Research Article

Venkateswarlu M*, Balusamy T, Murthy K S N, Jagadish M, and Vijayanand S

# Effect of magnesium sulfate on the electrochemical behavior of lead electrodes for lead acid batteries

https://doi.org/10.1515/eetech-2018-0007
Received Mar 23, 2017; accepted Oct 05, 2018

**Abstract:** The lead acid battery technology has undergone several modifications in the recent past, in particular, the electrode grid composition, oxide paste recipe with incorporation of foreign additives into the electrodes and similarly additives added in the electrolytes to improve electrical performance of the lead acid battery. In this paper, the electrochemical behavior of the lead electrodes with different weight/volume percentages (wt./v%) of $MgSO_4$ (0.0., 0.5., 1.0., 2.0., and 5.0) added into the electrolyte have been investigated with cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). The CV profile showed better redox behavior of the lead electrodes which was attributed to the increased active surface area of the electrode. Further studies of the gas evolution found a mixed trend and a considerable drop in the impedance as observed by LSV and EIS analysis as compared to the blank electrolyte solution. The influence of a modified electrolyte on the electrochemical activity of the lead electrodes is correlated and discussed.

## 1 Introduction

The dc power source has been in great demand for automotive, consumer and industrial applications [1]. Lead acid batteries are the most promising power sources in terms of reliability, safety and also economy among all commercial batteries in the market. However, some newer applications like renewable, stop and start, hybrid, electric vehicles, etc. require batteries with superior performance of charging efficiency (CE) with enhanced life cycle (ELC). The improved version of battery is in demand for the mentioned applications because of usage pattern and operating environment conditions. One of the reasons for inadequate charging of the lead acid battery is the accumulation of lead sulfate in the negative electrode and subsequent sulfation of the electrode meaning that the lead sulfate crystals become too large. Efforts were made to control the size of the lead sulfate crystals with the help of organic and inorganic additives in the expander formula of the negative electrode of the lead acid battery [1].

To improve further the battery parameters like capacity, charge acceptance, cold cranking performance, cycle life, etc., several additives in the electrode and electrolyte have been tested [2–11]. Some of the additives like sulfates of sodium, magnesium, aluminum, iron, etc., and acids such as oxalic acid, tetracetic acid, succinic acid, boric acid, etc., into the electrolyte have shown specific advantages on the performance and life of the lead acid batteries [3–5]. A water-soluble poly-aspartate (PASP) polymer into negative electrode and also to the electrolyte was found to be beneficial even under high rate partial state of charging (HRPSoC) of the battery, attributed to control/modification of lead sulfate crystal size and shape [6–8]. Recently, ionic liquids were considered as an effective additive in the electrolyte which obviously enhances the rate of conversion of the lead sulfate to the lead dioxide and vice versa [9].

The effective conversion of active material prevents the formation of hard lead sulfate crystals which in turn improves rechargeability and also enhances the cycle life of the battery. There are reports on different metal ion effects in the electrolyte pertaining to influence on the performance of the lead acid batteries [10, 11]. However, electrochemical study of the lead electrodes in the magnesium sulfate-containing electrolyte solution is of interest for practical applications. Therefore, an attempt has been made to study the effect of magnesium sulfate in the blank

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***Corresponding Author: Venkateswarlu M:** Technology Centre, Amara Raja Batteries Ltd., Karakambadi – 517 520, Andhra Pradesh, India; Email: mvu@amararaja.co.in; Tel.: +91-877-2265000 Extn. 7682; Mobile: +91-9985738746 and Fax: +91-877-228600
**Balusamy T:** Department of Applied Chemistry, Sri Venkateswara College of Engineering, Sriperumbudur – 602 117 Tamil Nadu, India
**Murthy K S N, Jagadish M, Vijayanand S:** Technology Centre, Amara Raja Batteries Ltd., Karakambadi – 517 520, Andhra Pradesh, India

electrolyte solution on the electrochemical behavior of the lead electrode for lead acid battery.

# 2 Experimental

The electrochemical behavior of the lead electrode has been investigated in the modified electrolyte with magnesium sulfate at ambient conditions. The lead (Pb) samples were prepared by polishing with SiC coated abrasive papers of different grades (800, 1200, 2000 grit size) to obtain mirror finishing. The resultant samples were washed with de-ionized water followed by ethanol and then dried. The electrochemical studies were carried out using a three electrode cell system consisting of pure lead (working electrode), a platinum foil (counter electrode) and a saturated calomel electrode (SCE) (reference electrode). All the three electrodes were arranged in a customized flat type cell and design was made such that one sq. cm area of the working electrode (pure lead) was exposed to the electrolyte solution. Different percentages (wt./v%) of magnesium sulfate (0.0, 0.5 , 1.0, 2.0 and 5.0) were added to the electrolyte and then the electrochemical studies such as CV, LSV and EIS on the blank and modified electrolyte solution with magnesium sulfate were carried out. The electrochemical measurements have been carried out in an aqueous sulfuric acid electrolyte, with a specific gravity of 1.245, using multi-function cycle tester (Won a Tech & VMPG 1000, Korea).

CV studies were performed in the potential range of −0.8 V to −0.4 V and 1.2 V to 2.2 V, respectively, for the negative and positive electrodes at a scan rate of 10 mV/s. LSV was recorded in the potential range −0.7 V to −1.4 V and 1.65 V to 2.1 V at 10.0 mV/s on both positive and negative electrodes, respectively. The early battery failure is a result of accumulation of hard lead sulfate crystals during charge-discharge processes, which is predominant in the negative electrode rather than positive electrode of the lead acid battery. The formation of hard sulfate crystals on the negative electrode leads to increase in internal resistance of the battery. In order to understand the change in the internal resistance in the different electrolyte environments EIS studies were carried out on the negative electrode using Zahner BAS (Model IM6) in the frequency range of 0.1Hz to 10 KHz at ambient temperature.

# 3 Results and Discussion

## 3.1 Electrochemical behavior of the negative electrode

CV behavior of the negative electrode was evaluated with different electrolyte solutions at ambient temperature. The electrochemical reactions during forward and reverse scans are similar to those of the charge and discharge processes of the battery. Figure 1 shows the CV profile of the negative electrode in the blank and modified electrolyte solution. From Figure 1, it is clear that strong anodic and cathodic peaks were observed respectively at −0.56 V to −0.58 V and −0.62 V to −0.65 V during the forward and reverse sweep. The redox peaks were attributed to the oxidation and reduction of lead. It is noteworthy to mention that the peak height increases with increase of percentage of magnesium sulfate in the electrolyte solution indicating an effective increase in electrode surface area. The basic electrochemical reaction at the electrode surface is redox reaction, which is the formation of lead sulfate and lead during forward and reverse scans. The formation of hard sulfate crystals on Pb electrode reduces the activity of negative electrode during charge-discharge cycle. Addition of appropriate additives in an electrolyte solution leads to the specific adsorption of additives on the electrode surface which is expected to reduce the formation of hard sulfate crystals (large in size), thus increase the active surface area of the electrode due the formation of small lead sulfate crystals [8]. Greene has reported an increase in chargeability of lead acid batteries with the addition of magnesium sulfate to the mixture of ethylene tetracetic acid and ferrous sulfate [3]. The addition of magnesium sulfate in elec-

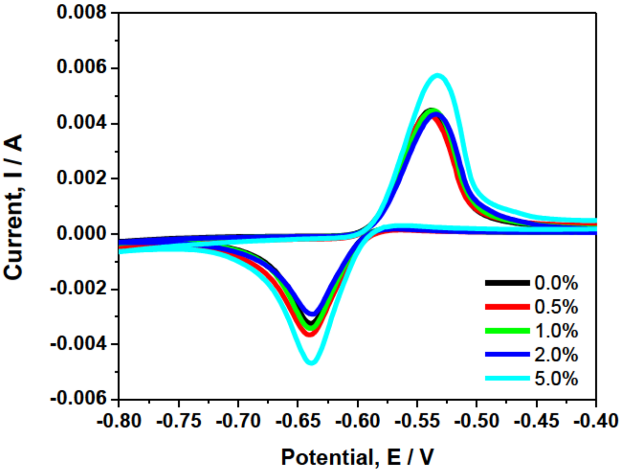

**Figure 1:** CV of negative electrode

trolyte enhances the electrochemical performance and kinetics of the Pb electrode which was in good agreement with charge and discharge characteristics of the lead acid battery.

LSV behavior of the lead electrode is presented in Figure 2. The evolution of gases in the lead electrode is observed when the battery is charged to higher voltages because of the presence of impurities either in electrode or electrolyte which imbalances the forward and reverse flow and then leads to potential failure of the battery. In order to understand the evolution of hydrogen gas in the modified electrolyte solution; the lead electrode was polarized in the potential range of −0.7 V to −1.4 V. The LSV results were compared with those obtained with blank electrolyte solution to figure out the effectiveness of the additive. Observed results showed a mixed trend in the hydrogen evolution in the modified electrolyte solution. From Figure 2, it is notably observed that the salt concentration of 2.0% has significant effect in inhibiting the evolution of hydrogen as compared to blank electrolyte solution as well as other additive concentrations such as 0.5%, 1.0% and 5.0% of $MgSO_4$ containing electrolyte solution. It can be seen from Figure 2 (marked with arrow) that the addition of additive at concentration 2.0% has shifted the hydrogen evolution potential to the negative side. Therefore, it can be concluded that the addition of $MgSO_4$ at an optimum concentration would retard the formation of hydrogen at Pb electrode, reduce the self-discharge of battery and ultimately help meeting the performance requirements of the battery.

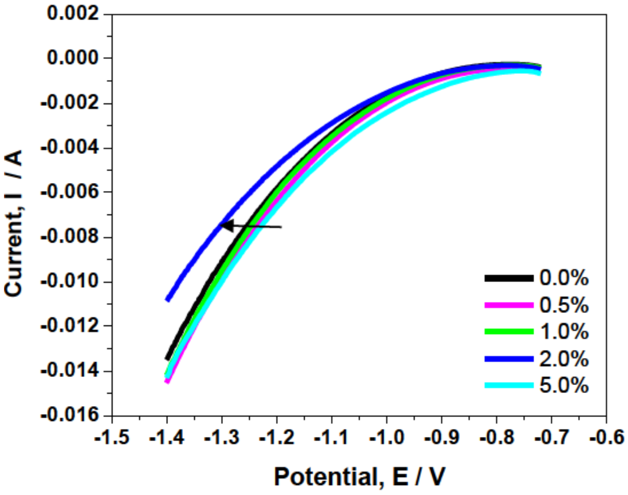

**Figure 2:** LSV of negative electrode

## 3.2 Electrochemical behavior of the positive electrode

CV measurements were performed on the positive electrode to understand the electrode redox behavior in the blank and modified electrolyte solution with magnesium sulfate. Figure 3 shows the CV profiles of the blank and modified electrolyte solution. The CV result does not show significant influence on the oxidation of lead as observed in the anodic peaks. However, the rise of the current after anodic peak (1.9 V) was observed which corresponds to oxygen evolution at higher potentials. On the other hand, the cathodic peak height increases with the magnesium sulfate concentration in the electrolyte solution as compared to blank electrolyte solution. A well-defined cathodic peak at around 1.4 V was attributed to the formation of the lead sulfate. In order to understand the evolution of gas in the modified electrolyte solution; the positive lead electrode was polarized in the potential range from 1.65 V to 2.1 V and observed LSV results are shown in Figure 4. They show that the oxygen evolution increases (marked as arrow) with increase of the additive concentration in the electrolyte solution. But, the current at Pb electrode with the 2.0% magnesium sulfate in the electrolyte solution remained unchanged as compared to blank electrolyte solution. It is further evident from Figure 4 that the oxygen evolution potential (marked as arrow) shifts to the lower side by the addition of $MgSO_4$ to electrolyte solution except at 2%. Thus, it is clear that the appreciable concentration in electrolyte solution is expected to be beneficial to the electrochemical behavior of the electrode of the battery.

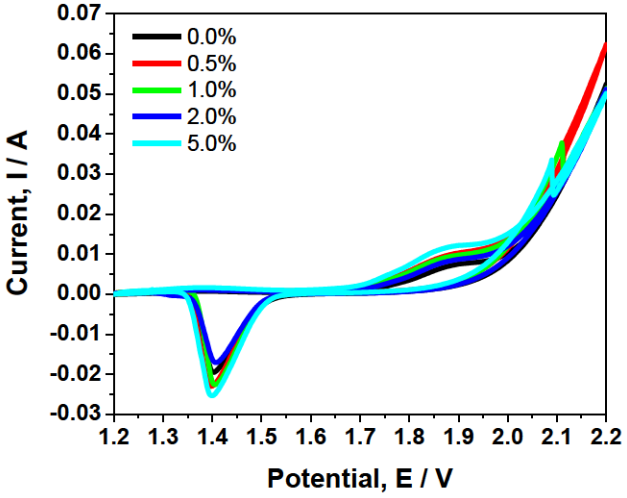

**Figure 3:** CV profile of positive electrode

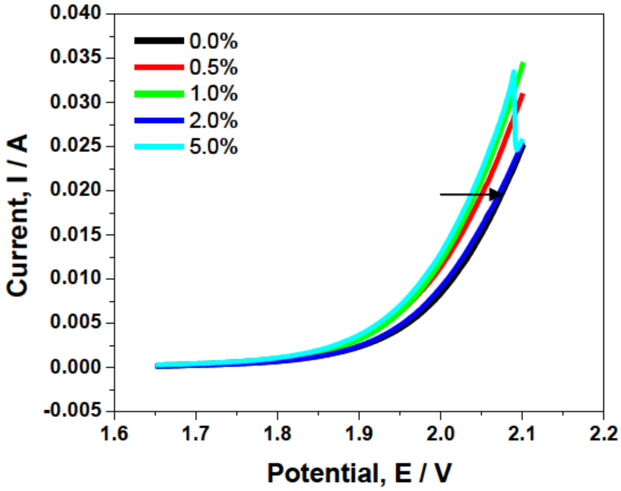

**Figure 4:** LSV of positive electrode

### 3.3 Electrochemical impedance spectroscopy of the negative electrode

The battery design consists of both passive and active components and each component contributes some resistance to battery which impedes the flow of electrons during operation. The increase of the internal resistance has serious impact on the charge acceptance and life of the battery. One of the contributions to the internal resistance is the formation of hard sulfate crystals which is predominant in the negative electrode rather than positive electrode of the lead acid battery. Hence, EIS studies have been carried out on the negative electrode only and results are presented in Figure 5. An expanded view in the higher frequency region of the spectra is shown as inset in Figure 5. It is evident from Figure 5 that the total impedance of the lead electrode in 1.245 g/cm$^3$ specific gravity $H_2SO_4$ electrolyte is decreased considerably with magnesium sulfate concentrations except 0.5%. This has been clearly indicated in Figure 5 with the decrease in semicircle size in impedance spectra (marked as arrow) with addition of $MgSO_4$ in electrolyte. However, 0.5% addition of $MgSO_4$ electrolyte shows only the capacitive behavior, which increases the resistance of the electrode. These inferences clearly indicate that the drop in total impedance of the electrode in turn reduces the internal resistance of the battery. The total impedance of electrode determines internal resistance of the battery. Yu et al. have also reported that the lower concentration of $Na_2SO_4$ in an electrolyte increases the total resistance of electrode system, whereas at higher concentrations considerably reduces the total resistance of the electrode system [12]. Moreover, in the present study, at 2.0% of the $MgSO_4$ additive in electrolyte less hydrogen evolution was observed compared to other concentrations which is evidently shown in LSV curves (Figure 2) at negative electrode. In case of positive electrodes, the oxygen evolution of 2.0% additive in the modified electrolyte solution is comparable with blank electrolyte solution. Thus, the experimental results (from EIS and CV studies) suggest that the optimal concentration of magnesium sulfate (1-2%) in the electrolyte solution is expected to be beneficial to the electrochemical behavior of the electrodes of the lead acid battery.

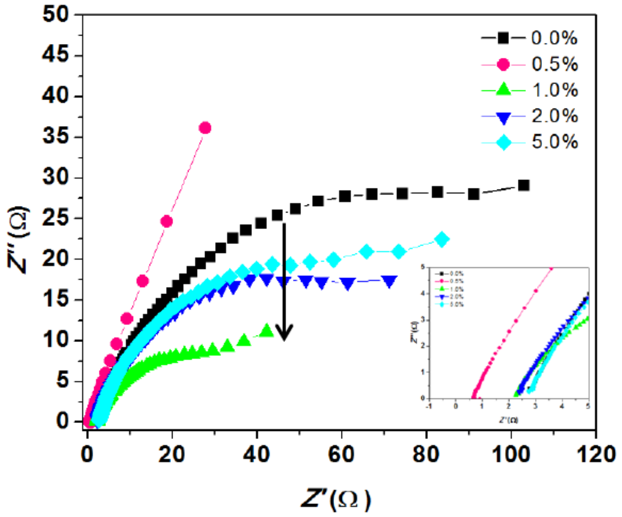

**Figure 5:** Nyquist plots of the lead electrode

## 4 Conclusions

The effects of the presence of magnesium sulfate in the electrolyte solution and the electrochemical behavior of the lead electrodes were studied. The specific adsorption of additives on the electrode surfaces is expected to reduce the formation of large sulfate crystals. However, the optimal concentration of magnesium sulfate in the electrolyte solution would retard the formation of hydrogen at lead electrode, whereas the oxygen evolution at Pb electrode remains unchanged as compared to that of blank and also other concentrations in the electrolyte solution. The drop in impedance of the electrode is expected to reduce the total resistance of the electrode which is expected to enhance the charge acceptance and life of battery. Thus, the optimum concentration of the magnesium sulfate in the electrolyte solution is expected to be beneficial to the electrochemical behavior of the electrodes of the lead acid battery.

**Acknowledgement:** Authors are grateful to the management of Amara Raja Batteries Ltd. for their constant support and encouragement. Authors also would like to thank Prof. Rudolf Holze for healthy discussion on the experimental results.

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