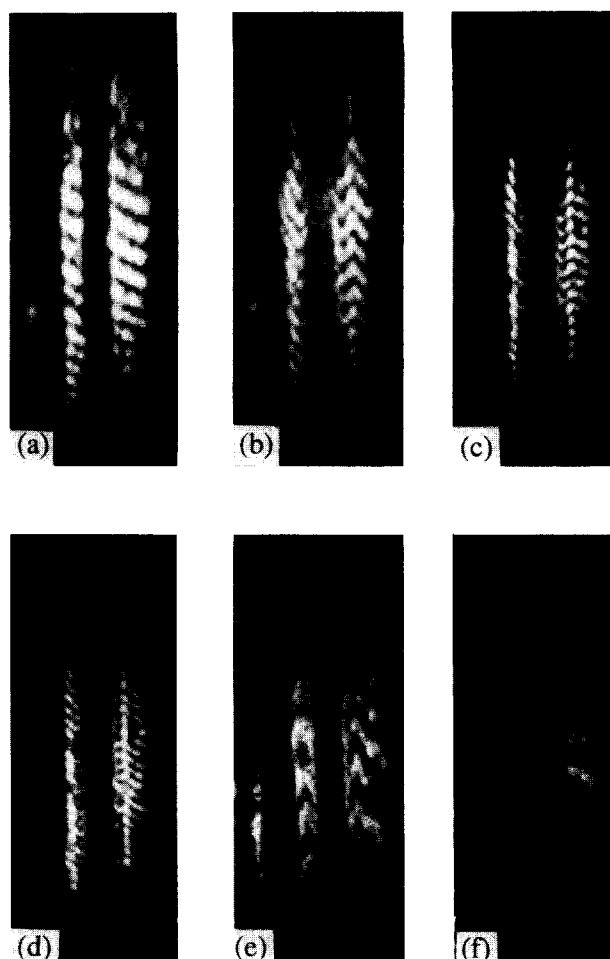


Fig. 1. Acid concentration distribution during charging. Monitor location: central region. Time (in min): (a) 0, charge initiated; (b) 5; (c) 60; (d) 180; (e) 300, and (f) 390, end of charge.

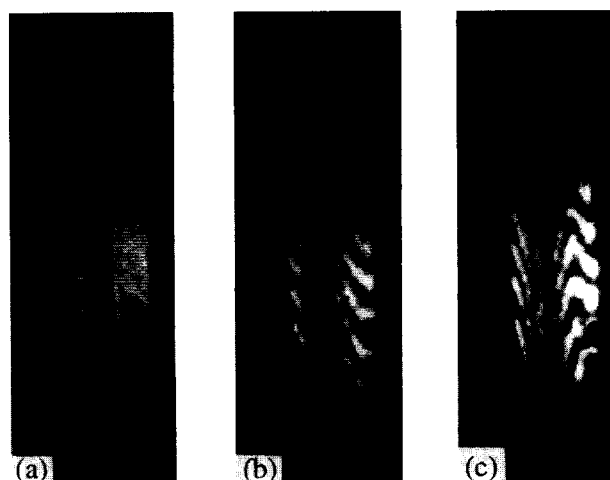


Fig. 2. Acid distribution in interval between charge and discharge. Monitor location: central region. Time (in min): (a) 0; (b) 1, and (c) 10.

(ii) Second half of charging period

During this period, gas bubbles generated from the electrode became apparent. These bubbles tend to agitate the electrolyte and reduce the stratification phenomena, as shown in Fig. 1 (d) to (f). Hence, the stratification phenomenon is most serious mid-way through a full-charging process.

(iii) Interval between charging and discharging

Once the charging is stopped, the originally quite uniform distribution of acid, that was caused by gas agitation, became non-uniform again, as shown in Fig. 2 (a) to (c). This result is quite remarkable and has only been rarely mentioned. At first, it was suspected that the phenomenon is due to insufficient gas agitation. It was later proved, however, that both 10% and 100% overcharge produce the same result. Hence, the re-emergence of acid stratification is not related to the degree of overcharge.

The monitoring position was shifted from the central region to the bottom region of the cell. It was found

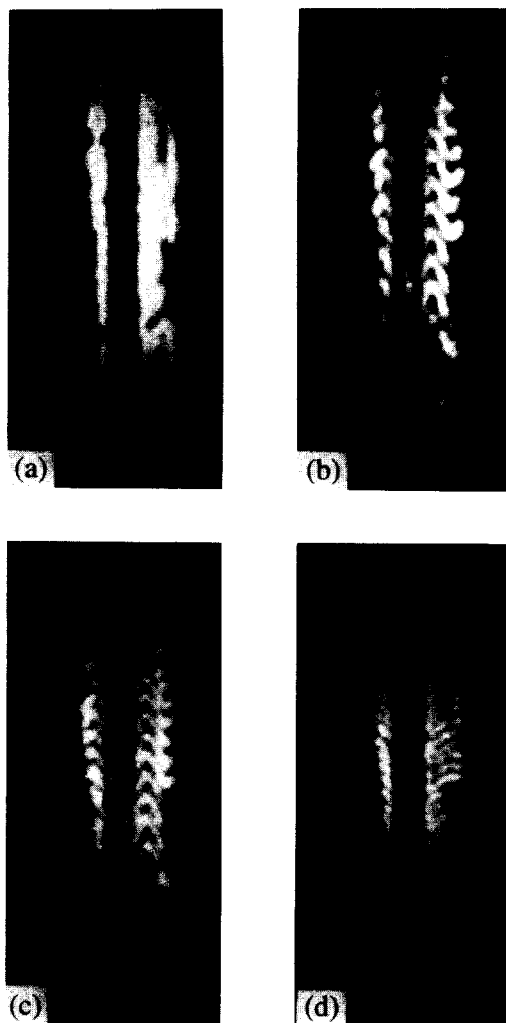


Fig. 3. Acid distribution during charging and monitored at the bottom region of cell. Time (in min): (a) 0; (b) 30; (c) 120, and (d) 420.

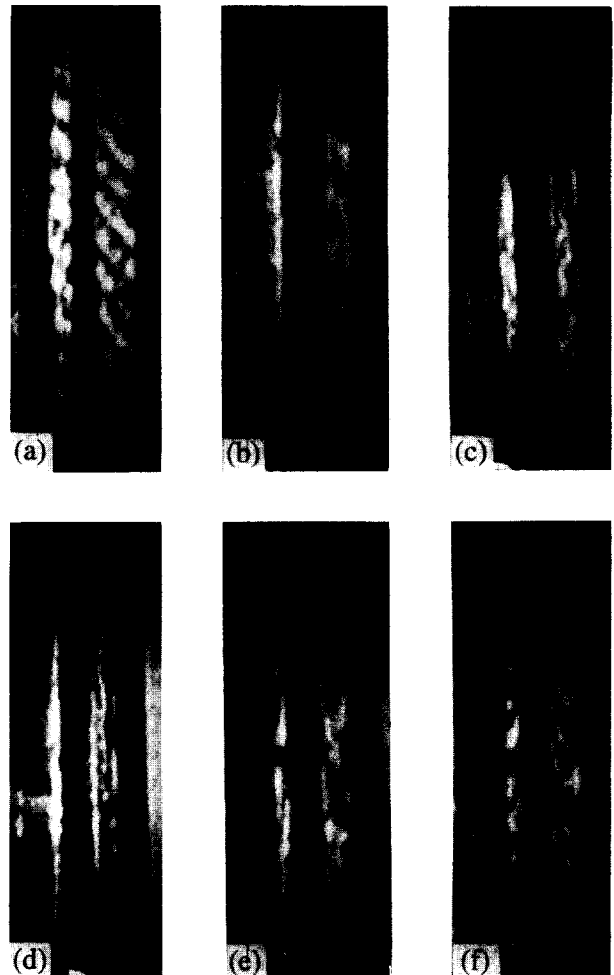


Fig. 4. Acid distribution during discharging process. Monitor location: central region. Time (in min): (a) 0; (b) 10; (c) 60; (d) 90; (e) 240, and (f) 360.

that the acid distribution here varied differently from that observed in the central region. The results are given in Fig. 3 (a) to (d). Clearly, the uneven distribution becomes increasingly more serious from the beginning to the end of charging. This indicates that the gas evolution which is apparent during the second half of charging is effective only in the upper part of the cell. There is little electrolyte agitation due to gas evolution near the bottom of the cell. Hence, prolonged overcharging has little effect on the acid distribution in the lower part of the cell. This creates an unsteady state near the end of charging, namely, uniform acid distribution in the upper part and non-uniform distribution in the lower part. Once the charging stops, the gas agitation also stops. The uneven acid distribution naturally progresses upward to reach an equilibrium.

(iv) First part of discharge

The results of this period are presented in Fig. 4 (a) to (c). The acid distribution becomes more uniform as the discharge proceeds. It appears that the high content of acid stored in the lower part of the cell

Table 2
Change in PbO₂ content (wt.%)

Location	Before discharging	After discharging for 1 h
Top	80.4	74.1
Bottom	73.9	52.8

facilitates the discharge process although the lower part of the electrode suffers a larger ohmic resistance than the upper part. The change in PbO₂ in the two regions also supports this statement: the amount of PbO₂ reacted at the bottom is much larger (Table 2).

(v) Second half of the discharge

In this period, the uneven distribution reappeared, as demonstrated in Fig. 4 (d) to (f). This is because near the end of discharge, the upper part becomes the major reaction region under a constant-current discharge operation, as the active material in the lower part is almost totally consumed. This causes a faster consumption of the acid in the upper than in the lower part and, consequently, a higher acid concentration is induced near the bottom and an uneven acid distribution develops.

If the discharge stops at stage (iv), i.e., at a low depth-of-discharge, there is little acid stratification. The uneven acid distribution becomes serious only under deep-discharge operation. This may be one of the reasons why the cycle life of a battery is closely related to the depth-of-discharge.

4. Conclusions

During charging, the upper part of the plate is favoured and quickly reaches full charge. The gas generated tends to reduce the uneven acid distribution. By contrast, the bottom region does not enjoy the benefit of gas agitation and uneven distribution becomes more serious throughout the process.

During discharging, the lower part is the first to undergo reaction and this makes the acid distribution more uniform. When the upper part becomes the major reaction zone, uneven distribution appears.

The lower part of the electrode is more difficult to charge and tends to discharge first. Hence, after repeated cycling, it gradually forms inactive crystals of lead sulfate that are not convertible.

References

- [1] H. Bode, *Lead-Acid Batteries*, Wiley, New York, 1977.
- [2] K. Tomantschger, *J. Power Sources*, 13 (1984) 137.
- [3] A.D. Turner and P.T. Moseley, *J. Power Sources*, 9 (1983) 19.
- [4] W.G. Sunu and B.W. Burrows, *J. Electrochem. Soc.*, 128 (1981) 1405.
- [5] W.G. Sunu and B.W. Burrows, in J. Thompson (ed.), *Power Sources 8*, Academic Press, 1981, p. 606.
- [6] A. Eklund, F. Alavyoon, D. Simonsson, R.I. Karlsson and F.H. Bark, *Electrochim. Acta*, 36 (1991) 1345.
- [7] F. Alavyoon, A. Eklund, F.H. Bark, R.I. Karlsson and D. Simonsson, *Electrochim. Acta*, 36 (1991) 2153.
- [8] A. Eklund and R.I. Karlsson, *Electrochim. Acta*, 37 (1992) 681.
- [9] R.H. Muller, *Advances in Electrochemistry and Electrochemical Engineering*, Interscience, New York, Vol. 9, 1973, p. 281.