# Effect of mixed additives on lead–acid battery electrolyte

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## Abstract

This paper describes the corrosion behaviour of the positive and negative electrodes of a lead–acid battery in 5 M $H_2SO_4$ with binary additives such as mixtures of phosphoric acid and boric acid, phosphoric acid and tin sulphate, and phosphoric acid and picric acid. The effect of these additives is examined from the Tafel polarisation curves, double layer capacitance and percentage of inhibition efficiency. A lead salt battery has been fabricated replacing the binary mixture with an alternative electrolyte and the above electrochemical parameters have been evaluated for this lead salt battery. The results are explained in terms of $H^+$ ion transport and the morphological change of the $PbSO_4$ layer.
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## 1. Introduction

During the last two decades the lead–acid battery has been widely used in battery driven vehicles and for storing electrical energy from non-conventional sources.

In spite of rapid improvement in its performance and design, there remain some problems of the battery which are yet to be solved. These problems have drawn the attention of the battery scientists which has resulted in an annual publication of more than 150 papers in the scientific journals and a good number of patents.

The use of additives in the electrolyte is one of the approaches which offers improvement of the battery without much alteration of other factors. The major problem lies with selecting a suitable additive which is chemically, thermally and electrochemically stable in highly corrosive environment. Among the additives used so far the most widely investigated is $H_3PO_4$ [1,2] which has been reported as a beneficial additive in terms of improving cycle life, decreasing self discharge and increasing the oxygen over potential on the positive electrode. Among the other additives, $H_3BO_3$ [3] and $SnSO_4$ [4] are also prominent. In the present research, an attempt has been made to use a mixture of additives (instead of single additive as studied earlier) to the electrolyte and to examine the performances of the electrode and the battery in the presence of these additives. The mixed additives used in the present study are: (a) $H_3PO_4$ and $H_3BO_3$, (b) $H_3PO_4$ and $SnSO_4$, (c) $H_3PO_4$ and picric acid

($C_6H_3N_3O_7$). It is expected that these additives will improve the electrochemical behaviour of the individual electrodes and the battery as a whole. In this study, a lead salt battery is also investigated. In three different types of lead salt battery we used: (i) $(NH_4)_2SO_4$ alone, (ii) hydrogel (agar agar) with $(NH_4)_2SO_4$, and (iii) U-foam soaked with $(NH_4)_2SO_4$ instead of 5 M $H_2SO_4$ as electrolyte.

## 2. Experimental

The electrochemical performance of the electrodes and the electrolyte (5 M $H_2SO_4$, as blank), with and without mixed additives, has been examined from Open Circuit Potential (OCP) data, and polarisation, cyclovoltammetric and galvanotransient studies. These studies have been carried out using conventional techniques with a potentiostat/galvanostat (Vibrant, Model VSMCS 30, Lab India) and a multimeter. The detailed experimental set-up has been described in our earlier paper [5]. In all these studies a Hg/$Hg_2SO_4$ reference electrode in $H_2SO_4$ of the same molarity (5 M) and a Pt foil counter electrode are used. The working electrode was either pure Pb (99.28% pure, Johnson Mathey) or $PbO_2$ (electrochemically prepared by anodic oxidation using standard techniques).

## 3. Results and discussions

Many reports have been published on the use of $H_3PO_4$ as additive to the electrolyte. In our study with mixed additives

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Table 1
OCP values (vs. Hg/Hg$_2$SO$_4$; mV) of Pb and PbO$_2$ electrodes in lead–acid 5 M H$_2$SO$_4$ with and without different mixed additives at 298 K

| Electrodes | OCP in 5 M H$_2$SO$_4$ (mV) | OCP in 5 M H$_2$SO$_4$ + 0.5% (v/v) H$_3$PO$_4$ + 0.5% (v/v) H$_3$BO$_3$ (mV) | OCP in 5 M H$_2$SO$_4$ + 1% (v/v) H$_3$PO$_4$ + 1% (w/v) SnSO$_4$ (mV) | OCP in 5 M H$_2$SO$_4$ + 1% (v/v) H$_3$PO$_4$ + 10% (v/v) C$_6$H$_3$N$_3$O$_7$ (mV) |
|---|---|---|---|---|
| Pb | −948[a] | −969 | −877 | −366 |
| PbO$_2$ | 1154[b] | 1108 | 1110 | 1040 |
| Cell: Pb–PbO$_2$ | 2102 | 2077 | 1987 | 1406 |

[a] Literature value: −0.95 V vs. Hg/Hg$_2$SO$_4$ in [11].
[b] Literature value: 1.10–1.30 V vs. Hg/Hg$_2$SO$_4$ in [12].

we have used H$_3$PO$_4$ mixed with other components like H$_3$BO$_3$, SnSO$_4$ and picric acid (C$_6$H$_3$N$_3$O$_7$). The positive and negative electrode potentials and the cell potentials in the presence of the mixed additives are shown in Table 1.

It may be noted that the electrode and the cell potentials are shifted to some extent in the presence of these additives. With picric acid and H$_3$PO$_4$, the cell potential and the negative electrode potential are sharply reduced. The electrode reaction at the negative electrode in the electrolyte with and without additives is represented by the following equation:

$$Pb + SO_4{}^{2-} = PbSO_4 + 2e \qquad (1)$$
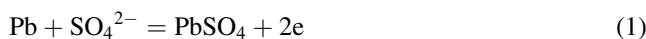
There are three factors which may alter the electrode potentials: (i) the activity of solid Pb may be changed due to the specific adsorption of additives (single additive or mixture of additives). Thus, if the surface coverage is $\theta$, the active surface taking part in the reaction will be $(1-\theta)$. (ii) The activity of SO$_4{}^{2-}$ ion may be altered due to the presence of the additive in the electrolyte. (iii) The activity of the PbSO$_4$ layer may also be changed due to the morphological changes.

Since the concentration of the additives is relatively small, the change of activity of SO$_4{}^{2-}$ ion may not be significant. However, it seems that factors (i) and (iii) are often important in understanding the functioning of the electrodes in the presence of the additives. The poor performance of the Pb electrode with picric acid and H$_3$PO$_4$ as additives seems to arise from the strong adsorption of picric acid at the electrode surface. For the positive plate (PbO$_2$) the situation is much more complex because there are at least five different layers over the surface [6,7]. However, the basic reactions may be represented as follows:

$$PbO_2 + 2H^+ + SO_4{}^{2-} = PbSO_4 + H_2O \qquad (2)$$

It seems that morphological changes of the PbSO$_4$ layer (vide factor (iii) above) seem to play an important role in dictating the potential of these electrodes.

Typical Tafel polarisation curves are as shown in Figs. 1 and 2.

Results of the analysis of Tafel plots are presented in Tables 2 and 3 below.

Analysis of the inhibition efficiency (IE%) of these additives reveals that picric acid and H$_3$PO$_4$ act as good corrosion inhibitors of the electrodes but they also inhibit the

electrode reaction. So, the performance of the battery will also be reduced because of a decrease in the rates of the reactions. Ideally for the negative electrode an inhibitor should inhibit the corrosion by retarding the hydrogen evolution reaction (HER) and not the metal dissolution reaction which is important for the functioning of the battery. Similarly, for the positive electrode an inhibitor should inhibit the oxygen evolution reaction (OER) and not the PbO$_2$ reduction reaction. Therefore, we have studied the oxygen evolution overpotential of the positive electrode in the presence of mixed additives and these are tabulated as shown in Table 4.

The mixture of H$_3$PO$_4$ and H$_3$BO$_3$ [8] reduced the oxygen overpotential to a small extent but the mixture of H$_3$PO$_4$ and SnSO$_4$ [9,10] increased it. The exchange currents for the OER apparently seem to be anomalous because these values have not behaved as expected from the oxygen evolution potentials.

From Table 4 it seems that H$_3$PO$_4$ and SnSO$_4$ may be a good additive combination for the lead–acid battery. The charging behaviour of the cell using H$_3$PO$_4$ and SnSO$_4$ is very interesting. The Sn$^{2+}$ ion has been found to deposit at the negative plate during charging (Sn$^{2+}$ + 2e ⇌ Sn, $E = -0.136$ V and Pb$^{2+}$ + 2e ⇌ Pb, $E = -0.126$ V). However, the situation may be overcome by using a controlled concentration of SnSO$_4$ and using a complexing agent. The model of specific adsorption of additives on the electrode
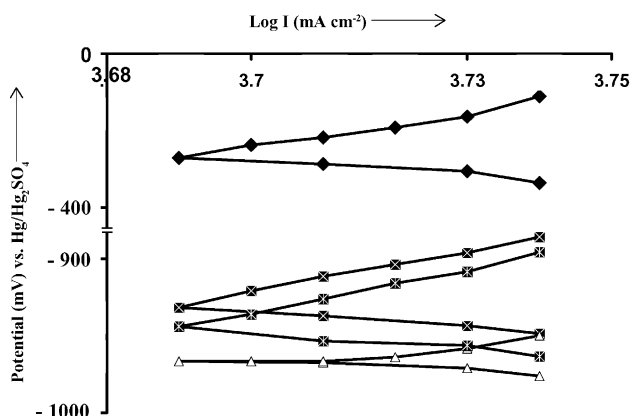


Fig. 1. Tafel polarisation curves of negative plate for the following: (⊠) blank (5 M H$_2$SO$_4$); (△) 5 M H$_2$SO$_4$ + 0.5% (v/v) H$_3$PO$_4$ + 0.5% (v/v) H$_3$BO$_3$; (⊠) 5 M H$_2$SO$_4$ + 1% (v/v) H$_3$PO$_4$ + 1% (w/v) SnSO$_4$; (◆) 5 M H$_2$SO$_4$ + 1% (v/v) H$_3$PO$_4$ + 10% (v/v) C$_6$H$_3$N$_3$O$_7$.
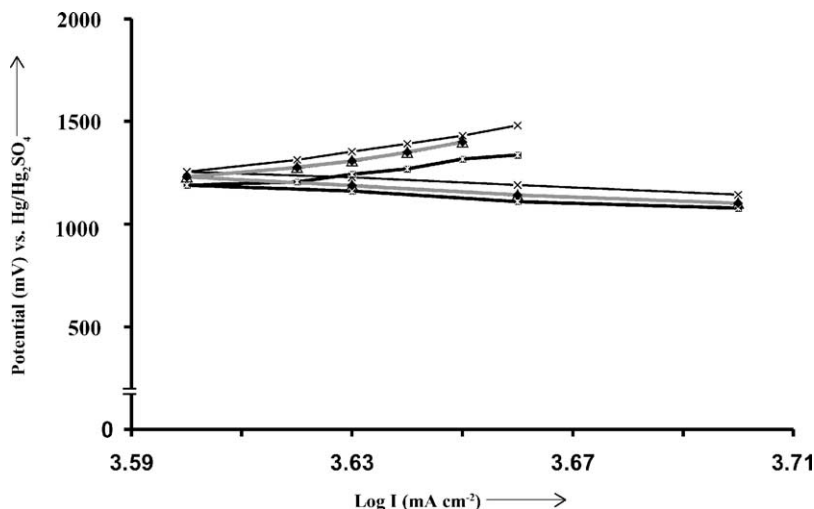
Fig. 2. Tafel polarisation curves of positive plate for the followings: (✗) blank (5 M $H_2SO_4$); (△) 5 M $H_2SO_4$ + 0.5% (v/v) $H_3PO_4$ + 0.5% (v/v) $H_3BO_3$; (▨) 5 M $H_2SO_4$ + 1% (v/v) $H_3PO_4$ + 1% (w/v) $SnSO_4$; (◆) 5 M $H_2SO_4$ + 1% (v/v) $H_3PO_4$ + 10% (v/v) $C_6H_3N_3O_7$.

surface and the morphological changes of the $PbSO_4$ layer which regulate $H^+$ ion transport through different layers have been identified as key factors governing the functioning of the electrodes in the presence of additives.

These factors have been studied through measurement of the double layer capacitance of the electrodes in the presence of additives and by fabricating a cell replacing the acid by a salt, $(NH_4)_2SO_4$. The model of $H^+$ ion transport through $PbSO_4$ layer as has been proposed to explain the alteration of

the rates of the electrode reactions in terms of corrosion current has been further studied with laboratory test cells without using 5 M $H_2SO_4$. Three different types of cell have been studied.

(1) Replacing 5 M $H_2SO_4$ by 20% (w/v) $(NH_4)_2SO_4$ as electrolyte.
(ii) Replacing 5 M $H_2SO_4$ by hydrogel (agar agar) with 20% (w/v) $(NH_4)_2SO_4$ as electrolyte.

Table 2
Potentiodynamic polarisation parameters for the corrosion of the negative plate (Pb) in lead–acid battery electrolyte with and without different mixed additives at 298 K

| Electrolyte | Corrosion potential $E_{corr}$ (mV) | Corrosion current $I_{corr}$ (mA cm$^{-2}$)[a] | Tafel slopes (mV per decade) | | Inhibition efficiency (IE, %) |
|---|---|---|---|---|---|
| | | | $b_c$ | $b_a$ | |
| 5 M $H_2SO_4$ (blank) | −924 | 5.01 | 50 | 59 | – |
| 5 M $H_2SO_4$ + 0.5% (v/v) $H_3PO_4$ + 0.5% (v/v) $H_3BO_3$ | −917 | 4.89 | 30 | 55 | 2.4 |
| 5 M $H_2SO_4$ + 1% (v/v) $H_3PO_4$ + 1% (w/v) $SnSO_4$ | −855 | 4.57 | 37 | 54 | 8.8 |
| A: 5 M $H_2SO_4$ + 1% (v/v) $H_3PO_4$ + 10% (v/v) $C_6H_3N_3O_7$ | −328 | 4.27 | 27 | 32 | 14.8 |

[a] With apparent geometrical surface area = 1 cm$^2$.

Table 3
Potentiodynamic polarisation parameters for the corrosion of the positive plate ($PbO_2$) in lead–acid battery electrolyte with and without different mixed additives at 298 K

| Electrolyte | Corrosion potential $E_{corr}$ (mV) | Corrosion current $I_{corr}$ (mA cm$^{-2}$)[a] | Tafel slopes (mV per decade) | | Inhibition efficiency (IE, %) |
|---|---|---|---|---|---|
| | | | $b_c$ | $b_a$ | |
| 5 M $H_2SO_4$ (blank) | 1149 | 5.01 | 108 | 62 | – |
| 5 M $H_2SO_4$ + 0.5% (v/v) $H_3PO_4$ + 0.5% (v/v) $H_3BO_3$ | 1103 | 4.47 | 128 | 43 | 10.8 |
| 5 M $H_2SO_4$ + 1% (v/v) $H_3PO_4$ + 1% (w/v) $SnSO_4$ | 1105 | 4.27 | 113 | 60 | 14.8 |
| 5 M $H_2SO_4$ + 1% (v/v) $H_3PO_4$ + 10% (v/v) $C_6H_3N_3O_7$ (picric acid) | 1026 | 3.90 | 114 | 54 | 22.2 |

[a] With apparent geometrical surface area = 1 cm$^2$.

Table 4
Electrochemical parameters of positive (PbO$_2$) plate obtained from cyclovoltammogram studies at the scan rate of 15 mV s$^{-1}$

| Electrolyte | Oxygen evolution reaction (OER) potential (mV) | Exchange current for OER (mA) |
|---|---|---|
| 5 M H$_2$SO$_4$ (blank) | 1312 | 5.60 |
| 5 M H$_2$SO$_4$ + 0.5% (v/v) H$_3$PO$_4$ + 0.5% (v/v) H$_3$BO$_3$ | 1200 | 5.39 |
| 5 M H$_2$SO$_4$ + 1% (v/v) H$_3$PO$_4$ + 1% (w/v) SnSO$_4$ | 1388 | 5.75 |
| 5 M H$_2$SO$_4$ + 1% (v/v) H$_3$PO$_4$ + 10% (v/v) C$_6$H$_3$N$_3$O$_7$ (picric acid) | 1317 | 5.51 |

In 5 M H$_2$SO$_4$ (blank), 5 M H$_2$SO$_4$ containing aqueous solution of 0.5% (v/v) H$_3$PO$_4$ and 0.5% (v/v) H$_3$BO$_3$, 5 M H$_2$SO$_4$ containing aqueous solution of 1% (v/v) H$_3$PO$_4$ and 1% (w/v) SnSO$_4$ and 5 M H$_2$SO$_4$ containing aqueous solution of 1% (v/v) H$_3$PO$_4$ and 10% (v/v) C$_6$H$_3$N$_3$O$_7$ at 298 K.

Table 5
Potentiodynamic polarisation parameters for the corrosion of a commercial negative plate in 20% (w/v) (NH$_4$)$_2$SO$_4$, 20% (w/v) (NH$_4$)$_2$SO$_4$–agar gel and 20% (w/v) (NH$_4$)$_2$SO$_4$–foam at 298 K

| Electrolyte | $E_{eqm.}$ | $E_{corr}$ (mV) | $I_{corr}$ ($\mu$A cm$^{-2}$)[a] |
|---|---|---|---|
| 20% (w/v) (NH$_4$)$_2$SO$_4$ | −365 | −353 | 70 |
| 20% (w/v) (NH$_4$)$_2$SO$_4$–agar gel | −305 | −256 | 46 |
| 20% (w/v) (NH$_4$)$_2$SO$_4$–foam | −345 | −323 | 62 |

[a] With apparent geometrical surface area = 1 cm$^2$.

Table 6
Specific conductance of 20% (w/v) (NH$_4$)$_2$SO$_4$, 20% (w/v) (NH$_4$)$_2$SO$_4$–agar gel and 20% (w/v) (NH$_4$)$_2$SO$_4$–foam (m (m$\Omega$ cm)$^{-1}$) at 298 K

| | Specific conductance (m (m$\Omega$ cm)$^{-1}$) |
|---|---|
| 20% (w/v) (NH$_4$)$_2$SO$_4$ | 24 |
| 20% (w/v) (NH$_4$)$_2$SO$_4$–agar gel | 21 |
| 20% (w/v) (NH$_4$)$_2$SO$_4$–foam | 9 |

(iii) Replacing 5 M H$_2$SO$_4$ by U-foam soaked with 20% (w/v) (NH$_4$)$_2$SO$_4$ as electrolyte.

Polarisation studies of commercial plates in these systems were carried out. The different kinetic and equilibrium parameters in these systems are shown in Table 5. It may be noted that electrodes dipped in the electrolyte with 20% (w/v) (NH$_4$)$_2$SO$_4$ exhibit poor kinetic and equilibrium parameters. This indicates that the H$^+$ ion plays an important role in dictating the electrode reactions of the plate. It may be mentioned that the low $I_{corr}$ values may not be due to poor conductance of the solution. The specific conductance of a 20% (w/v) (NH$_4$)$_2$SO$_4$ solution and such solution within a gel have been determined and are presented in Table 6. Based on our polarisation and conductance studies we conclude that the transport of the H$^+$ ion across the PbSO$_4$ membrane of the positive plate plays an important role in the electrode reactions as mentioned earlier.

In our double layer capacitance studies using a galvano-transient technique we have injected a current pulse of 5 mA and the resulting potential–time transients are as shown in Figs. 3 and 4. From the slope of the transient curve the double layer capacitance of the electrode has been determined using the following relation

$$C = \frac{i}{dV/dT}$$

and the differential capacitance values at the equilibrium potential are shown in Tables 7 and 8. It should be mentioned that the double layer capacitance values are important in understanding the presence or absence of adsorbed additives.
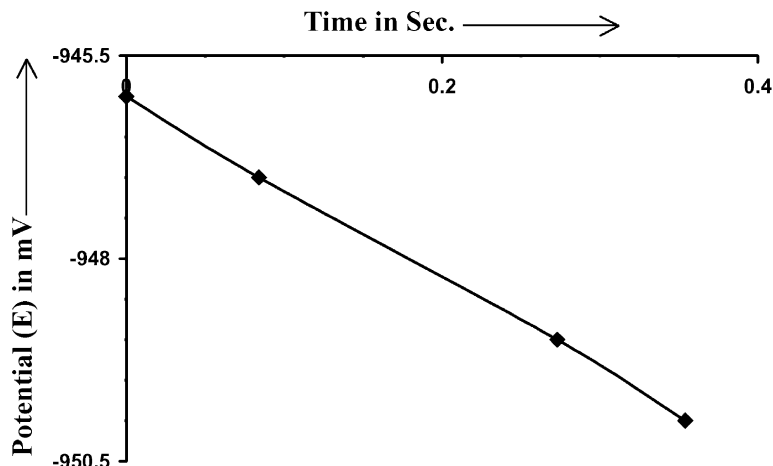


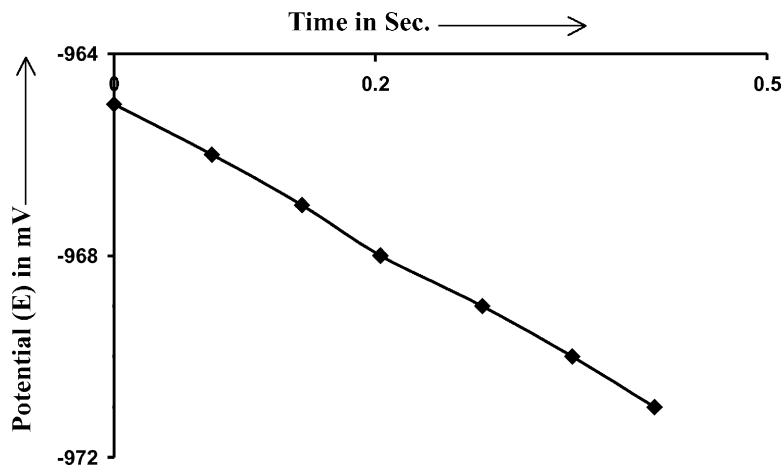Fig. 3. Galvanotransient polarisation curve of negative plate for the solution 5 M H$_2$SO$_4$ (blank).

Fig. 4. Galvanotransient polarisation curve of negative plate for the solution 5 M $H_2SO_4$ containing aqueous solution of 0.5% (v/v) $H_3PO_4$ and 0.5% (v/v) $H_3BO_3$.

It may also be mentioned that these values will also reflect contact adsorption of additives ions (like $Sn^{2+}$ ions) at the outer Helmholtz plane (OHP). The differential capacitance of the negative electrode in the presence of these additives is decreased significantly. This shows that these additives adsorbed firmly at the electrode surfaces. Galvanotransient behaviour of the picric acid + $H_3PO_4$ system is again unusual and strong adsorption results due to soft–soft interaction between the large picric acid molecules and the Pb atom. Unlike the negative plate the double layer capacitance of the positive plate is slightly increased in the presence of the

additives which may be due to the fact that the positive active material ($PbO_2$) deposited on the outer surface of the lead (Pb) may not be selective to the strong adsorption of the additives. It seems that the $PbSO_4$ layer formed over the grid material and the active mass of the plate play an important role and the observed slight increase in double layer capacitance may be due to the enhanced contact adsorption of ions over the modified $PbSO_4$ layer.

For the system of $H_3PO_4$ and picric acid we noted an anomalous drop in the double layer capacitance (Tables 7 and 8) which indicates the strong adsorption

Table 7
Electrochemical parameters of negative (Pb) plate[a] obtained from galvanotransient studies

| Electrolyte | Differential capacity ($C$, µF cm$^{-2}$) | Charging time ($T$, s) | Voltage (mV) |
|---|---|---|---|
| 5 M $H_2SO_4$ (blank) | 54 | 0.20 | −948 |
| 5 M $H_2SO_4$ + 0.5% (v/v) $H_3PO_4$ + 0.5% (v/v) $H_3BO_3$ | 30 | 0.20 | −936 |
| 5 M $H_2SO_4$ + 1% (v/v) $H_3PO_4$ + 1% (w/v) $SnSO_4$ | 31 | 0.21 | −890 |
| 5 M $H_2SO_4$ + 1% (v/v) $H_3PO_4$ + 10% (v/v) $C_6H_3N_3O_7$ (picric acid) | – | – | −366 |

In 5 M $H_2SO_4$ (blank), 5 M $H_2SO_4$ containing aqueous solution of 0.5% (v/v) $H_3PO_4$ and 0.5% (v/v) $H_3BO_3$, 5 M $H_2SO_4$ containing aqueous solution of 1% (v/v) $H_3PO_4$ and 1% (w/v) $SnSO_4$, and 5 M $H_2SO_4$ containing aqueous solution of 1% (v/v) $H_3PO_4$ and 10% (v/v) $C_6H_3N_3O_7$ (picric acid) at 298 K.
[a] With apparent geometrical surface area = 1 cm$^2$.

Table 8
Electrochemical parameters of positive ($PbO_2$) plate[a] obtained from galvanotransient studies

| Electrolyte | Differential capacity ($C$, µF cm$^{-2}$) | Charging time ($T$, s) | Voltage (mV) |
|---|---|---|---|
| 5 M $H_2SO_4$ (blank) | 11 | 0.11 | 1254 |
| 5 M $H_2SO_4$ + 0.5% (v/v) $H_3PO_4$ + 0.5% (v/v) $H_3BO_3$ | 16 | 0.10 | 1248 |
| 5 M $H_2SO_4$ + 1% (v/v) $H_3PO_4$ + 1% (w/v) $SnSO_4$ | 14 | 0.11 | 1210 |
| 5 M $H_2SO_4$ + 1% (v/v) $H_3PO_4$ + 10% (v/v) $C_6H_3N_3O_7$ (picric acid) | 75 | 0.10 | 1205 |

In 5 M $H_2SO_4$ (blank), 5 M $H_2SO_4$ containing aqueous solution of 0.5% (v/v) $H_3PO_4$ and 0.5% (v/v) $H_3BO_3$, 5 M $H_2SO_4$ containing aqueous solution of 1% (v/v) $H_3PO_4$ and 1% (w/v) $SnSO_4$ and 5 M $H_2SO_4$ containing aqueous solution of 1% (v/v) $H_3PO_4$ and 10% (v/v) $C_6H_3N_3O_7$ (picric acid) at 298 K.
[a] With apparent geometrical surface area = 1 cm$^2$.

of picric acid over the positive active material (PAM) and the grid.

## 4. Conclusions

Based on these studies we may conclude that mixed additives, viz. $H_3PO_4 + H_3BO_3$ and $H_3PO_4 + SnSO_4$ improve the electrolyte of the lead–acid battery. The corrosion of both the negative and the positive plates are significantly reduced in the presence of these two additive mixtures. The electrode and the cell potentials are not much disturbed using these two additives in the electrolyte. The mechanism of corrosion inhibition by these additives involves:

(i) alteration of the physical structure of the $PbSO_4$ layer on the electrode surface;
(ii) adsorption of the additives on the electrode surface;
(iii) regulating the transport of the $H^+$ ion from the solution to the corrosion layer (CL) through the $PbSO_4$ coating.

Any one of the above factors may be prominent depending on the nature of the additives used. For picric acid and $H_3PO_4$, adsorption of the additives on the electrode surface may be important but for $Sn^{2+}$ ion as additive also with $H_3PO_4$ at the positive electrode, the alteration of the structure of the $PbSO_4$ layer seems to be a key issue.

The transport of the $H^+$ ion from the solution to the corrosion layer through the $PbSO_4$ coating is also a key factor in dictating the kinetics and the equilibrium of the electrode reactions. The results obtained from our laboratory model $Pb–(NH_4)_2SO_4$ battery also support the views that the $H^+$ ion plays an important role in the electrode reactions of the positive electrode. The double layer capacitance values provide information on the nature of the adsorption of the additives.

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