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# An electrometric method for evaluation of the corrosion of lead alloys

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# Abstract

In an electrometric method, the lead electrode is subjected to electrolyte and temperature conditions, as well as various states of polarization that simulate the service of lead/acid batteries. The resulting corrosion layer is first reduced to lead sulfate then to sponge lead. A linear relation is observed between the weight of the corroded lead and the surface area of the sponge lead after cathodic reduction of the corrosion layer. This surface area is determined by measuring the time required to cover the lead completely again with lead sulfate at a specified current density and standardized conditions, irrespective of the test solution and test temperature. The results are very reproducible. The application of the electrometric method proves to be effective for the evaluation of lead–antimony–arsenic alloys in a wide range of sulfuric acid concentrations and at temperatures between 25 and 60°C. The study also suggests that the recommendation to reduce the acid's relative density (rel. dens.) in lead/acid batteries operated in tropical climates may be harmful to battery life. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lead/acid batteries; Electrometric method; Corrosion; Relative density

# 1. Introduction

The main challenge for lead/acid batteries to become effective power sources for vehicle is the need to increase specific energy and to extend deep cycle life. To this end, efforts have been made to reduce significantly the dead weight from non-energy producing components (i.e., grids, connectors, terminals, etc.) and to increase both the electrode-material utilization and battery cycle life [1,2]. These objectives are approached through the use of thin positive and negative plates which are produced from highly corrosion-resistant alloys. The challenge to thin plate design is more pronounced at elevated temperatures.

The sulfuric acid concentration is of major importance in battery design, especially under tropical conditions; various manufacturers recommend lower acid relative density (rel. dens.) under such conditions. The effect of sulfuric acid concentration has been included in some earlier studies but under conditions not related to battery service conditions [3–11].

In this work, series of studies have been planned to develop a mathematical model for lead/acid batteries designed for tropical applications. The aims of the present work are to develop a method for quantitative evaluation of the corrosion resistance of the lead and its alloys in sulfuric acid solutions and to determine the effect of temperature and sulfuric acid concentration on the corrosion of the pure lead and a lead-antimony-arsenic alloy.

Lead/acid battery service life is affected markedly by increasing temperature. It is usually limited by the corrosion of the positive grid. Such corrosion increases the internal resistance of the battery, causes the growth of the positive grid and eventually loss of the contact between the grid and the active material. The corrosion of lead-antimony grids also releases antimony which increases the self-discharge and increases the rate of hydrogen evolution and, hence, water loss.

Several authors [12–18] have recently studied the corrosion of lead at constant potential or under certain service conditions. These studies aimed to reveal the corrosion mechanism of various alloys and to make qualitative evaluation of the corrosion resistance of various alloys. The anodic oxidation of lead electrodes in sulfuric acid has been studied extensively and the electrochemical method used in the work reported here has been reported a long time ago [19–25]. The method is only applicable, however, under the condition that the quantitative reduction of the oxide layer is possible and most of the results reported cannot be correlated on a quantitative basis under condi-

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tions similar to service conditions. There is a need for quantitative evaluation of lead alloy electrodes in sulfuric acid solutions to develop the thinnest possible durable grids for plates with high specific energy and deep cycling service.

# 2. Experimental

# 2.1. Electrodes

The electrodes were prepared by casting pure lead or a lead–antimony alloy. The composition of the alloy was determined by atomic absorption spectroscopy. The results are given in Table 1. The electrodes were in the form of rods, each with a cross-sectional area of  $0.54 \text{ cm}^2$ . Unless otherwise stated, the surface pre-treatment and the polishing of the electrode was similar to that described previously [18]. The electrode was then quickly immersed in the electrolyte and cathodically reduced at 2 mA for 2 min. The counter electrode swere platinum plates (a1 and a2, Fig. 1) and the electrode potential was measured against a  $Hg/Hg_2SO_4$  reference electrode. The electrode potentials were then calculated with respect to the standard hydrogen electrode potential.

#### 2.2. Test cell

The arrangement of the test cells and the electrodes is shown in Fig. 1. The test cell, C1, was filled with 1.28 rel. dens. sulfuric acid. A 'reference cell' denoted in the diagram by C2 was filled with 3 N sulfuric acid. The temperature of the 'reference cell', C2, was always kept at  $25 \pm 0.5^{\circ}$ C, while the temperature of the cell, C1, was controlled at the test temperature within  $\pm 0.5^{\circ}$ C by using a thermostatic water bath.

#### 2.3. Experimental technique

The weight of metal oxidized during anodic polarization was calculated as follows:

$$W = \frac{iMT_{\rm P1}}{NF} \tag{1}$$

where: W is the weight in grams (g) of metal anodically dissolved; i is the current in amperes (A); M is the gram

Table 1 Composition of electrodes

Element	Pure lead	Lead-antimony	
Antimony	0.0576	5.5486	
Arsenic	0.0055	0.1117	
Tin	0.0014	0.0760	
Copper	0.0008	0.0200	
Bismuth	_	0.0125	
Iron	_	0.0050	
Silver	_	0.0032	

al E Reference electrodytic a2 bridge c1 C2

Fig. 1. Arrangement of test cells and electrodes.

molecular weight of the metal;  $T_{P1}$  is the time in seconds (s) to cover completely the lead electrode with lead sulfate; N is number of Faradays per gram mole; F is the Faraday number.

Dividing W by the density of the metal (d) results in the volume of the metal dissolved. If the volume of the metal is divided by the electrode area (A), then the average depth of attack,  $D_0$ , can be obtained, i.e.,

$$D_o = \frac{iMT_{\rm Pl}}{NFAd}.$$
 (2)

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This calculation is valid when lead is converted to lead sulfate with no gas evolution. Subjecting the lead electrode to anodic polarization until the end of the lead/lead sulfate potential plateau allows determination of the amount of lead oxidized to lead sulfate. Cathodic reduction of this corrosion layer will result in a layer of sponge lead. The surface of the resulting sponge lead provides a measure of the quantity of lead sulfate formed or the depth of attack. Thus, the time of passivation,  $T_{P2}$ , of the resulting lead is a measure of the lead sulfate weight or the depth of attack:  $T_{P2} \propto D_0$ .

Subjecting the electrode to varying current densities results in varying  $T_{\rm Pl}$ . At each current density,  $T_{\rm Pl}$  was measured and the depth of attack ( $D_{\rm o}$ ) was calculated by the use of Eq. (2). Also for each current density, the corrosion layer was reduced and  $T_{\rm P2}$  for the resulting sponge lead surface was measured. Using standard regression equations to relate the values of  $D_{\rm o}$  and  $T_{\rm P2}$ , a linear relation was found with an excellent correlation coefficient. The regression equation is as follows:

$$D_{\rm c} = mT_{\rm P2} + b \tag{3}$$

where  $D_c$  is the calculated average depth of attack from the regression calculations,  $T_{P2}$  is the time needed to completely cover the surface of the treated electrode with lead sulfate in a specific solution under standardized conditions in a 'reference cell', *m* and *b* are experimental constants. The values of *m* and *b* were found to be dependent on the electrode and electrolyte composition and the prevailing temperature. It was found that if  $T_{P2}$ was always measured in a reference cell, preferably 3 M sulfuric acid, irrespective of the test solution, the results were reproducible.

All these measurements were carried out in the lead/lead sulfate potential area (Fig. 2). Once the values of m and b were determined for a given lead alloy and specific sulfuric acid concentration, additives, temperature, etc., the working electrode could be subjected to a controlled corrosion environment which is similar to battery service conditions until oxygen evolution commences. At this point, the current was reversed at a higher value and the corrosion layer was reduced to lead sulfate which contained isolated patches of lead dioxide. The electrode was then moved to the reference cell (C2) to complete the reduction of the corrosion layer to lead sulfate and then to sponge lead. The time needed to cover this sponge lead with lead sulfate was indicated by a sharp rise in electrode potential (Fig. 2) and was denoted  $T_{P2}$ . From Eq. (3) the average depth of attack  $(D_c)$  can be determined for a specific electrolyte and an electrode with known m and bvalues.

In the reference cell, C2, an anodic current of 1.85 mA cm<sup>-2</sup> was chosen to allow an accurate determination of the end of the Pb/PbSO<sub>4</sub> potential plateau (Fig. 2), while the cathodic current density, 3.7 mA cm<sup>-2</sup>, was higher in order to minimize the effect of local action before reduction of the lead dioxide layer. The duration of the cathodic reduction was always 120 s for a freshly polished electrode, but for a test electrode, subjected to anodic corrosion, the cathodic duration was much longer and depended on the quantity of anodic polarization products. It was found that reproducible results could be obtained if the quantity of electricity was equal to, or larger than, three times the theoretical value. Thus, the following relation was used to determine the proper reduction period:

$$T_{\rm c} = \frac{3I_{\rm a}T_{\rm a}}{I_{\rm c}} \tag{4}$$

where:  $I_{\rm a}$  and  $I_{\rm c}$  are the anodic and cathodic currents;  $T_{\rm a}$  and  $T_{\rm c}$  are the periods of anodic and cathodic polarization in seconds (s), respectively.



Fig. 2. Measurement of time required to cover the electrode surface with lead sulfate.

In the lead/acid battery, the positive grids are subjected to corrosion both during charging and at rest. Therefore, the corrosion evaluation in the present study was carried out under conditions of repeated cycles of charge and rest. The test electrodes were polished, wiped with filter paper, left for 15 min exposed to the air, dipped in the test solution for 5 min and then subjected to 20 cycles of charge and rest. Each cycle comprised 2 min anodic polarization at a current density of  $1.85 \text{ mA cm}^{-2}$  and a rest period at open circuit for 2 min. The anodic treatment was sufficient to passivate the electrodes in the first half cycle and ensure the onset of oxygen evolution. This provided test conditions similar to those prevailing during battery service. The solutions were prepared by dilution of concentrated AR sulfuric acid. To simulate battery service conditions, the solution of the test cell was saturated with lead sulfate. To maintain saturation of the test cell, cathodic pre-treatment, in contrast to work described above, was carried out in a cell that was dedicated for this purpose. Measurements were carried out at constant temperatures in the range 25 to  $60 \pm 0.5^{\circ}$ C.

At the end of the 20th cycle, the anodic circuit was switched on instantaneously to reduce the PbO<sub>2</sub> film in the test solution at a current density of 3.70 mA cm<sup>-2</sup> until the end of the PbO<sub>2</sub>/PbSO<sub>4</sub> potential plateau. The electrodes were then rinsed in 3 M sulfuric acid solution and subjected to further cathodic reduction in the reference cell which contained 3 M sulfuric acid, at a current density of 3.70 mA cm<sup>-2</sup> for more than 20 min. The average depth of attack,  $D_c$ , was calculated according to Eq. (3). The values, *m* and *b*, are constants which depend upon the acid concentration and temperature of the 'test cell'. These values were first determined at various temperatures for each acid concentration according to a method described previously.

#### 3. Results and discussion

### 3.1. Evaluation of a lead-antimony-arsenic alloy

In a preliminary investigation, the electrode was subjected to anodic corrosion in 3 M  $H_2SO_4$  by passing a current of 0.4 mA for 30 min at 25°C. A typical galvanostatic cathodic polarization curve for such an electrode is shown in Fig. 3. The curve exhibits three potential arrests at about +1.6, -0.1 and -0.3 V before the hydrogen evolution potential [10]. The potential of the first and the third arrests are comparable, respectively, with those of the PbO<sub>2</sub>/PbSO<sub>4</sub> and PbSO<sub>4</sub>/Pb reactions. The curve reveals that the first arrest is reduced considerably, relative to the third arrest, although both reactions involve the transfer of two electrons. This is due to the fact that after interrupting the anodic current, the lead dioxide coating forms a number of small galvanic cells with the underlying lead, with subsequent formation of lead sulfate. Therefore, the differ-



Fig. 3. Potential-time curve during reduction of the corrosion layer.

ence between the duration of both arrests is due to the following. (i) The number of coulombs equivalent to the formed lead sulfate are subtracted from the first arrest and added to the third arrest. (ii) During the first arrest, since the  $PbSO_4$  was formed under the  $PbO_2$  layer, due to interaction with underlying lead, some of the  $PbO_2$  should be expected to remain unchanged and electronically isolated from the electrode by the newly formed  $PbSO_4$ . This isolated  $PbO_2$  does not contribute to the first potential arrest which was markedly shorter than the third arrest. (iii) Some of the lead dioxide deep in the corrosion layer can be reduced to  $PbO \cdot PbSO_4$  instead of  $PbSO_4$ .

The marked deviation of the two potential arrests in the curve shown in Fig. 3 illustrates the need for this new approach to evaluation of electrometric corrosion. These sources of error are specific for the lead anode. Another source of error, common for many metals including lead, is the evolution of hydrogen on a partly reduced surface.

The duration of the first arrest has been considered by some investigators [19–25] to be a measure of the corrosion of the lead anode. Ruetschi and Cahan [25] used the electrometric method to determine the quantity of PbO<sub>2</sub> formed on the electrode, taking in consideration the unreduced PbO<sub>2</sub> and local action. They estimated, by microtitration, the amount of PbO<sub>2</sub> left in the layer. In order to eliminate local action under given conditions, they performed several runs at different current densities and extrapolated the results to zero time of cathodic reduction. In the present work, the electrode was completely reduced to sponge lead by extending cathodic reduction sufficiently after hydrogen evolution. Then the duration needed to cover the resulting surface with lead sulfate in the reference bath was determined as shown in Fig. 2. It was found that the time of passivation  $(T_{\rm P2})$  was a measure of the degree of attack exerted on the electrode. This procedure was quite reliable when sufficient cathodic reduction was carried out and the measurement in the 'reference bath' was undertaken at fixed current density and temperature.

#### Table 2

Values of  $D_{\rm o}$  determined by Eq. (2) and  $D_{\rm c}$  calculated from slope and intercept values of the regression of  $D_{\rm o}$  values (pure lead electrode)

$T_{\rm P1}$ (s)	$D_{\rm o}$ (µm)	$T_{\rm P2}$ (s)	<i>D</i> <sub>c</sub> (μm)	
42.5	7.44	77.4	7.50	
59.8	10.47	98.0	10.54	
73.2	12.81	112.4	12.66	
86.6	15.16	127.8	14.93	
96.2	16.84	141.7	16.98	
107.3	18.78	154.6	18.88	
118.3	20.71	167.0	20.71	
127.8	22.37	178.4	22.39	
137.0	23.98	188.5	23.88	
159.4	27.90	215.8	27.91	
175.0	30.63	235.2	30.77	
192.4	33.67	255.6	33.78	
207.2	36.26	271.4	36.11	
219.2	38.37	286.5	38.34	

3.1.1. Lead electrode in 1.28 rel. dens. sulfuric acid solution

To determine the values of m and b in Eq. (3), a series of tests were performed that comprised the anodic polarization of a lead surface until the end of the Pb/PbSO<sub>4</sub> potential plateau was reached (Fig. 2). The average depth of attack  $D_0$  was determined by measuring the time required to cover the lead surface with lead sulfate  $(T_{P1})$  and applying Eq. (2) and then reducing the formed lead sulfate layer at 3.7 mA for a period according to Eq. (4) until it was reduced completely to sponge lead. The time required to cover this sponge lead surface with lead sulfate in the reference cell is called  $T_{P2}$ . The constants *m* and *b* in Eq. (3) for lead in 1.28 rel. dens. sulfuric acid solution were determined by regression of the  $T_{P2}$  data against the average depth of induced attack  $D_{\rm o}$ . The measurements  $T_{\rm P1}$  and  $T_{\rm P2}$  are taken as 'one cycle'. Several cycles were carried out. Each time the same electrode was used and repeated anodic and cathodic reductions increased the depth of corrosion. On each cycle,  $T_{P1}$  was measured in the test cell and  $T_{P2}$  was measured in the 'reference cell'. The results are given in Table 2.



Fig. 4. Linear relation between average depth of attack  $D_{\rm o}$  and  $T_{\rm P2}$  for pure lead.

Table 3 Average depth of attack of pure lead electrode in 1.280 rel. dens. sulfuric acid

Exposure time (h)	$T_{\rm P2}$ (s)	$D_{\rm c}$ (µm)	
0.08	89.7	9.3	
0.17	101.0	11.0	
0.45	118.2	13.5	
1.00	163.0	20.1	
2.33	235.5	30.8	
3.40	285.2	38.1	
20.00	1108.0	159.4	
43.33	1523.0	220.6	



Fig. 5. Linear relation between average depth of attack  $D_0$  and  $T_{\rm P2}$  for lead-antimony-arsenic alloy.

The values of *m* and *b* calculated from the data in Table 2 are 0.147 and -3.90, respectively. The results show strong linear relation between the average depth of attack  $D_0$  and  $T_{P2}$  which is presented in Fig. 4. The coefficient of correlation is 0.999 and the coefficient of determination amounted to 99.98%. In other words, the variation in the value of  $T_{P2}$  accounted for the variation in the depth of attack by 99.98%. The standard error in the depth for this series of measurements was 0.13  $\mu$ m.

After determining the value of each of the constants m and b in Eq. (3), it is now possible to measure the depth of attack in the test cells. The pure lead electrode was subjected to anodic corrosion at 1.85 mA cm<sup>-2</sup> and 25°C for different periods of time, after which  $D_c$  was determined in each case from the values of m and b derived from Table 2 according to Eq. (3). The period of exposure to corrosion varied from 5 to 2600 min. In all these tests, oxygen started to evolve after about 0.02 h. The results are given in Table 3.

# 3.1.2. Lead-antimony-arsenic electrode in sulfuric acid solution (1.28 rel. dens.)

The values of m and b, calculated from the data in Table 4 are 0.136 and -5.42, respectively. The results also show strong linear relation between the average depth

Table 4

Values of  $D_o$  determined by Eq. (2) and  $D_c$  calculated from slope and intercept values of the regression of  $D_o$  values (Pb–Sb–As electrode)

$T_{\rm P1}$ (s)	$D_{\rm o}$ ( $\mu$ m)	$T_{\rm P2}$ (s)	$D_{\rm c}$ (µm)
22.5	4.10	72.2	4.43
42.5	7.75	94.5	7.48
60.0	10.95	115.0	10.27
81.4	14.85	147.8	14.75
105.5	19.24	182.5	19.49
128.4	23.42	215.0	23.92
150.4	27.44	241.0	27.47
168.9	30.81	267.8	31.13
186.4	34.00	290.0	34.16
201.5	36.76	308.5	36.69
218.3	39.82	334.7	40.26
238.0	43.42	351.8	42.60
251.3	45.84	374.8	45.74

of attack  $D_{\rm o}$  and  $T_{\rm P2}$ , which is presented in Fig. 5. The coefficient of correlation is 0.9996 and the variation in the value of  $T_{\rm P2}$  accounted for the variation in the depth of attack by 99.96%. The standard error for this series of measurements was 0.42  $\mu$ m.

The lead-antimony-arsenic electrode was then subjected to anodic corrosion at 1.85 mA cm<sup>-2</sup> and 25°C for various periods. In each case,  $D_c$  was determined from the values of *m* and *b* according to Eq. (3). The period of exposure to corrosion varied from 5 to 2600 min. The results are given in Table 5.

Although both the lead and the alloy electrodes were passivated after about 0.01 h and oxygen started to evolve in both cases after about 0.02 h, the results in Tables 3 and 5 for either the pure lead or the lead–antimony–arsenic alloy indicate that corrosion continued after passivation and most of the attack occurred after oxygen evolution. To gain further insight into the mode of attack of both electrodes, the results were calculated in terms of the rate of penetration per hour. As the rate of attack varied greatly with time, the results are represented in Fig. 6 in three sets of X-Y scales. The curves reveal that the rate of penetration on the metal surface slows down with time. The first set of curves shows the rate of penetration of a fresh metal surface. The second phase is characterized by passing through a minimum and a maximum. This appears to be

Table 5

Average depth of attack of Pb-Sb-As electrode in 1.280 rel. dens. sulfuric acid

Exposure time (h)	$T_{\rm P2}$ (s)	$D_{\rm c}$ (µm)			
0.08	84.7	6.1			
0.17	88.8	6.7			
0.45	116.4	10.5			
1.00	151.0	15.2			
2.33	220.5	24.7			
3.40	278.6	32.6			
20.00	973.6	127.5			
43.33	1543.1	205.2			



Fig. 6. Variation of corrosion rate of lead and alloy with time.

the same for both the lead and the alloy electrodes. In the third phase, the electrode is covered completely by an impervious layer of lead dioxide. At this stage, the corrosion rates finally diminish to very low values. The curves also indicate that the alloy is more corrosion resistant in the first two phases. During the third phase, when the electrode is covered by the lead dioxide layer, the difference in the substrate is not significant. The three phases repeat with time when the lead dioxide layer cracks under the stress of the more voluminous lead dioxide formed from the more dense lead substrate.

# 3.2. Effect of temperature and acid relative density on lead–antimony–arsenic alloy

In lead/acid battery applications, it is common practice for the acid concentration to be expressed as the relative density of  $H_2SO_4$ . The results of measuring the depth of attack in various relative densities are summarized in Table 6 and plotted in Fig. 7. It is found that the relative density of  $H_2SO_4$  has a marked effect on the corrosion of

Table 6 Average depth of attack (in µm) of lead-antimony-arsenic anode after 20 cycles of anodic polarization and rest

Sulfuric acid relative density 25°C/25°C	Average depth of attack at $25^{\circ}$ C $\mu$ m <sup>-1</sup>	Average depth of attack at $60^{\circ}$ C $\mu$ m <sup>-1</sup>
1.02	51.7	125.7
1.05	60.0	134.5
1.09	59.7	125.7
1.15	41.3	108.5
1.22	21.6	76.1
1.24	18.7	64.1
1.26	15.5	62.6
1.28	12.9	41.8
1.30	10.7	40.5
1.32	11.1	33.7
1.35	8.8	28.9
1.40	5.2	16.6



Fig. 7. Effect of sulfuric acid relative density on the depth of attack of lead alloy at 25 and  $60^{\circ}$ C and on the solubility of PbSO<sub>4</sub> at 25°C.

lead. At very low sulfuric acid concentrations, the corrosion increases with increasing relative density. It then decreases at relative density values beyond 1.050 up to 1.400. This range of acid relative density is that used at different stages of battery manufacture and service in various applications. If the values of the solubility of lead sulfate in sulfuric acid [26] are also plotted for comparison, it becomes clear that the corrosion of the lead anode, even after passivation, is governed by the solubility of lead sulfate or the solubility of divalent lead ion.

The calculated values of m and b in each acid concentration and at each temperature are shown in Table 7. The experimental results show a strong polynomial relation (of order three) between the depth of attack and the relative density. This relation is plotted in Fig. 8. At 25°C, the coefficient of correlation is 0.991 and the coefficient of determination is 98.16%. At 60°C, the coefficient of correlation is 0.990 and the coefficient of determination is 98.06%. Therefore, the variation in the depth of attack accounted for the variation of the relative density of sulfuric acid by 98.16% and 98.06% and 25 and 60°C, respectively.

There has been considerable effort devoted to the improvement of lead/acid battery performance at tempera-

Table 7										
Values of m	and h	in in	different	acid	relative	densities	at	25	and	60°C

Sulfuric acid	25°C		60°C		
relative density 25°C/25°C	$m(10^{-3})$	$-b(10^{-2})$	$m(10^{-3})$	$-b(10^{-2})$	
1.02	2.106	5.8351	2.270	9.9375	
1.05	2.164	7.2689	2.399	10.0172	
1.09	2.165	7.6871	2.508	9.3102	
1.15	2.156	10.6843	2.287	10.1160	
1.22	1.883	9.2903	2.039	7.8365	
1.24	1.795	7.0200	2.039	8.4240	
1.26	1.736	8.2448	1.915	6.9105	
1.28	1.480	5.5861	1.871	8.7526	
1.30	1.465	6.9503	1.769	8.0357	
1.32	1.504	8.6729	1.652	6.2632	
1.35	1.195	6.6018	1.545	5.4169	
1.40	0.936	6.0243	1.112	3.7440	



Fig. 8. Effect of sulfuric acid relative density and temperature on the value of m.

tures below 0°C. There are many other applications, however, in which high-temperature environments are encountered, such as standby and solar power systems and electric vehicles. In automotive battery applications, most manufacturers recommend decreasing the acid gravity in tropical areas from 1.280 to 1.240. The results in Fig. 7 indicate, however, that the depth of attack increases not only with increasing temperature but also with decreasing acid relative density. This result is in agreement with the potentiostatic study carried out by Dasoyan and Aguf [27] who found that the rate of corrosion decreased with increase in the concentration of sulfuric acid. Thus, automotive batteries are subjected to much more severe conditions in tropical climates than in cold climates, especially when a lower acid relative density is employed. The same should also apply to stationary and solar applications to varying degrees. The effect of reducing acid gravity in high-temperature applications is indicated by the increase in the level of the two arrows in Fig. 7. Table 6 shows that the depth of attack after 20 cycles of charge and rest was 12.9  $\mu$ m in 1.28 rel. dens. acid at 25°C and 64.1  $\mu$ m in 1.24 rel. dens. acid at 60°C.

The engine compartment of modern vehicles is becoming increasingly packed with components all of which serve to increase the temperature in this compartment. Some engines are even designed to run at temperatures higher than 100°C. The present results indicate that these trends in vehicle design should be considered in tropical battery designs. The electrolyte temperature during service in hot climates has been found to vary between 54 and 93°C, depending on the design of the engine compartment.

#### 4. Conclusions

In the electrometric method used here, the electrode is subjected to electrolyte, temperature and various states of polarization that simulate the service conditions of head/ acid batteries. The resulting corrosion layer is first reduced to lead sulfate then to sponge lead.

A linear relation is found to exist between the average depth of corrosion of the corroded lead or lead alloy electrode and the surface area of the sponge lead resulting from cathodic reduction of the corrosion layer. The surface area is determined by measuring the time required to cover completely this surface with lead sulfate in a specific solution under standardized conditions. The corrosion of the lead anode take places in three phases. Initially, there is a high rate followed by a minimum and a maximum during the second phase. Finally, the rate markedly slow downs with time during the third phase. The lead-antimony-arsenic alloy is more corrosion resistant than pure lead during the first two phases. After 43.33 h of continuous polarization of a polished surface, the depth of attack at a current density of 1.85 mA  $cm^{-2}$  is 220.2 and 205.1 μm, for pure lead and alloy, respectively.

The application of the new electrometric method is an effective method for the evaluation of the lead– antimony–arsenic alloy over a wide range of acid concentrations which cover most battery applications and at temperatures between 25 and 60°C. It allows a quantitative evaluation of the depth of attack on the lead and lead alloy anodes during anodic polarization cycles, with each cycle followed by a rest period. The results also indicated that the solubility of the Pb<sup>+2</sup> ions is the major factor in the corrosion of lead anodes even after passivation and during conditions similar to those prevailing during the service life of the lead/acid battery.

The study also suggests that the recommendation to reduce acid relative density in tropical climates could enhance deterioration of the positive plates. The reduction in relative density and the elevated temperature combine to affect markedly lead/acid battery life under tropical service conditions.

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