Improvement of the performance of the positive electrode in the lead/acid battery by addition of boric acid

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Abstract

A major disadvantage of the lead/acid battery is the decrease in voltage during operation which makes it unsuitable for systems sensitive to voltage fluctuations. Additives like $BaSO_4$ or $SrSO_4$, which are isomorphous to $PbSO_4$, have been used to overcome this problem. Phosphoric acid and the various phosphates have long been used to improve the performance of the positive electrode of the battery. A beneficial effect of phosphoric acid is to inhibit the rate of the self-discharge reaction of the positive electrode in the lead/acid battery. However, adverse effects of phosphoric acid include capacity loss in the initial cycles, excessive mossing, especially at high H_3PO_4 concentrations, and poor low-temperature performance (decrease in the rate of $PbSO_4$ oxidation). The effect of boric acid as an additive substituting for H_3PO_4 has been investigated using linear sweep voltammetry, constant potential and impedance measurements. The results show that boric acid markedly improves the kinetics of the $PbO_2/PbSO_4$ couple and removes the problems encountered during the usage of H_3PO_4.

Keywords: Lead/acid batteries; Boric acid; Positive electrodes

1. Introduction

One of the main disadvantages of the lead/acid battery is the decrease in voltage during discharge making them unsuitable for systems that require a stable power supply, e.g., relays used in telephone or railway stations. Addition of various species like $BaSO_4$ and $SrSO_4$ to the positive plate were used to overcome this problem since these materials are isomorphous to $PbSO_4$ [1].

Phosphoric acid and various phosphate derivatives have been used for the same purpose [2,3], and the effect of phosphoric acid on the performance of the positive electrode has been extensively investigated by various well-known electrochemical techniques [4–10]. It has been concluded that the phosphate ions are adsorbed reversibly on the PbO_2 electrode during the charging process. The adsorption of phosphate ions modifies the crystalline structure of PbO_2 by the inhibition of the three-dimensional crystal growth in favour of the two-dimensional growth of the nuclei. The PbO_2 crystals formed by two-dimensional growth are more difficult to reduce than those formed by three-dimen-

sional crystal growth. The modified PbO_2 undergoes self-discharge at slower rate. The rate-determining step in that reaction was given by [11]:

$$PbO_2 + H_2SO_4 \longrightarrow$$
$$PbSO_4 + H_2O + 0.5O_2 \quad \text{(slow reaction)} \quad (1)$$
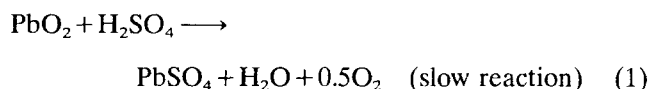
In agreement with this reaction is the observation made by Davang and co-workers [6,12,13] that the sulfate layer was not formed in cells containing phosphoric acid.

Although the presence of phosphoric acid or phosphates inhibits the self-discharge reaction, it leads to serious disadvantages, e.g., capacity loss, excessive mossing, and decrease of the charging efficiency [14–16]. In the presence of phosphate ions, the potential required to oxidize the lead sulfate to lead dioxide is higher than in the absence of phosphate. At this higher voltage, the rate of the oxygen-evolution reaction is also higher and therefore the charging efficiency is lower [14]. Decreasing the temperature has a similar effect on the charging efficiency [14]. It follows that the presence of phosphoric acid intensifies the problems already present in low-temperature charging. Therefore, there is a need to test other additives which can overcome the problems arising with the positive electrode of the lead/acid

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battery, i.e., decreasing the charging efficiency or the creation of new problems. In this respect, boric acid may be a suitable additive. Previous results showed that the presence of boric acid in sulfuric acid improves the corrosion resistance of the lead and lead alloys [17]. Further, treating the positive grid of the lead/acid batteries with aqueous boric acid solutions for 10–50 s was found to prevent cracking and drying of the grid [18].

In the present paper, the effect of boric acid on the kinetics of the $PbO_2/PbSO_4$ couple was investigated using linear sweep voltammetry, constant potential, and impedance techniques.

2. Experimental

Massive lead discs (Aldrich Chemie) with a surface area of 0.237 cm^2 were used as working electrodes. The electrochemical cell, electrode preparation and pretreatment were as described in Refs. [19,20]. The potential sweep measurements were made using a fast response potentiostat in conjunction with a linear sweep generator. The electrode impedance was measured using IM5d-AMOS system (Zahner Elektrik GmbH & Co., Kronach, Germany). The frequency range of the system is from 0.1 Hz to 100 kHz. Since the electrode reaction is fast and very sensitive, one frequency of 1 kHz and a 10 mV amplitude signal were always used to minimize the time required for the full frequency range. The electrode potential was measured against a $Hg/Hg_2SO_4/$ H_2SO_4 (0.5 M) as reference.

3. Results and discussion

3.1. Linear sweep voltammetry

Linear sweep voltammetry has been widely used for the examination of reactions or changes occurring at the electrode/electrolyte interface. For the lead electrode in sulfuric acid solutions, the linear sweep voltammograms are well identified [21–25]. In our investigations, the lead electrode was cycled in 4.5 M H_2SO_4 containing different concentrations of boric acid at 45 °C and with a slow scan rate of 0.1 mV S^{-1}. Under these conditions, the reaction is reasonably fast and the measurements are slow enough; the reaction appeared to be reversible. Before recording the cyclic voltammograms, five cycles were made at a scan rate of 1 mV S^{-1} in the potential range 1.53 to 0.975 V in order to develop a dense PbO_2 coating on the working electrode surface, and to allow the electrode reaction to reach a steady state. The recorded voltammograms were limited to a maximum of 1.425 V. Typical voltammograms of the lead electrode in 4.5 M H_2SO_4

containing different concentrations of boric acid are shown in Fig. 1. On the anodic scan, the wave corresponding to the reduction of PbO_2 to $PbSO_4$ is present. The values of the anodic and cathodic peak potentials and peak currents are presented in Table 1. From the values given in this Table, it can be seen that the addition of a low concentration of boric acid ($\leqslant 0.4$ wt.%) had a negligible effect on the position of the peaks, i.e., the peak potentials of both the anodic and cathodic scans remained unchanged. On the other hand, the peak current is markedly affected. The reduction peak current showed a decrease of more than 30% of its initial value in the absence of boric acid. Fig. 1 shows also that even at the concentration of boric acid $\geqslant 0.4\%$ there is a complete separation of the anodic peak from the oxygen-evolution region, which means that the efficiency of the anodic oxidation of $PbSO_4$ to PbO_2 is unaffected by the presence of boric acid. Fig. 2 shows a linear decrease in the cathodic peak current with a concentration of boric acid up to 0.4 wt.%. Above this limit, the behaviour was reversed.

The present results may be explained, as was suggested earlier for phosphoric acid [11], by the adsorption of boric acid on the PbO_2 surface during the charging process leading to a modification of the crystal growth; hence, the PbO_2 formed in the presence of boric acid is not easily reduced to $PbSO_4$.

In contrast to the behaviour of H_3PO_4 [11], the addition of boric acid did not affect the position of the anodic peak and hence did not affect the oxidation efficiency. It follows that the addition of boric acid had no effect on the low-temperature performance of the lead/acid battery.

The data of the constant potential corrosion data were correlated with the results of cyclic voltammetry by holding the potential of the lead electrode at 1.425 V for 3 h, then reducing it to 0.975 V at a scan rate of 0.2 mV S^{-1}. During the potentiostatic corrosion test, the current was monitored with time. Fig. 3 shows cyclic voltammograms of lead corroded at 1.425 V in 4.5 M H_2SO_4 containing different concentrations of boric acid. On the first cathodic scan, the reduction of PbO_2 to $PbSO_4$ at 1.193 V (peak (a)) was followed by an anodic peak (peak (b)), which resulted probably from a subsurface corrosion reaction. On subsequent cycling between 0.975 and 1.425 V, peak (b) disappeared and simultaneously, peak (c), which corresponds to the oxidation of $PbSO_4$ to PbO_2, is shifted to lower potential. The voltammograms no longer changed markedly after the third cycle. In the steady state, peak (a) appeared at 1.103 V, and peak (c) at 1.253 V. The anodic and cathodic peak potentials and currents for the lead electrode cycled in 4.5 M H_2SO_4 solution containing 0, 0.2 and 0.4 wt.% H_3BO_3, are presented in Table 2. The most important result is that the position of the peaks has not been altered by the the addition of boric
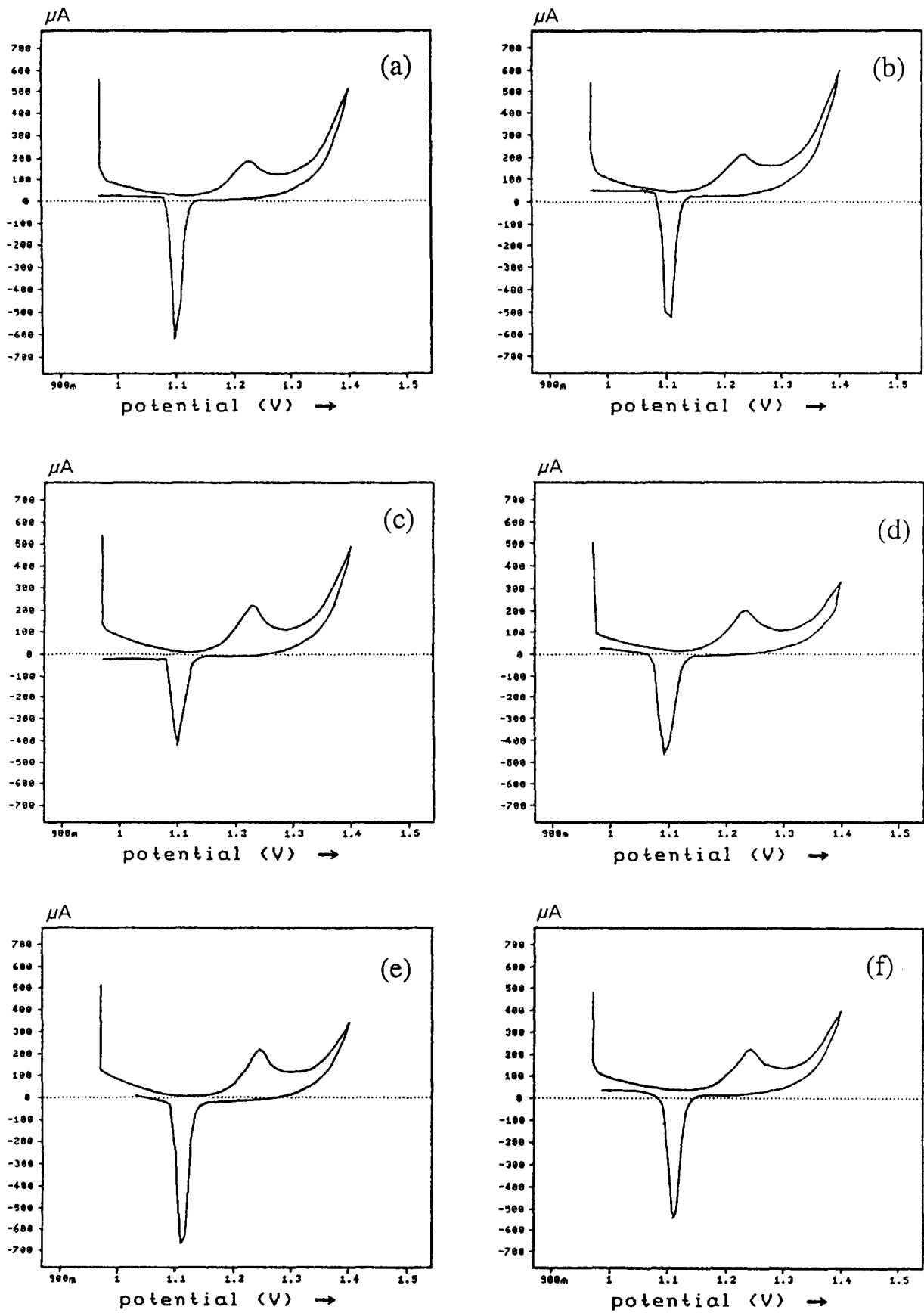
Fig. 1. Cyclic voltammograms of the lead electrode in 4.5 M H₂SO₄ containing: (a) 0%; (b) 0.2%; (c) 0.4%; (d) 0.6%; (e) 0.8%, and (f) 1.0% H₃BO₃.

Table 1
Effect of boric acid concentration on the peak potentials and peak currents of the cyclic voltammograms of the lead electrode in 4.5 M H_2SO_4

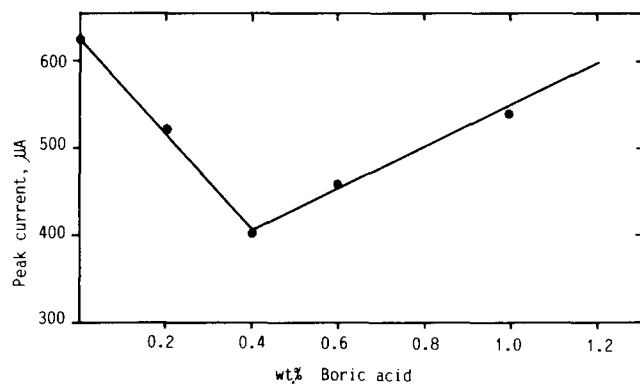| H_3BO_4 (wt.%)	Anodic peak		Cathodic peak	
	E_p (V)	I_p (μA)	E_p (V)	I_p (μA)
0	1.227	184.76	1.099	−620.68
0.2	1.235	214.00	1.108	−523.46
0.4	1.244	218.45	1.108	−407.00
0.6	1.244	210.00	1.108	−468.36
1.0	1.244	222.80	1.108	−546.46

Fig. 2. Reduction peak current of Fig. 1 as a function of boric acid concentrations.

acid. The peak heights, on the other hand, increased markedly with an increasing concentration of boric acid. This indicates that the presence of boric acid causes increased corrosion of the lead surface into PbO_2, and that a higher percentage of the PbO_2 in the corrosion film discharges.

3.2. Potentiostatic measurements

Although the potentiodynamic technique can be considered as an accelerated electrochemical test to provide useful information on corrosion characteristics, it may lead to incorrect predictions about the efficiency of oxide formation or reformation. The details of the cyclic voltammograms depend on the pretreatment, anodization time, acid activities, etc. [11]. For these reasons, it is useful to study the effect of boric acid on the PbO_2 positive electrode by carrying out potentiostatic measurements and subsequent self-discharge.

The lead electrode was corroded in 4.5 M H_2SO_4 without and in one containing 0.4 wt.% H_3BO_3 for 3 h at a constant potential of 1.425 V. During the corrosion process, the current was monitored as a function of time. At the end of the corrosion process, the potentiostat was switched off and the electrode was allowed to self-discharge in the same solution and at the same temperature. The results are presented in Figs. 4–6.
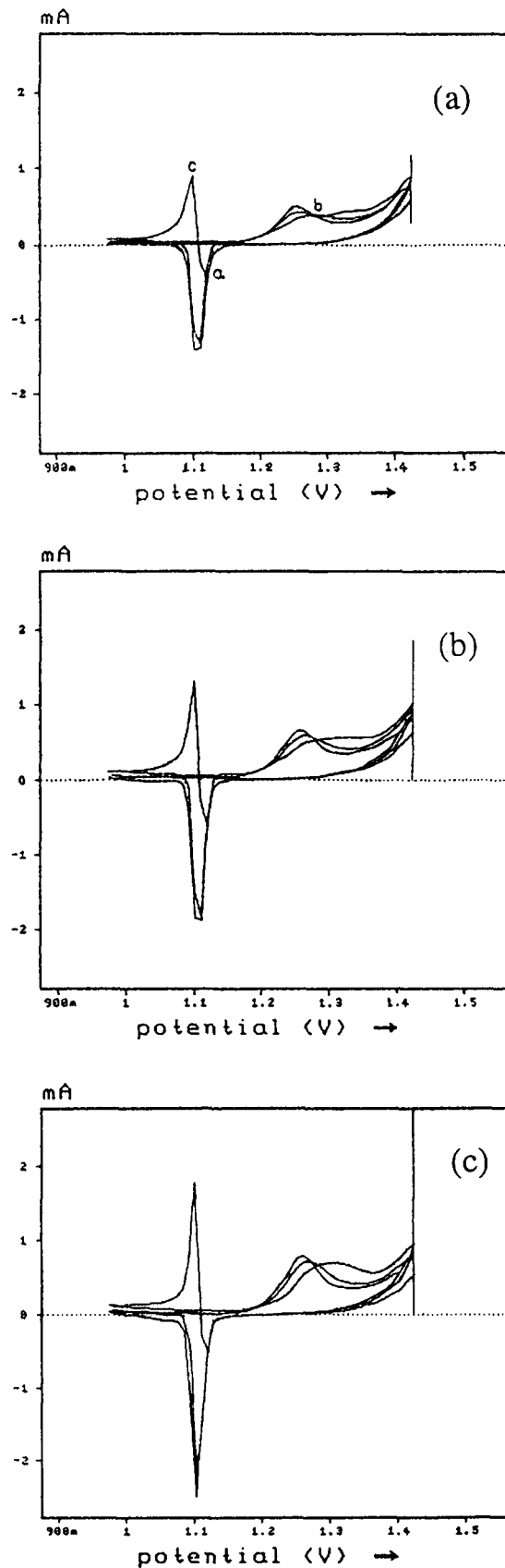

Fig. 3. Cyclic voltammograms (first, second and third cycles) of lead corroded at 1.425 V for 3 h in 4.5 M H_2SO_4 containing: (a) 0%; (b) 0.2%, and (c) 0.4% H_3BO_3. Scan rate: 0.2 mV S^{-1}.

Table 2
Anodic and cathodic peak potentials and peak currents for the third cycle of the lead electrode cycled in 4.5 M H_2SO_4 with different concentrations of H_3BO_4

H_3BO_3 (wt.%)	Anodic peak		Cathodic peak	
	E_p (V)	I_p (mA)	E_p (V)	I_p (μA)
0	1.103	1.394	1.253	−498.90
0.2	1.103	1.850	1.253	−666.24
0.4	1.103	2.487	1.262	−793.85

Fig. 4 shows the current–time transients for the potentiostatically anodized lead electrode in 4.5 M H_2SO_4 without and in one containing 0.4 wt.% boric acid. The current shows an extremely fast initial rise, followed by a gradual decay to a minimum, then increases again and a new peak due to the oxidation of $PbSO_4$ to β-PbO_2 in the outer part of the corrosion layer is obtained. The presence of boric acid is accompanied by a decrease in the current. This indicates passivation of the lead electrode and modification of the PbO_2 deposit. In Figs. 5 and 6, the voltage decay and impedance characteristics of the corroded lead electrode in the same solution are presented. The open-circuit self-depassivation process is clearly demonstrated. The addition of boric acid to a 4.5 M H_2SO_4 solution shifts the electrode potential towards more positive values (Fig. 5). The cell impedance in the first 30 min is lower in the presence of boric acid than in the absence of boric acid. At longer periods of time, the reverse trend was observed (Fig. 6). This behaviour can be attributed to the fact that, under our experimental conditions, the oxidation was carried out in 3 h, a time which is too short to form a dense layer. The film formed in the presence of boric acid seems to be thinner, homogeneous and adherent to the electrode surfaces [11]. Under open-circuit conditions, the PbO_2 film formed in the presence of H_3BO_3 discharges at a slower rate leading to low total impedance. Once the outer lead dioxide layer has been discharged (this depends on the pre-anodization time), higher impedance was observed (cf., Fig. 6). This behaviour is a good indication that the presence of boric acid modifies the morphological structure of the PbO_2 crystals, which delays its self-discharge to $PbSO_4$.

4. Conclusions

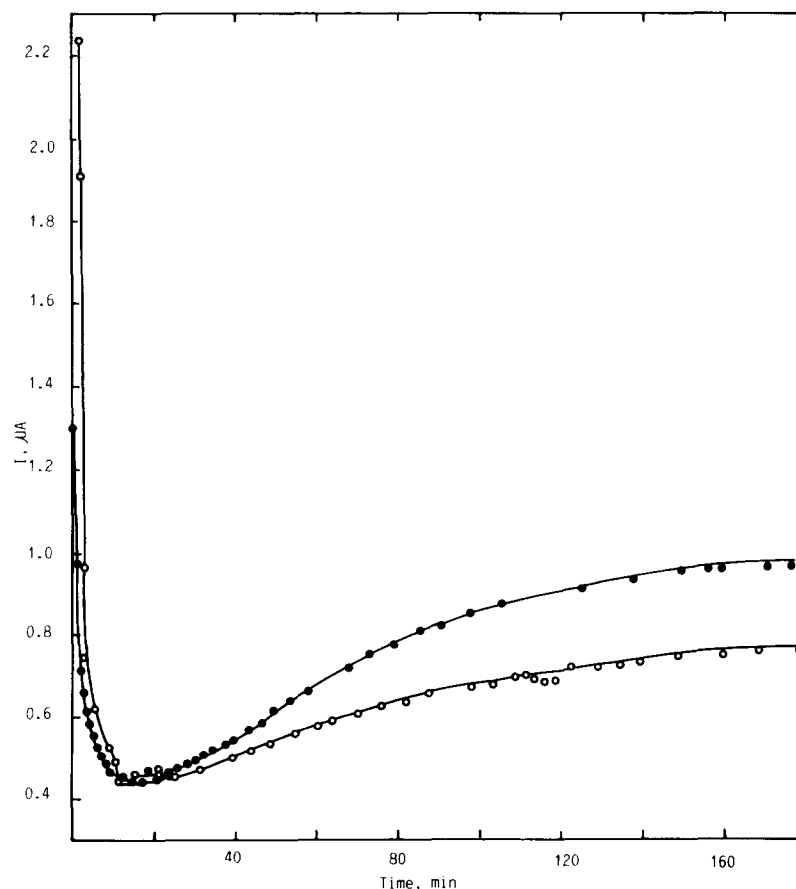Boric acid can be used as an additive to improve the performance of the positive electrode of the lead/

Fig. 4. Constant potential corrosion curves showing current vs. time for lead electrode corroded at 1.425 V in 4.5 M H_2SO_4: (●) without addition, and (○) containing 0.4 wt.% H_3BO_3.
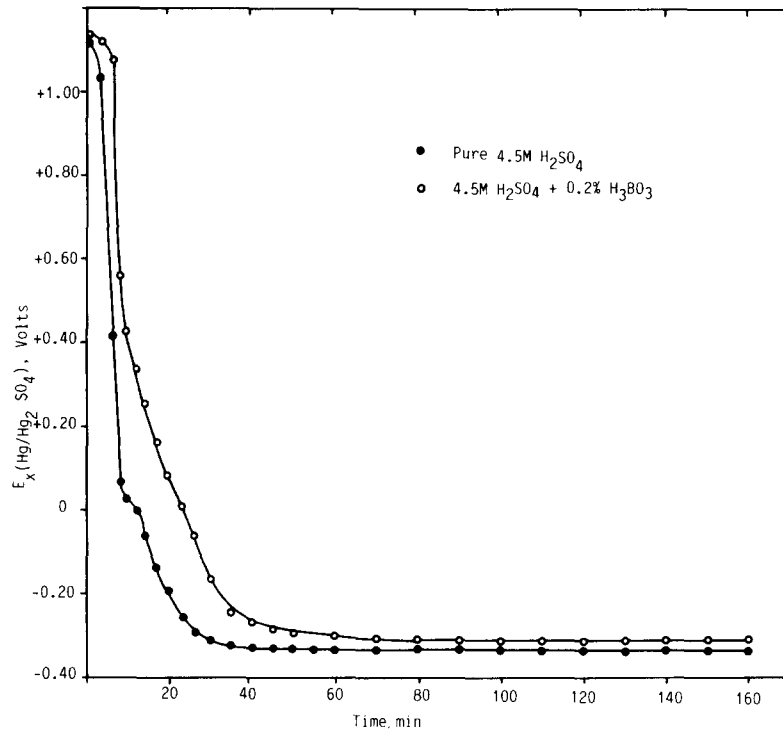
Fig. 5. Voltage decay curves in 4.5 M H₂SO₄ for lead electrode corroded at 1.425 V: (●) without addition, and (○) containing 0.4 wt.% H₃BO₃.
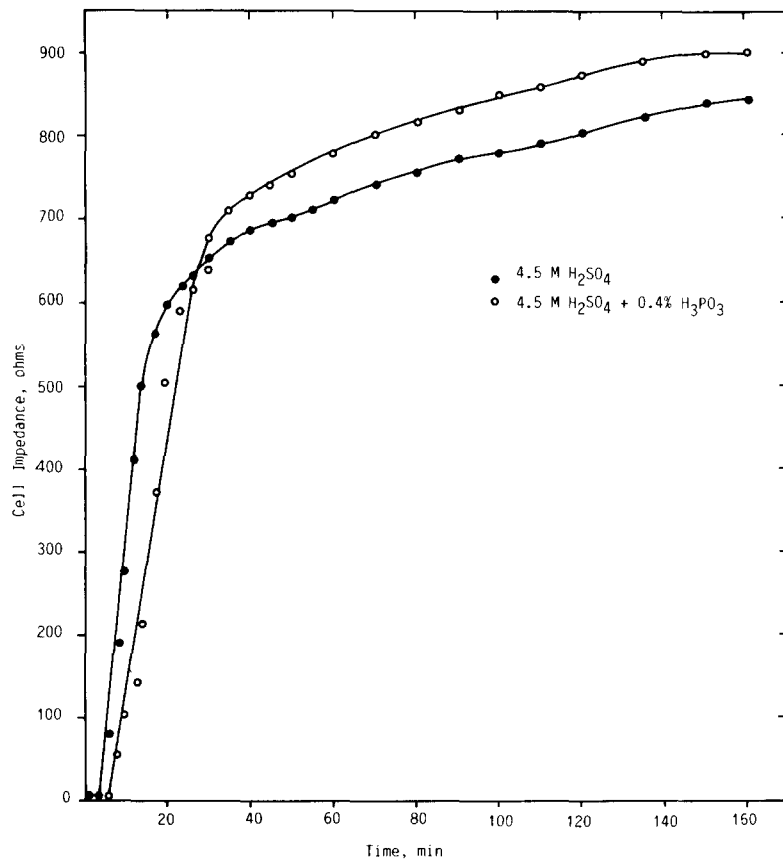

Fig. 6. Variation of cell impedance with time during self-discharge of the lead dioxide electrode in 4.5 M H₂SO₄: (●) without addition, and (○) containing 0.4 wt.% H₃BO₃.

acid battery. The presence of boric acid has advantages over phosphoric acid, in that it modifies the PbO_2 deposit without decreasing its formation efficiency from $PbSO_4$. H_3BO_3 inhibits the formation of the insulating $PbSO_4$ phase and, hence, decreases the self-discharge of the formed PbO_2.

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