The Anodic Oxides of Lead

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ABSTRACT

The anodic oxides formed on lead under varying potential and *p*H were identified by x-ray and electron diffraction. Pure lead specimens were anodized at selected constant potentials to develop anodic coatings of sufficient thickness to give strong x-ray patterns. The domains of occurrence of: α and β PbO_2, yellow and red PbO, and the intermediate oxides, Pb_3O_4, and PbO_x were determined for acid and alkaline electrolytes. The intermediate oxides are not believed to be direct anodic oxides, but to represent chemical reaction products. The occurrence of certain of the oxides may be attributable to an initial electrochemical oxidation of water. The identifications have been presented in potential-*p*H phase diagrams.

Coincident with a study of the positive grid corrosion of the lead-acid storage cell, the anodic oxides formed on lead at various potentials in H_2SO_4 were identified by x-ray and electron diffraction (1, 2). Considered in the light of the potential-*p*H phase diagrams for the system (3), it became evident that certain aspects of the diagrams could be verified by application of diffraction techniques to anodic products formed on lead under controlled conditions of potential and *p*H. Furthermore, it was of interest to know which of the many oxides of lead occur as direct anodic products.

The potential-*p*H diagram is an isothermal phase diagram showing the various valence states of a metal, solubilities of oxides and salts, areas of thermodynamic stability of solid phases, ionic species, and their homogeneous and heterogeneous equilibria. The original presentation of the diagrams for the lead system (3) was based on available thermodynamic information. This present study was undertaken to identify the solid oxide phases appearing on lead as anodic products and to expand the usefulness of the diagrams by verification of the stable and metastable equilibria. In addition, it was desired to clarify the apparent thermodynamic anomaly of the simultaneous occurrence of the two crystallographic modifications of PbO_2 and of tetragonal PbO as anodic products on lead in acid solutions, and relate the known corrosion domains to those predicted on the basis of the diagrams.

Lead forms a number of oxides and Table I presents selected references (4-24) and the designations used in this report. An exhaustive listing has not been attempted. The hydrated lead monoxides have not been included because these materials are not well-established crystallographic identities. Bystrom (25) has presented a survey of the sterochemistry of the lead oxides.

Previous studies have indicated that the corrosion processes on the lead anode in H_2SO_4 at selected positive potentials included a group of reactions quite distinct from the reversible PbO_2, $PbSO_4$ and Pb, $PbSO_4$ electrode reactions (1, 2, 26-28). In order to clarify further the anodic corrosion reactions on lead, this detailed identification of the anodic products was undertaken.

Experimental

The anodic deposits formed on lead at controlled potential and *p*H were determined by polarizing pure lead sheet under fixed conditions and identifying the anodic products by x-ray and electron diffraction patterns taken by reflection from the anodized surfaces. The standard diffraction patterns used for identification are found in the X-ray Powder Data File (29) or in one or more of the references cited for each oxide in Table I.

The electrolytes used in this study were made from C. P. chemicals and distilled water. In the solutions near neutral limited amounts of CO_2 did not interfere with the observations. In order to check this a few experiments were carried out with freshly boiled distilled water and KOH very low in CO_2, in a closed cell. The results of these anodic tests were identical with those obtained in fresh solutions with nominal concentrations of CO_2. Fresh KOH solution was prepared for each run in which it was used. Values of reference electrode potentials were taken from the literature (30-33).

A Beckmann *p*H meter using a glass electrode, saturated calomel reference electrode, and standard buffer solutions were used to monitor the *p*H of the electrolytes. Solutions were made with C. P. reagents to approximate values and their actual *p*H's determined. Whenever feasible, the reference electrodes were used in the same solutions during anodization to eliminate liquid junctions. In sulfuric acid solutions, the electrode was Hg_2SO_4, Hg and in KOH solutions, HgO, Hg. Potentials were converted to the standard hydrogen electrode for this report.

Anodizations were carried out in glass cells, and usually only a few hours were required to develop coatings sufficiently heavy to give excellent x-ray diffraction patterns. Some specimens were anodized for longer periods of time, and as much as one week. The constant potential regulator described by Work and Wales (34) was used as the source of polarizing potential. A negative electrode of Pb or Pt gauze

Table I. Some known oxides of lead

	Formula*	Lattice	Other designations	Reaction with Acids	References
	PbO_y*	Orthorhombic	Litharge, yellow		(4, 5)
	PbO_t*	Orthorhombic-pseudotetragonal	Distorted PbO, yellow, brown, red	$PbO + 2H^+ = Pb^{++} + H_2O$	(6)
	Red PbO	Tetragonal	Massicot, red		(7, 8)
	PbO	Hexagonal	Yellow Litharge		(9)
$PbO \cdot xPbO_2$* or PbO_x*	Pb_3O_4*	Tetragonal	Minimum-orange Red lead	$Pb_3O_4 + 4H^+ = 2Pb^{++} + \beta PbO_2 + 2H_2O$	(6, 9-11)
	Pb_7O_{11}	Orthorhombic-pseudotetragonal	Black minium		(6, 12-17)
	Pb_5O_8		$PbO_{1.33-1.51}$ maroon to	$PbO_x + 2H^+ = Pb^{++} + \alpha PbO_2 + H_2O$	
	Pb_2O_3	Orthorhombic-pseudocubic	$PbO_{1.47-1.57}$ black	$1.33 \leqq x \leqq 1.57$	
		Monoclinic			(16, 18, 19)
	βPbO_2*	Tetragonal	Beta; $PbO_{1.87-2.02}$	Insoluble or dissolves as divalent Pb	(6, 13, 20, 21)
	αPbO_2*	Orthorhombic	Alpha; $PbO_{1.94-2.02}$		(22-24)

* Symbols used in this report.

was of such area that a constant positive polarization potential was obtained.

C. P. lead sheet to be anodized was annealed at 100°C for six weeks, cleaned of its air-formed oxide film by washing in saturated ammonium acetate solution, rinsing in water and inserting into the electrolyte while wet. Anodic polarization was begun simultaneously with insertion into the electrolyte, and the first few minutes of polarization was monitored carefully with a bench potentiometer and reference electrode to determine that the desired anodic potential was applied to the positive electrode.

At the termination of polarization, the electrode was removed from the solution, and rinsed in water, blotted dry on tissue, and placed immediately in the diffraction apparatus. The patterns were recorded as soon as possible after mounting.

GE-XRD-5 x-ray diffraction equipment was used with copper and iron targets, and electron diffraction examination was carried out with the diffraction attachment of an RCA-EMU-2 electron microscope.

In order to determine whether the two polymorphic forms of PbO_2 were readily interconvertible by crystallization from alkaline or acid media several tests were made on C. P. βPbO_2. Beta PbO_2 was dissolved in KOH solution, in concentrated HNO_3 solutions, and filtered with water aspiration. Water was added dropwise to the filtrates and, when sufficient material had hydrolyzed, it was collected on a filter and identified by x-ray diffraction examination.

C.P. βPbO_2 was treated with solid KOH and sufficient water to form a slurry. After several days' digestion at room temperature, large water-clear crystals formed up to 2 cm in diameter. These were washed free of excess PbO_2 with distilled water, and then placed in contact with a few drops of *N* KOH solution. They were slowly converted to dark brown powder which was examined by x-ray diffraction. The residual unconverted PbO_2 was also examined by diffraction.

Large clear crystals up to 6 mm in diameter formed from C.P. PbO_2 when treated with concentrated HNO_3. These were washed free of excess PbO_2, and placed in contact with dilute HNO_3 at room temperature. They were converted gradually to a brown powder that was examined by x-ray diffraction.

Essentially identical potential arrests are reported in many polarization studies of lead anodes in alkalies and only a few are cited here (35-38). Consider-

Table II. Electrolytes and anodic potentials used in this study

pH	Electrolyte Composition	Potential in volts with respect to standard hydrogen electrode — Anodic lead specimens			
—0.63	3.5*N* H_2SO_4	2.08	1.87	1.62	1.30
		2.07	1.86	1.59	1.10
		1.90	1.70	1.56	1.06
2.5	*N* $NaSO_4$	1.85	1.19	0.32	
	H_2SO_4*	1.57	1.17	0.02	
7	M K_2SO_4	1.33	1.05	1.00	
	N Na_2SO_4	1.4	1.00	0.51	
		1.20	0.80	—0.30	
12	*N*/1000 KOH	0.85	0.45	—0.41	
14.5	3*N* KOH	1.03	0.67	0.38	0.27
		0.98	0.45	0.36	—0.57
		0.85	0.43	0.33	—0.66
		Platinum anode potentials			
2.5	0.1M $Pb(NO_3)_2$	2.3	1.47	1.32	
8	0.1M $Pb(NO_3)_2$ KOH*	1.8	1.30	1.1	
14.5	3*N* KOH PbO**	1.06	0.34		

* Sufficient quantities of these reagents were added to adjust the pH to the indicated values.
** Excess solid PbO was present in the cell during electrolysis.

ation of such reports enabled judicious choice of the potentials used for the anodic treatments of this study.

Table II is a list of the electrolytes, and the potentials, employed in these anodization studies. Certain experiments were rerun many times in order that the identification should be conclusive. Certain other areas, where there seemed no possibility of question, were identified with only a few runs. The anodic products formed on lead in H_2SO_4 solutions have been reported earlier (1,2).

Some anodic coatings were laminated, and the material at the solution interface was removed by wiping the electrode with dry tissue, or by scoring around the edge of the electrode and lifting off the outer layer.

By using spot tests (39) it was possible to detect the appearance of a highly oxidizing material on the electrode surface considerably below the potentials where PbO_2 or the intermediate oxides became apparent in the x-ray diffraction patterns from specimens anodized in the strong acid range. Sheet lead specimens were anodized in H_2SO_4 solutions at carefully monitored potentials within a range ± 0.1 v to the theoretical reversible O_2,H_2O potential. After anodizations as long as 24 hr, the electrodes were removed from the electrolyte and dropped into the selected reagent: acetic acid when the benzidine test was used and starch-KI solution when this was used.

In order to verify the reported deposition of α and β PbO_2 as residues from the intermediate oxides, Pb_3O_4 and PbO_x were extracted with H_2SO_4, $NH_4C_2H_8O_2$ (saturated solution), HNO_3, and $HC_2H_8O_2$. The residues were rinsed in water, sucked dry on a filter, and the diffraction patterns recorded.

Neutral, acid and alkaline solutions of lead were electrolized between platinum electrodes. The potentials at which lead dioxide first deposited on the anode were observed, and the initial and final deposits were examined by x-ray diffraction.

αPbO_2 was heated in air at temperatures between 150° and 400° and the decomposition followed by x-ray diffraction examination of the products. The temperature range between 290°-305° was examined in steps of 2° with heating times of 48 hr. The decomposition was compared with that reported and verified for C.P. βPbO_2 (6, 13, 17).

Results and Discussion

The solid anodic products formed on lead at fixed *p*H and potential are divided into two categories: (*a*) the product of the anodic reaction at the solution interface; and (*b*) the product of the anodic reaction at the metal interface. These may be the same or different reactions, and there may or may not be other reactions between cell components. Thorough familiarity with the potential-*p*H diagram originally published (3) for the system is assumed, and this report deals mainly with the solid oxide phases associated with certain conditions of potential and *p*H at room temperature, but does not include solubility data.

Free energy values have been used to calculate the equilibrium potentials of this report in conformity with the original presentation of the potential-*p*H diagram; however, the free energy of formation of PbO_2 used by Delahay, Pourbaix, and Van Ryssel-berghe was only −50.86 kcal. Latimer gives a value of −52.34 kcal (40).

The domain of thermodynamic stability of metallic lead may approach that of PbO_2, and the equilibrium expected between the metal and this oxide has been calculated (28)

$$\beta PbO_2 + 4H^+ + 4e^- = Pb + 2H_2O \qquad [1]$$
$$E = 0.6775 - 0.0591\ pH$$

However, it is known that metallic lead usually tends to dissolve in the presence of PbO_2 and will be oxidized in a mixture containing excess higher oxide; or if metallic lead is in excess, the higher oxide will be discharged (41, 42). The electrochemical instability of PbO_2 in strong H_2SO_4 solutions at potentials below the reversible $PbSO_4$, PbO_2 electrode has been discussed by Lander (28). But at the potential of reaction [1], metallic lead is thermodynamically stable in the presence of PbO_2. However at this potential PbO_2 is not thermodynamically stable with respect to PbO_t or Pb^{++}. Therefore when the potential of a lead anode is raised above that of reaction [1], any formation of PbO_2 from metallic lead would tend to undergo the reaction

$$PbO_2 + 2H^+ + 2e^- = PbO_t + H_2O \qquad [2]$$
$$E = 1.107 - 0.0591\ pH$$

until the reversible potential for this reaction is exceeded. At potentials above those of reaction [1], metallic lead is unstable with respect to both PbO_t and PbO_2.

Anodic oxides at the solution interface.—It has been reported and was verified in this study that electrolysis of Pb^{++} solutions between platinum electrodes develops deposits largely of βPbO_2 from acid and αPbO_2 from alkaline solutions. Either or both polymorphs may be deposited from certain solutions depending on current density (potential) (23, 24).

Figure 1 shows the anodic oxides identified in this study at the electrode-solution interface on lead polarized in solutions of varying *p*H at several potentials. The lines for the oxidation of water to ozone and H_2O_2 have been added for reference. The effect of anions other than sulfate has not been indicated on the diagram; however, the corresponding salts will precipitate at the solution interface. The accumulations of solid products on the anode surfaces appear as oxides or hydrated oxides intermixed with the salts owing to depletion of the anolyte in anions.

The areas designated as PbO_y, βPbO_2, and the hydrous oxides (43) indicated on the diagram, Fig. 1, are not at thermodynamic equilibrium. Lead dissolves in solutions of *p*H less than 9.4 as the divalent Pb^{++} to form a saturated solution adjacent to the electrode, and when the rate of solution exceeds the rate of diffusion of anions from the bulk of the electrolyte the oxide crystallizes as a chemical deposit from this solution. The deposits designated in Fig. 1 of the hydrous oxides and the yellow glistening crystals of orthorhombic PbO_y are in this category and form normal and basic salts with anions present.

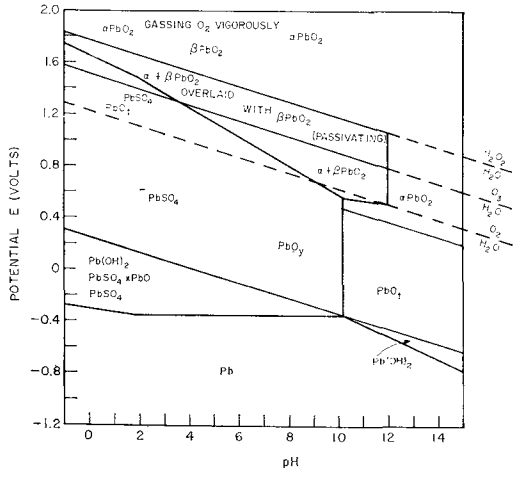

Fig. 1. Anodic oxides on lead at the solution interface. This diagram indicates the areas of occurrence of the solid oxide phases identified by x-ray and electron diffraction, and obtained on anodization of lead metal at fixed pH and potential. The lines for the following equilibria have been added

$$O_3 + 6H^+ + 6e^- = 3H_2O$$
$$E = 1.51 - 0.0591\ pH \quad P_{O_3} = 1\ atm$$
$$H_2O_2 + 2H^+ + 2e^- = 2H_2O$$
$$E = 1.77 - 0.0591\ pH \quad a_{H_2O_2} = 1M$$

Anions present in the electrolytes will form normal and basic salts with the lower oxides as indicated in the original potential -pH diagram of the system (3).

The open-circuit potential of the lead electrode is controlled by the amount of Pb^{++} in solution and is independent of *p*H. Above *p*H of 9.4 lead passes into solution as biplumbite ion, and the reaction has a slope 0.089 vs. *p*H. By impressing anodic potential on the system, more and more salt and oxide will be deposited unless a uniform coherent coating forms on the surface (passivation). These phenomena have been described in detail by Wolf and Bonilla for a large number of anions (44).

The crystals of PbO_y deposit in platelets shown by x-ray diffraction to be parallel to the c_o face typical of solution-grown crystals of this material. It does not form dense passivating films but grossly crystalline deposits. It is an anodic oxide in the sense that it is the solid deposited from saturated lead ion solutions.

At more elevated potentials such an electrode becomes covered with a layer of PbO_t in which the crystals of PbO_y are embedded. The domains of solubility of the two polymorphs of PbO_2 intrude into this area at higher *p*H, and a mixture of the four oxides is obtained. It is in this area that the intermediate oxides Pb_3O_4 and PbO_x as chemical reaction products will form after a time, but the electrode does not passivate. Only above the line indicated in Fig. 1 corresponding to the theoretical reversible O_3/H_2O reaction does passivation appear. The corrosion reaction of the metal surface is primarily a divalent one up to a potential corresponding to the reversible ozone reaction, while the deposition of tetravalent oxide takes place at the solution interface, resulting in a mixture of di- and tetravalent products.

In solutions of *p*H 12 and higher, a lead anode becomes covered with a deposit of hydrated lead oxide designated as $Pb(OH)_2$ in Fig. 1, and subsequently with a tetragonal oxide designated as PbO_t. If the potential is increased, plumbate ion is formed in the solution, and the surface of the electrode becomes covered with a layer of αPbO_2. There is an underlying layer of PbO_t which may react with the αPbO_2 formed at the solution interface to produce the intermediate oxides.

It may be possible to limit the deposition of αPbO_2 from alkaline solutions to a rate comparable to its chemical reaction rate with PbO_t and thereby obtain a deposit at the solution interface of the intermediate oxides, but such a condition was not observed in this work during anodization. Self-discharge may also produce such a surface. These intermediate oxides do not appear to be deposited directly from oxidation-reduction reactions, but from chemical combinations, i.e.

$$\left.\begin{aligned} PbO + PbO_2 &= Pb_2O_3 \\ 2PbO + PbO_2 &= Pb_3O_4 \end{aligned}\right\} \text{designated } PbO_t \cdot xPbO_2$$

An infinitude of stoichiometries is possible in such anodic products.

X-ray diffraction examination shows that βPbO_2 is obtained by hydrolysis of both acid and alkaline solutions of tetravalent lead ion, and is the main product deposited electrolytically from acidic Pb^{++} solutions at elevated potentials. Anodization of metallic lead, however, produces a mixture of α and βPbO_2 at elevated potentials. The anodic deposition of βPbO_2 in alkaline solutions occurs simultaneously with the evolution of O_2 gas. It therefore probably deposits by hydrolysis at the local areas on the anode where alkalinity is reduced by the gassing reaction.

Anodic oxides at the metal interface.—The x-ray and electron diffraction examination of the anodic products developed on Pb at various *p*H and potential conditions showed that the metal-coating interface exhibited the same oxides throughout the *p*H range, at the same potentials relative to the reversible hydrogen electrode in the same solutions (not the standard electrode). This means that the anodic reactions have slopes of 0.059 vs. *p*H. The solid phases identified in this study are indicated in Fig. 2.

When the potential of a lead surface exceeds the line bounding the lower extent of the area designated as $Pb(OH)_2$, a film of the solid hydrous oxide forms on the metal surface.

When the potential of a lead anode is raised above the line representing the reaction:

$$PbO_t + 2H^+ + 2e = Pb + H_2O \qquad E_o = 0.248$$

in Fig. 2, the lead becomes covered by a layer of PbO_t. This oxide has a tetragonal lattice showing a characteristic combination of sharp and diffuse lines in its diffraction patterns (6,13, 14). It is considered more reactive than either of the normal monoxides, and it appears on a lead anode in both acid and alkaline media. Katz described this as orthorhombic pseudotetragonal PbO (6). In alkaline solutions heavy coatings of this material appear yellow when wet with electrolyte, but are pale peach in color when dry and may form beautiful glossy coatings on a lead electrode. It has been described as a yellow

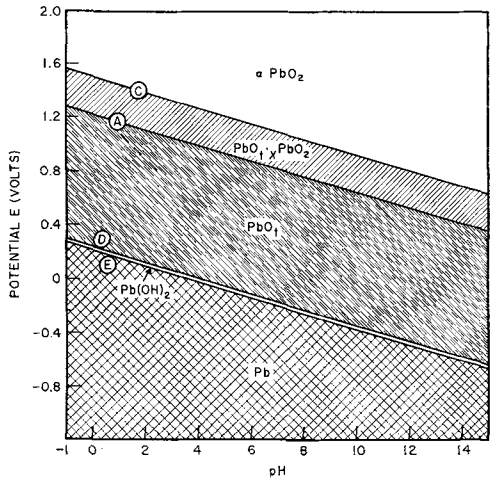

Fig. 2. Anodic oxides of lead at the metal interface. This diagram indicates the areas of occurrence of the solid oxide phases obtained at the metal-coating interface on anodization of lead at fixed potential and pH. The reactions represented by the lines D and E bounding Pb and the phases $Pb(OH)_2$ and PbO_t will be recognized from the original diagram (3), and were found to occur at essentially their reversible potentials throughout the pH range. The exception is the boundary between PbO_t and PbO_2. The intermediate region labeled $PbO \cdot xPbO_2$, representing oxides and mixtures of oxides of di- and tetravalent lead, was found to appear between the reversible oxygen and ozone potentials, lines A and C. Above line C, αPbO_2 is the principal anodic oxide at the metal interface. The reactions are represented as follows

(A) $O_2 + 4H^+ + 4e^- = 2H_2O$
$E = 1.228 - 0.0591\ pH \qquad P_{O_2} = 1\ atm$

(C) $O_3 + 6H^+ + 6e^- = 3H_2O$
$E = 1.51 - 0.0591\ pH \qquad P_{O_3} = 1\ atm$

(D) $PbO_t + 2H^+ + 2e^- = Pb + H_2O$
$E = 0.258 - 0.0591\ pH$

(E) $Pb(OH)_2 + 2H^+ + 2e^- = Pb + 2H_2O$
$E = 0.242 - 0.0591\ pH$

scum (37). Thermodynamically this oxide is stable up to a potential described by the reaction:

$$PbO_2 + 2H^+ + 2e = PbO_t + H_2O \qquad E_o = 1.107$$

The area associated with PbO_t is one of rapid corrosion of the anode unless there is a passivating layer of salt at the solution interface that permits establishment of metastable equilibrium. In sulfuric acid $PbSO_4$ serves this purpose, but in alkaline solutions no passivation occurs and the anode continues to corrode at high rates.

The area designated in Fig. 2 as $PbO \cdot xPbO_2$ is determined by both diffraction examination and spot tests. In this area PbO_2 as such is not detected by diffraction examination at the metal interface. In acid solutions the product is PbO_t giving a spot test for a highly oxidizing material after polarization above a potential corresponding to the theoretical reversible oxygen potential. The highly oxidizing material is considered in this report to be tetravalent lead. It appears immediately above the O_2/H_2O electrode potential and is not observed in the area where H_2O_2 could form from O_2 reduction. In neutral and alkaline solutions a mixture of the oxides Pb_3O_4, PbO_x, and PbO_t is observed. The reason for the difference in anodic materials developed in highly acid and in neutral or alkaline solutions is that PbO_2 varies in solubility with the pH at the solution interface. It is discharged in strong acid solutions, preventing accumulation of significant amounts of tetravalent lead. Both forms of PbO_2 are formed at the solution interface at higher pH so that larger amounts of tetravalent material do accumulate. In the alkaline solutions of $pH > 9.4$, the electrode is covered with a gray or black film of PbO_2 which is loose and may be lifted off the electrode revealing a layer colored bright orange, yellow, and peach giving the diffraction patterns for PbO_t, Pb_3O_4, and PbO_x. Lead is corroding under these conditions by a divalent mechanism (26, 28, 35, 36) forming PbO_t, part of which is being oxidized to PbO_2, and acted on at the solution interface by plumbate ion. The anodic products designated $PbO_t \cdot xPbO_2$ at the metal interface represent the mixture obtained by chemical reaction of these materials.

The existence of this area is belived to be caused by the relative rates of these several reactions

$$Pb + H_2O = PbO_t + 2H^+ + 2e^-$$

$$2H_2O = 2(O)_{aq} + 4H^+ + 4e^-$$

$$PbO_t + (O)_{aq} = PbO_2$$

$$\left.\begin{aligned} PbO_t + PbO_2 &= Pb_2O_3 \\ 2PbO_t + PbO_2 &= Pb_3O_4 \end{aligned}\right\} \text{Designated } PbO_t \cdot xPbO_2$$

The following mechanism is suggested: The anodic current may take two paths: (*a*) it corrodes Pb to form PbO_t or divalent products; (*b*) it oxidizes H_2O to $O_{2(aq)}$ which reacts with PbO_t to form the intermediate oxides (6, 13). Lander (26, 28) showed that within experimental limits all the current went to a divalent corrosion mechanism up to a potential of 1.58 v in acid solutions, and only above that potential did a tetravalent corrosion mechanism become significant. Grube and Glasstone (35, 36) showed a similar divalent corrosion mechanism in NaOH solutions up to a corresponding potential. It is suggested that the kinetics of the electrochemical reactions determine the anodic corrosion rate, and above potentials expressed by line C, Fig. 2, PbO_2 is present directly on the metallic surface. Line C corresponds to the reversible oxidation potential of water to ozone.

$$O_3 + 6H^+ + 6e^- = 3H_2O \qquad E_o = 1.51$$

The fact that the passivation of Pb in both acids and alkalies occurs just above this potential, that the reaction has a slope of 0.059 vs. pH, that it exceeds the potentials for formation of PbO_2 from Pb and PbO_t indicates that the corrosion reactions occurring at this potential may be related to water oxidation reactions.

The kinetic analyses of Lander (26) show that when lead is polarized above the potential for oxidation of water to O_2, the reaction mechanism changes. It was further determined that the anodic corrosion rates were related to the square of the water activity up to a potential corresponding to the maximum in the rate. Above this potential the relationship of the corrosion rate to water activity has values "ranging between two and four" (27). The water oxidation reactions to give O_2 and O_3 depend on the square and cube of the water activity, respectively.

The steps in the over-all water oxidation mechanisms are not known at the present time. The relation of the oxidation processes of the lead anodes to the water activity does not prove that $O_2(aq)$ or $O_3(aq)$ is liberated in these reactions; however, it does suggest that the anodic processes depend on the simultaneous reaction of two and more water molecules. It is possible that Pb or PbO_t catalyzes the water oxidation reaction, and that the subsequent step is reaction of Pb and PbO_t with the water oxidation product to form the intermediate oxides rather than molecular gas evolution.

If the lead anode in alkaline solutions is disturbed while in the laminated condition, before polarization above line C, Fig. 2, so that PbO_2 is mechanically brought into physical contact with the base lead metal, oxygen gas begins to be evolved at a potential lower than it will be from an undisturbed electrode. This effect, described by earlier workers (35), was verified in this study. With this positive identification of the anodic materials, it is concluded that PbO_2 must be in direct contact with the metal surface for the oxygen gas liberation reaction to take place and that the reaction may be associated with oxidation of H_2O or $(OH)^-$ to H_2O_2.[1]

It should be emphasized that this is a study of the dynamic anodization of lead under the potential and pH conditions indicated. Polarization of lead within the area designated $PbO \cdot xPbO_2$ does not establish a passivating coating on the surface, and anodic corrosion rates are high. Deposition of PbO_2 at the solution interface does not comprise a protective coating.

The area indicated at αPbO_2 in Fig. 2 is characterized by a heavy deposit of this material directly on the electrode, providing other reactions do not interfere. This material has not been well characterized chemically, and is probably the low-temperature polymorph (45).

X-ray diffraction examination of the residues obtained on air ignition of αPbO_2 at temperatures corresponding to those reported for thermal degradation of βPbO_2 (6, 17) showed evidence that prior to decomposition α converted to βPbO_2. The conversion temperature lies between 296° and 301°C. Subsequent thermal decomposition, determined by x-ray diffraction examination, follows the same path as βPbO_2.

It may be concluded from this examination of the oxides occurring at the metal-coating interface on anodic lead specimens that the oxides formed are: $Pb(OH)_2$; PbO_t and αPbO_2. The potentials for these reactions have a slope of 0.0591 vs. pH and are believed to represent the electrochemical reactions of lead with water and its oxidation products.

The reaction of metallic lead with water to form PbO_t takes place near the calculated reversible potential. Arrests appear near the theoretical potential in both acid and alkaline solutions on both anodic and cathodic treatment, and PbO_t is observed by diffraction examination of the surface. This indicates that the oxidation proceeds by direct reaction with water molecules or hydroxyl ions at the electrode interface and that no preliminary oxidation of water occurs in this reaction. But the reaction forming PbO_2 at the metal interface should probably be written to indicate that water is first oxidized to an oxygen species and the solid anodic products result from secondary reactions. This suggests that the anodic studies of lead may offer a method for kinetic analysis of the water, oxygen electrodes.

Anions and passivation.—As pointed out previously and discussed extensively by Wolf and Bonilla (44) anions present in the solutions will react with the lead ion and/or the lower oxides, and the corresponding salt will be deposited at the solution interface. If the anion is suitable, a tight passivating film is deposited on the anode surface [i.e., $Pb_3(PO_4)_2$, PbI_2, $PbSO_4$] (44, 46), and continued polarization of the electrode will result in the characteristic anodic oxide at the metal-coating interface. If the lead salt of the anion is not passivating, the electrode process may be changed by only very high current densities or cell potentials (47).

A picturization of a cross section of an anodic lead surface is shown in Fig. 3. This indicates the reaction products identified on the anode surface at pH = 0, and the reference potentials are presented in the left margin. The cross section is schematic;

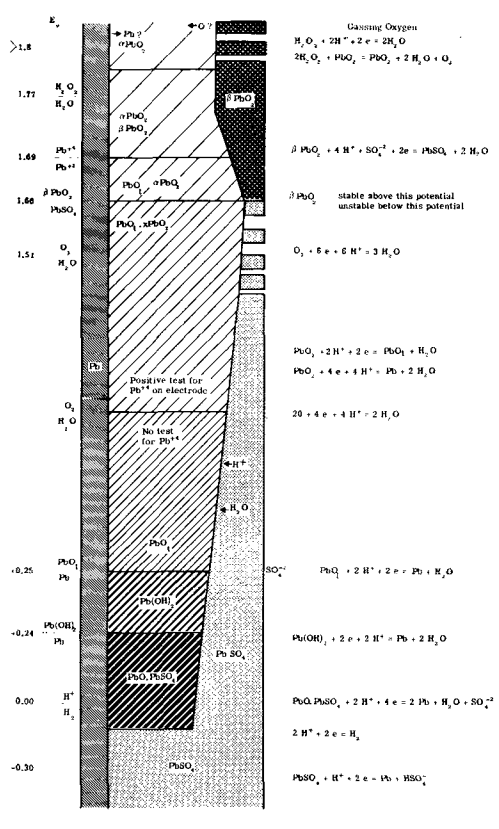

Fig. 3. Schematic cross-section of an anodic lead surface in H_2SO_4 at pH = 0. Anodic products identified by diffraction techniques on a lead surface held at constant potential in sulfuric acid are indicated. Electrochemical reactions are shown at the right within the areas where they were observed to occur. Some E_0 values are indicated at the left for orientation purposes. At the potential 1.8 v oxygen gas is evolved, and a hydrogen peroxide reaction mechanism is indicated as suggested by the potential. At this potential lead is represented as corroding by either migration of Pb or O in the film. The mechanism of this corrosion process is not known at the present time.

[1] The reactions in alkaline solution may be written with $(OH)^-$ rather than H^+, and the HO_2^- reactions have different slopes, but for simplicity these are not included in this discussion.

however, it indicates that as the potential is increased the $PbSO_4$ coating appears to become thinner while the PbO_t layer becomes increasingly thicker. Some suggested reactions are indicated at the right of the drawing. The solid phases identified by diffraction examination are indicated within the potential ranges where they were observed. Areas corresponding to high corrosion rates are indicated as porosity in the outer coating. These rates were determined by Lander under constant potential anodization (26, 28). Several reactions appear near their reversible potentials, exhibiting little polarization, and it is thought that the superficial $PbSO_4$ coating is permeable to H^+ ion and water, but not to SO_4^- ion (26, 44). The action of this passivating film is to permit establishment of pseudo equilibrium in an electrochemical reaction in an environment where the reaction would normally be driven in a destructive direction. This, of course, describes the condition called metastable equilibrium.

As the potential is increased, the lead sulfate present on the surface may be converted to βPbO_2. Electron diffraction examination of the anodic products indicates that the βPbO_2 is a polycrystalline coating at the solution interface. Beneath this is a thin layer of a mixture of the two polymorphs of PbO_2 (1, 2). These materials are believed to arise from two reactions forming PbO_2, one from the base lead and PbO_t and the other from $PbSO_4$.

The oxygen gassing reaction at elevated potentials has been indicated as going by way of the formation of H_2O_2 (possible at these potentials) and being decomposed catalytically by the PbO_2. This is merely a representation and suggestion of a possible oxygen liberation mechanism which potential appears to be related to the peroxide reaction in both acid and alkaline solutions (48, 49). The lead metal is represented as corroding by migration of an oxygen species in and lead outward through an αPbO_2 coating at very elevated potentials. Lead exhibits an increased corrosion rate (26, 28), and αPbO_2 comprises the major portion of the anodic product at these potentials, but it is not known whether the mechanism involves attack of the lead through fissures in the coating or migration through a continuous film.

Conclusions

The areas of occurrence of the anodic lead oxide phases are indicated on the potential-pH phase diagrams of Fig. 1 and 2. There appear to be two sets of anodic reactions, producing different anodic products. Some of the observed oxides are believed to be electrode species, and some deposits from saturated solutions and chemical reactions.

The occurrence of αPbO_2 as an anodic product on lead in acid solutions has been attributed to oxidation of PbO_t and lead metal by the preliminary oxidation of water.

It is suggested that the corrosion rate of lead depends on the kinetics of these water reactions, and that inhibition of corrosion depends on the imposition of a "corrosion" current and potential that results in a steady-state condition in which PbO_2 is maintained in direct contact with the base metal. Upon anodic polarization of a clean lead surface, it is necessary to "overshoot" the steady-state potential and current in order to generate the required materials, but once the materials are formed in the solution and on the electrode surface then only a minimal current is required to maintain passivation. The low corrosion rate of telephone battery service (50) is believed to be a reflection of this requirement.

The passivation domains originally outlined to correspond to the domains of thermodynamic stability of PbO_2 and $PbSO_4$ (3) should be modified to indicate two areas of passivation: one where the composite coating of $PbSO_4$ and PbO_t is protective below line A in Fig. 2; and the other above line C. These passivation domains are separated by an area of intense corrosion believed to be caused by the electrochemical oxidation of water at the metal interface at a rate insufficient to maintain a passivating coating of PbO_2 on the metal surface.

X-ray diffraction examination of calcined αPbO_2 suggests that it is the low-temperature polymorph and is converted to βPbO_2 at approximately 300°C in air.

The potentials associated with gassing oxygen from a PbO_2 electrode indicate that the reaction may go by way of peroxide in both acid and alkaline media.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1959 JOURNAL.

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Evidence for a Logarithmic Oxidation Process for Stainless Steel in Aqueous Systems

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ABSTRACT

Upon immersion of a passive stainless steel electrode into an oxidizing ferrous-ferric aqueous solution, the mixed potential of the electrode gradually approaches the reversible redox potential of the solution. During this period, an oxidation process occurs, the rate of which decreases with time. The process is most likely oxidation of metal since the potential range over which it occurs is more active than the estimated reversible oxygen potential for the system, and no other oxidation reaction is likely. The kinetics of oxidation of stainless steel are similar to kinetics reported for anodic oxidation of metals which form thin amorphous oxides. Therefore, it is believed that evidence has been obtained for growth of a similar type of oxide on stainless steel. At constant potential, the oxidation process can be described closely by a logarithmic oxidation equation. Also, the kinetics are consistent with equations which describe ion current through thin oxides as a function of the field across the oxide.

A study of ferrous-ferric electrode kinetics on stainless steel surfaces has been reported (1). The data supported theoretical equations which describe potential-current relationships for such a system. All rate measurements were conducted on electrodes whose potential, with no applied current, was very close to the reversible ferrous-ferric potential. However, it was also shown that stainless steel does not exhibit this potential immediately after immersion in the oxidizing solution. The electrode is initially more active than a platinum electrode in the same solution and slowly approaches the platinum potential over a period of several thousand minutes in a manner already illustrated (1). No effort was made to explain the processes occurring during this time interval; however, pertinent data were obtained which, at that time, were not particularly clear. A better understanding of the nature of the system now provides a reasonable explanation of this initial potential-time dependence, and the purpose of this discussion is to describe the kinetics of the processes which occur.

Experimental

The experimental procedure was described earlier (1, 2) and only pertinent details are repeated. The environment was either a mixture of ferrous and ferric sulfate in water or a mixture of ferrous and ferric chloride containing sodium nitrate as a pitting inhibitor. Solutions were oxygen-free. Platinized platinum was used as reference and as auxiliary electrodes during polarization. The material was commercial Type 304 stainless steel. Sample preparation involved thorough degreasing, activation in concentrated HCl until hydrogen evolution was ob-