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THE CONSTANT-POTENTIAL ANODIZATION OF LEAD IN SULFURIC ACID SOLUTIONS

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ABSTRACT

The rate of attack on pure lead, anodized at various constant potentials in sulfuric acid solutions, was studied. It was found that, below potentials for PbO_2 formation, tetragonal PbO is formed at rates given by the activation equation,

$$w = nke^{\alpha zFV/RT} \int_0^t adt.$$

The PbO is attacked chemically by the electrolyte to form an outer layer of $PbSO_4$. At higher potentials, PbO_2 is formed as a protective film.

The inflection in the curve for the constant current-potential anodization of lead (occurring at about 0.23 to 0.24 volt anodic to the standard hydrogen electrode) corresponds to that calculated thermodynamically for PbO formation.

An analysis of the problem of positive-grid corrosion in the lead-acid cell is included.

PROBLEM STATUS

This is an interim report on the grid corrosion problem; work is continuing.

AUTHORIZATION

NRL Problem C05-16R
NS 677-059

THE CONSTANT-POTENTIAL ANODIZATION OF LEAD IN SULFURIC ACID SOLUTIONS

BACKGROUND

The experimental work with which this report is concerned was conducted in an attempt to obtain information about the mechanism of corrosion of the positive grid in the lead-acid battery. It was hoped that the results might indicate methods of slowing down or preventing the corrosion, thus extending battery life. A previous report[1] gives more detailed background and references to earlier work done at this Laboratory and elsewhere. It was decided to confine the present study to the rate of corrosion of pure lead rather than of alloys, since lead is the simplest system possible and therefore might be the easiest from which to obtain fundamental information.

THEORY

The theoretical aspects may conveniently be considered from two viewpoints. First, what is the chemical reaction and its mechanism, and second, since an insoluble corrosion product forms which adheres more or less firmly to the metallic lead, what is the physical nature of this product and what is the mechanism of its production?

The chemical nature of the products formed may, in general, be determined by chemical analysis or physical analytical methods (such as those using X-rays or electron diffraction), and, if the original substances present in the system are known, then the over-all reaction is usually evident. However, if the reaction takes place in several steps, succeeding one another in time, the nature of these steps (the chemical mechanism) is not necessarily apparent, particularly in a heterogeneous process such as electrochemical reaction at an anode. The situation may, indeed, be quite complex. For example, water in the electrolyte may furnish several ions for reaction, depending on potential and pH, or a metal having more than one oxidation state will form two or more products, depending on potential. In the case of lead in sulfuric acid electrolyte, it would be expected that, above the equilibrium potential for the PbO_2-$PbSO_4$ couple, a PbO_2 film would be formed, while below that potential $PbSO_4$ would be formed.

Previous work[2] has shown that, in electrolytes the anion of which forms an insoluble salt with lead, an outer coating of the salt will be formed, together with an underlying coat

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[1] *Power, W.H., Rabideau, S.W., Kern, R.A., Pierce, R.T. and Lander, J.J., "Investigation of Methods of Increasing Life and Capacity of Lead Acid Storage Batteries, I," NRL Report No. P-2908, January 9, 1947, and previous reports there referred to.*

[2] *Wolf and Bonilla, Trans. Electrochem. Soc. 79, 307, 1941, and references there quoted.*

of tetragonal PbO. The mechanism offered for the formation of the PbO film may be stated in the following steps:

1. Initial formation of Pb^{++} at the anode, with deposition of the lead salt when the solubility product is exceeded.

2. Depletion of the anions of the solute in the salt, together with migration of H^+ out of and OH^- into the reaction area, bringing about an increase in pH until the value for the formation of PbO is reached, whereupon the lead salt and PbO will be formed simultaneously.

3. Further depletion of the anion of the salt until almost all of the current goes to the formation of PbO. Under these conditions the electrode reaction must consist of discharge of OH^- ions, or the decomposition of water, from which it follows that the current is carried through the dense coating of PbO by H^+ and OH^- ions.

In the present report the physical nature and mechanism is considered to be associated with such phenomena as the continuity or porosity of the film; rates of nucleation and growth in the crystal aggregate making up the film; orientation effects; diffusion speeds of ions, atoms, or molecules through the film itself or through the electrolyte in the pores of the film; and the nature and distribution of any potential differences involved. From the standpoint of rates, the physical side of the picture may be more important than the chemical because the physical nature of the film might determine the rate of attack. For example, the formation of a perfectly continuous and electrically insulating film would make the corrosion rate negligible.

Wolf and Bonilla[3] show that the very nature of the electrochemical reaction may be changed by diffusion limitations. Implicitly they give other information as to the physical mechanism, since it may be presumed that the reaction is taking place at the bottom of pores or discontinuities in the film (OH^- ion is described as migrating into the reaction area). Furthermore, if Pb^{++} ion were to reach the film-electrolyte interface, the salt would be formed in preference to the oxide unless there is considerable concentration polarization of the anion of the salt, an improbable condition for other than initial rates.

Two possible modes of film growth are at once apparent: either the film is continuous or it is porous. If the film is continuous, the rate of reaction is limited either by the reaction rate at one of the interfaces or by migration of ions through the film. In the first case the film would build up linearly with time[4] as given by the equation,

$$w = Bt, \qquad (1)$$

where w is the weight of the film, B is a constant, and t is time. If the rate is limited by migration of ions, the situation is analogous to the high-temperature oxidation of metals, where it has been shown[5,6] that in the simplest case the relation between weight and time

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[3] *Ibid.*

[4] *Mott, N.F. and Gurney, R.W., "Electronic Processes in Ionic Crystals," Oxford at the Clarendon Press, 1940, p. 250.*

[5] *Hoar, T.P. and Price, L.E., "Chemical Reactions Involving Solids," The Faraday Society, 34, 867-874, April 1938.*

[6] *Wagner, C., Beitrag zur Theorie des Anloufvorganges, II, Z. Physik. Chem., B32, 447-462 (1936).*

is parabolic. That is,

$$w^2 = kt, \tag{2}$$

wherein the constant k contains V_o, the potential existing across the film, to the first power, so that the relation between w and V_o for constant time should also be parabolic.

If the film is porous, the theoretical analysis is much more complex because of the variety of factors involved. If the intrinsic rate of the reaction itself is controlling, then the activation equation[7,8,9,10] for the rate may be expected to apply at potentials sufficiently removed from equilibrium:

$$i = k e^{\alpha zFV/RT}, \tag{3}$$

where:

i = the current density;

k = a constant related to the specific reaction velocity constant;

α = a constant, the nature of which is still problematical;

F = the Faraday;

R = the gas constant;

T = the absolute temperature;

z = the electron change for the reaction; and

V = the voltage.

Experimentally, a plot of log i vs. V should result in a straight line at constant temperature. The total current, I, is equal to the current density times the available area, a, so:

$$I = ake^{\alpha zFV/RT} \tag{4}$$

If a film is formed and Faraday's law applies, we may use:

$$w = n\int_o^t I\,dt, \tag{5}$$

where w is the weight of metal attacked (or the film weight), and n is the equivalent weight divided by the Faraday, to obtain:

$$w = nke^{\alpha zFV/RT}\int_o^t a\,dt, \tag{6}$$

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[7] *Glasstone, S., "Introduction to Electrochemistry," Van Nostrand Co., Inc., New York City, 1942, p. 251.*

[8] *Audubert, "Electrode Processes," Discussion of the Faraday Society No. 1, 1947, p. 73.*

[9] *Randles, Ibid, p. 13*

[10] *Durdin, Uchenye Zapiski Lenigrad. Gosudarst Univ., Ser. Khim. Nauk 1939, No. 4 (40), pp. 3-18, C. A. 43, 506d.*

for a reaction where the rate is controlled by an activated process. If it were known how a varies with time, the integral could be evaluated. But this variation involves knowledge of rates of nucleation and growth. Such theory is in a very undeveloped state, although an attempt has been made[11] to relate the mechanism to area-vs.-time curves. Where the area term is unobtainable, such equations are not of much help.

If, after an initial period, a should become constant, then equation 6 is applicable to the case where the reaction products are soluble and diffuse away fast, because then the weight loss of the anode should be linear with time and its logarithm should vary linearly with voltage. This amounts to stating that Faraday's law may be used in the form $w = nIt$, or that current is constant. However, where a film is formed, log w will, at constant t, vary linearly with V only if the integral term is constant. If such is found to be the case, then the activation equation, modified by modes of nucleation and growth, may be assumed to control the rate of attack, unless another theoretical equation could be obtained which would give the same relation between w and V.

Two other factors can be visualized as controlling[12] the rate of formation of porous films: one, ohmic resistance of electrolyte in the pores, and two, the rate of diffusion of molecular (or atomic) reactants and products.

In the first case, an equation for the rate may be developed. Of course,

$$I = V/R, \tag{7}$$

and

$$R = \rho l/a', \tag{8}$$

where R is the total resistance of all pores, ρ is the specific resistance of the electrolyte in the pores, a′ is the total pore area, l is the pore length, and V is the potential difference across the pores. Combining these,

$$I = V\, a'/\rho\, l. \tag{9}$$

Then at any given potential, if ρ is constant, a′ will be some function of time and $l \cong$ a constant times the film weight. Using Equation 5,

$$w^2 = nV/k\rho \int_o^t a'dt. \tag{10}$$

If the same conditions apply to the integral,

$$\int_o^t a'dt,$$

as were previously applied to the integral,

$$\int_o^t a\,dt,$$

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[11] *Evans, U. R., "An Introduction to Metallic Corrosion," Arnold and Co., 1948, p. 197 et. seq.*

[12] *Randles, op. cit.*

then the relation between w and V at constant time is parabolic. However, V in this case is not necessarily the electrode potential nor related to it in a linear fashion. Possibly V might be a concentration polarization across the pore length or some fraction of the potential drop across the total electrolyte path between the two electrodes. Regardless of the nature of V in this instance, if it can be assumed constant for a constant measured potential, then at constant time w^2 should be linear with $1/\rho$. Since ρ can be varied experimentally by changing the concentration and temperature, the equation may be tested for fit to the data.

If, on the other hand, the rate is dependent on a molecular diffusion process through the pores, then.[13]

$$j = \frac{a'D\,(C_o - C_i)}{l}, \tag{11}$$

where

j = the rate of diffusion through the pores;

D = the diffusion constant;

$C_o - C_i$ = the concentration gradient; and

l = the pore length.

The corrosion current will be:

$$I = kj, \tag{12}$$

or

$$I = \frac{k\,a'D\,(C_o - C_i)}{l}, \tag{13}$$

and the rate should be independent of the potential. Such an equation might apply, for example, if water were the reacting substance, the rate being limited by its rate of diffusion through the pores to the metal surface.

Other more complicated mechanisms might be imagined — for example, parallel corrosion proceeding by migration of ions through the film and by any of the above processes through the pores themselves. In this case a suitable combination of the applicable equations would have to be developed. There is, however, a case which may be more likely here because it has been found that the corrosion results in two products arranged in layers. It would be necessary to consider this process if the electrolyte and the underlayer were reacting chemically so that the thickness of the overlying film was increasing with time. Then one of the equations for the porous film would apply, except that it would be modified by the rate of the chemical reaction. A nonporous underfilm would be expected to grow at some rate faster than parabolic, but slower than linear, resulting in a log w vs. log t plot with a slope between 0.5 and 1. Another complicated process would result from a repeated recrystallization of a nonporous film as it reached a limiting thickness, thus maintaining some constant effective thickness. This should lead to a linear rate of growth if the recrystallized portion has no inhibiting effect on the rate. It would be possible in such a case to obtain a linear log w vs. V plot also.

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[13] *Agar, "Electrode Processes," p. 27; see also Randles, op. cit.*

In addition to these effects, there are others [14] which may be used to obtain some idea of the rate-controlling factors in electrode processes. Stirring, for example, will have little effect on the rate of a process which may be expressed by the activation equation, but it will have a large effect if concentration polarization or diffusion effects are controlling. In the case of film formation, such an effect would not be expected to be evident because the stirring would have to take place in the pores. Again, concentration of solution has only a small effect on activation processes, but it should have a large effect on concentration polarization. Finally, the temperature effect is generally large for activation processes but comparatively small for others. All these effects would require a very careful analysis of the data before conclusions could be drawn, but they may be used to obtain indications of the mechanisms involved.

THE GENERAL METHOD

Samples of cold-rolled lead sheet, cut always to the same dimensions (giving 34 sq. cm. area), were maintained at constant potential for suitable times in various concentrations of sulfuric acid electrolyte under constant temperature conditions. The rates of attack were followed either by stripping the films formed in ammonium acetate solution and obtaining weight losses or by measuring the current flowing through the sample. X-ray patterns were obtained for the anodized samples to relate the nature of the corrosion product with the potential. Some lead samples were anodized at various constant currents to determine the potential-time curves.

APPARATUS AND TECHNIQUES

The circuit diagram of the apparatus used for constant-potential anodization is shown in Figure 1. A resistor, R_1, consisting of several feet of copper wire, was connected in series with a hot plate, R_3, and another variable resistor, R_4, so that currents of 2.4 to 4.5 amperes could be made to flow through R_1, producing potential drops up to about 1.1 volts. The sample to be anodized is at B. It was contained in a beaker of sulfuric acid electrolyte and could be connected to any position on R_1 through R_2, a two-ohm resistor from which leads ran to a G.E. Potentiometer Recorder with a range of 0.2 to 500 mv. Parts A and A′ were sections of positive plate from a lead-acid cell having a very large capacity such that currents of the order of magnitude drawn by the samples produced little or no polarization. They were connected through switches S_1 and S_2 to either end of the slide wire, R_1, so that a given potential either positive or negative with respect to the PbO_2 plates could be applied to the sample. At C was a mercury-mercurous sulfate reference electrode. Leads from it and the sample were connected to a portable Rubicon Null-point potentiometer with a range of 1.5 volts. The potential of the sample was adjusted manually by sliding the contact from R_2 along R_1, or by adjusting the resistors R_3 and R_4.

To make a run, the sample was connected to R_2, the recorder was started, and the slide-wire contact was adjusted to a predetermined position such that the desired potential would be obtained approximately within a few seconds after lowering the sample into the bath. The manual control allowed attainment of potentials with ± 0.01 volt within one-half minute after putting the sample into the bath. Within a few minutes the potential could be controlled easily to ± 0.001 volt, and after fifteen minutes to an hour or so, depending on conditions, it was necessary to adjust potential less and less frequently. For overnight

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[14] *Bowden, F. P. and Agar, J.N., "The Kinetics of Electrode Reactions-I," Proc. Roy. Soc. A169, 206-220 (1938).*

runs, the potential was adjusted to 0.01 volt lower than the nominal potential, because it had a tendency to creep up very slowly. After sixteen hours the potential seldom exceeded a value of 0.01 volt higher than the nominal potential.

These variations affected the rate by but a small amount in comparison with the variations found for the over-all potential range studied, and the method was considered satisfactory below 1.0 volt. Between 1.0 volt and about 1.2 volts, potential had to be controlled much more closely, and no overnight runs were attempted. Current-time curves were plotted from the record, and weight-loss vs.time curves were then calculated using small increments of the current-time curves and Faraday's law. The X-ray patterns were obtained with apparatus previously described.[15]

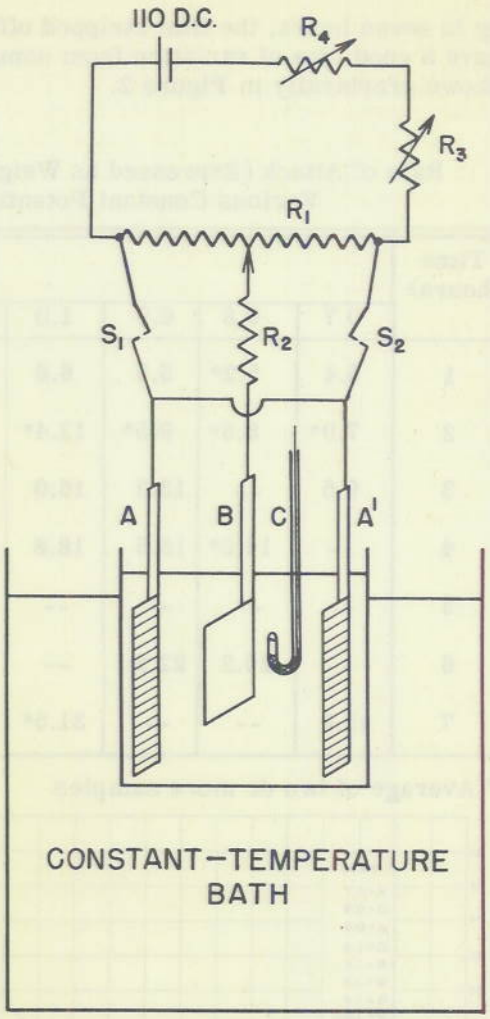

Figure 1 - Constant-potential apparatus

THE POTENTIAL SCALE

With reference to the standard hydrogen electrode, the mercury-mercurous sulfate reference electrode has a potential of +0.566 volt in 40.8% sulfuric acid solution at 20°C. Under the same conditions, the reversible potential of the PbO_2-$PbSO_4$ couple is approximately +1.1 volts with respect to the mercury-mercurous sulfate reference electrode. A 1.0 volt difference between the reference electrode and the anodizing sample under these conditions was selected as a standard voltage for these experiments, and all voltage data is corrected for concentration and temperature to this reference value using the data of Harned and Hamer.[16] This standard potential is thus about 0.1 volt lower than the PbO_2-$PbSO_4$ reversible potential in the most concentrated solutions used in these experiments, although this comparison depends somewhat on temperature. The effect of the corrections is to eliminate variations in the reference electrode potential with concentration and temperature.

RESULTS AND DISCUSSION

The first experiment was preliminary in nature and was designed to show the rates of attack which might be expected at potentials from 0.7 to 1.55 volts. Weighed samples were run at a series of potentials in that range in sulfuric acid of specific gravity 1.30 (approximately 40% by weight) at 30°C. Individual samples were removed at the end of each hour

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[15] *Lander, J. J., "First report on Investigation of the Plate Materials of the Lead Acid Cell," NRL Report No. C-3262, March 22, 1948.*

[16] *J.A.C.S. 57, 33 (1935).*

up to seven hours, the film stripped off and the weight loss determined. This method gave a good idea of variation from sample to sample. The results given in Table 1 are shown graphically in Figure 2.

TABLE 1
Rate of Attack (Expressed as Weight Loss, mgs, in 34 sq. cm.) of Pb Anodes at Various Constant Potentials in H_2SO_4 (sp. gr. 130) at 30°C.

Time (hours)	Potential (volts)										
	0.7	0.8	0.9	1.0	1.2	1.3	1.35	1.4	1.45	1.5	1.55
1	5.4	5.2*	5.5	6.6	--	4.5	--	4.0	--	--	5.2
2	7.9*	8.6*	9.5*	12.4*	--	5.4	--	4.4*	--	--	6.4
3	9.5	--	13.3	16.0	7.0	5.6	4.7	5.1	--	--	7.7
4	--	14.0*	15.5	18.6	--	6.3	5.7	5.4	--	--	11.6
5	--	--	--	--	8.0	6.1	5.2*	--	6.2*	7.5	16.0*
6	--	20.2	22.8	--	9.0	6.0	--	--	6.7	8.5*	19.2
7	15.9	--	--	31.5*	9.5	6.1	--	7.0*	7.0	--	22.0

* Average of two or more samples

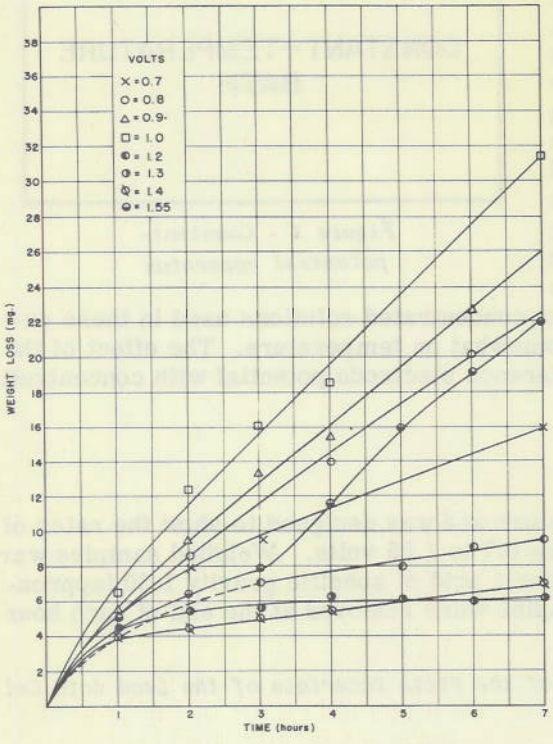

Figure 2 - Rate of attack of Pb anodes at constant potential in H_2SO_4 (sp. gr. 1.300) at 30°C

These results show that the rate of attack of the metal increases rapidly with potential and reaches a maximum at about 1.0 volt, after which it falls off rapidly giving a broad minimum from about 1.2 to 1.5 volts. At 1.55 volts the rate begins to increase rapidly again. This is shown in Figure 3, where weight losses at the end of three and seven hours respectively are plotted against potential. The samples begin to gas oxygen visibly at 1.40 volts under these conditions. At 1.3 volts the corrosion current falls rapidly (within an hour or so) to 1.0 to 0.2 ma. Using Faraday's law and assuming the production of PbO_2, this gives conversion of about 1 to 2 mg. of Pb per 34 sq. cm. of surface per hour, a value slightly larger than the measured weight losses. Hence, some current must be going to O_2 gas.

X-ray patterns obtained for these samples showed that the heavier coatings obtained at 1.0 volt for seven hours consisted primarily of $PbSO_4$, even though the samples were reddish-brown in color. No pattern could be obtained from the films formed at the higher voltages (1.2 to 1.4 volts). Assuming a roughness factor of one for the surface, the

weight loss figures indicate a PbO_2 film thickness of 3000 Å. Such a thickness should reduce the intensity of the original Pb lines in the patterns by about one-half and should give a pattern. The fact that it does not give an X-ray pattern indicates that the film may be amorphous or so oriented that a line does not appear within a 2θ value of 85°, or that the roughness factor is considerably too low. If the roughness factor were 10, for example, the film thickness would be 300 Å, and no pattern would be expected.

The films formed at 1.2 volts and above were dark brown to black in color. If allowed to stand in water after removal from the oxidizing bath, they rapidly turned greyish white. X-ray analysis showed that the greyish-white material was $PbSO_4$.

The minimum in the rate vs. potential curve[17] shows that the film formed on pure lead at the potentials concerned is protective. Several samples were run for longer periods of time (16 to 24 hours); the weight losses were still very low as shown in Table 2.

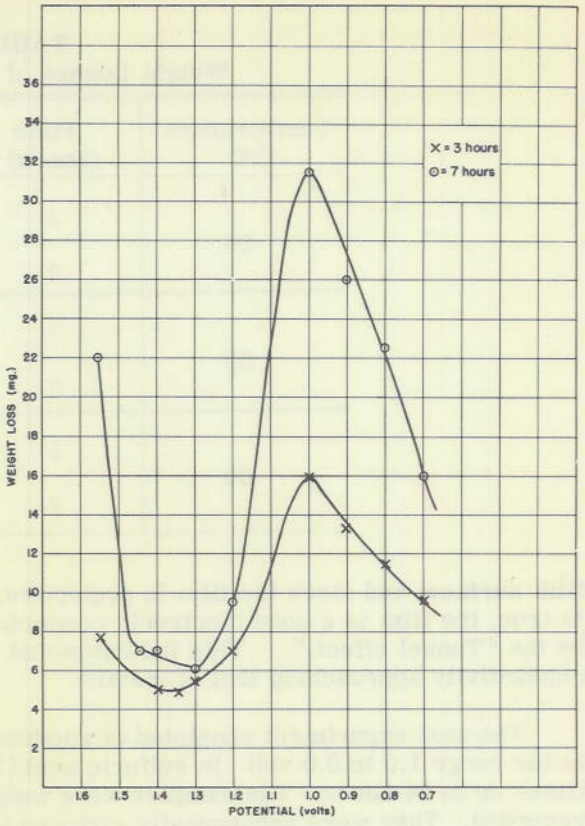

Figure 3 - Total attack of Pb anodes after 3 and after 7 hours in H_2SO_4 (sp. gr. 1.300) at 30°C

Another experiment was run to determine whether or not higher temperatures would break down the protective films. At 50°C and at 60°C in the same acid, weight losses were determined for one and three hours. The results are shown in Table 3 where values at 30° C are included for comparison.

TABLE 2
Weight Losses of Pb Anodes (mg.)

Time (hours)	Potential (volts)		
	1.2	1.3	1.4
16	9.5	9.4	9.1
24	11.8	--	9.9

It is concluded that the film does not break down within three hours at the higher temperatures, although the amount of initial formation is higher. The samples at 1.3 volts gassed visibly at the higher temperatures and vigorously at 1.4 volts. It may be presumed that these films are also of the order of 300-3000 Å thick, according to the previous analysis. The gassing means that 0_2 is being discharged either at the Pb surface or the

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[17] *This minimum is also exhibited at lower concentrations and higher temperatures. See the data for 1.3 volts, 10% acid, and 50°C (Figure 12).*

TABLE 3
Weight Losses of Pb Anodes (mg.)

Temperature °C	Time (hours)	Potential (volts) 1.3	1.4
30	1	4.5	4.0
	3	5.6	5.1
50	1	6.6	6.9
	3	7.9	8.0
60	1	7.0	8.4
	3	8.5	9.8

film surface, and since the film is protective, the latter situation is quite likely. If this is true, the film is a good electronic conductor, because it is too thick to pass electrons by the "Tunnel effect." This indicates that the film is PbO_2, which as an electronic conductivity approaching that of metals.

The next experiment consisted of anodization of a few Pb samples at several potentials in the range 1.0 to 0.0 volt in sulfuric acid (1.300 sp. gr.) at several temperatures for times up to 24 hours. The samples were weighed initially, and the current passing was recorded. They were subsequently stripped and weight losses determined and checked against calculated values from the current-time data. In every case the corrosion was found within experimental error to follow Faraday's law for the reaction $Pb - 2e \longrightarrow Pb^{++}$. The heavier films obtained at the higher voltages were also analyzed with the X-ray apparatus.

The surface film consisted almost entirely of $PbSO_4$. It was loosely adherent and could be wiped off with cotton or a soft wooden wedge, whereupon a brown to black underfilm was exposed which proved to be tetragonal PbO, thus checking the previous work.[18] This film is apparently protected from electrolyte chemical action by the $PbSO_4$ film which must pass $SO_4^=$ ion only comparatively slowly. The PbO film was observed at potentials as low as 0.1 volt on the arbitrary scale used in this report, and this potential corresponds approximately to that at which PbO was found previously in H_2SO_4 solutions by Wolf and Bonilla.

Since PbO is formed in the anode process, it must be due ultimately to reaction of the lead with the water of the electrolyte. An ion such as OH^-, or some other ion or substance derivable from water, might be the attacking species. However, reference to Latimer[19] on oxidation-reduction potentials indicates that, at the potentials concerned, H_2O or OH^- would be the most likely reacting species. Of these, H_2O is present in far greater concentrations in the bulk solution and when no current is passing should be present in about the same

[18] *Wolf and Bonilla, op. cit.*

[19] *Latimer, W. M. "Oxidation Potentials," Prentice-Hall, Inc., New York, 1938, pp. 294-298.*

concentration near the reaction interface. When current flows, this surface may be depleted of H^+ ions for an anodic process unless they are furnished by the reaction (which could be the case here). This would indicate that OH^- ion concentration is not increased appreciably in the immediate vicinity of the reaction site, especially in such strongly acid solutions as were used in this work. Thus, water is favored as the attacking species.

Nevertheless, three simple reactions may be written for the electrochemical formation of PbO with either of these substances:

$$Pb + OH^- \rightarrow PbO + H^+ + 2e$$

$$Pb + 2OH^- \rightarrow PbO + H_2O + 2e$$

$$Pb + H_2O \rightarrow PbO + 2H^+ + 2e.$$

Using the equation, $\Delta F = -n F V$, it can be shown that for all of these reactions $V_o = +0.250$ volt on the hydrogen scale. This is about -0.4 volt on our arbitrary scale — which means that the potentials of +0.1 volt used here are well above the reversible potential for the formation of PbO by any of the above reactions. The reversible potential for experimental conditions which depends on the activity of the reactants and products under those conditions, is given by the equation,

$$V = 0.250 + 0.0293 \log \left[H^+\right]^2, \qquad (14)$$

where PbO, H_2O, and Pb are assumed to have an activity of 1, so that the less acidic the solution, the less noble the potential for the reaction becomes. Using data given by Lewis and Randall[20] for the activity of sulfuric acid solutions, the equilibrium potential for the reaction in 10 weight percent sulfuric acid at 30°C is calculated to be +0.218 volt on the hydrogen scale.

Previous work in this Laboratory[21] showed an unexplained inflection in the potential-time curve in the constant-current anodization of pure lead which corresponds approximately to the +0.218-volt potential. Further work was done to obtain potential-time curves which would more accurately fix the value of the inflection in 10% solutions at 30°C so that comparison could be made with the calculated value.

Lead sheets of constant area (34 sq. cm.) were anodized at constant currents in the range 0.1-4.0 ma. Potentials were measured against the mercury-mercurous sulfate reference electrode, which has an equilibrium potential of +0.668 on the hydrogen scale under these conditions. The voltage-time curves in the neighborhood of the inflection are shown in Figure 4. The mean value of the inflection determined for these curves is about -0.43 to -0.44, which corresponds to about +0.23 to 0.24 on the hydrogen scale. Since these are not values for reversible conditions, some polarization may be involved, a factor which would tend to make the values somewhat more positive than the calculated equilibrium value (although in the curves no change in the potential is evident with increasing current density). At any rate, the agreement with the calculated value is good, so that the inflection could be due to PbO formation by any of the electrochemical reactions.

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[20] *Lewis, G. N. and Randall, M., "Thermodynamics," McGraw-Hill Book Co., Inc. New York, 1923, p. 357.*

[21] *Work done in connection with Reference 1 and some other unreported work.*

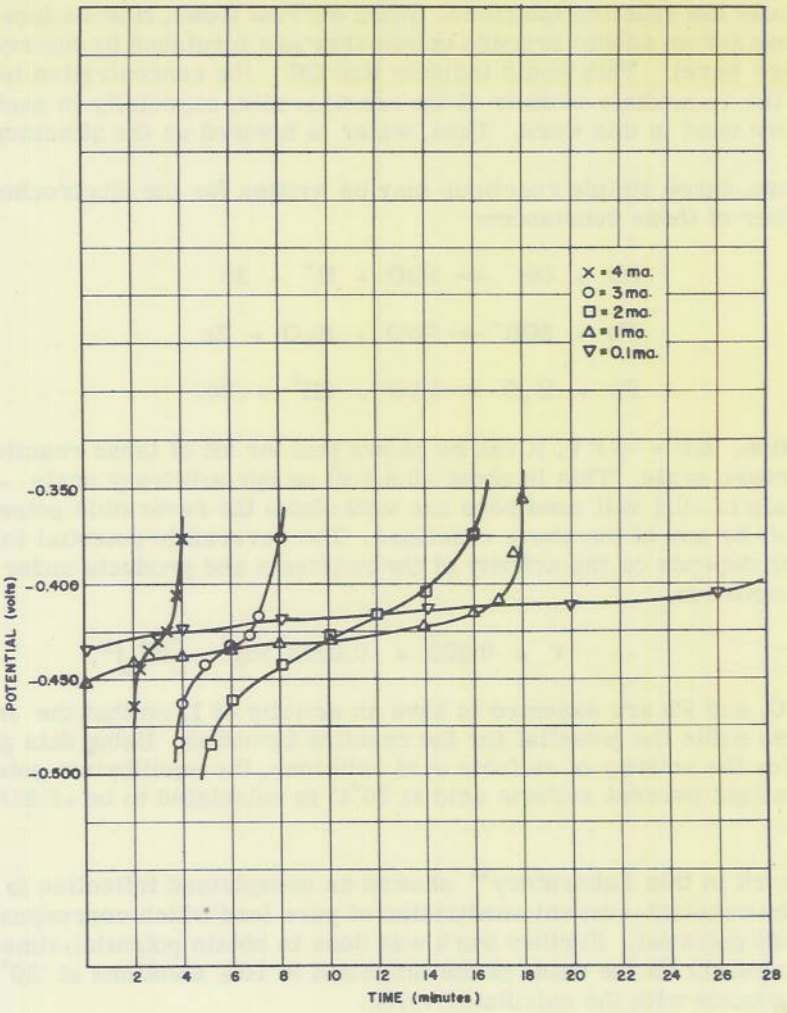

Figure 4 - Potential-time relationship at constant current in 10% H_2SO_4 solutions at 30°C

Most of the experimental work was concerned with rate studies for the anodic process at constant potentials in the range 1.0 to -0.1 volt. Since it was shown that the reaction follows Faraday's law, the rates could be obtained conveniently in terms of weight loss by running current-time curves at various constant potentials and calculating weight-loss data from them. The results were compared with the equations previously given to see if any of the simple cases applied.

In the voltage range specified, rate curves were determined up to 25 hours for 30% acid at 30° and 50°C and for 10% acid at 30° and 50°C. The current-time curves for the three sets of conditions are given in Figures 5, 6, 7, and 8, and the weight loss data calculated from them are given in Figures 9, 10, 11, and 12. Two obvious comparisons are that increase in temperature and decrease in concentration both markedly increase in rate of attack. Since the conductivity of the electrolyte is higher at the higher concentration, it is concluded that the rate is not limited by the conductivity ($1/\rho$).

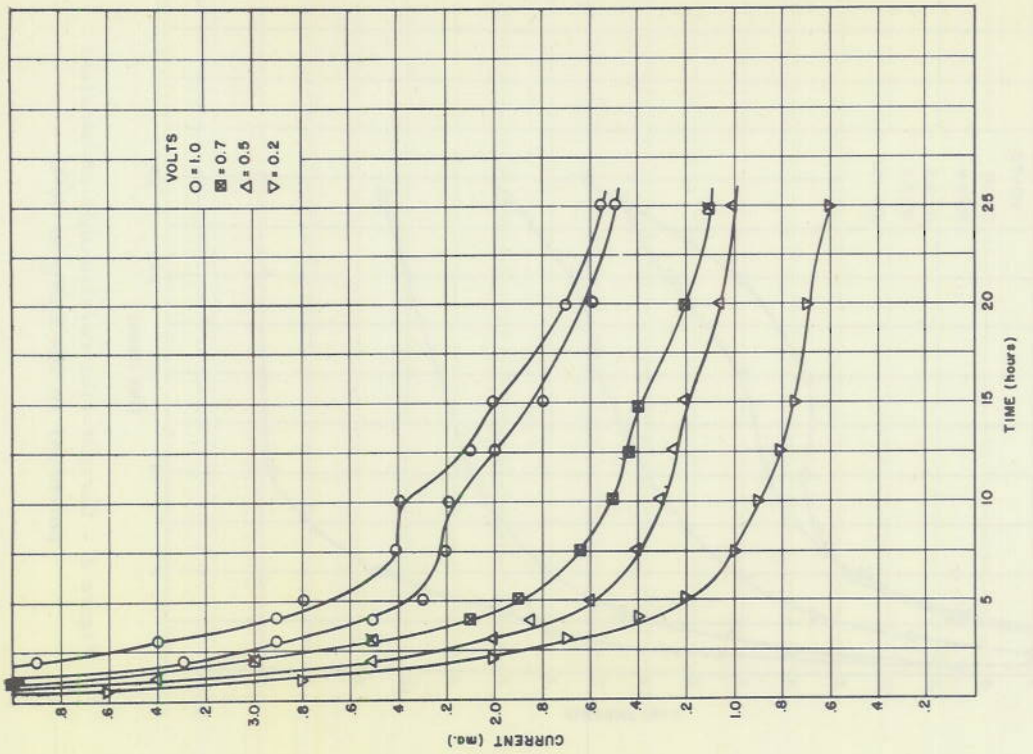

Figure 6 - Current-time relationship at constant potential in 30% H_2SO_4 at 50°C

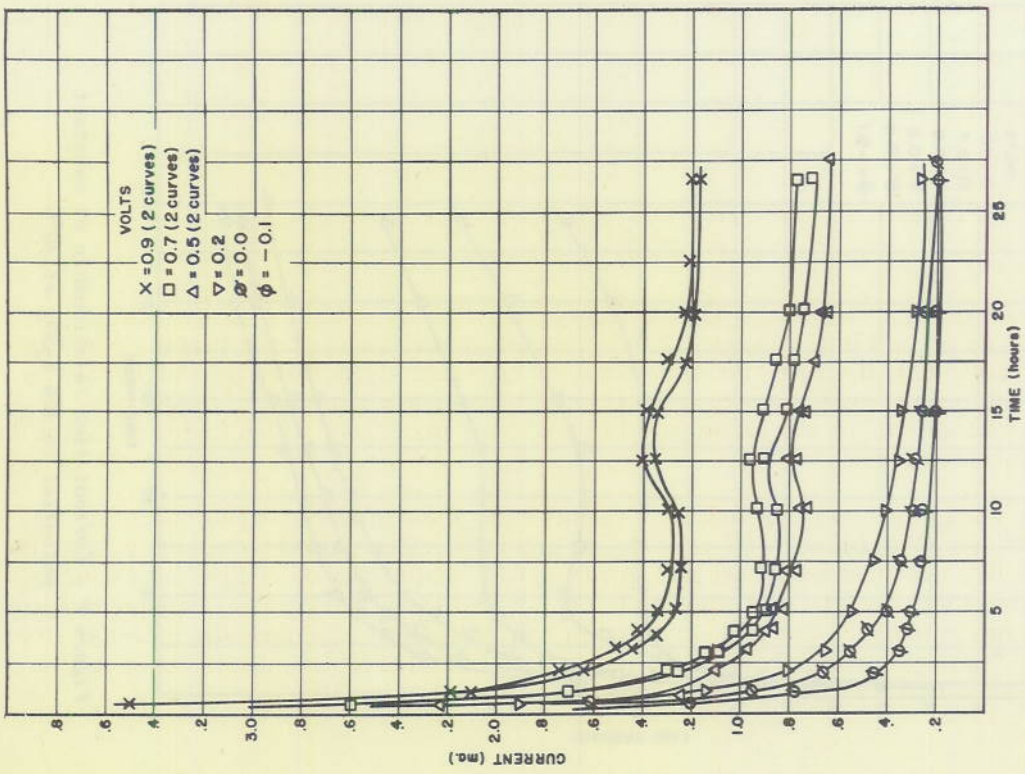

Figure 5 - Current-time relationship at constant potential in 30% H_2SO_4 at 30°C

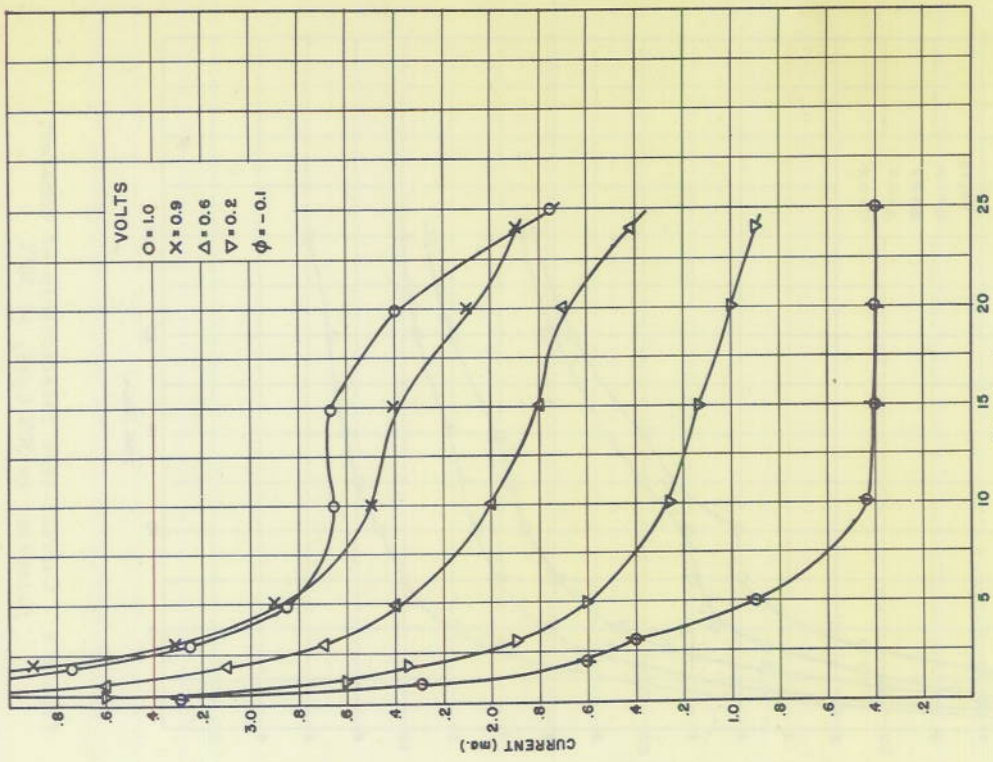

Figure 8 - Current-time relationship at constant potential in 10% H_2SO_4 at 50°C

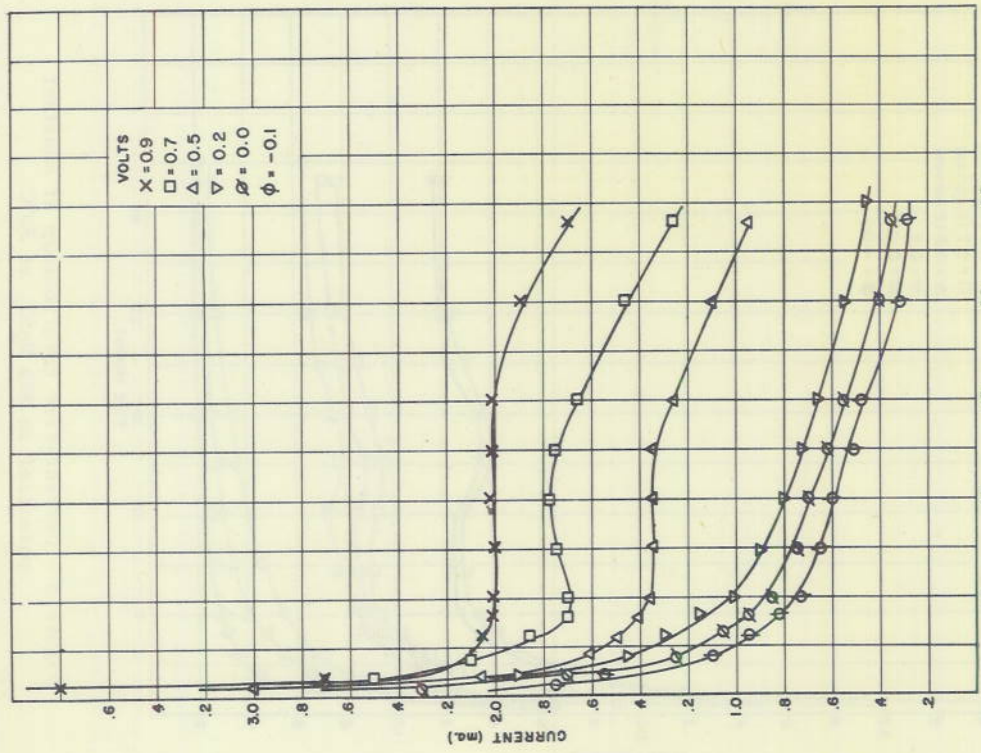

Figure 7 - Current-time relationship at constant potential in 10% H_2SO_4 at 30°C

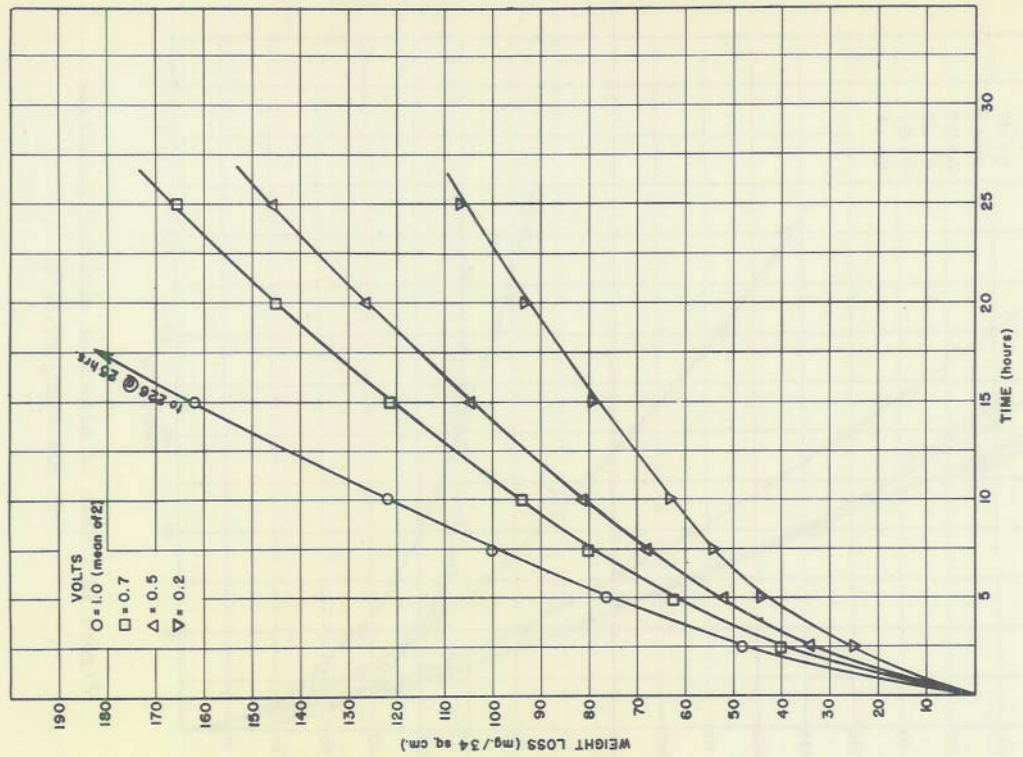

Figure 10 - Rate of attack at constant potential in 30% H_2SO_4 at 50°C

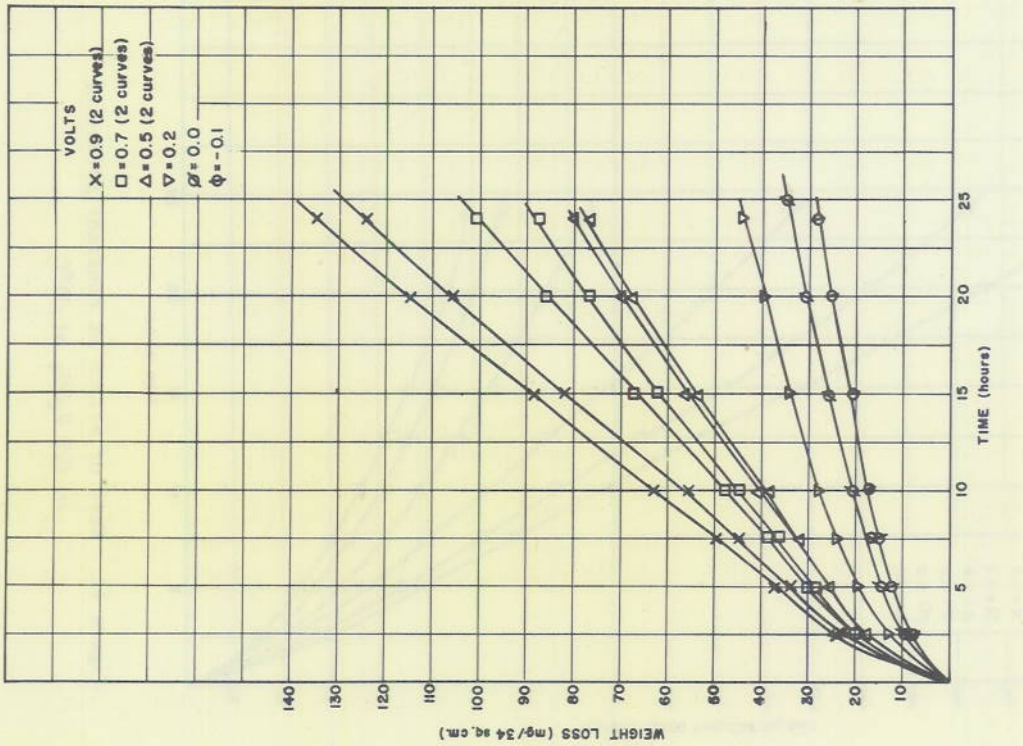

Figure 9 - Rate of attack at constant potential in 30% H_2SO_4 at 30°C

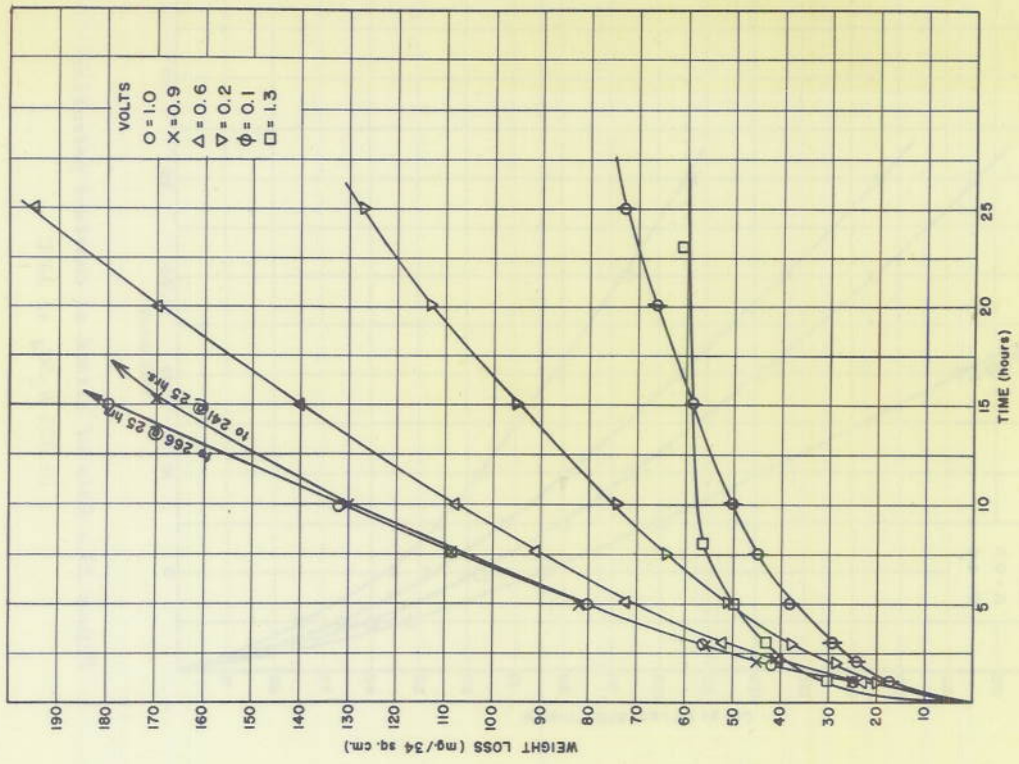

Figure 12 - Rate of attack at constant potential in 10% H_2SO_4 at 50°C

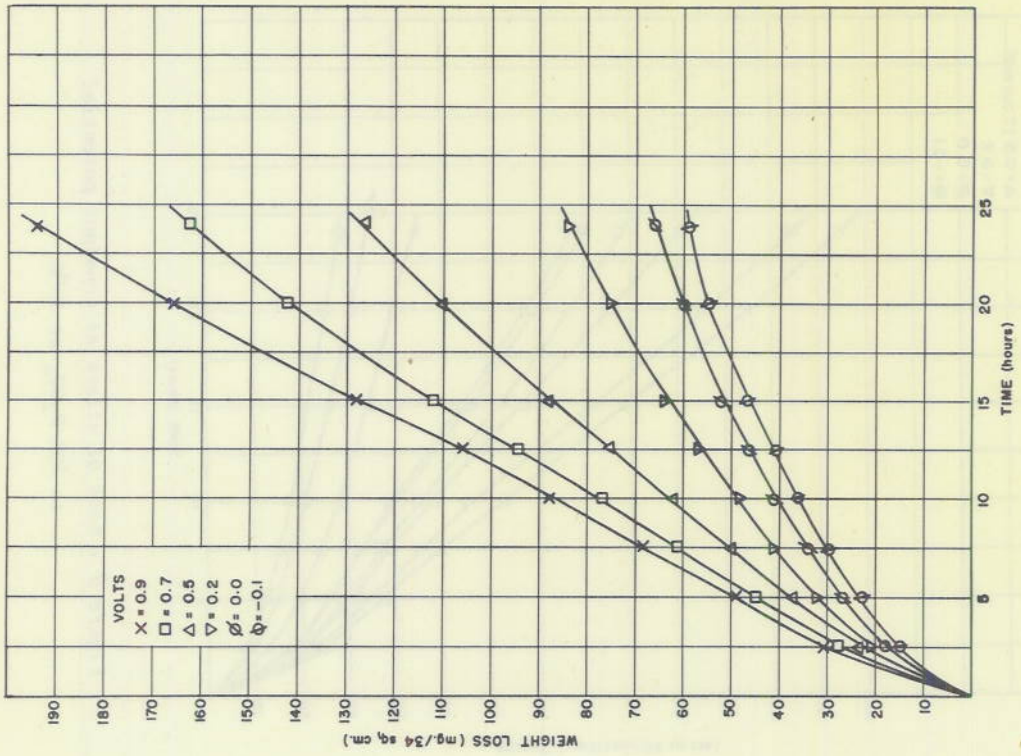

Figure 11 - Rate of attack at constant potential in 10% H_2SO_4 at 30°C

Figures 13, 14, 15, and 16 are log-log plots of w vs. t for the three conditions. If the slopes of these were 0.5, then the simple parabolic relation might apply. Actually they vary between about 0.55 and 0.9 so that the relation is something between parabolic and linear. This effect could possibly be due to chemical reaction of the electrolyte with the PbO film as previously discussed, but it does not seem likely that the underlying film is continuous.

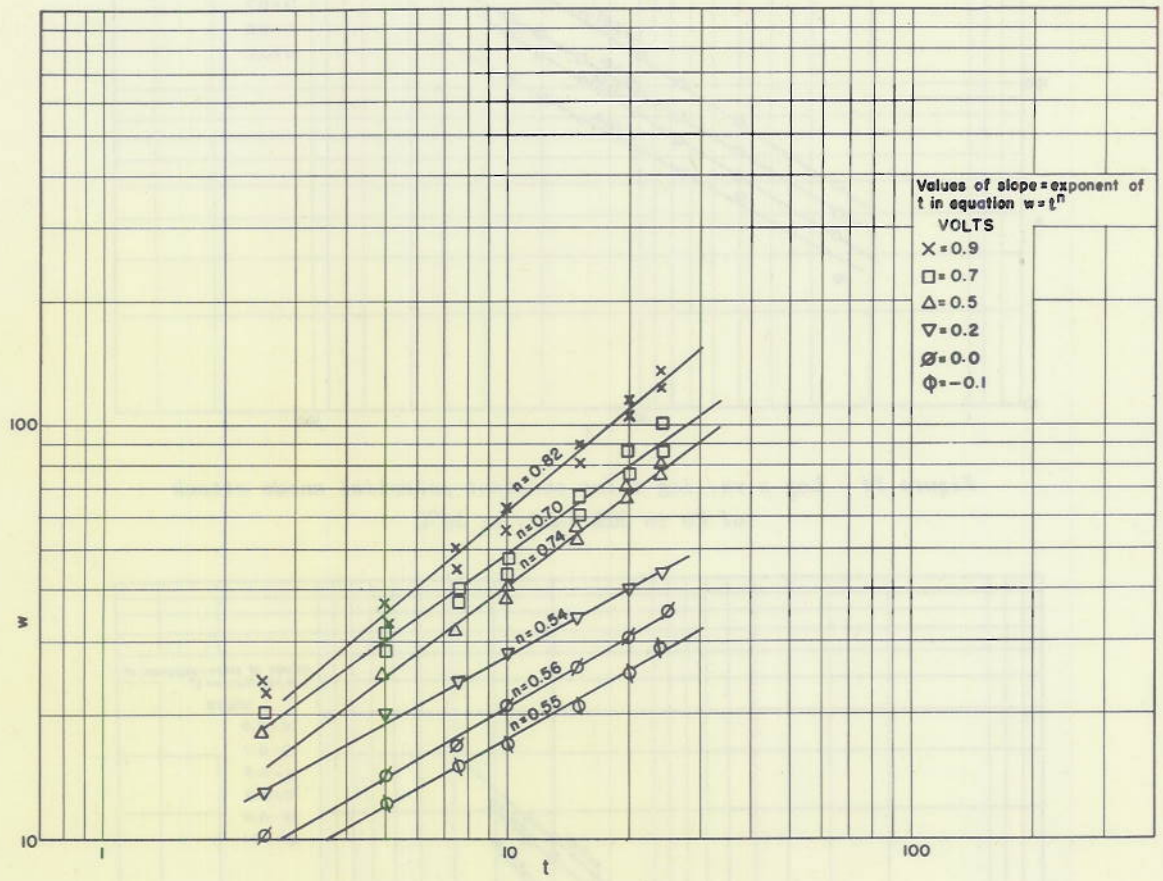

Figure 13 - Log w vs. log t for constant potential anode attack of Pb in 30% H_2SO_4 at 30°C

Figures 17, 18, 19, and 20 show plots of low w vs. V at various times for the three conditions. The curves are linear within experimental error, so it may be concluded that the rate of the total electrode process is governed by the intrinsic rate of the electrode reaction and not by diffusion effects or conductivity of the electrolyte. The rate is modified, however, by the manner in which the film forms on the surface, i.e., by nucleation and growth. This conclusion indicates that the reaction is taking place at the Pb-solution interface at the bottom of pores in the film. The linear relation also shows that the value of the integral, $\int_0^t a\,dt$, for any given temperature and electrolyte concentration, is constant at constant time regardless of potential within the range measured. This is a very interesting development because it means that the available area does not depend on the amount of film formed but is only a function of time under the limitations imposed.

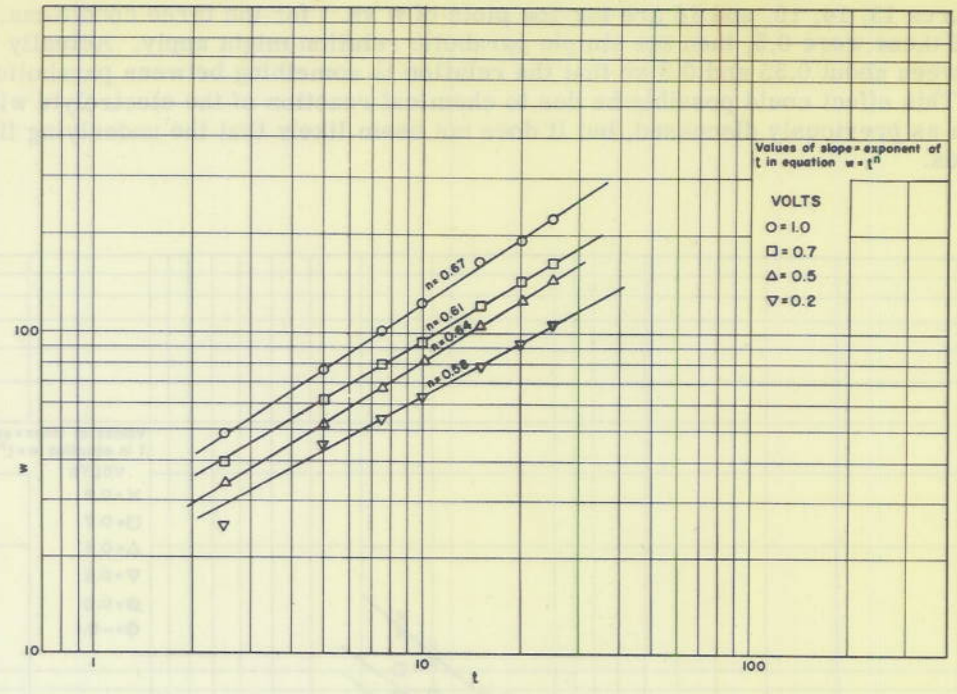

Figure 14 - Log w vs. log t for constant potential anode attack of Pb in 30% H_2SO_4 at 50°C

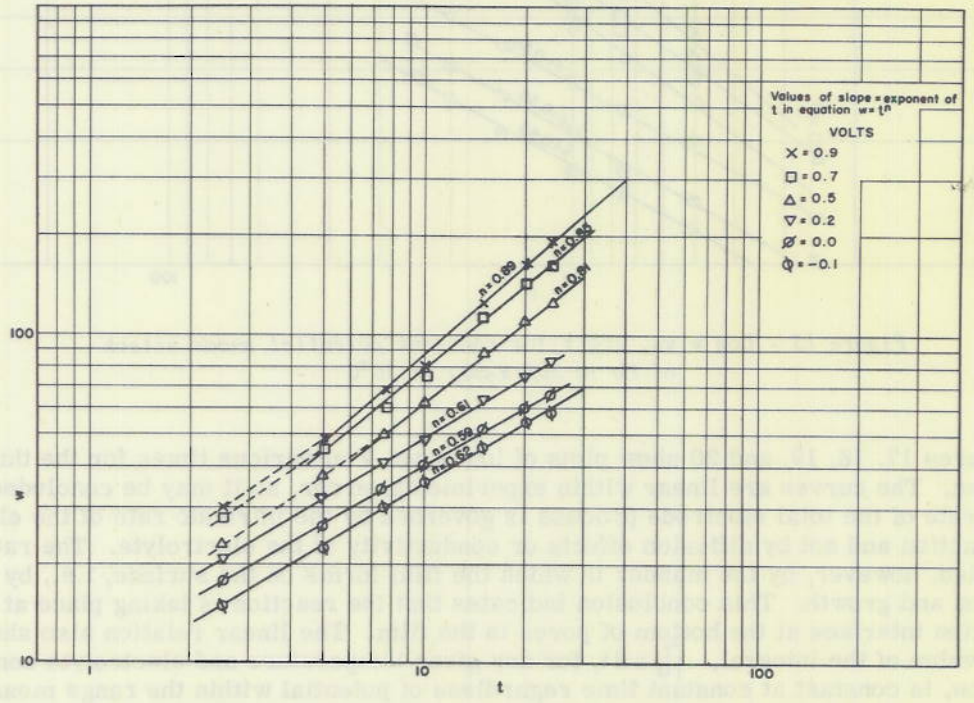

Figure 15 - Log w vs. log t for constant potential anode attack of Pb in 10% H_2SO_4 at 30°C

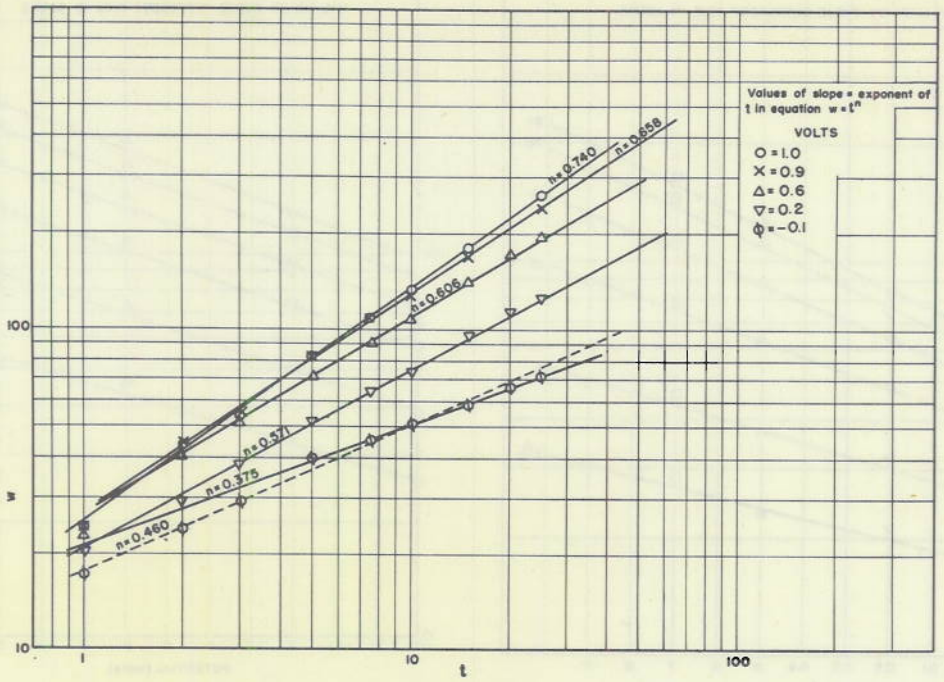

Figure 16 - Log w vs. log t for constant potential anode attack of Pb in 10% H_2SO_4 at 50°C

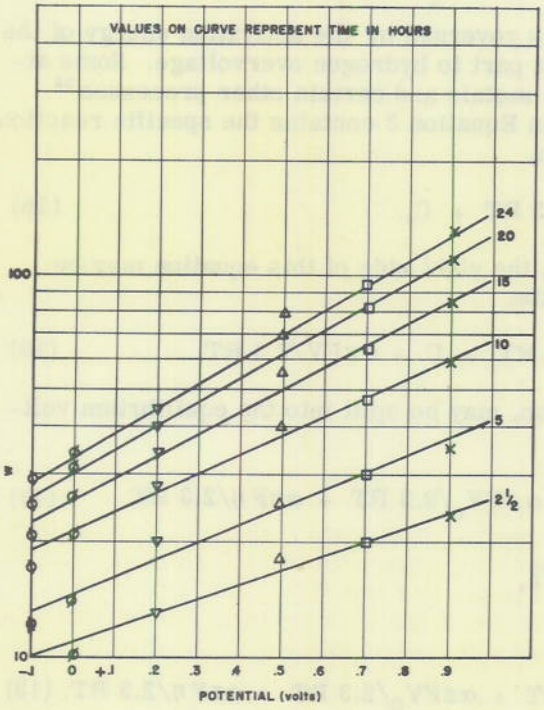

Figure 17 - Log w vs. V at constant t for 30% H_2SO_4 at 30°C

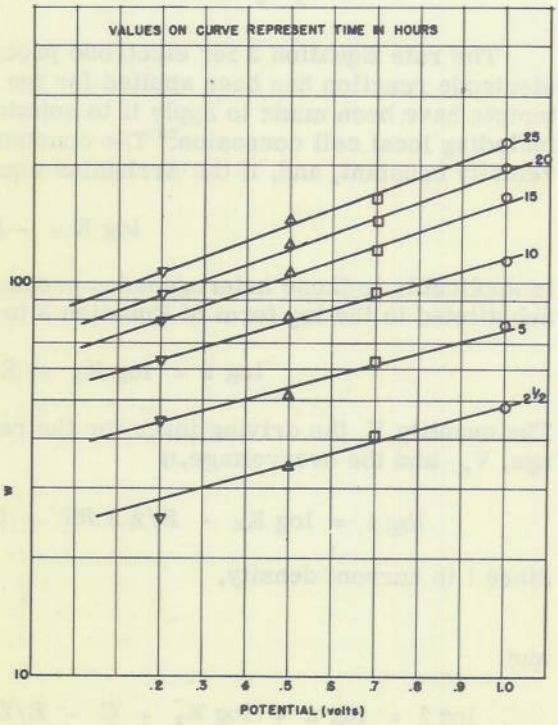

Figure 18 - Log w vs. V at constant t for 30% H_2SO_4 at 50°C

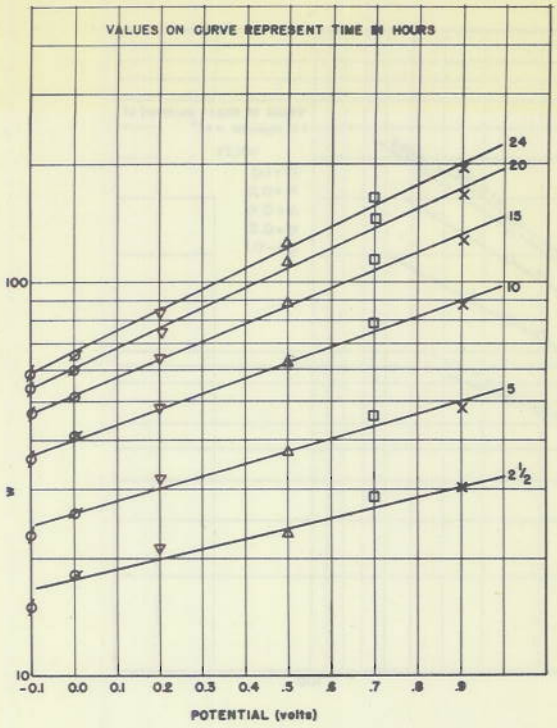

Figure 19 - Log w vs. V at constant t for 10% H_2SO_4 at 30°C

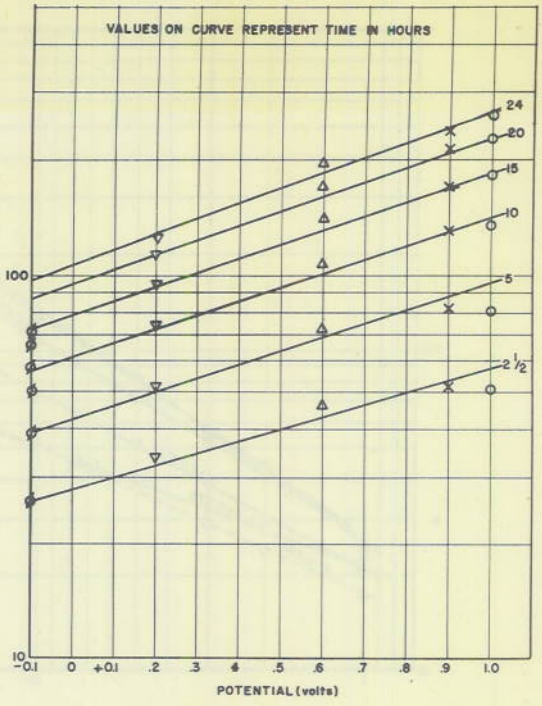

Figure 20 - Log w vs. V at constant t for 10% H_2SO_4 at 50°C

The rate Equation 3 for electrode processes governed by the activation energy of the electrode reaction has been applied for the most part to hydrogen overvoltage. Some attempts have been made to apply it to solution of metals and certain other processes [22] including local cell corrosion.[23] The constant k in Equation 3 contains the specific reaction velocity constant, and, if the Arrhenius equation,

$$\log K = - E/2.3\ RT + C, \tag{15}$$

is applicable to these heterogeneous processes, the right side of this equation may be substituted in the log form of Equation 3 to obtain:

$$\log i = \log K_2 - E/2.3\ RT + C + \alpha zFV/2.3\ RT. \tag{16}$$

The quantity V, the driving force for the reaction, may be split into the equilibrium voltage, V_o, and the overvoltage, η

$$\log i = \log K_2 - E/2.3\ RT + C + \alpha zFV_o/2.3\ RT + \alpha zF\eta/2.3\ RT. \tag{17}$$

Since i is current density,

$$i = I/a,$$

and

$$\log I = \log a + \log K_2 + C - E/2.3\ RT + \alpha zFV_o/2.3\ RT + \alpha zF\eta/2.3\ RT. \tag{18}$$

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[22] *Andubert, op. cit.*

[23] *Durdin, op. cit.*

If no film is formed and the area term remains constant, and if the equilibrium value can be calculated (i.e., if the reaction is known), then a plot of η vs. log I should give a straight line, the intercept of which on the log I axis (log I_o) is equal to the sum of the terms on the right, except that containing the overvoltage which becomes zero. If all these terms are constant with T except $-E/2.3\,RT$, then, since the slope of the resulting straight line is equal to $-E/2.3R$, several such curves at various temperatures enable calculation of E by plotting the log I_o values against 1/T.

If a film is formed, then the modification of Equation 18 (from Equation 5) is

$$\log w = \log\int_o^t a\,dt + \log K_2 + C - E/2.3\,RT + \alpha z F(V_o + \eta)/2.3\,RT. \qquad (19)$$

In this case there is no apparent justification for assuming the area term to be constant at constant time at various temperatures. However, since it was found experimentally that log-log plots of w vs. t are approximately linear,

$$\log w - n \log t = \log c, \qquad (20)$$

where n is the slope for the log-log plot. Comparing this with Equation 19, it is evident that

$$\log c = \log K_2 + C - E/2.3\,RT + \alpha z F V_o/2.3\,RT + \alpha z F \eta/2.3\,RT. \qquad (21)$$

If a plot of log c values is made against η, then the intercept on the log c axis at $\eta = 0$ is log c_o and

$$\log c_o = \log K_2 + C - E/2.3\,RT + \alpha z F V_o/2.3\,RT. \qquad (22)$$

All the terms on the right are constant with temperature except that containing E, so that by plotting values of log c_o at various temperatures vs. 1/T, E is obtained from the resulting slope which is equal to $-E/2.3\,R$.

Table 4 shows the values of log c calculated from the data for 30% and 10% electrolyte at 30° and 50°C for various potentials. The log c values are plotted against η in Figure 21. Straight lines are drawn through the points to an η value of zero. In the case of the 30%, 30°C curve, adjustment was made in drawing the line because the slope of the log w vs. log t curves for overvoltage values 0.546 and 1.046 (0.2 and 0.7 on the arbitrary scale) seem to be too low when compared with those for the other potentials. This of course would lead to a high value of log c as can be seen from Equation 20. Log c_o values are plotted against 1/T in Figure 22, from which it is found that $-E/2.3\,R = -1900$ and -1238 for the 30% and 10% solutions respectively; E is calculated from these values to be about 8670 and 5660 calories per mole in the same order.[24]

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[24] *These values can by no means be considered accurate because only two temperatures were used over a narrow range and the data for 30%, 30°C is quite scattered. So far as is known, there is no value with which to compare the data, and the calculations serve therefore only to illustrate the method.*

TABLE 4
Calculated Values of Log c

Voltage	Temperature, °C			
	30		50	
	Concentration, %		Concentration, %	
	30	10	30	10
-0.1	0.688	1.028	--	1.302
+0.0	0.760	1.075	--	--
+0.2	0.902	--	1.220	1.318
+0.5	0.871	1.058	1.270	--
+0.6	--	--	--	1.433
+0.7	0.997	1.082	1.365	--
+0.9	0.956	1.095	--	1.465
+1.0	--	--	1.416	1.305

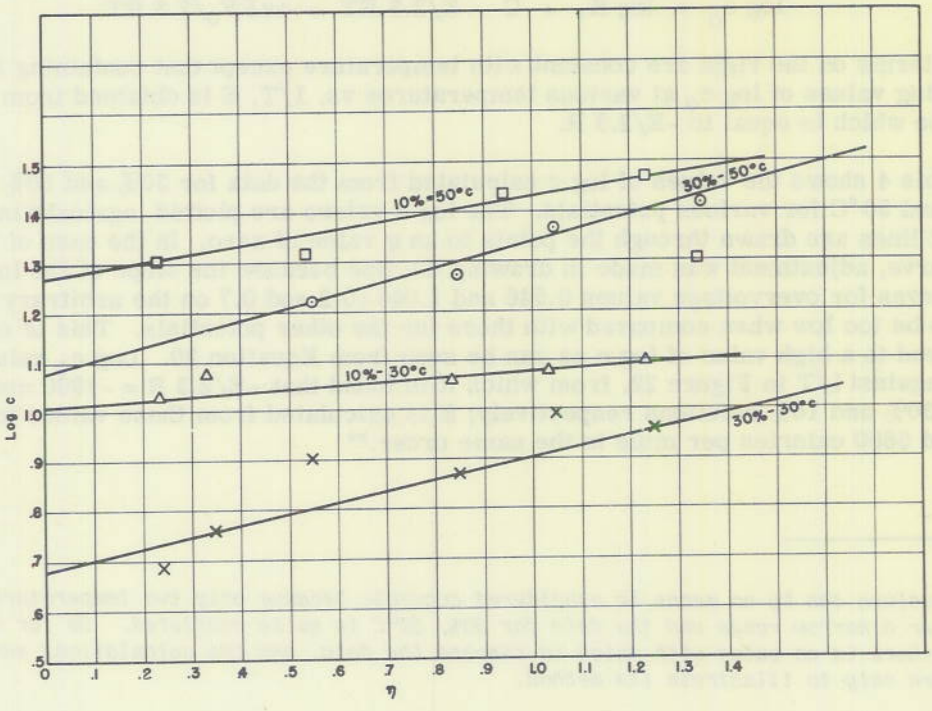

Figure 21 - Log c vs. η

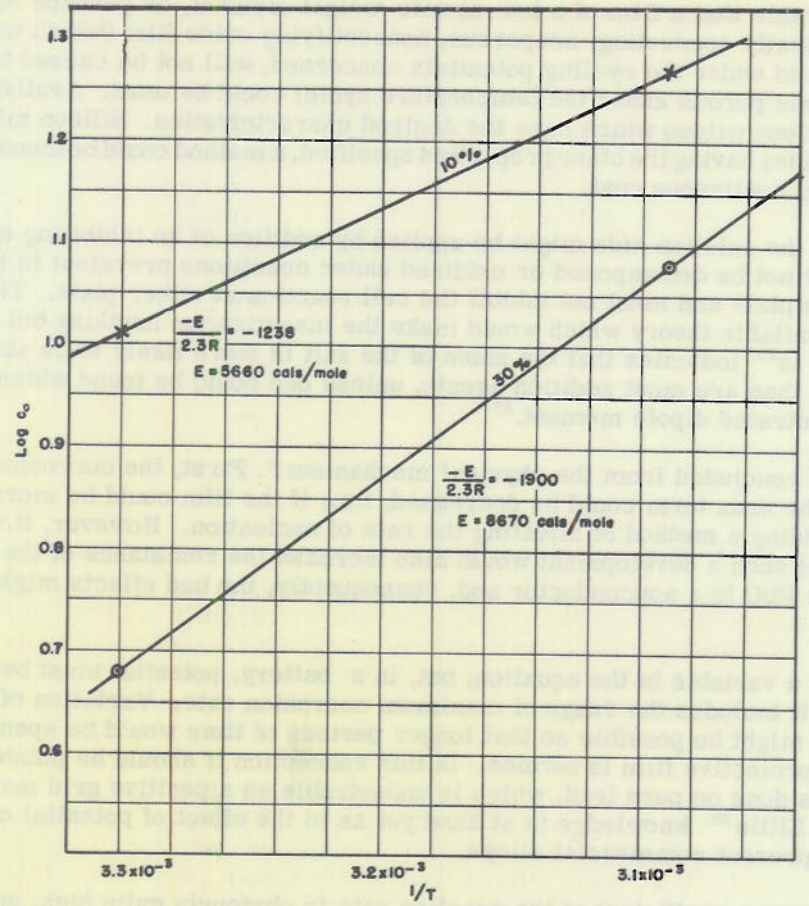

Figure 22 - Log c_o vs. 1/T

ANALYSIS OF THE CORROSION PROBLEM

The question needs examination as to whether or not such knowledge as has been obtained indicates lines of attack for further investigation directed toward slowing down or preventing corrosion. First, it is evident that, as long as the grid material is lead, nothing can be done about the chemical reaction itself because water cannot be removed from the electrolyte. Indeed, nearly all the common metals form sulfates or oxides which are soluble in the sulfuric acid electrolyte and consequently may be presumed to be attacked much more rapidly than lead itself. Even the use of films of some of the more noble metals, such as gold over a lead grid, would not be indicated because of their rapid intermetallic diffusion with lead; moreover, Latimer[25] shows that gold, platinum and palladium would not be expected to be completely immune from attack since their oxidation potentials are lower than the PbO_2 -$PbSO_4$ equilibrium voltage. Because of their low hydrogen overvoltages, the presence of even small amounts of these substances in the electrolyte would be very damaging to the negative plate.

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[25] *Latimer, op. cit.*

It is conceivable that a film of a low-atomic-weight element, or perhaps some insoluble, electronically conducting, nonporous, nonrectifying oxide film (which will not be oxidized or reduced under the cycling potentials concerned, will not be caused to flake off, and will not become porous under the temperature cycle) could be used. Available references fail to disclose oxides which have the desired characteristics. Silicon might be a possibility if, besides having the other properties specified, a method could be found to apply it in a conducting, continuous coat.

A film from the solution side might be applied by addition of an inhibiting agent. Such a substance must not be decomposed or oxidized under conditions prevalent in the battery or at the positive plate and must not inhibit the cell reaction at either plate. There is as yet very little available theory which would make the investigation anything but empirical. What little there is[26] indicates that the anion of the salt is more likely to be absorbed at the positive grid than are most addition agents, unless one could be found which has a very high, very concentrated dipole moment.[27]

What can be concluded from the physical mechanism? First, the corrosion could be slowed down if the area term could be decreased, i.e., if the film could be more continuous. This involves finding a method of affecting the rate of nucleation. However, it must be remembered that such a development would also increase the resistance of the film-pore network because PbO is a nonconductor and, consequently, the bad effects might off-set the good.

Potential is a variable in the equation, but, in a battery, potential must be cycled in such a way that it includes the range of maximum corrosion rate. Variation of the charge-discharge cycle might be possible so that longer periods of time would be spent at potentials where the protective film is formed. In this connection it should be pointed out that work to date was done on pure lead, which is undesirable as a positive grid material for other reasons. Little[28] knowledge is at hand yet as to the effect of potential on the rates of corrosion of present commercial alloys.

The temperature coefficient of the reaction rate is obviously quite high, so that anything which can be done to reduce the temperature of operation will be beneficial as far as the corrosion is concerned. Generally speaking, however, batteries must operate under ambient temperature conditions, so that not much improvement may be expected with regard to this factor.

The experimental results indicate that operation of the cell employing electrolyte concentrations higher than are normally used might be beneficial from the corrosion standpoint. This effect should be studied for antimonial grids. However, where antimonial grids are used, it would probably have an adverse influence on the negative plate because of self-discharge.

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[26] *Butler, J.A.V., "Electrocapillarity," Methuen and Co., Ltd., London, 1940, p. 85.*

[27] *Although the discussion up to this point in no way eliminates as the best answer to the problem any of the general possibilities, it does indicate several very stringent conditions limiting the nature of whatever protective device is considered.*

[28] *One test at one potential (1.3 volts) and one concentration and temperature shows that, under the conditions used, 6% Sb-Pb alloy does not form a protective film.*

The remaining terms in the equation are supposedly constant, and there is too little theory available to enable much discussion of them at this time. Suppose, however, that the value of E, the activation energy, could be appreciably affected by alloying lead. Obviously, even a small increase in E might bring about a comparatively large decrease in the rate, because the rate is dependent on E in an exponential fashion. It is because of this effect that an intimate knowledge of the chemical mechanism might possibly be of great value. The value of E might also be affected by lattice strain. It is, for example, perhaps to be expected that a strained lattice will have made up some of the necessary activation energy, since it is in a higher energy state. If so, the same value of potential might possibly be expected to give higher corrosion rates.

The corrosion rate might be reduced as a result of studies of alloying (or some of its attendant metallurgical effects such as grain size and orientation and precipitation of impurities and alloy additions within grains and in grain boundaries) and of casting methods to obtain optimum properties concerned. Much of this has been done in other systems without having produced as yet any reliable general theory.

SUMMARY

X-ray data for anode films formed on lead show that, for a range of potential of 0.9 to 1.0 volt below the value for PbO_2 formation, the film consists of an outside layer of $PbSO_4$ and an underlying coating of tegragonal PbO. The $PbSO_4$ film, after an initial period, is probably formed by chemical reaction of the electrolyte with the underlying PbO film. Comparison of experimental data with thermodynamic calculations shows that the attacking agent from solution could be H_2O or OH^- ion. Other conditions might indicate that H_2O is the more likely one.

Comparison of experimental data on rates of PbO formation with various equations for simple modes of film formation indicates that the PbO film is essentially porous to the attacking substance. Hence, the reaction may be considered to take place at the metal surface at a rate limited by the activation energy of the electrode reaction itself. Where this is true, the value of the activation energy may be determined. If rates of nucleation and growth were obtainable, then the actual weight loss could be calculated.

The details of the chemical mechanism still are not clarified.

The film formed above the PbO_2 potential is a good conductor, is protective over a limited voltage range, and very likely consists of a relatively nonporous film of PbO_2.

Analysis of the problem, considering presently available fact and theory, suggests no logical direction for future work. That is to say, future investigations must still be on an empirical basis.

* * *

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