

## FORMATION OF BARRIER OXIDE FILM ON LEAD IN BORATE SOLUTIONS

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Galvanostatic anodization of lead in borate solutions reveals that lead can form a barrier type oxide film. The rate of growth,  $R$ , fulfils the empirical relation,  $R = ai^b$  within the current density  $i$  range from  $1.16 \cdot 10^{-4}$  to  $3.19 \cdot 10^{-4}$  A cm<sup>-2</sup>. The magnitudes of the parameters  $a$  and  $b$  are  $6.9 \cdot 10^3$  and 1.6, respectively, it has been found that the high field approximation is applicable for the oxide growth on lead. The coefficients of the dependence of  $R$  on solution temperature,  $T$ , pH and borate ion concentration,  $c$ , viz.  $(\partial R/\partial T)$ ,  $(\partial R/\partial \text{pH})$  and  $(\partial R/\partial \log c)$  are  $-18 \cdot 10^{-4}$ ,  $-0.13$  and 0.41, respectively.

Lead oxides are important in electrochemical technology owing to their cheapness and wide reactivity<sup>1</sup>. Therefore there is a great effort to understand the electrochemistry of lead oxides<sup>2</sup>. Great attention has recently been paid to elucidate the nature of the lead oxide films in weakly alkaline solutions<sup>3</sup>. However, little work has been made to elucidate the conditions that give rise to the formation of the barrier type oxide film<sup>4</sup>.

### EXPERIMENTAL

Galvanostatic anodic polarization was performed with a power source combined with a X-Y recorder. Current densities were calculated on the basis of the apparent geometric area. Solutions were prepared from analytical grade chemicals. Solution pH was adjusted by the addition of carbonate free concentrated sodium hydroxide solution.

A three-electrode double jacket glass cell with a Luggin capillary leading to a saturated calomel reference electrode (SCE) was used. The auxiliary electrode was a platinum wire. The test electrode was a pure lead rod fixed to a glass tube with epoxy resin such that only the cross sectional area of the rod (0.69 cm<sup>2</sup>) was exposed to the solution.

Before each run the electrode surface was polished mechanically with increasingly fine grades of metallurgical emery papers down to 4/0. The electrode was finally polished with a soft cloth then rinsed

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with distilled water and dried with a fine tissue. The electrode was then immersed in the test solution while cathodically polarized at the selected current density. This treatment took ten minutes. It was undertaken to remove any residual surface oxide films. Afterwards, the electrode polarity was reversed. The test solution was used under natural convection condition and air saturation<sup>3</sup>.

The temperature was controlled at  $25 \pm 0.2$  °C by a water thermostat. The procedure involves the construction of the potential time ( $E-t$ ) curve at a constant current density  $i$ .

## RESULTS AND DISCUSSION

### Polarization Curves

Figure 1 shows a typical potential–time curve for the galvanostatic anodization of lead in 0.1 M  $\text{Na}_2\text{B}_4\text{O}_7$  at 25 °C. This curve has the following features:

1. At the beginning of polarization, there is a sudden potential increase that may be attributed to the decay of hydrogen evolution overvoltage and the subsequent charging of the electrical double layer<sup>5</sup> (region 1).

2. Then there is an arrest which can be attributed to the formation of a divalent basic salt film<sup>6</sup>.

3. After the first arrest, the potential increases linearly with time owing to the formation of a barrier oxide film. This process is limited by the film dissolution. The second arrest indicates the onset of formation of  $\text{PbO}_2$ . The slope of the linear region A represents the barrier oxide formation rate,  $R = \partial E / \partial t$ .

4. Finally oxygen evolves<sup>7,8</sup> (region 0).

A similar feature has been observed during the galvanostatic anodization of tin in weakly alkaline solutions<sup>9</sup>.

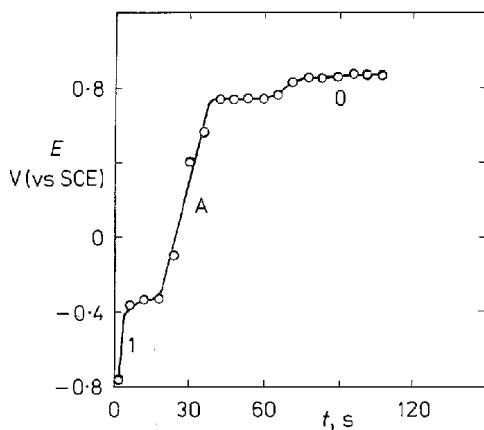


FIG. 1  
Galvanostatic anodic charging curve of lead in 0.1 M  $\text{Na}_2\text{B}_4\text{O}_7$  at 25 °C. The current density is  $217 \mu\text{A cm}^{-2}$

## Kinetics of Oxide Growth

The rate of barrier oxide film growth,  $R$ , increases with the anodizing current density,  $i$ , as shown in Fig. 2, according to the empirical relation  $R = ai^b$ , where  $a$  and  $b$  are constants characteristic of the metal/solution system<sup>10</sup>. These constants have been calculated from Fig. 2 and found to be  $6.9 \cdot 10^3$  and 1.6, respectively, comparable to those obtained for the other valve metals<sup>4</sup>.

The growth of this barrier oxide film proceeds mainly by the ionic conductance mechanism. It is generally accepted that the rate determining step is the transport of oxygen vacancy through the oxide phase<sup>11</sup>. Under this condition, the formation rate, defined as  $(1/i) (\partial E/\partial t)$ , is related to  $i$  by the equation

$$1/i (\partial E/\partial t) = r/B \ln i/A,$$

where  $A$  and  $B$  are called the electrolyte parameters<sup>12</sup>.

The physical units of the rate are  $V C^{-1} cm^2$ . It tells how much oxide is formed by unit electricity per unit area. The formed oxide develops a potential difference due to its resistance. The obedience of the anodic oxide film formation to the last equation indicates that the high field approximation is applicable. This has been observed ex-

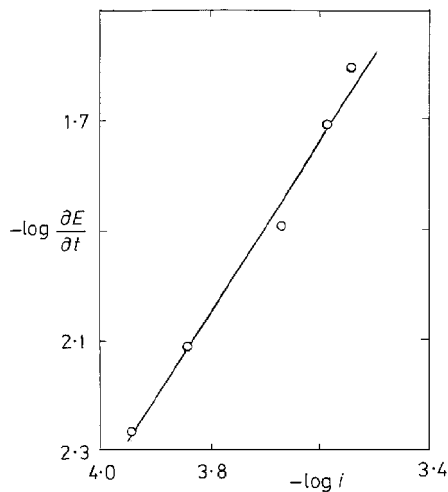


FIG. 2

Increase of the oxide formation rate,  $R$ , with the anodizing current density,  $i$ , in a logarithmic plot. The solution composition and temperature are 0.1 M  $Na_2B_4O_7$  and 25 °C, respectively

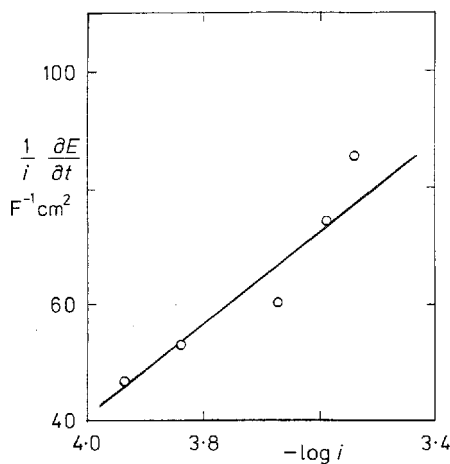


FIG. 3

Semilogarithmic plot for the increase of the unitary formation rate with the anodizing current density for lead in 0.1 M  $Na_2B_4O_7$  at 25 °C

perimentally (Fig. 3). The quantity  $r$  is the volume of oxide in  $\text{cm}^3$  formed per coulomb of electricity.

It has been estimated on account of the similarity between Sn and Pb. Assuming a reverse proportionality between  $r$  and the molar mass of the oxide. For  $\text{SnO}_2$ ,  $r = 5.6 \cdot 10^{-5} \text{ cm}^3 \text{ C}^{-1}$  (ref.<sup>9</sup>), therefore for  $\text{PbO}_2$ ,  $r = 3.5 \cdot 10^{-5} \text{ cm}^3 \text{ C}^{-1}$ . Consequently  $A = 2.8 \cdot 10^{-5} \text{ A cm}^{-2}$  and  $B = 11 \cdot 10^{-7} \text{ cm V}^{-1}$ .

The parameter  $A$  is an exponential function of the standard free energy of activation for oxygen vacancy transport, and hence it is a measure of the height of the energy barrier for this process. The parameter  $B$  is related to the activation distance  $a^*$  by  $B = zF a^*/RT$ .  $a^*$  was found to be  $2.8 \cdot 10^{-8} \text{ cm}$  at  $25^\circ \text{C}$ , assuming that  $z = 2$ . The constants  $F$  and  $R$  have their usual significances,  $z$  is the charge of the moving ion in the oxide.

### Effect of Temperature

The rate of oxide growth,  $R$ , decreases with the temperature as shown in Fig. 4. The differential quotient  $\partial R/\partial T$  amounts to  $-1.8 \cdot 10^{-4} \text{ V s}^{-1} \text{ deg}^{-1}$ , i.e. rise of temperature inhibits the oxide formation process.

The oxide grows as a result of the directional motion of the oxygen ion vacancy under the influence of the applied electric field. So it moves in the field direction. Rise of temperature increases the amplitudes of vibrations of all the atoms constituting the oxide<sup>13</sup>. The chaotic vibrational motion will lead to collisions thus impeding the ordered oxide growth.

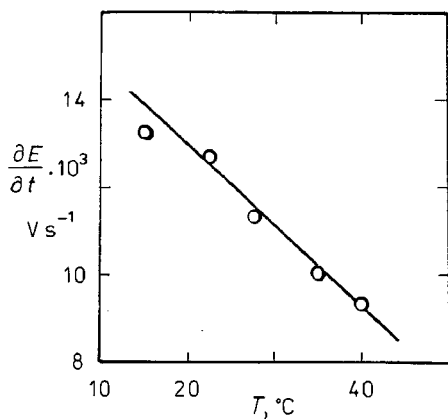


FIG. 4  
Decrease of the rate of oxide growth on lead in  $0.1 \text{ M Na}_2\text{B}_4\text{O}_7$  with temperature. The anodizing current density  $i = 217 \mu\text{A cm}^{-2}$

Thermal activation can influence the oxide formation in another way, that is by activating the oxide dissolution. The two processes are conjugate. The rate of the latter one is negligible under mild anodization condition.

### *Effect of pH*

Increase of pH of the anodizing solution causes decrease of the rate of oxide growth as shown in Fig. 5, owing to the higher solubility of  $\text{PbO}_2$  in the more alkaline solutions<sup>14</sup>.

### *Effect of Borate Ion Concentration*

Borate ions increase the rate of oxide growth as shown in Fig. 6. This effect can be attributed to their adsorption at the oxide/solution interface, causing increase of the rate of oxide growth<sup>15</sup> and decrease of the rate of oxide dissolution.

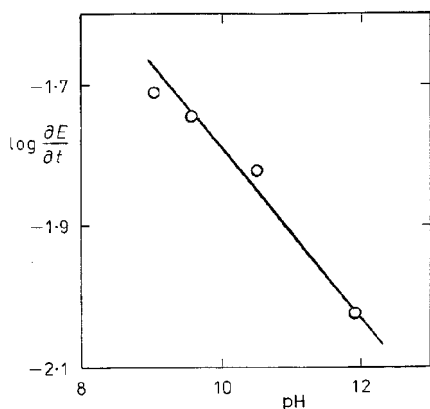


FIG. 5

Decrease of the rate of oxide growth on lead in 0.1 M  $\text{Na}_2\text{B}_4\text{O}_7$  with the increase of pH in a semilogarithmic plot. The anodizing current density  $i = 217 \mu\text{A cm}^{-2}$ ,  $T = 25^\circ\text{C}$

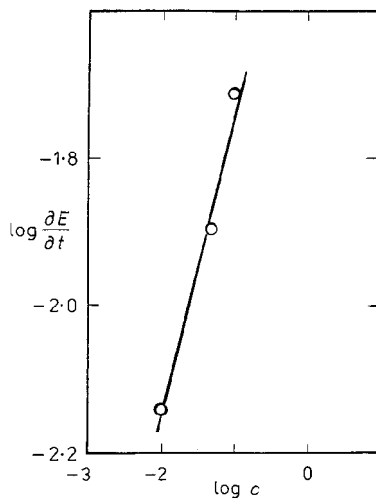


FIG. 6

Increase of the rate of oxide growth on lead with the borate ion concentration ( $\text{mol l}^{-1}$ ) in a logarithmic plot. The anodizing current density and temperature are  $217 \mu\text{A cm}^{-2}$  and  $25^\circ\text{C}$ , respectively

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