



Dependence of Lead Acid Battery Performance on Electrolyte Stratification and Electrolyte Agitation

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Abstract

Lead acid battery is the most successful storage battery developed, its main application being in the automotive field. Despite its great versatility, storage characteristics and high degree of reversibility, it suffers from loss of water, stratification of electrolyte, grid corrosion, degradation of the active material etc. application of lead acid battery to electric vehicles and other repetitive deep cycle services produces an undesirable state in the cells of the battery known as electrolyte stratification. This is with the changes of the specific gravity of the sulphuric acid associated with the concentration changes during charge and discharge. It causes severe problems such as decrease in capacity and life in case of lead acid battery. Overcharging of the battery has been found to minimize the problem of stratification to some extent, but leads to deleterious effects. Hence, efforts have been made to design a simple and low power consuming electrolyte circulation system. Many researchers have tried and reported their results. In this paper, the authors present a detailed review regarding the consequences of electrolyte stratification on battery life and its capacity, about the methods employed to minimize its effect and also the results of the work.

Keywords: Lead acid battery, cycling, acid stratification capacity and life.

Introduction

The wide use of the lead acid batteries in many designs, sizes and system voltage is accounted for by the low price and ease of manufacture of the battery system. The lead acid battery is almost always the least expensive storage battery for any application, providing good performance and life characteristics. In view of the current interest in electric vehicles as a means of conserving oil reserves and the fact that the lead acid battery is the only system available for motive power, a high level of support for lead acid battery research and development has been received. Research of the lead acid battery was directed along the following lines – improvement of the utilization of the active material, which is far below the theoretical limits at present, improvement of the cycle life and

reduction of the maintenance expenditure by developing peripheral equipment. To achieve this, continued effort in these areas are being employed. Electrolyte stratification is one of the most important problems in static electrical storage. Charging process in lead acid battery causes this typical multi-layer configuration as sulfuric acid density. Since the density of sulfuric acid is greater than that of water, as and when sulfuric acid is formed it starts moving down resulting in concentration gradient. Electrolyte stratification is best defined as the development of a vertical concentration gradient of sulfuric acid within the cell container height.

Only very recently, was the focus on the effect of agitation of electrolyte received any attention though the problem was defined well back in 1897. Acid stratification is disadvantageous for lead-acid cells since it causes inhomogeneous current distribution and non-uniform utilization of the active materials. These lead to reduced efficiency and performance of lead acid battery. These effects could be avoided by agitation.

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Employment of overcharging method was found to be detrimental for the cell because of the elevated corrosion and shedding rate of the positive active material hence, efforts are made to design a simple and low power consuming electrolyte circulation system. The overall goal in the design of the electrolyte circulation system is to achieve mixing of the electrolyte by retaining the isolation of electrolyte by not removing or introducing electrolyte from one cell to the other.

H.Tuphorn [1] has noticed severe stratification effects in flooded cells of 55 cm height and observed that this affects the negative plates, which are prone to sulphation when working too high an acid concentration at the bottom.

E.Voss and W.Kappus [2] explain the flow of high-density acid to the bottom of the cells of traction batteries during discharge – charge cycles. In the case of flooded traction batteries overcharging by 10 to 20% per cycle has been recommended as a remedy against stratification [3]. During overcharge, the evolved gases exert a pumping action thereby equalizing the acid concentration. Hence, it was first understood that the gas evolution during overcharge was the efficient method of overcharge was the efficient method of combating electrolyte stratification. However, overcharging results in an increased water loss, corrosion of positive grid and generation of heat. In order to facilitate the mixing of acid use of air-lift pumps has been in common use for many years in submarine [4] batteries, load leveling applications [5], batteries for electric vehicles (EVs) [6] and also for solar applications. By inserting airlift pumps to maintain an electrolyte flow in traction battery cells, E.Voss [7], J.Pierson and C.Weinlein [8] demonstrate that active material utilization, available discharge energy and life time could be improved.

Sunu and Burrows [9] have investigated the effects of electrolyte stratification in 400 Ah traction batteries during cycling. As the number of cycles increases they have noticed an enhancement of stratification indicating the accumulation of concentration changes. Based on calculations they report the extent of stratification to be 0.15 specific gravity. They have noted that for each 0.01 specific gravity. They have noted that for each 0.01 specific gravity unit of stratification, there is a decrease in capacity by 1% and this capacity loss very much depends on the depth of the depth of discharge (DOD) and charge – discharge coefficient. Sunu and Burrows have also observed that equalization of electrolyte concentration through free consuming process and hence imposed a forced equalization of the acid concentration through gas lift stirring by overcharging.

D.Barrett [10] et al have performed tests on electric vehicle batteries by subjecting them to EV duty cycles ad report that

forced stirring of the electrolyte increase the rate of shedding of active material.

Klaus Tomantscheger [11] has designed an effective pump system and investigated the flow patterns of the electrolyte in commercially available lead acid batteries. A comparison in the performance among the agitated and unagitated batteries reveals that there is a faster decrease in the top than at the bottom of the cell. It is also pointed out that there is an improved discharge performance at temperatures above 20°C in the agitated battery, however, below 20°C the agitated batteries exhibit a decrease in discharge performance over unagitated batteries and it is attributed that in agitated batteries the heat developed at the electrode surface is removed by the flow of electrolyte at low temperatures. It is concluded that considering the energy needed for operating the pump system, the improved performance observed in agitated system is still comparable with that obtained in the case of unagitated system. The overall view is that agitated batteries however show significant increase in life cycles.

Doria et al [12] have studied the effect of electrolyte flow on the performance of a lead acid cell by employing a magnetic pump. It is reported that the stratification in non-circulating system causes an inhomogeneous mass distribution, voltage gradient and capacity reduction while circulating system results in homogeneous mass distribution thereby increasing the capacity. It is pointed out that the electrolyte circulation provides and improved performance, about 20% higher efficiency. It is observed that a higher efficiency. It is observed that a favorable effect could be obtained from electrolyte circulation in batteries which are regularly cycled without being deeply discharged thereby preventing damage from a substantial low state of charge.

Based on their inspiration from research conducted on premature capacity loss (PCL) in lead acid battery [13-16], L.Apateanu, et al have monitored the extent of stratification in an EV battery by subjecting it to a repetitive deep discharge cycling and explain the relationship between capacity loss and electrolyte stratification. Also, they have reported the results of a more detailed study of stratification experienced by cells based on antimony free positive plate grids and antimony containing cells. It is observed that the capacity loss begins very early in the cycle life and it is more severe for Pb-Ca than for Pb-Sb alloys. It is also reported that the antimonial cells maintain a higher discharge capacity while there is a decrease in capacity in Pb-Ca cells and remains at a lower level for much of the remainder of the service life. However, it is noted that within life. However, it is noted that

within approximately 20 discharge-charge cycles the electrolyte in both the cells become markedly stratified.

K.Higashimoto et al [17] have investigated the effects of stratification in a stationary sealed lead acid battery during the life pattern of recharging after a deep discharge. The test batteries are of 200 Ah capacity using plates with heights of 140, 220, 440 and 660 mm and employ a non-woven fabric composed mainly of minute glass fibers for electrolyte retention as well as separator. It is demonstrated that during cycling the stratification makes a large difference in the electrolyte specific gravity and also a great amount of lead sulphate is produced in the lower parts of the plates resulting in a decreased battery capacity. It is observed that with the increase in height of the plates there is an increase in the extent of stratification. It is concluded that the tendency for stratification in a sealed type battery is very much similar to that of a flooded cell.

Liebenow [18] has explained the relationship existing between the poor utilization of active materials in lead acid batter during high current discharges and sulfuric acid deficiency in the pore system of the electrodes. By passing the electrolyte through a negative plate, it is reported that the available capacity could be increased thrice. Using a scanning X-ray microprobe technique, Haebler et al [19] have studied the lead sulphate distribution within the partially discharged lead dioxide plates. Their results show that a very small flow of sulphuric acid through the porous plate causes intense deformation of the lead sulphate distribution particularly under high current load.

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References

1. H.Tuphorn, 'Advances in Lead Acid Batteries', *The Electrochemical Soc.*, Pennington, NJ, (1984) 441
2. E.Voss and W.Kappus, Recent Lead acid Research at Varta, Progress in Batteries and Solar Cells, Vol4, JEC Press, Cleveland, Ohio, (1982) 187
3. D.Berndt Maintenance-free Batteries, Research Studies press, John Wiley & Sons, (1997) 145
4. N.E.Bagshaw, 'Batteries on Ships', Research Studies Press, John Wiley & Sons, (1982) 106
5. G.D.Rodriguez, W.C.Spindler and D.S.Carr, *J. Power Sources*, 31 (1990) 311
6. K.R.Bullock, B.K.Mahato, G.H.Brilmeyer and GLWierschem "Advances in Lead Acid Batteries", the *Electrochem. Soc. Proceedings*, Vol. 84-14, 451
7. E.Voss, Recent Advances in Lead Acid Cell Research and Development, Electric Vehicle Exposition, EVE 80, Adelaide, Australia, August 26-29 (1980) Conference papers 161-198.
8. J.Pierson and C.Weinlein, J. Thompson (Ed), *Power Sources 9*, Academic Press, London and New York (1983)
9. W.G.Sunu and B.W.Burrows, J. Thompson (Ed), *Power Sources 8*, Academic Press (1981) 601
10. D.Barret, M.T.Frost, J.A.Hamilton, K.Harris, J.F.Moresby and D.A.J.Rand, ILZRO Project No: LE-290, International Lead Zinc Research Organization, Progress report Ni:2, Dec. 1, 1979-July 15, 1980
11. Klaus Tomantschger, K.E. Johnson Environmental and Energy Center, University of Alabama, Huntsville, J. *Power Sources*, 13 (1984) 137
12. J.Doria, M.C.DEAndrest C.Armenta, *J. Power Sources*, 22 (1988) 115
13. K.K.Constanta, A.F.Hollenkamp, A.M.Huey & DAJ Rand, ILZRO Project Le-371, Progress Report No.2, CSIRO Division of Mineral Products, Melbourne, Commun, July (1991) 1-28
14. K.K.Constanta, J.A.Hamilton, A.F.Hollenkamp, A.M.Huey and L.H.Vu, ILZRO Project LE-371, CSIRO Division of Mineral Products, Melbourne, Commun, Jan (1992) 1-68
15. A.F.Hollenkamp, M.J.Koop, A.M.Huey, K.Constant, J.A.Hailton, L.Apateanu and L.H.Vu, ILZRO Project: 371, CSIRO Division of Mineral Products, Melbourne, Commun, Aug (1991) 1-58
16. A.F.Hollenkamp, M.J.Koop, L.Apateanu, CSIRO Division of Mineral Products, Melbourne, Vic, 3207 (Australia), *J. of Power Sources*, 46 (1993) 239-250.
17. K.Higashimoto, A.Miura, t.Hayakaw & A.Komaki, *Prog. Batt. Sol Cells*, 8 (1989)
18. C.Liebenow, *Z.Electrochem* 4 (1897) 61
19. H.Haeblear, P.Panesar and E.Voss, *Electrochim Acta*, 15 (1970) 1421.