

The initial stages of lead oxidation in pH 9 to 14 aqueous solutions

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The initial stages of lead oxidation in a range of alkaline solutions of varying pH and ion content have been investigated with the use of cyclic voltammetry and potential step techniques. In both carbonate and borate buffered solutions (pH > 9), and in more alkaline solutions, Pb oxidation commences at a potential of ca. 140 mV vs. RHE. The initial product is considered to be Pb(OH)₂, due to the proximity of this potential with the theoretically predicted one, and due to its invariance (vs. RHE) with pH. In pH 14 solutions, Pb(OH)₂ is soluble, producing Pb(OH)₃⁻ and only a small amount of a stable surface film. At lower pH's, Pb(OH)₂ is not predicted to be soluble, and in borate-buffered solutions, a stable, reducible film appears to form. In carbonate-buffered solutions, the surface film is very difficult to remove electrochemically. Although XPS analyses show the film to be essentially free of carbonate, it is clear that carbonate must be involved in some way in inhibiting film reduction.

Key words: lead, lead hydroxide, lead oxide, surface films, carbonate solutions, borate solutions, alkaline solutions, cyclic voltammetry.

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Utilisant des techniques de voltamétrie cyclique et opérant dans des solutions alcalines de pH et de contenus ioniques divers, on a étudié la nature des étapes initiales de l'oxydation du plomb. Dans des solutions tamponnées avec des ions carbonate ou borate (pH > 9) ainsi que dans des solutions plus alcalines, l'oxydation du plomb commence à un potentiel d'environ 140 mV vs. RHE. En se basant sur le fait que ce potentiel est très proche de celui prédit sur une base théorique ainsi que sur le fait qu'il ne varie pas (vs. RHE) avec le pH, on considère que le produit initial est du Pb(OH)₂. Dans des solutions de pH 14, le Pb(OH)₂ est soluble et il conduit à la formation de Pb(OH)₃⁻ ainsi qu'à une très faible quantité d'une couche superficielle stable. A des pH plus bas, il n'est pas prévu que le Pb(OH)₂ soit soluble et, dans des solutions tamponnées au borate, il semble se former une couche stable qui peut être réduite. Dans des solutions tamponnées au carbonate, il est très difficile d'enlever la couche superficielle d'une façon électrochimique. Même si des analyses par XPS démontrent que la couche superficielle ne contient essentiellement pas de carbonate, il est évident que le carbonate doit être impliqué d'une façon quelconque dans l'inhibition de la couche superficielle.

Mots clés : plomb, hydroxyde de plomb, oxyde de plomb, couches superficielles, solutions de carbonate, solutions de borate, solutions alcalines, voltamétrie cyclique.

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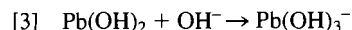
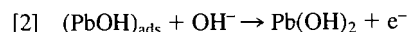
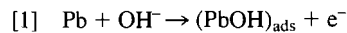
Introduction

Quite a number of studies concerning the electrochemical behaviour of lead have been carried out in the past (1–3), with emphasis on acidic environments. Lead has a variety of applications in industry, particularly as a lining and piping material because of its good corrosion resistance in acidic media (4). It has also played a major role in the development of electrical power sources, e.g. in lead–acid batteries (5).

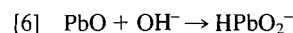
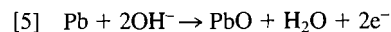
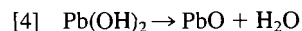
Relatively little has been reported in the literature regarding the fundamental electrochemistry of lead in alkaline media. Early research (6) concerning the anodic behaviour of lead in alkaline solutions, carried out under galvanostatic conditions, has indicated that lead can be dissolved to form Pb²⁺ at low applied current densities. At higher current densities, a PbO₂ film is expected to form at the electrode surface, with the subsequent evolution of oxygen. A more recent study carried out by Ptitsyn *et al.* (7), using potentiostatic and potentiometric methods, has indicated that the oxidation of lead in alkaline solutions involves first the formation of Pb(OH)₂, which subsequently dissolves as Pb(OH)₃⁻, with the latter dissolution step being rate determining.

More recently (8), it has been suggested on the basis of results obtained with cyclic voltammetry as well as steady state and transient potentiostatic techniques, that the first stage in the anodic oxidation of lead in 1 M NaOH solutions involves the formation of a surface intermediate, PbOH, followed by the deposition of a thin Pb(OH)₂ film on the Pb electrode surface, as shown in reactions [1] and [2]. The Pb(OH)₂ film then dissolves

to form a soluble species, Pb(OH)₃⁻ (reaction [3]), as was also suggested by Ptitsyn *et al.* (7).



Following reaction [3], it has been suggested (9) that a PbO film forms at higher potentials, both by the dehydration of Pb(OH)₂ and also via a nucleation and growth process at the free Pb surface, according to reactions [4] and [5], respectively. PbO is also thought to be somewhat soluble (reaction [6]).



These suggested reactions pathways and products are supported by thermodynamic calculations (8–10) which indicate that Pb(OH)₂ is predicted to form at a potential more negative than that for PbO formation.

The electrochemistry of lead in somewhat less alkaline solutions has also been investigated recently (11, 12). In borate buffered solutions (pH 9.0), it has been suggested (11) that the initial stage of Pb oxidation involves the formation of a lead borate surface film, followed by PbO deposition. In carbonate solutions (pH 10 to 12), a small anodic peak preceding the main peak in cyclic voltammetric experiments has been attributed to the formation of a lead hydroxy–carbonate surface compound (12). It has been suggested that within the potential range of this small peak, some Pb dissolution may also occur, possibly via a

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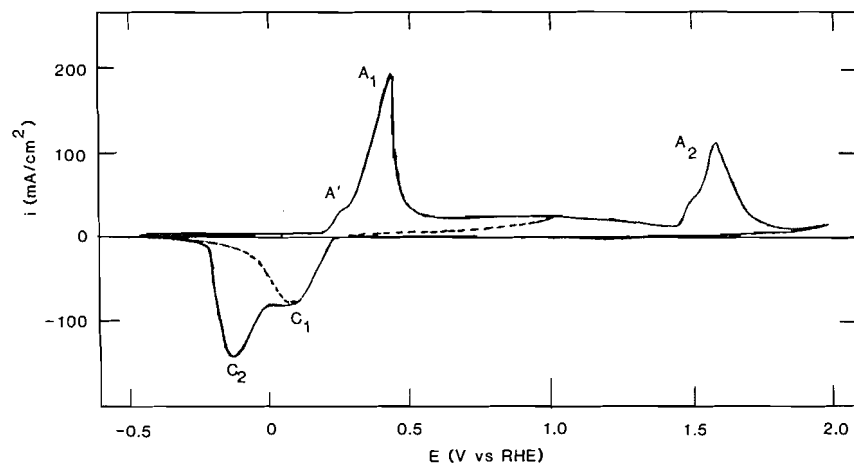


FIG. 1. Cyclic voltammogram of Pb chip electrode (0.015 cm^2) in 1 M NaOH at $s = 20 \text{ mV/s}$.

surface intermediate, while at higher anodic potentials, further surface film formation occurs and the rate of dissolution diminishes.

Interest in the behaviour of lead in alkaline carbonate-containing solutions is growing due to the possible use of lead to precipitate ^{14}C -containing carbonate ions, a radioactive contaminant produced in CANDU D_2O -containing nuclear reactors (13). Lead may also be used as a storage material for nuclear waste in deep underground vaults in the future (14).

This paper focuses on the initial stage of lead oxidation in a number of alkaline solutions. These include NaOH (pH 14) solutions, as well as buffered (primarily pH 9 to 10) carbonate and borate solutions. It will be shown that the initial step in the oxidation process in all of these solutions is likely to involve the formation of the same species, i.e. $\text{Pb}(\text{OH})_2$, as seen partly from the fact that the potential at which Pb oxidation commences (vs. the RHE) is independent of the nature of the electrolyte and the solution pH.

Experimental

Cyclic voltammetry (CV) and chronoamperometry (I/t) experiments were carried out using standard three electrode circuitry and an EG&G PARC 173 potentiostat coupled to an EG&G PARC 175 function generator. The current (I) vs. potential (E) profiles were plotted on a HP 7045B X/Y recorder at slow potential sweep rates (s), while all I/t data, and I/E curves at sweep rates greater than ca. 300 mV/s , were monitored on a Nicolet 3091 digital oscilloscope, and then transferred to the X/Y recorder.

A three compartment electrochemical cell was used in all of this work. The electrolytic contact between the working electrode (WE) and the reference electrode (RE) compartments was maintained via a luggin capillary. The counter electrode (CE), a large area platinum gauze, was placed in the third compartment. The RE was either a platinized Pt/hydrogen electrode placed in the same solution as that in the main compartment of the cell (RHE) or a saturated calomel electrode (SCE). All potentials are given with respect to the RHE in this work.

The WE consisted of either a Pb chip (from a Pb rod, 99.99% purity; Johnson and Matthey), having a geometrical area of ca. 1.5 to 3.0 mm^2 , embedded in epoxy in a Pyrex tube, or a Pb disc (ca. 0.385 cm^2) press-fitted into a Teflon holder. In some of this work, the WE surface was mechanically polished in stages with various grades of emery paper (250 to 600 grit), then with 0.1 alumina paste on a polishing cloth, ultrasonically cleaned in acetone, and then finally rinsed with distilled water. The true surface area of the WE could be obtained from double layer capacitance measurements in $0.1 \text{ N Na}_2\text{SO}_4$ solutions (15), in order to compare the surface areas of different electrodes.

However, because Pb is roughened by repeated oxidation/reduction cycles in high pH (>13) solutions, all current and charge densities are given with respect to the apparent electrode surface area in this work.

All solutions used were prepared from Analar grade chemicals and triply distilled water, and all experiments were carried out at room temperature. The solutions were deoxygenated by bubbling argon through the cell prior to, and over the cell solution, during the electrochemical experiments. Several runs were also carried out in carbonate-free NaOH , but no differences were seen in these results vs. those obtained in normal NaOH solutions.

X-ray photoelectron spectroscopy (XPS) analyses were carried out with a VG ESCA III instrument at the Alcan International Limited laboratories in Kingston, Ontario.

Results and discussion

(i) General behaviour of lead in 1 M NaOH solutions

Figure 1 shows a typical CV obtained with a mechanically polished Pb chip electrode in 1 M NaOH at a sweep rate of 20 mV/s . When the potential is extended positively towards the oxygen evolution reaction (OER) at ca. 2.0 V , and then negatively towards the range of hydrogen evolution (HER), two main anodic peaks (A_1 and A_2) and corresponding cathodic peaks (C_1 and C_2) are observed. A shoulder (A') is also seen on the cathodic side of peak A_1 .

(a) Shoulder, A'

In earlier work (8), it was proposed that this shoulder, A' , is related to $\text{Pb}(\text{OH})_2$ film formation and its subsequent dissolution, as shown by reactions [1]–[3]. A recent thermodynamic calculation has shown (8, 9) that $\text{Pb}(\text{OH})_2$ can be expected to form at ca. 115 mV vs. RHE , while PbO is not predicted to form until ca. 255 mV (10, 16). At a higher current scale sensitivity than in Fig. 1, the potential at the foot of shoulder A' is seen to be ca. 150 mV , which is at only a small overpotential relative to the theoretical value for $\text{Pb}(\text{OH})_2$ formation. It should be noted that when a positive going potential sweep (at $s < 200 \text{ mV/s}$) is reversed in the region of A' , very little cathodic current is seen (8). This evidence for the dissolution of the product formed in the anodic reaction (i.e. $\text{Pb}(\text{OH})_3^-$, reaction [3]) under the conditions of these experiments was also supported by the results of ring-disc electrode experiments (9, 10).

To confirm $\text{Pb}(\text{OH})_2$ dissolution in this potential range and in pH 14 solutions, new experiments were focussed on the use of high potential sweep rates and small area Pb electrodes. It should be noted that a small electrode area was chosen for the present work primarily to maintain low cell currents and thereby

TABLE 1. Potentials and charge densities in region of peaks A'/C'

Solution/pH	s (V/s)	E_+ (mV vs. RHE)	E_{foot}^* (mV vs. RHE)	$q_{A'}$ (mC cm^{-2})	$q_{C'}$ (mC cm^{-2})	$q_{A'}/q_{C'}$
1 M NaOH pH = 14	0.02	175	140	2.44	0.44	5.5
	0.10	175	140	1.30	0.40	3.3
	2.0	300	150	2.20	1.70	1.3
	10.0	400	150	2.40	2.40	1.0
Na borate pH = 9.6	0.05	450	150	4.70	4.20	1.1
Na carbonate pH = 9.6	0.10	350	130	4.60	0.40	11.5

*At foot of A'.

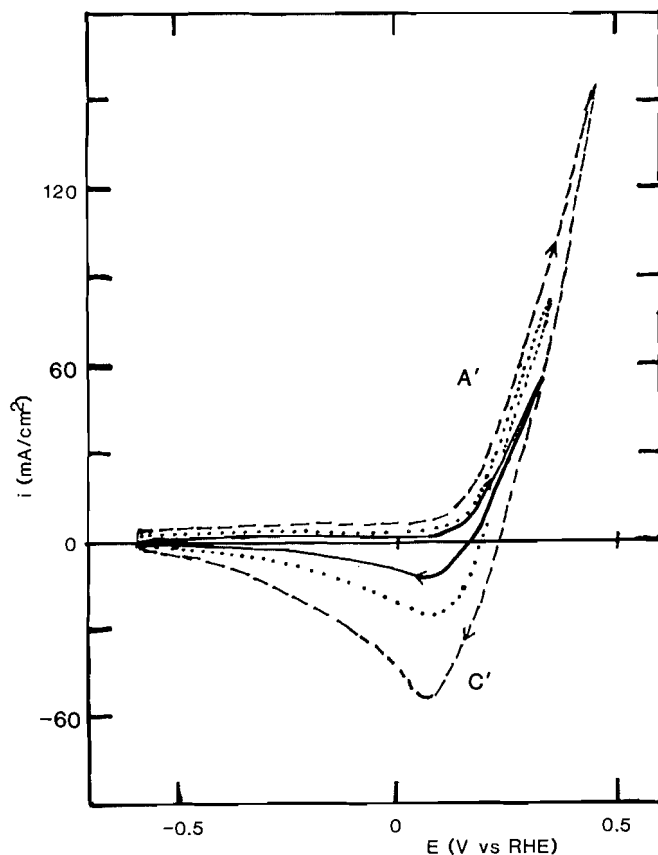


FIG. 2. Cyclic voltammetric response of Pb chip electrode (0.02 cm^2) at high sweep rates in 1 M NaOH. $s = 2 \text{ V/s}$ (—), 5 V/s (⋯) and 10 V/s (---).

minimize IR drops and distributed potential effects (18), which were present in our prior work (8, 9).

The first series of experiments involved the use of high potential sweep rates as a test of the suggested reaction mechanism (reactions [1]–[3]) in pH 14 solutions. Figure 2 shows the CV response obtained in the region of A' at high sweep rates (2 to 10 V/s) at a Pb chip electrode. With increasing sweep rates, the potential at the positive end of the scan had to be incremented somewhat in order to reach all of A' in each scan.

In contrast to the large $q_{A'}/q_{C'}$ ratios observed at low sweep rates (Table 1), it can be seen that as the sweep rate is increased, the anodic (A') and cathodic (C') charge densities become similar in value (Fig. 3). The charge density passed in A' and C'

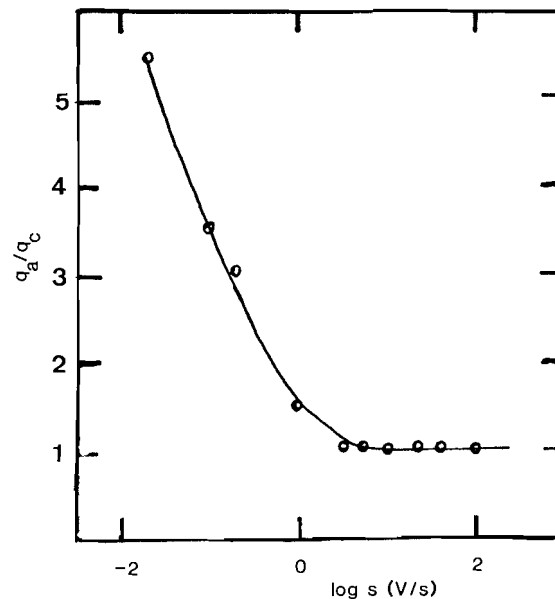


FIG. 3. Ratio of anodic to cathodic charge densities passed in the region of A'/C' in 1 M NaOH as a function of potential sweep rate.

is ca. $2.3 \pm 0.2 \text{ mC/cm}^2$ at high sweep rates, i.e. a charge density equivalent to ca. 5 to 10 monolayers of $\text{Pb}(\text{OH})_2$ (19, 20), assuming a surface roughness factor (true surface area/apparent surface area) of unity. The similarity of the anodic and cathodic charge densities at high sweep rates indicates that insufficient time is available for any dissolution of $\text{Pb}(\text{OH})_2$ (reaction [3]) to occur, so that only the formation and reduction of $\text{Pb}(\text{OH})_2$ is monitored in A'/C'. Table 1 summarizes the principal features of A'/C', including the charge densities and the potential at the foot of A', as a function of potential sweep rate.

(b) Peaks A_1 and A_2

The potential obtained by extrapolating the current to the foot of peak A_1 in Fig. 1 is ca. 220 mV. Since this potential is reasonably close to the calculated potential for PbO formation (255 mV), it was suggested (8, 9) that peak A_1 depicts the formation of a PbO surface film, while peak C_1 reflects its reduction. When the potential is extended to peak A_2 , considered to represent PbO_2 film formation, peak C_2 begins to develop (Fig. 1), while peak C_1 then decreases somewhat. This indicates that PbO_2 is reduced in peak C_2 , and that more PbO is converted to PbO_2 in peak A_2 than is formed along with PbO_2 in

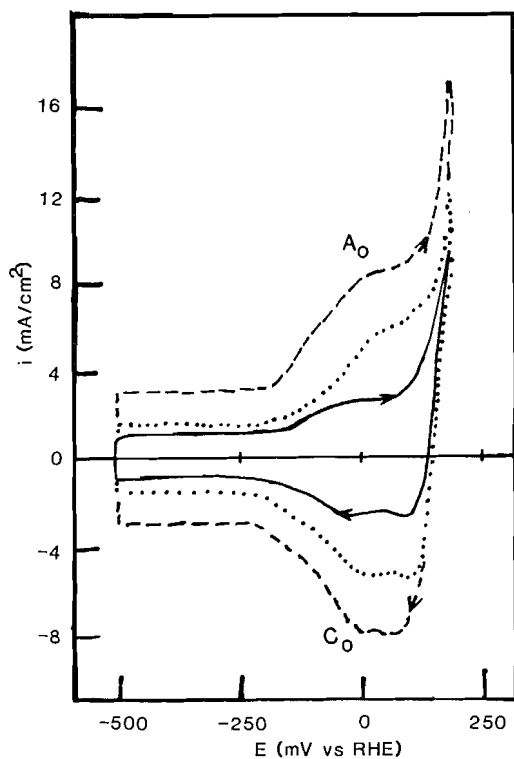


FIG. 4. Cyclic voltammograms of Pb chip electrode (0.02 cm^2) at high sweep rates after several hours of electrochemical experimentation in 1 M NaOH . $s = 10 \text{ V/s}$ (—), 20 V/s (···), and 30 V/s (---).

the potential range of peak A_2 . The reduction of PbO (C_1) at a potential positive of that for the reduction of PbO_2 (C_2) is unusual, and may indicate that film reduction occurs first at the metal/inner film (PbO region) interface and then moves outward towards the outer film (PbO_2)/solution interface.

(c) Peaks A_0/C_0

After several hours of experimentation with a Pb electrode in the same 1 M NaOH solution, a new phenomenon was seen to develop in the potential range just negative of A' . Figure 4 shows that at high sweep rates, a matching pair of small peaks (A_0/C_0) appear, centred at a potential of ca. 0 V vs. RHE, i.e. at an underpotential of ca. 115 mV relative to the calculated potential for Pb(OH)_2 formation. An analysis of the relationship between the peak current densities of peaks A_0 and C_0 and the potential sweep rate reveals a linear dependence between these parameters (Fig. 5 depicts the case for peak A_0). The charge density contained in the peaks in Fig. 4 is ca. $40 \mu\text{C}/\text{cm}^2$, if the apparent electrode area is again assumed. If the electrode area is higher by a factor of 2 or 3, which would be more realistic, the charge density would be still smaller than this.

It should be noted that the formation of a monolayer of Pb(OH)_2 would be expected to be seen at an underpotential. Also, a linear i_p/s relationship would be consistent with monolayer formation and removal. However, a single monolayer of Pb(OH)_2 , having the same density as the bulk material, would be expected to involve a charge density of ca. $220 \mu\text{C}/\text{cm}^2$ (19, 20). As the charges are sufficiently less than this, peaks A_0/C_0 may represent the formation of a two-dimensional layer of Pb(OH)_2 on only part of the electrode surface, or the deposition of two-dimensional Pb(OH)_2 having a very open structure (lower density than phase Pb(OH)_2 over the entire electrode surface).

Peaks A_0/C_0 may also reflect the adsorption of OH^- on the Pb surface, as suggested in reaction [1], followed by a partial

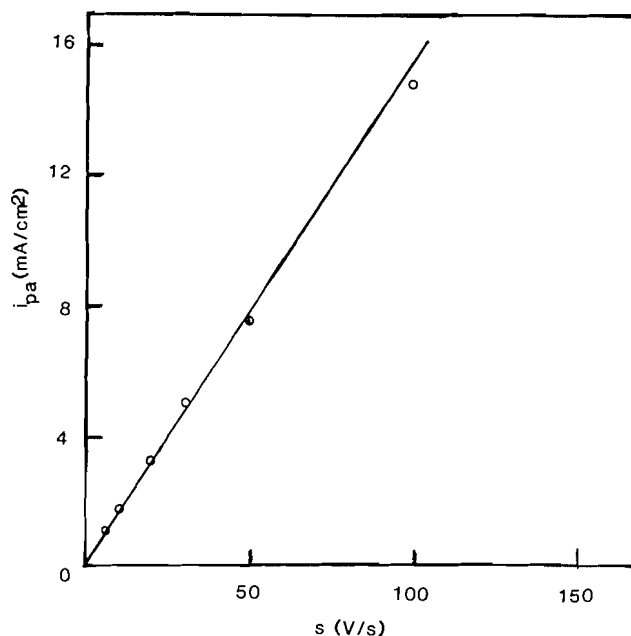


FIG. 5. Relationship between anodic peak current density of A_0 and potential sweep rate in 1 M NaOH .

charge transfer reaction (21). This type of process could also be observed at an underpotential, and would be expected to involve a lower charge density than that for the formation of a monolayer of Pb(OH)_2 film. These two possibilities cannot be distinguished from the data presented here. In a study of the electrochemistry of Ag electrodes in chloride-containing solutions (22), a similar difficulty was encountered in distinguishing adsorption with partial charge transfer from the formation of a low density monolayer.

The fact that peaks A_0/C_0 are only seen after some time of experimentation, during which many sweeps of potential are made to positive potentials, was originally thought to indicate that the Pb electrode had become activated, perhaps by an etching process, with time of potential cycling in these alkaline solutions. However, the appearance of peaks A_0/C_0 with time may also be related to the gradual deposition of high energy Pb nuclei on the Pb electrode surface by the reduction of Pb(OH)_3^- at negative potentials. It is reasonable to suggest that Pb sites of this kind would be more active towards either two-dimensional film formation and/or anion (OH^-) absorption, as they would be likely to have a different surface energy from the original Pb electrode surface.

The suggestion that the newly deposited Pb nuclei, rather than a surface etching process, are responsible for the gradual appearance of peaks A_0/C_0 is supported by the following observation. A fresh Pb electrode, placed into a solution which had been studied previously, and therefore would be expected to contain dissolved Pb, probably in the form of Pb(OH)_3^- , rapidly developed peaks A_0/C_0 . In contrast, a fresh Pb electrode placed in a fresh 1 M NaOH solution required several hours of continuous potential cycling before peaks A_0/C_0 appear. As the rate of Pb surface etching should depend only on time spent in the solution (and the potential), this result rules out an etching process as the cause of the development of peaks A_0/C_0 .

(ii) Behaviour of Pb in less alkaline solutions

The cyclic voltammetric response obtained with lead in pH 9.6 bicarbonate and borate solutions is shown in Figs. 6a and b,

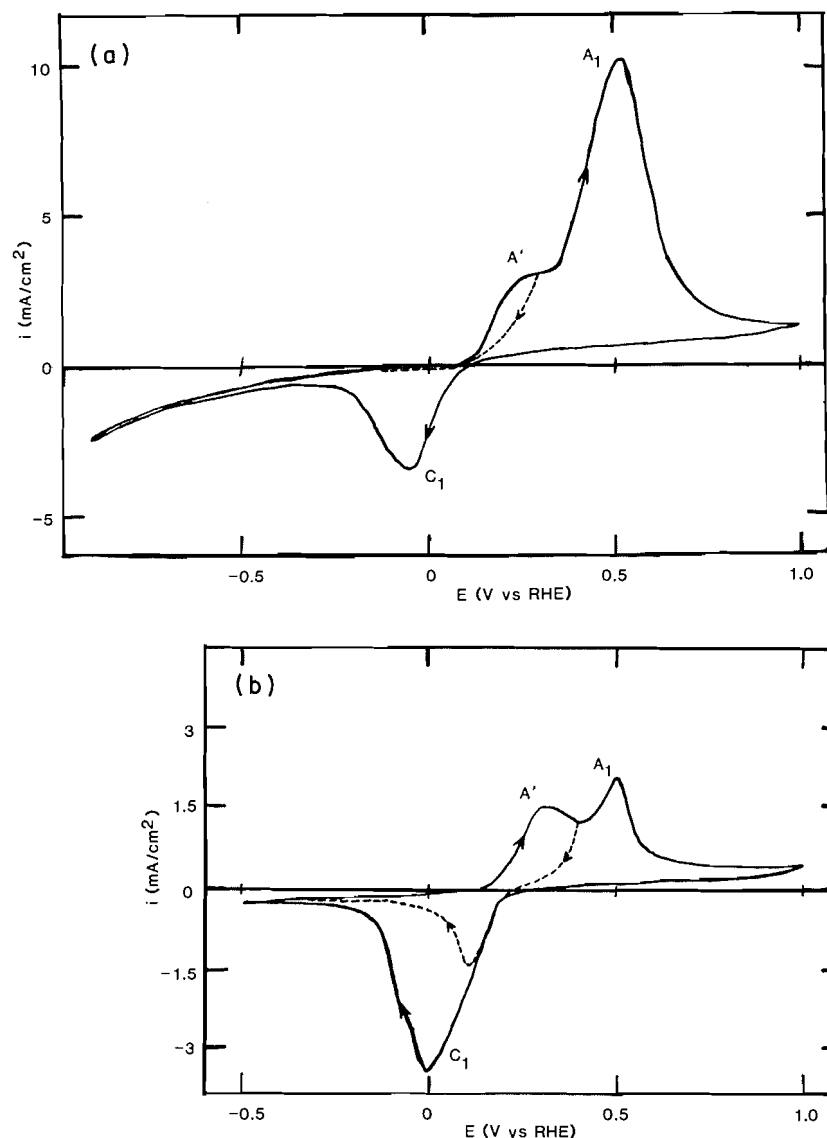


FIG. 6. Cyclic voltammograms obtained with Pb chip electrode in buffered pH 9.6 solutions: (a) 0.05 *M* sodium bicarbonate at $s = 50$ mV/s; (b) 0.025 *M* sodium borate at $s = 20$ mV/s.

respectively. In these experiments, the positive potential limit has been extended to only ca. 1.0 V. The general appearance of the CVs in these pH 9.6 solutions is similar to that at pH 14, although A' now appears as a more distinct peak rather than a shoulder, and peak A₁ is significantly smaller at pH 9.6 than at pH 14. This indicates that the extent of PbO formation (A₁) is diminished at lower OH⁻ concentrations.

The similarity of the CVs in the carbonate and borate solutions is striking, lending support to a common reaction sequence and products. One noticeable difference in Figs. 6a vs. 6b, however, is that the anodic charge is substantially greater than the cathodic charge in carbonate solutions, while in the borate medium, the charges are similar. Figures 6a and b display this more clearly when the potential is reversed just positive of A'. In the carbonate solution, almost no cathodic charge is observed under the conditions of this experiment, while in borate solutions, the charges are very similar. It will be shown below that this difference in the anodic and cathodic charges in the carbonate solution is not the result of Pb dissolution, but rather the incomplete removal of the oxidation products from the electrode

surface during each cathodic sweep. In fact, the electrochemistry of Pb in these dilute carbonate solutions is very complex, in that the magnitude of the anodic peaks, as well as their response to sweep rate, depends significantly on the electrochemical history of the electrode (23). Also, the ease of film reduction depends on both the upper potential limit utilized and the time of oxidation (23). A detailed mechanistic analysis of the oxidation of lead in pH 9 to 10 carbonate-buffered solutions will be presented in a future publication.

Despite these complexities, it is of interest to note that the onset of A' occurs at ca. 140 mV vs. RHE under all conditions in the carbonate solutions and also in the borate-containing solutions investigated in this work (Table 1). This value is very similar to the potential at the foot of A' in pH 14 solutions. The charge passed in peaks A'/C' in borate solutions and also in carbonate solutions after numerous cycles of potential, are also given in Table 1, for comparison with the pH 14 case. It can be seen that the charge densities are of a similar order at pH 9.6 at low sweep rates to those in pH 14 solutions at high sweep rates. It should also be noted that Pb(OH)₂ is not expected to be very

soluble at pH 9.6 (8, 10), consistent with the matching anodic and cathodic charge densities in Fig. 6b.

A' was also seen to commence at a similar potential (vs. RHE) over the range of pH from ca. 10 to 14, and with either (or neither) carbonate/bicarbonate or borate ions present. This is strong evidence for the formation of the same phase in A' in all of these solutions, i.e. at least in the early stages of A'. As A' has been correlated with Pb(OH)₂ formation in pH 14 solutions (from thermodynamic calculations), it is therefore assumed that the first step of Pb oxidation in these dilute borate and carbonate solutions also involves Pb(OH)₂ formation.

Our hypothesis that the same phase, i.e. Pb(OH)₂, is formed initially in a range of alkaline solutions is similar to that made in recent studies of the Zn electrode (24). During the oxidation of Zn in various alkaline solutions, using a range of buffer solutions, the potential at the onset of Zn oxidation was also found to be independent of the nature of the electrolytes used. It was therefore proposed that the initial stage of Zn oxidation must also involve the formation of the same oxide phase, i.e. Zn(OH)₂, in all solutions.

Our suggestion that peak A' reflects Pb(OH)₂ formation, at least initially, is in partial disagreement with two prior studies in the literature. Shoosmith *et al.* (12) have recently studied the oxidation of lead in carbonate solutions (1 M carbonate, pH 12). At this comparatively high pH, the CV response appears quite similar to our results at pH 14, including the presence of an anodic shoulder (A') preceding the main anodic peak (A₁). It was suggested in their work that the formation of a hydroxycarbonate complex of lead (e.g. plumbonacrite (PN) or hydrocerussite (HC), Pb₁₀O(OH)₆(CO₃)₆ or Pb₃(OH)₂(CO₃)₂, respectively) occurs in A', as determined by XRD analyses after long times of oxidation. However, the potential obtained by extrapolating to the foot of peak A' in their data also yields a potential of ca. 130 to 150 mV vs. RHE, as is observed in both carbonate and borate-buffered solutions in our work.

If a PN or HC phase is indeed the equilibrium phase formed in peak A' in pH 12, 1 M carbonate solutions, it is possible that the initial step in the reaction is still the formation of Pb(OH)₂, hence defining the thermodynamic conditions, and that Pb(OH)₂ subsequently transforms to the carbonate/Pb oxide phase after reaction with carbonate. The high carbonate concentrations (ca. 1 M) used in their work would favor such a process. It is also feasible that the free energy of formation of the PN or HC phase is similar to that of Pb(OH)₂ in these carbonate-containing solutions, and that this is the case of the similar potentials observed in their work as in our solutions.

In a study of the electrochemical behavior of Pb in 0.1 M sodium borate solutions (11), the foot of the first anodic peak observed (very similar to peak A' in Fig. 6b) was also observed at a potential of ca. 150 mV vs. RHE, while the second anodic peak was considered to reflect PbO film formation. In this paper (11), peak A' was attributed to the formation of a lead borate surface film, although no supporting evidence (eg. surface analysis) was provided for this assignment. Under certain conditions during the reduction of this film, two cathodic peaks were seen, thought to depict two forms of Pb borate formation and reduction. We have carried out a series of experiments to determine the pH dependence of A' in borate solutions, and have found that when the borate concentration was held constant, while the pH was varied from ca. 9.5 to 12, peaks A' and A₁ both moved negatively with increasing pH in an identical manner. On the basis of all of our results, we believe it is more likely

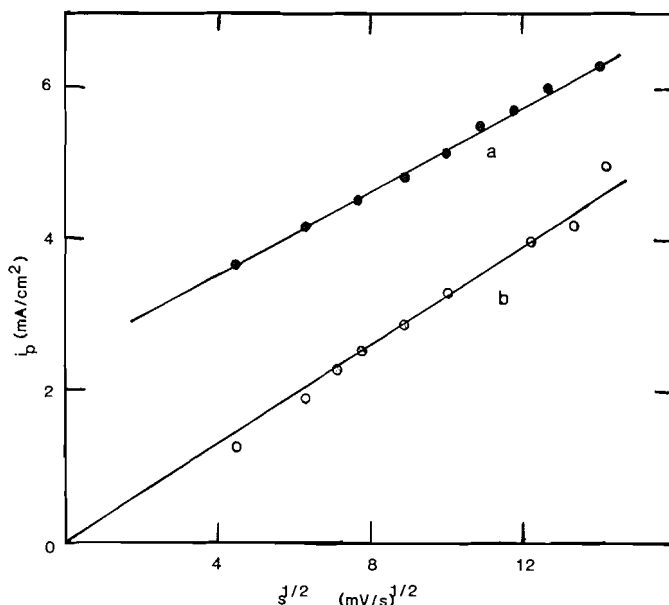


FIG. 7. Dependence of the peak current density of A' on sweep rate in pH 9.6 bicarbonate (a) and borate (b) solutions.

that the first peak (A') in borate solutions reflects Pb(OH)₂ deposition, followed by PbO formation in peak A₁.

Further support for the hypothesis that Pb(OH)₂ is formed in peak A' in carbonate solutions comes from the results of XPS analyses. In a typical experiment, a Pb electrode, which had been oxidized in a single sweep from -1.0 V to 0.35 V in a pH 9.6 carbonate solution, was removed from the solution at the positive potential limit, and was examined by XPS. The nature of the surface film was assessed by comparing the binding energy shift for Pb(4f) and the O(1s)/Pb(4f) intensity ratios of the electrode surface with a number of standard materials, e.g. various lead oxides. As Pb(OH)₂ is not an equilibrium phase, it could not be produced as a standard material. Nevertheless, the results showed that the binding energy and intensity ratios of the surface film were essentially equivalent to that of PbO. This would be the likely dehydration product of Pb(OH)₂ after transferring the electrode into a vacuum chamber. Some carbon was observed at the electrode surface, but no more than at the PbO standard. Sputtering through the material at the electrode surface showed a sharp drop in carbon, and no evidence was obtained for carbonate at any points in the film. This result implies that an oxide film forms in A' in pH 9 to 10 carbonate-buffered solutions, and by inference, this supports the same conclusion in borate-buffered solutions.

An analysis of the sweep rate dependence of peak A' in carbonate (first sweep after holding the potential at the negative limit for controlled periods of time) and borate solutions was carried out to further probe similarities in the identity and nature of the surface products. This type of analysis could not be done in pH 14 solutions, as A' did not form as a peak in this solution, even at high sweep rates (Fig. 2). Figure 7 demonstrates a generally similar behavior in the two solutions, although the non-zero intercept on the current density axis in Fig. 7 (curve a) is consistent with the more complex electrochemistry of Pb in the bicarbonate vs. borate solutions. These plots cannot be interpreted as being indicative of simple diffusion control by a species in solution. This is because the peak currents are essentially independent of solution stirring, and also as the diffusion

coefficients obtained from the slopes of these plots are anomalously large. It is perhaps more likely that the linear $i_p/s^{1/2}$ behavior is indicative of rate control by transport of species within pores of a surface film (25).

When the potential is reversed at ca. 0.35 V (see Fig. 6a), almost no cathodic charge passes, even at high sweep rates. An analysis of the solution after several hours of cycling of the potential between ca. -1.0 and 0.3 V revealed that virtually no Pb had dissolved during this time. The electrode surface, however, appeared to be covered with a grey, porous coating. Therefore, in pH 9.6 carbonate solutions, it appears that peak A' initially involves the formation of $Pb(OH)_2$, which then interacts with carbonate species in some way so that the surface films are very difficult to reduce, as compared to the ease of reduction (in peak C') of the material formed in A' in borate solutions.

Overall, it is proposed that the initial step in the oxidation of lead in the range of pH from ca. 9 to 14, i.e. in solutions containing low concentrations of borate or carbonate ions as the buffering species, involves $Pb(OH)_2$ formation, as seen primarily by the common potential at the foot of peak A' in all solutions. Also, the XPS result obtained for surface films formed in pH 9.6 carbonate solutions showed the presence of only oxide species, and essentially no carbonate was observed in the surface films. In pH 14 solutions, $Pb(OH)_2$ is soluble and repeated cycling of the potential in these solutions leads to the redeposition of lead on the electrode surface at negative potentials. A new pair of peaks is observed at an underpotential on such a lead electrode surface, perhaps reflecting OH^- adsorption with partial charge transfer, or the formation of a dilute monolayer of Pb hydroxide.

Summary

An investigation of the electrochemistry of Pb in three types of alkaline solutions of varying pH and ion content show a strong similarity in the initial stages of Pb oxidation. This is seen from cyclic voltammetry experiments, where a shoulder (A') in pH 14 solutions occurs at the same potential (vs. the RHE) as the small peak (A') in borate and carbonate solutions of lower pH. The potential at the onset of this shoulder (or peak) is ca. 140 ± 10 mV vs. RHE in all solutions. As the shoulder in pH 14 solutions has been suggested previously to be due to $Pb(OH)_2$ formation, it is proposed that the same reaction occurs in all of these solutions. The surface film formed in peak A' in carbonate solutions was found by XPS to be an oxide film, containing essentially no carbonate. In pH 9.6 solutions, significantly less dissolution of $Pb(OH)_2$ is observed than at pH 14. In borate-buffered solutions, the $Pb(OH)_2$ surface film can be reversibly removed, while in carbonate solutions, the $Pb(OH)_2$ film must interact in some way with carbonate species in solution, making it difficult to remove electrochemically.

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