Cyclic voltammetry and passivation behaviour of lead in Na_2HPO_4 solution

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Abstract

The electrochemical and passivation behaviour of lead electrode in $0.10 \, mol \, dm^{-3}$ Na_2HPO_4 solution was studied using cyclic voltammetric technique and complemented by X-ray surface analysis. The anodic half-cycle of the voltammogram exhibits active, pre-passive, passive and transpassive regions before the oxygen evolution. Passivity is due to the formation of thick porous PbO film by three-dimensional nucleation and growth on the electrode surface. The transpassive region is attributed to the electroformation of PbO_2. The cathodic half-cycle shows two cathodic peaks as well as a small shoulder at the extreme negative potential just before the hydrogen evolution. The mechanism of formation of the passive film is discussed.
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1. Introduction

The electrochemical behavior of lead in alkaline media has attracted considerable attention. According to the literature, it was generally agreed that PbO and PbO_2 were the only two anodic oxides formed on the electrode surface before the oxygen evolution [1,2]. On the other hand, there was no such an agreement regarding the formation of other oxide-forms of lead in alkaline solutions under the various experimental conditions such as Pb_2O_3 and Pb_3O_4 [3–6]. This situation arises from the fact that most of the early-published works on the electrochemical and passivation behaviors of lead in alkaline solutions were basically performed using galvanostatic as well as potentiostatic methods [4–7]. More recently studies [1,8–10] have used advanced techniques such as cyclic voltammetry, steady state and transit potentiostatic methods, rotating disk electrode techniques as well as surface analysis of film morphology. Still, there is an apparent disagreement about the presence or absence of $Pb(OH)_2$ and whether the first anodic oxidation is $Pb(OH)_2$ and/or PbO.

Although, it is well established that the passivity of lead in alkaline solutions is associated with film formation, yet the exact conditions leading to the development of the passive film are not well defined and are not fully understood. The present study has been undertaken to investigate more fully the exact conditions leading to the pre-passive and passive regions of lead in $0.10 \, mol \, dm^{-3}$ Na_2HPO_4 solution and

moreover to contribute a better understanding of both the nature and the mechanism of the passive film formation.

2. Experimental

A cylindrical lead electrode was used in experiments, with $0.385 \, cm^2$ cross-sectional area, directly made from 99.99% pure lead rod (Aldrich). It was embedded in the epoxy resin mold and only its cross-section surface area was allowed to contact the electrolyte. Prior to each experiment, the electrode surface was polished with different grads from emery papers, degrased with acetone and then washed with running doubly distilled water and finally dried with filter paper before use.

All the experiments were carried out in $0.10 \, mol \, dm^{-3}$ Na_2HPO_4 solution. The electrolyte solution was prepared from analytical grade chemicals (Merck) and doubly distilled water.

Experiments were conducted in the potentiodynamic mode at $25 \pm 1 \, ^\circ C$ using a three-electrode glass cell. The counter electrode was a platinum electrode and the reference electrode was a saturated calomel electrode (SCE) with a luggin capillary probe placed blew the surface of the working electrode to minimize the IR drop through the cell. A wenking potentioscan (type pos. 73) was the electrochemical instrumentation used to perform the potentiodynamic polarization behavior. The polarization curves

were recorded from −1.8 to +2.0 V using X–Y recorder (type pL 3). However, X-ray diffraction analyses of the lead surface were carried out after some experiments using a Philips diffractometer (40 kV, 25 mA) with a Ni filter and Cu radiation.

3. Results and discussion

3.1. General features of the voltammogram

The electrochemical and passivation behavior of lead electrode between the hydrogen and the oxygen evolution potentials in $0.10 \, mol \, dm^{-3}$ Na_2HPO_4 solution and at a voltage scan rate of $25 \, mV \, s^{-1}$ at $25 \, °C$ was investigated using cyclic voltammetric technique. The positive direction (forward) of the observed voltammogram (Fig. 1) consists of first an initial region of the hydrogen evolution reaction (HER), followed by a well-defined first anodic peak A, a small broad and ill-defined second anodic peak B, an elongated plateau region C, transpassive arrest D and finally oxygen evolution at E. By reversing the direction of potential after the oxygen evolution reaction (OER) at the vertex, the backward direction of the voltammogram consists of a broad first reduction peak F followed by a huge well-defined reduction peak G with an associated shoulder H just before the hydrogen evolution at I. In other words, the voltammogram of lead electrode in $0.10 \, mol \, dm^{-3}$ Na_2HPO_4 solution and at

a voltage scan rate of $25 \, mV \, s^{-1}$ and $25 \, °C$ consists of four anodic features (namely: A–D) preceding the oxygen evolution reaction at E and three cathodic features (namely: F–H) preceding the hydrogen evolution reaction at I.

In order to give a valuable discussion and more realistic explanations of the above-maintained features (Fig. 1), it would be of importance first to have a better understanding and deep insight into the mechanistic aspects and on the kinetics of film formation–dissolution as well as passivation. To gain such information the following studies were conducted namely: cyclization, sweep rate, reversal potential studies and X-ray surface analysis.

3.2. Cyclization studies

Fig. 2 shows three successively repeated sweep cyclic voltammograms of Pb electrode in $0.10 \, mol \, dm^{-3}$ Na_2HPO_4 aqueous solution traced between the hydrogen and the oxygen evolution potentials at a voltage sweep rate of $25 \, mV \, s^{-1}$ at $25 \, °C$. Curves 1–3 refer to the first, the second and the third repeated cycle, respectively. It can be clearly seen that repeated cyclization of the electrode gives essentially similar voltammograms with their characteristic features. The effect of cyclization depends on the magnitude of the anodic reactivation as well as changes in the solution concentration and composition. However, the main difference between these three curves could be summarized as given further.
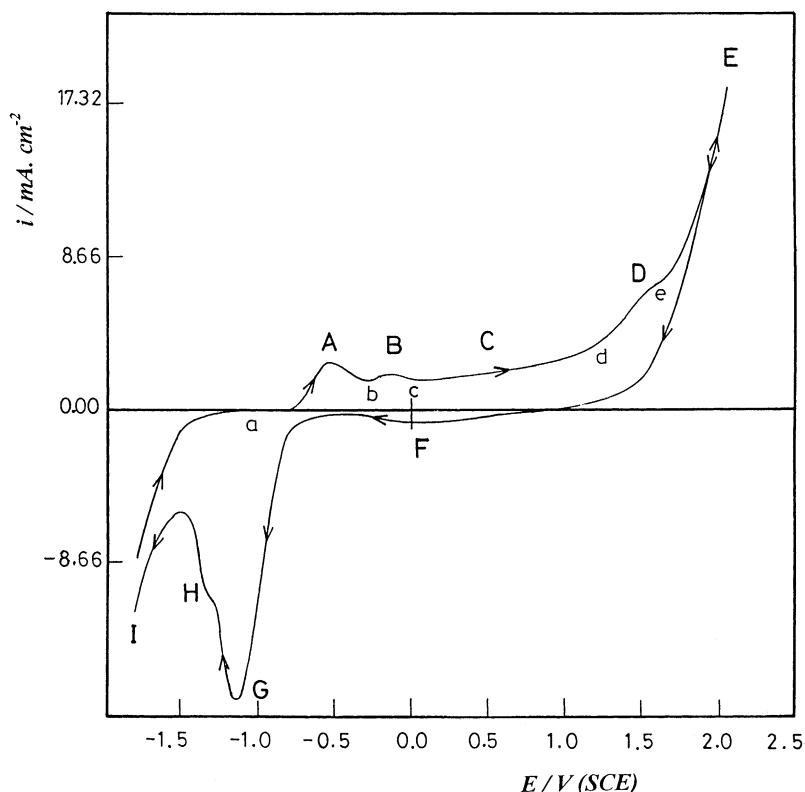

Fig. 1. Cyclic voltammogram of Pb electrode in $0.10 \, mol \, dm^{-3}$ Na_2HPO_4 solution at voltage scan rate of $25 \, mV \, s^{-1}$.
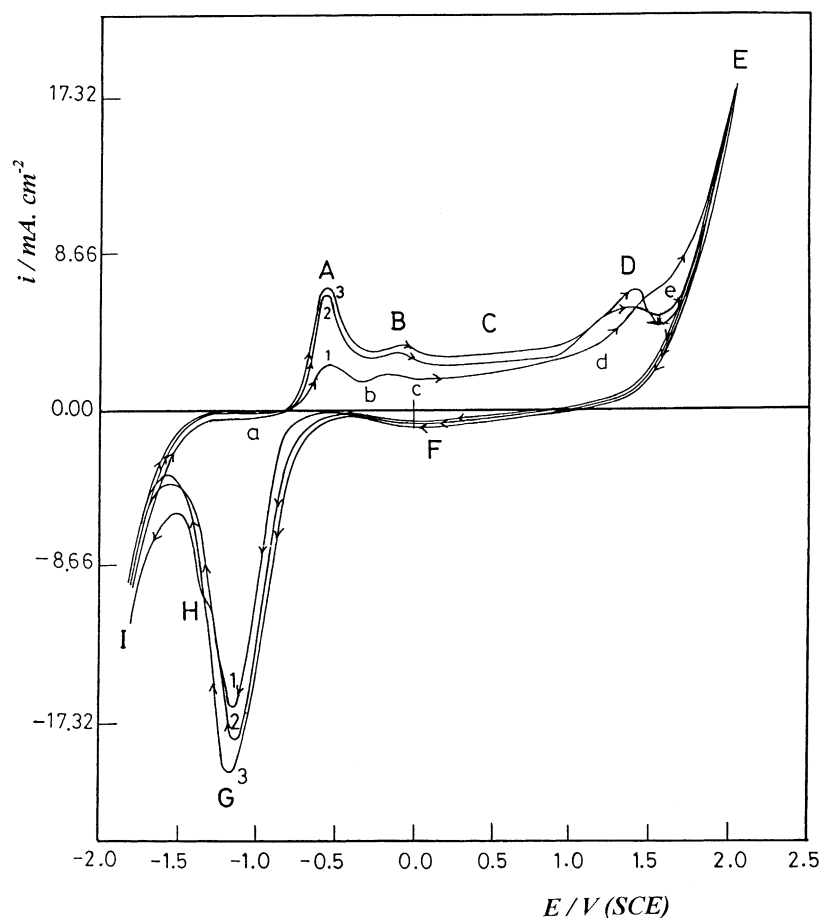
Fig. 2. Three successive sweeps of Pb electrode in $0.10\,mol\,dm^{-3}$ Na_2HPO_4 solutions at voltage scan rate of $25\,mV\,s^{-1}$: 1, first sweep; 2, second sweep; 3, third sweep.

1. The current densities during both the anodic and cathodic half-cycles of the repeated cyclization (curves 2 and 3) are higher than of the first cycle (curve 1).
2. The anodic arrest D, which precedes the oxygen evolution of the first cycle is transferred to an equivalent dissolution maximum in the successive cycles with nearly the same quantity of charges.
3. The cathodic shoulder H of the first cycle, which is the conjugate of the anodic arrest D disappears in the successive cycles.

In general, the difference between these three curves and, which can be recognized along both the anodic and the cathodic branches of the voltammograms, could be attributed to a difference in the initial state at the electrode surface at the beginning of each successive cycle. Generally, effect of cyclization probably increases the roughness of the electrode surface (i.e. reactivation) and also causes some changes in the solution concentration and composition. In conclusion, special emphasis should be given to the characterization of the transpassive region (arrest D) and of the cathodic shoulder H, which have been observed.

3.3. Sweep rates studies

Fig. 3 (curves 1–5) illustrates the effect of sweep rates in the range of 25–$120\,mV\,s^{-1}$ on the cyclic voltammograms traced for Pb electrodes in $0.10\,mol\,dm^{-3}$ Na_2HPO_4 solutions between the hydrogen and the oxygen evolution potentials. The main conclusions that could be drawn are the following.

1. A well-defined oxidation shoulder $A^\backslash$ appears preceding peak A in the active region only at sweep rate $\geq 70\,mV\,s^{-1}$. Appearance and disappearance of shoulder $A^\backslash$ seems to depend on the sweep rate.
2. The cyclic voltammogram curves obtained for several sweep rates (Fig. 3, curves 1–5) exhibits an Ohmic type of behavior as indicated from the leading slope of the first anodic peak A and that of the cathodic peak G. This type of behavior might be an indicative for an electrochemical process under resistance control at these two peaks.
3. It is illustrated that, the value of I_{pass} within the passive region C does not remain constant as the potential moves in the positive direction but rises gradually. This would indicate that nucleation and growth of passive film are
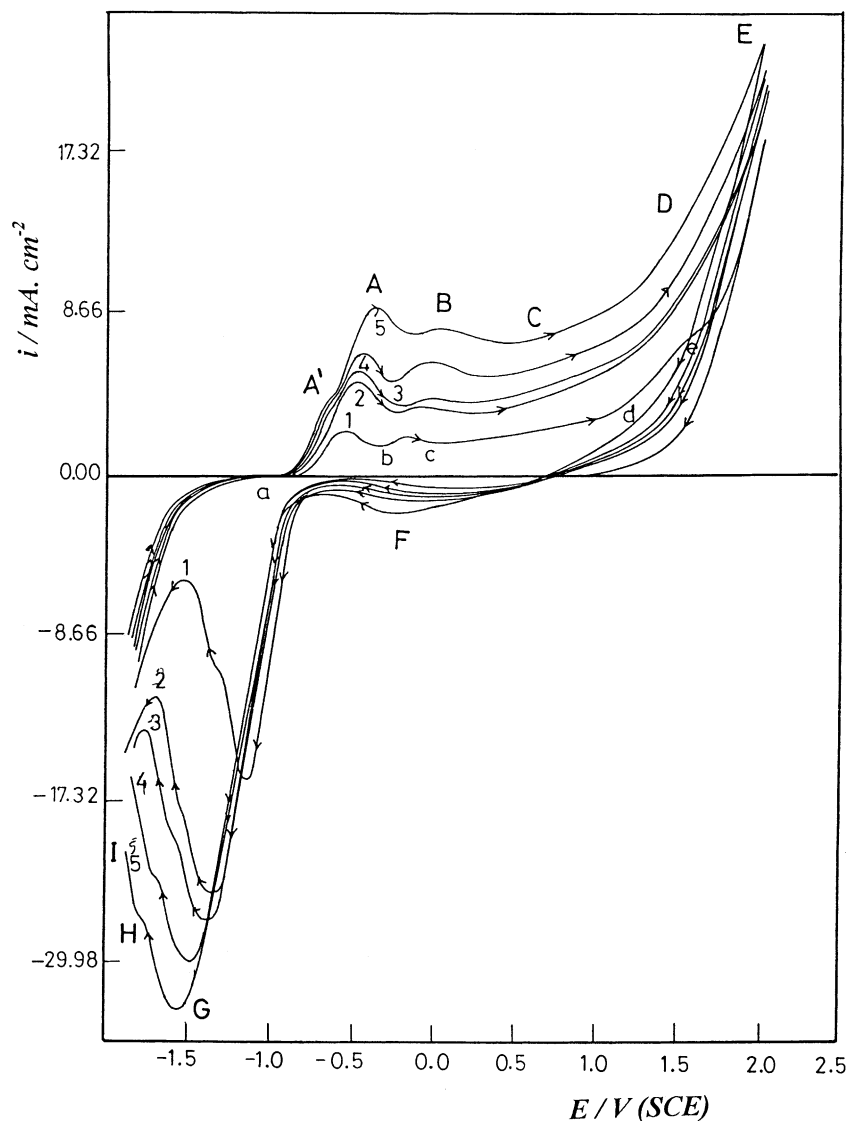
Fig. 3. Cyclic voltammograms of Pb in 0.10 mol dm^{-3} Na$_2$HPO$_4$ solutions at different voltage scan rate: 1, 25 mV s^{-1}; 2, 55 mV s^{-1}; 3, 70 mV s^{-1}; 4, 100 mV s^{-1}; 5, 120 mV s^{-1}.

more significant than chemical dissolution (i.e. thickening of the passive film along C-span).

4. Further inspection of the cyclic voltammograms shown in Fig. 3 reveals that an increase in the scan rate causes an increase in the peak current density of peak A ($I_{peak\,A}$) and shifts its peak potential ($E_{peak\,A}$) to more positive value. The plot of peak current density of the first anodic peak A versus the square root of scanning rate ($v^{1/2}$) gives a straight line as shown from Fig. 4. This result suggests that the anodic process within the potential range of the anodic peak A appear to involve in part, diffusion processes [11,12].

5. Also, the voltammogram curves presented in Fig. 3 reveal that, the appearance and disappearance of the anodic arrest D that preceding the oxygen evolution seems to be dependent on the sweep rate. The anodic arrest D is not observed at sweep rate >70 mV s^{-1}. This might in-

dicate that, transpassive-dissolution occurs with the oxygen evolution reaction, in which the overlapping of the two processes precludes its separation.

In conclusion, special emphasis should be given to the characterization of the two significant situations in the active region A and in the transpassive region D, which depend on the sweep rate.

3.4. Sweep reversal studies

In order to define the origins of the reduction peaks subsequent to the anodic oxidation, a number of sweep-reversal experiments were performed. Fig. 5 (CV$_1$–CV$_4$) shows the effect of reversing the potential at different anodic limits. The curves manifests a number of interesting features, which are summarized as given further.
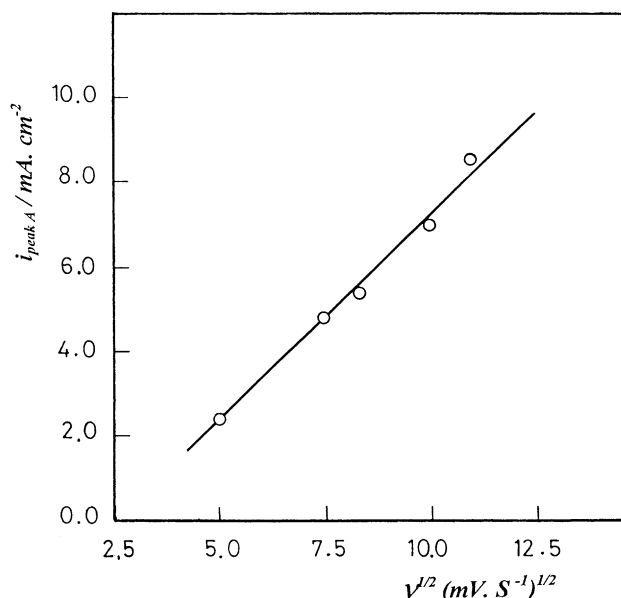
Fig. 4. Dependence of $I_{peak A}$ on $\nu^{1/2}$ for Pb electrode in 0.10 mol dm^{-3} Na$_2$HPO$_4$ solutions.

1. Peak G is related to peak A according to CV$_1$. The associated charge is very small value when compared with the corresponding anodic peak and this is thought to be due to chemical dissolution.
2. Further increase in charge under peak G is observed after reversing the potential just beyond peak B (CV$_2$).
3. Moreover, a considerable increase in charge under peak G is also observed after reversing the potential just before arrest D (CV$_3$). It can readily be seen that, the anodic and cathodic charge densities are more or less similar showing that most of the oxidation products formed as surface films under peaks (A and B) and arrest C are then reduced in the cathodic scan under peak G.
4. By reversing the direction of potential during the oxygen evolution (i.e. after the appearance of arrest D, Fig. 5, CV$_4$), the broad cathodic peak F, a further increase in charge under the cathodic peak G and the shoulder H are observed. Since peak G is related to the anodic peaks A, B and arrest C, thus the increase in the charge under peak G is related to the reduction of a surface layer, which exists under arrest D. This layer has the same structure as that formed under peaks A, B and arrest C. On the other hand, the appearance of peak F and shoulder H on the reverse scan could be related to the reduction of another surface layer that formed during arrest D. This layer could be reduced in two steps. Thus, it is concluded that the transpassive region (arrest D) consists of a mixture of two oxidation products.

3.5. X-ray diffraction analysis

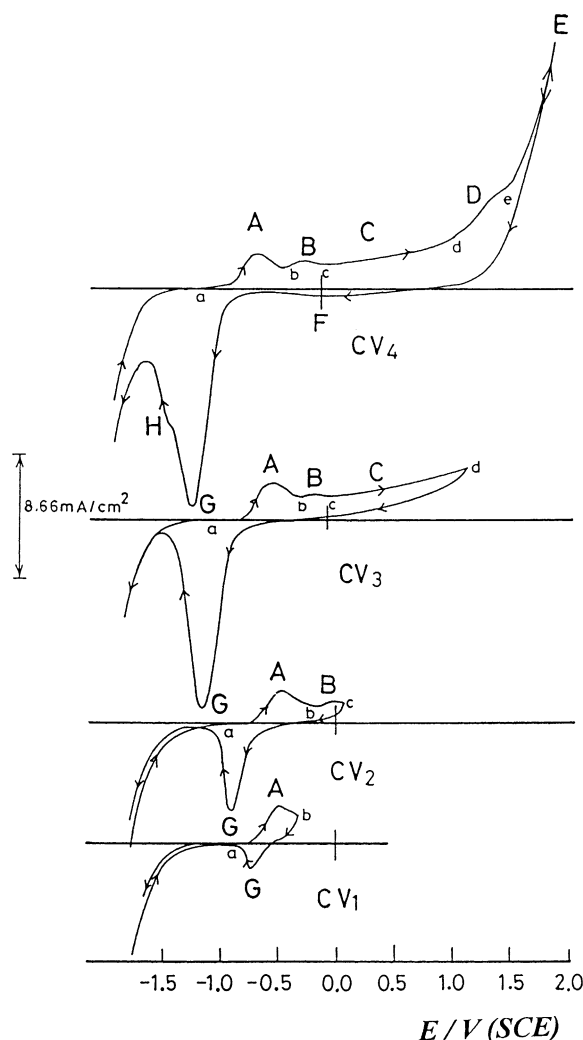Fig. 6(a) and (b) shows the X-ray diffraction analysis of the film formed on the Pb anode surface potentiodynami-

Fig. 5. Effect of increasing anodic reversal potential on Pb electrode in 0.10 mol dm^{-3} Na$_2$HPO$_4$ solutions at voltage scan rate of 25 mV s^{-1}.

cally polarized from the hydrogen evolution up to 0.00 V (peak B) and up to 0.50 V (during region C) with a scan rate of 25 mV s^{-1} in 0.10 mol dm^{-3} Na$_2$HPO$_4$ solutions. The results indicate that PbO is formed during peak B as well as the main passive region C. Moreover, it is clear that the peak intensities of PbO is increased considerably in the case of Pb sample subjected to anodic polarization up to region C (Fig. 6b) as compared with that obtained for Pb sample polarized anodically up to the second anodic peak B (Fig. 6a). These experimental findings would reveal that the PbO that formed along region C (main passive region) is thicker than that formed during the second anodic peak B.

3.6. Mechanism of passivation

The present study has been mainly directed to the establishment of the kinetics of the film formation on lead electrode surface in alkaline 0.10 mol dm^{-3} Na$_2$HPO$_4$ solution. The observed I–E relationship has been simulated
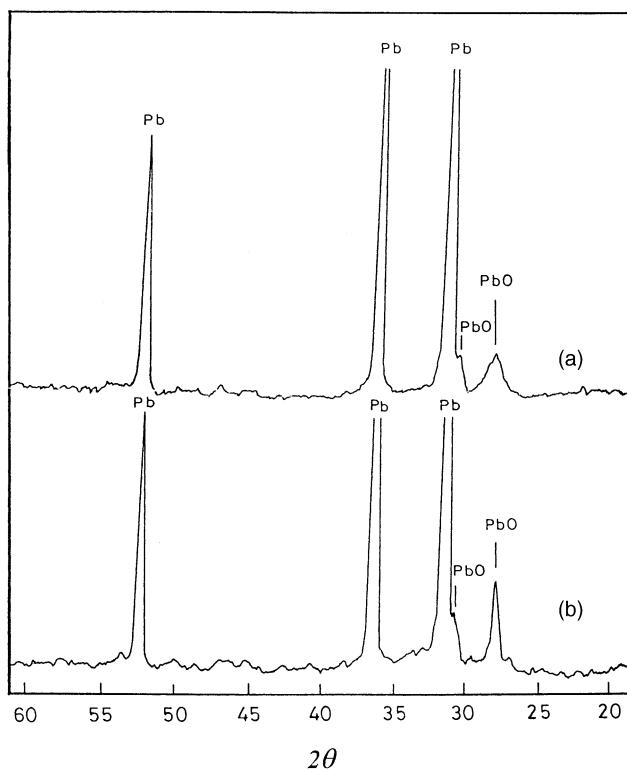
Fig. 6. X-ray diffraction of Pb surface after anodic polarization in $0.10\,\mathrm{mol\,dm^{-3}}$ Na_2HPO_4 solutions at voltage scan rate of $25\,\mathrm{mV\,s^{-1}}$: a, during peak B; b, during plateau C.

on the basis of a model of film growth, in which few nuclei of film are present [13,14]. As the nuclei spread, the pores between the growing nuclei of film becomes smaller. The increase resistance at the narrowing pores of the film begins to control reaction rate cause it to decrease. This is the origin of current peak and drop of current after peak. So that growth rate depends on pore-solution-resistance in pores and the resistance of pore-narrowing.

3.6.1. Composite peak (shoulder $A^\backslash$ and peak A)

It was reported that [8] the first step in the oxidation of lead in alkaline solution is the formation of a small amount of $Pb(OH)_2$ film. On the basis of this information shoulder $A^\backslash$ of the present study (see Fig. 3, curves 3–5) could be most probably attributed to the formation of $Pb(OH)_2$ according to the following equations:

$$Pb + OH^- = Pb(OH)_{ads} + e \qquad (1)$$

$$Pb(OH)_{ads} + OH^- = Pb(OH)_2 + e \qquad (2)$$
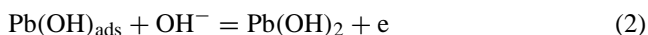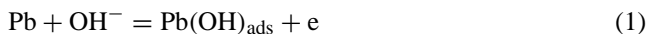
Most of the formed $Pb(OH)_2$ surface film is readily dissolves chemically as $Pb(OH)_3^-$ according to:

$$Pb(OH)_2 + OH^- = Pb(OH)_3^- \qquad (3)$$
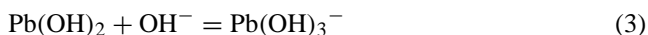
Moreover, some of the remaining $Pb(OH)_2$ can undergo dehydration producing PbO, leaving a small amount of lead hydroxide on the surface. Accordingly, peak A of the present

study could be most probably attributed to the formation of PbO according to:

$$Pb(OH)_2 = PbO + H_2O \qquad (4)$$

Some dissolution of PbO was also found to occur according to:

$$PbO + OH^- = HPbO_2^- \qquad (5)$$

Based on the thermodynamics and the kinetics of formation of the two compounds ($Pb(OH)_2$ and PbO) films it appears very probable that the first oxidation step could be attributed to the formation of a film, which is a mixture of $Pb(OH)_2$ and PbO (i.e. duplex peak A).

3.6.2. Peak B

Peak B is thought to corresponding to two-dimensional nucleation and lateral spreading of PbO film under the previously formed $Pb(OH)_2$ film. The charge density under peak B is much smaller than that under peak A indicating that much of the $Pb(OH)_2$ surface film formed under peak A has dissolved chemically to form $Pb(OH)_3^-$ (Eq. (3)) and/or dehydrated to form PbO (Eq. (4)). The remaining $Pb(OH)_2$ is thrown out as the result of PbO lateral spreading of constant height underneath it.

3.6.3. Region C (thickening of the passive film)

Region C is assumed to be the main passive region. The I_{pass} along region C does not remain constant as in similar cases but increases slightly and gradually as the potential increases in the positive direction indicating the growth and thickening of PbO surface film.

3.6.4. The transpassive region (arrest D)

The anodic arrest D could be attributed to the electroformation of PbO_2 according to the following overall reaction:

$$PbO + 2OH^- = PbO_2 + H_2O + 2e \qquad (6)$$

Evidence of existence of PbO_2 is indicated in reference with Pourbaix diagram since the threshold of the arrest D is very close to the equilibrium potential of PbO/PbO_2 system in the alkaline medium. However, it could be thought that the surface film at the end of the forward scan consists of an outer PbO_2 layer and an inner PbO layer. Thus, it is concluded that PbO_2 can be reduced firstly along peak F to produce $Pb(OH)_2$ according to the following reaction:

$$PbO_2 + 2H_2O + 2e = Pb(OH)_2 + 2OH^- \qquad (7)$$

Consequently, it appears most probable that the electroreduction of the passive layer begins at the level of PbO_2 layer and is subsequently followed by the electroreduction of PbO layer and finally $Pb(OH)_2$.

3.6.5. The oxygen evolution reaction

When the surface is entirely covered by the duplex layer (i.e. PbO and PbO_2), the current rises sharply most probably
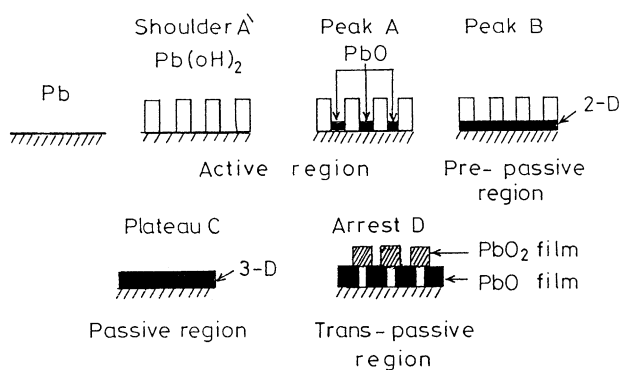
Fig. 7. Schematic simplified illustration of films formation on Pb.

due to oxygen evolution according to:

$$4OH^- = O_2 + 2H_2O + 4e \tag{8}$$

The mechanism of passivation, which is consistent with all the observations described above, is illustrated as shown from Fig. 7. According to this schematic illustration, when lead is anodically polarized, metal dissolution takes place as Pb^{2+} with the formation of porous $Pb(OH)_2$ film on the metal surface. Normally this occurs at a potential near the standard potential (shoulder $A^\backslash$). As porous $Pb(OH)_2$ film is deposited on the surface of the electrode, the current density of the free metal surface increases and subsequently the increases in potential to the extent that the commencement of PbO to be formed at the basis of the $Pb(OH)_2$ pores (i.e. under peak A).

Under peak B, the PbO is formed by two-dimensional nucleation as well as spreading laterally under $Pb(OH)_2$ film. Once PbO is completed it throws off remaining $Pb(OH)_2$ and starts to deposit under arrest C by three-dimensional nucleation and growth. Thickening of PbO under plateau C is evident from the gradual rise in the current density as the potential moves in the positive direction under plateau C.

When the formation of this thick porous PbO film is completed under plateau C, further oxidation of PbO to form PbO_2 under arrest D before the oxygen evolution takes place. Arrest D is a composite film with an outer PbO_2 layer and inner PbO layer. Both layers are porous but of different structure and properties. Moreover, each layer with centrally located pores. Central pores do not extent to the metal surface but it is possible that every few pores penetrates and reaching to the metal surface.

In conclusion, it is of interest to remark that PbO films formed under peaks A, B and arrest D by different mechanisms.

4. Conclusions

(a) The passivation behavior of lead in 0.10 M Na_2HPO_4 solution was studied using cyclic voltammetric technique.
(b) The main features of the anodic half-cycle branch are: mixture of $Pb(OH)_2$ and PbO (shoulder $A^\backslash$ and peak A), two-dimensional PbO nucleation and spreading (peak B), three-dimensional nucleation and growth PbO (region C) and PbO_2 electroformation (arrest D) before oxygen evolution. Peak B is considered as a separate region namely a pre-passive or transition active/passive region.
(c) X-ray diffraction analysis of the Pb surface proved the existence and formation of a thicker PbO film during region C.
(d) The main features of the cathodic half-cycle branch are: the reduction of PbO_2 (peak F), the reduction of PbO (peak G) and the reduction of $Pb(OH)_2$ (shoulder H) before the hydrogen evolution.

References

[1] V.I. Birrs, M.T. Shevalier, J. Electrochem. Soc. 137 (1990) 2643.
[2] L.M. Peter, J. Electroanal. Chem. Interfacial Electrochem. 182 (1985) 383.
[3] S. Glasston, J. Chem. Soc. 121 (1922) 1469.
[4] P. Jones, H.R. Thirsk, W.F.K. Wynne-Jones, Trans. Faraday Soc. 52 (1956) 1003.
[5] E.M. Khairy, A.A. Abdul Azim, K.M. El Sobki, J. Electroanal. Chem. 11 (1966) 282.
[6] E.E. Abd El Aal, Bull. Soc. Chim. Fr. 128 (1991) 351.
[7] M.V. Ptitsyn, G.S. Zenin, K.I. Tikhonov, Sov. Electrochem. 13 (1977) 1144.
[8] V.I. Birrs, M.T. Shevalier, J. Electrochem. Soc. 134 (1987) 802.
[9] V.I. Birrs, M.T. Shevalier, J. Electrochem. Soc. 134 (1987) 1594.
[10] S.S. Abd El Rehim, N.F. Mohamed, Corros. Sci. 40 (1998) 1883.
[11] H. Do Duc, P. Tissot, Corros. Sci. 19 (1979) 179.
[12] H.H. Hassan, S.S. Abd El Rehim, N.F. Mohamed, Corros. Sci. 44 (2002) 37.
[13] W. Muller, Trans. Faraday Soc. 27 (1991) 737.
[14] A.J. Calandra, N. de Tacconi, R. Pereiro, A.J. Arvia, Electrochim. Acta 19 (1974) 901.