

Short communication

Influence of phosphoric acid on the grid alloys of positive plates in the lead acid battery system: A comparative study

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Abstract

The effect of phosphoric acid in lead acid batteries was studied with potential sweep techniques. Lead–tin (2%) and lead–calcium (0.1%) tin (0.35%) alloys were used as the grids. The influence of phosphoric acid in the presence of tin, calcium and calcium alone on the grid were examined. Phosphoric acid inhibits the formation of β -PbO₂ in the alloys.

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1. Introduction

Deterioration of the positive plate is one of the main problems for the lead acid battery system (LAB) [1–3]. This deterioration or passivation of the positive plate shortens the life of the battery. In order to improve the life, much work has been done on the structure and electrochemical processes at the positive plate [4–6].

One of the most significant improvements is the reduction of the antimony level because of its electrochemical disadvantages [7]. To improve the electrochemical properties of the grid, Variety of metals have been added to replace antimony for example calcium, tin, etc.

It is well known that the addition of phosphoric acid also improves the performance of the LAB system. Phosphoric acid increases the cycle life but it decreases the capacity of the cell to a some extent. Still the loss of capacity can be compensated for by this improved cycle life [8]. Self-discharge of the positive plate is suppressed in the presence of phosphoric acid. This fact is supported by cyclic voltammetry data carried out by Vinoth [9].

Voss [10] and Meissner [11] reviewed the effect of phosphoric acid on the performance of the lead acid battery. Phosphoric acid significantly reduced the shedding of positive active material

and thus suppresses the anodic corrosion of the grid material and reduces self-discharge. According to Bullock et al. [12,13] phosphoric acid resists the formation of dense lead sulphate on the PbO₂ electrode. The beneficial effect of phosphoric acid has been tested with some lead alloys based on other than the usual antimony constituent.

Most manufacturers of lead acid batteries have opted for a Pb–Ca–Sn [6] ternary alloy in applications such as starting, lighting and ignition (SLI) of vehicles.

2. Experiment

The composition of selected binary and ternary alloys is presented in Table 1. Alloys (A1 and A2) of 4 mm diameter were press fitted in a Teflon rod, so that the exposed area was 0.5025 cm² and it was used as the working electrode. The working electrodes were polished using fine emery sheets with grit ranges sequentially of: 1/0, 2/0, 3/0, 4/0, 5/0, and 6/0, respectively, until a mirror like surface was obtained. Then it was degreased with trichloroethylene and then treated with a saturated solution of ammonium acetate to remove surface oxides. The electrode was washed with triple distilled water and then used for the studies. Hg/Hg₂SO₄ with 4.5 M sulphuric acid was used as the reference electrode. A platinum electrode of large surface area was used as the counter electrode. The AR grade sulphuric acid was diluted to 4.5 M using triple distilled water and was used as the electrolyte. Various concentrations of phos-

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Table 1
Composition of grid alloys

Alloys	Pb (wt.%)	Ca (wt.%)	Sn (wt.%)
A1	~98.00	–	~2.00
A2	99.55	0.1	0.35

phoric acid ranging from 0.05 to 0.2 M were used as the additive throughout the studies. All the experiments were carried out at room temperature.

2.1. CV studies

A PC controlled BAS 100 W instrument was used for cyclic voltammetry studies. A conventional all glass H-type cell was used for the electrochemical studies. The working electrode was kept in pure sulphuric acid at a potential of 2000 mV for several hours to facilitate the formation of PbO₂. The potential range studied was from 600 to 2200 mV against Hg/Hg₂SO₄ reference electrode at a fixed scan rate of 50 mV s⁻¹.

2.2. Discharge studies

The positive plate grid was prepared with alloys 1 and 2. Two positive plates with a 10 A h theoretical capacity, were coupled with higher capacity negative plates so that the capacity of the cell limited only by the positive plate performance. The paste compositions of the positive and negative plates are available in the literature [1,2]. The discharge studies were carried out at the C/10 rate.

3. Results and discussion

CV studies were performed from 600 to 2200 mV versus Hg/Hg₂SO₄ at a fixed scan rate of 50 mV s⁻¹ in the presence of various concentrations of phosphoric acid (additive) in 4.5 M sulphuric acid.

Table 2
Cyclic voltammogram (50 mV s⁻¹) of Pb–Sn alloy in 4.5 M sulphuric acid at various concentrations of phosphoric acid

S. No.	Composition of electrolyte	Anodic				Cathodic		ΔE_p	I_a/I_c
		A1		A2		C1			
		Potential (mV)	Current (mA)	Potential (mV)	Current (A)	Potential (mV)	Current (mA)		
1	4.5 M H ₂ SO ₄ (A)	1507	+8.273	1935.2	+5.310 × 10 ⁻²	1324	-88.72	183	0.0932
2	4.5 M H ₂ SO ₄ + 0.05 M H ₃ PO ₄ (B)	1478.3	+5.213	1865.5	+2.601 × 10 ⁻²	1361.5	-45.39	117	0.1148
3	4.5 M H ₂ SO ₄ + 0.1 M H ₃ PO ₄ (C)	1556.4	+2.053	–	–	1365.0	-33.76	191	0.0608
4	4.5 M H ₂ SO ₄ + 0.15 M H ₃ PO ₄ (D)	1662.2	+1.503	–	–	1369.2	-17.16	293	0.0875
5	4.5 M H ₂ SO ₄ + 0.20 M H ₃ PO ₄ (E)	1684.9	+0.9846	–	–	1344.9	-13.35	340	0.0737

S. No.	Composition of electrolyte	Oxygen evolution	
		Potential (mV)	Current (A)
1	4.5 M H ₂ SO ₄ (A)	2100	+9.104 × 10 ⁻²
2	4.5 M H ₂ SO ₄ + 0.05 M H ₃ PO ₄ (B)	2100	+1.390 × 10 ⁻²
3	4.5 M H ₂ SO ₄ + 0.1 M H ₃ PO ₄ (C)	2100	+9.077 × 10 ⁻³
4	4.5 M H ₂ SO ₄ + 0.15 M H ₃ PO ₄ (D)	2100	+8.589 × 10 ⁻³
5	4.5 M H ₂ SO ₄ + 0.20 M H ₃ PO ₄ (E)	2100	+4.865 × 10 ⁻³

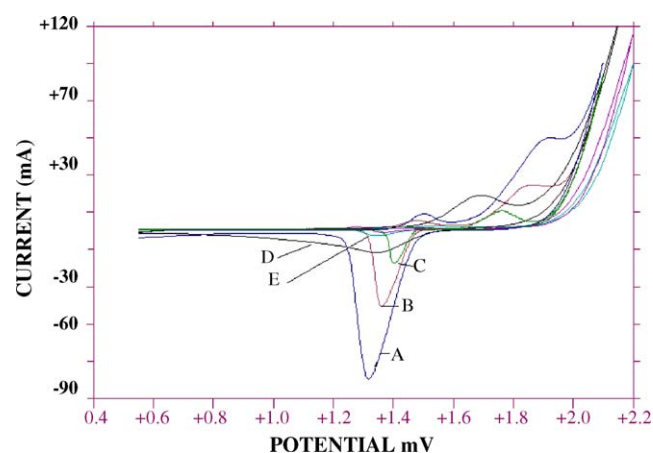


Fig. 1. Cyclic voltammogram (50 mV s⁻¹) of Pb–Sn alloy in 4.5 M sulphuric acid at various concentrations of phosphoric acid. A: 4.5 M sulphuric acid; B: 4.5 M sulphuric acid + 0.05 M phosphoric acid; C: 4.5 M sulphuric acid + 0.10 M phosphoric acid; D: 4.5 M sulphuric acid + 0.15 M phosphoric acid; E: 4.5 M sulphuric acid + 0.20 M phosphoric acid.

The potential window applied enables the formation of lead dioxide during oxidation and subsequent reduction in the reverse sweep. The peak current and peak potential values were noted and critically analyzed for the efficiencies.

3.1. Studies with Pb–Sn alloy (A1)

The cyclic voltammetry results for Pb–Sn alloy in 4.5 M sulphuric acid are presented in Table 2. With pure 4.5 M sulphuric acid (without phosphoric acid), two anodic peaks A1 and A2 corresponding to the formation of α -PbO₂ and β -PbO₂ [13] were encountered. The voltammograms for the successive additions of 0.05–0.2 M phosphoric acid are presented in Fig. 1 and the results are in Table 2.

In the presence of 0.05 M phosphoric acid, the peak currents correspond to A1 and A2 are decreased. When increasing the

concentration of phosphoric acid from 0.1 to 0.2 M, peak A2 slowly disappears, and peak A1 still appears but with diminished currents. This means that the addition of phosphoric acid in appreciable concentration inhibits the formation of $\beta\text{-PbO}_2$. Here, cathodic current is decreased with increasing phosphoric acid concentration. This indicates that the presence of phosphoric acid retards the reduction reaction, i.e., the discharge capacity of the positive plate is decreased. This has been reported as a welcome feature for only $\alpha\text{-PbO}_2$ enables the easy reduction to lead sulphate.

Another notable aspect on the anodic scan is the oxygen evolution at the extreme anodic potentials. The results are presented in Table 2. It is noted that in the presence of phosphoric acid, the oxygen evolution potential shifts to the positive direction with decreasing current. This is a good sign for the performance of the positive electrode.

3.2. Studies with Pb–Ca–Sn alloy

Calcium has been reported as one of the beneficial alloying elements in lead acid battery system. The electrochemical studies with the calcium-based alloy in phosphoric acid based electrolyte are presented in Fig. 2 and the corresponding data are presented in Table 3. As in the earlier study, here also in the absence of phosphoric acid, we have two anodic peaks A1 and A2 corresponding to the formation of $\alpha\text{-PbO}_2$ and $\beta\text{-PbO}_2$. With the addition of phosphoric acid from the lowest concentration, the formation of $\beta\text{-PbO}_2$ is suppressed. The results on the oxygen over voltage for this study are presented in Table 3. This alloy also has the ability to increase the oxygen over potential and retards oxygen evolution.

It is clear that from the results of ΔE_p and I_a/I_c values, the lead–calcium–tin alloy has better performance than lead–tin alloy in both plain sulphuric acid and sulphuric acid with phosphoric acid electrolytes.

Table 3
Cyclic voltammogram (50 mV s^{-1}) of Pb–Ca–Sn alloy in 4.5 M sulphuric acid at various concentrations of phosphoric acid

S. No.	Composition of electrolyte	Anodic		Cathodic		ΔE_p	I_a/I_c		
		A1	A2	C1					
		Potential (mV)	Current (mA)	Potential (mV)	Current (mA)				
1	4.5 M H_2SO_4 (A)	1444	+1.231	1690	$+5.231 \times 10^{-2}$	1303	−91.15	141	1.37
2	4.5 M H_2SO_4 + 0.05 M H_3PO_4 (B)	1639	+7.471	–	–	1363	−46.24	276	6.70
3	4.5 M H_2SO_4 + 0.1 M H_3PO_4 (C)	1522	+0.9161	–	–	1349	−29.32	173	0.60
4	4.5 M H_2SO_4 + 0.15 M H_3PO_4 (D)	1783	+2.239	–	–	1447	−16.58	336	2.13
5	4.5 M H_2SO_4 + 0.2 M H_3PO_4 (E)	1908	+10.02	–	–	1540	−12.65	368	3.40

S. No.	Composition of electrolyte	Oxygen evolution	
		Potential (mV)	Current (A)
1	4.5 M H_2SO_4 (A)	2100	$+1.238 \times 10^{-1}$
2	4.5 M H_2SO_4 + 0.05 M H_3PO_4 (B)	2100	$+8.942 \times 10^{-2}$
3	4.5 M H_2SO_4 + 0.1 M H_3PO_4 (C)	2100	$+6.497 \times 10^{-2}$
4	4.5 M H_2SO_4 + 0.15 M H_3PO_4 (D)	2100	$+5.027 \times 10^{-2}$
5	4.5 M H_2SO_4 + 0.2 M H_3PO_4 (E)	2100	$+1.761 \times 10^{-2}$

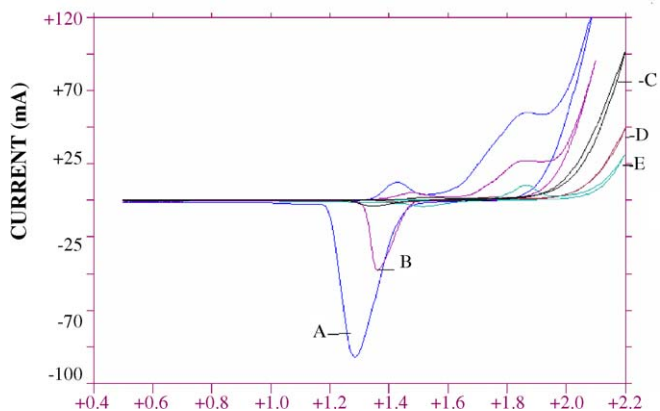


Fig. 2. Cyclic voltammogram (50 mV s^{-1}) of Pb–Ca–Sn alloy in 4.5 M sulphuric acid at various concentrations of phosphoric acid. A: 4.5 M sulphuric acid; B: 4.5 M sulphuric acid + 0.05 M phosphoric acid; C: 4.5 M sulphuric acid + 0.10 M phosphoric acid; D: 4.5 M sulphuric acid + 0.15 M phosphoric acid; E: 4.5 M sulphuric acid + 0.20 M phosphoric acid.

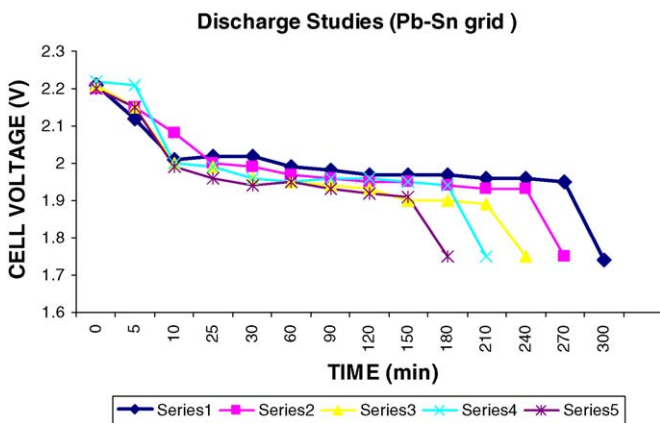


Fig. 3. Discharge studies LAB with Pb–Sn alloy (A1) grid in 4.5 M sulphuric acid with various concentrations of phosphoric acid. Series 1: 4.5 M sulphuric acid; series 2: 4.5 M sulphuric acid + 0.05 M phosphoric acid; series 3: 4.5 M sulphuric acid + 0.10 M phosphoric acid; series 4: 4.5 M sulphuric acid + 0.15 M phosphoric acid; series 5: 4.5 M sulphuric acid + 0.20 M phosphoric acid.

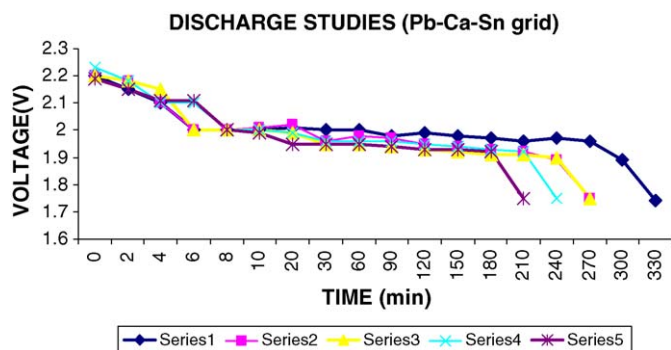


Fig. 4. Discharge studies LAB with Pb–Ca–Sn alloy (A2) grid in 4.5 M sulphuric acid with various concentrations of phosphoric acid. Series 1: 4.5 M sulphuric acid; series 2: 4.5 M sulphuric acid + 0.05 M phosphoric acid; series 3: 4.5 M sulphuric acid + 0.10 M phosphoric acid; series 4: 4.5 M sulphuric acid + 0.15 M phosphoric acid; series 5: 4.5 M sulphuric acid + 0.20 M phosphoric acid.

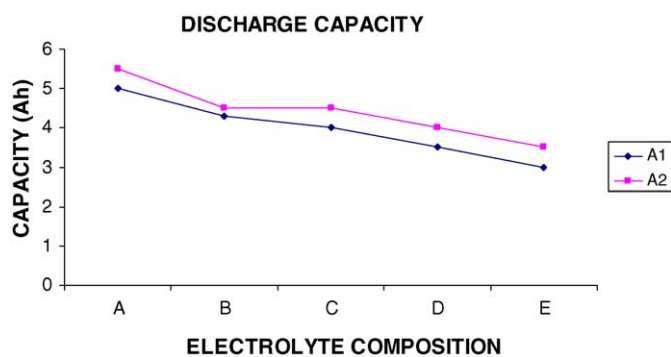


Fig. 5. Discharge capacity comparison for both alloys. A: 4.5 M sulphuric acid; B: 4.5 M sulphuric acid + 0.05 M phosphoric acid; C: 4.5 M sulphuric acid + 0.10 M phosphoric acid; D: 4.5 M sulphuric acid + 0.15 M phosphoric acid; E: 4.5 M sulphuric acid + 0.20 M phosphoric acid.

4. Discharge studies

The discharge data for both grids are presented in Figs. 3 and 4. The discharge capacity trend is presented in Fig. 5 when increasing the concentration of phosphoric acid, the capacity of the cell is decreased to some extent. The discharge capacity graph confirms the trend. The decreasing capacity is compensated by a long life of the plate. The fading of the capacity may be due to the disappearance of β -PbO₂. Mark [14] studied the discharge properties of pure α -PbO₂ in sulphuric acid. He concluded that the lead sulphate film may be the only

cause for the poor discharge of pure α -PbO₂. Here, both the tin and phosphate ions in the alloy may improve the conductivity through the passive film to some extent. So, compared with both alloys A1 and A2, the alloy A2 (Pb–Ca–Sn) performs well [15–21].

5. Conclusion

In the absence of phosphoric acid, both the alloys Pb–Sn or Pb–Ca–Sn uniformly give two anodic peaks A1 and A2 corresponding to the formation of α and β -PbO₂.

In the presence of sulphuric acid and an optimum concentration of 0.1 M phosphoric acid, the formation of β -PbO₂ was inhibited for both the alloys.

For both the alloys, the phosphoric acid additive enables the shifting of the oxygen evolution potential to more positive values and reduces the rate of oxygen evolution.

In the presence of phosphoric acid, Pb–Ca–Sn alloy showed good performance.

In the presence of phosphoric acid, the discharge capacity of the positive plate was decreased.

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