Potentiodynamic and Cyclic Voltammetric Behaviour of a Lead Electrode in NaOH Solution

S. S. Abd El Rehim[1,*], **L. I. Ali**[2], **N. H. Amin**[2], and **N. F. Mohamed**[2]

[1,*] Faculty of Science, Ain Shams University, Cairo, Egypt
[2] Faculty of Education, Ain Shams University, Cairo, Egypt

Summary. The electrochemical behaviour of lead in NaOH solution was studied by potentiodynamic and cyclic voltammetric techniques in combination with X-ray diffraction analysis. The active dissolution of lead involves a small shoulder $A1'$ followed by a peak **A1** prior to a passive region. The shoulder $A1'$ is assigned to the electroformation of a $Pb(OH)_2$ film, whereas peak **A1** is due to the formation of PbO. Beyond the passive region, the current density increases again, forming a small shoulder $A2'$ and a peak $A2$ prior to the oxygen evolution potential. The shoulder $A2'$ and the peak $A2$ are correlated to the electrooxidation of PbO to Pb_3O_4 and PbO_2, respectively. The intensity of the anodic peaks increases with increasing alkali concentration, temperature and scan rate. In cyclic voltammetry, the reverse scan shows two cathodic peaks $C1$ and $C2$ which are corrrelated to the electroreduction of PbO and PbO_2 respectively, to Pb.

Keywords. Cyclic voltammetry, Lead electrode; Alkaline solutions.

Potentiodynamisches und cyclovoltammetrisches Verhalten einer Bleielektrode in NaOH-Lösung

Zusammenfassung. Das elektrochemische Verhalten von Blei in NaOH wurde mittels potentiodynamischer und cyclovoltammetrischer Techniken unter Zuhilfenahme der Röntgenbeugungsanalyse untersucht. Die aktive Auflösung von Blei verläuft über eine Schulter $A1'$, die von einem einer passiven Region vorgelagerten Peak $A1$ gefolgt wird. Die Schulter $A1'$ wird der elektrochemischen Bildung eines $Pb(OH)_2$-Films, der Peak $A1$ der Bildung von PbO zugeschrieben. Jenseits der passiven Region steigt die Stromdichte wieder an, und vor Erreichen des Sauerstoffpotentials treten eine kleine Schulter $A2'$ und ein Peak $A2$ auf, die mit der Elektrooxidation von PbO zu Pb_3O_4 und PbO_2 korrelieren. Analog dazu beobachtet man in der cyclischen Voltammetrie zwei kathodische Peaks $C1$ und $C2$, die der Elektroreduktion von PbO und PbO_2 zu Pb entsprechen. Die Intensität der anodischen Peaks steigt mit steigender Alkalikonzentration, Temperatur und Scangeschwindigkeit.

Introduction

The electrochemical behaviour of lead in alkaline media has attracted the attention of several authors [1–10]. A review of the literature shows that the anodization of lead in alkaline electrolytes is a complex process, and the results contain a number

of contradictions. Early research work done under galvanostatic conditions revealed that at low current densities lead can be dissolved to form Pb^{2+} ions [1] or HPO_2^- ions [2], whereas at higher current densities a PbO_2 film is expected to form at the electrode surface. More recent work [3–5] indicated that both PbO and PbO_2 films are formed on the lead surface. *Tourkey et al.* [6] have demonstrated that the galvanostatic anodic polarization curves show three arrests corresponding to the oxidation of Pb to $Pb(OH)_2$, Pb to PbO, and PbO to PbO_2 in $NaOH$ solutions. On the other hand, *Abd El Aal* [7] reported that the galvanostatic potential *vs.* time curves of Pb in $NaOH$ solutions exhibit two oxidation arrests before the potential reaches the value of oxygen evolution. These two plateaus are related to the formation of PbO and PbO_2, respectively.

Ptitsyn et al. [8] have studied the behaviour of Pb in alkaline solutions using potentiostatic and potentiodynamic techniques. The authors pointed out that the initial stage of anodic dissolution of Pb involves the formation of $Pb(OH)_2$ and PbO. The same results have been obtained by *Birss* and *Shevalier* [9, 10] using the potentiostatic method. The first step in the potential range of active dissolution of Pb involves the formation of a $PbOH$ surface intermediate, followed by the deposition of a $Pb(OH)_2$ film on the anode surface. A major portion of this film dissolves, whereas the remaining part dehydrates to form a PbO film. At more positive potentials, further PbO film growth occurs.

The present work was carried out to investigate the anodic dissolution and film formation processes occurring on a Pb electrode surface over a potential range up to oxygen evolution potential under the influence of alkali concentration, temperature, scan rate, and successive cycling using potentiodynamic and cyclic voltammetric techniques.

Results and Discussion

Typical E *vs.* i curves of a Pb electrode in $NaOH$ solutions of various concentrations (0.05–1.5 M) at 25°C are shown in Fig. 1. The curves were swept from -2000 mV to 2000 mV at 100 mVs^{-1}. Hydrogen evolution commences at the starting potential. During the positive scan, the cathodic current decreases gradually and changes its sign at $E_{i=0}$. However, the anodic excursion exhibits a complex feature characterized by the contribution of two main anodic peaks $A1$ (in the potential region from -600 to -250 mV) and $A2$ (600 to 800 mV) prior to oxygen evolution potential. In addition, two small shoulders $A1'$ and $A2'$ can also be seen on the cathodic sides of the peaks $A1$ and $A2$ respectively. The shoulder $A1'$ is tentatively related to the formation of a thin film of $Pb(OH)_2$ on the electrode surface according to the following two step mechanism (for further details, see Refs. [10, 11]):

$$Pb + OH^- = PbOH_{ads} + e^-$$
$$PbOH_{ads} + OH^- = Pb(OH)_2 + e^-$$
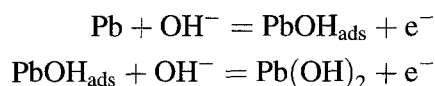
Most of the formed $Pb(OH)_2$ film dissolves chemically and yields $Pb(OH)_3^-$ ions, whereas the remaining $Pb(OH)_2$ undergoes dehydration and transforms into PbO. At a more positive potential than that required for the formation of $Pb(OH)_2$, the PbO film forms directly on the anode surface by nucleation and a growth mech-
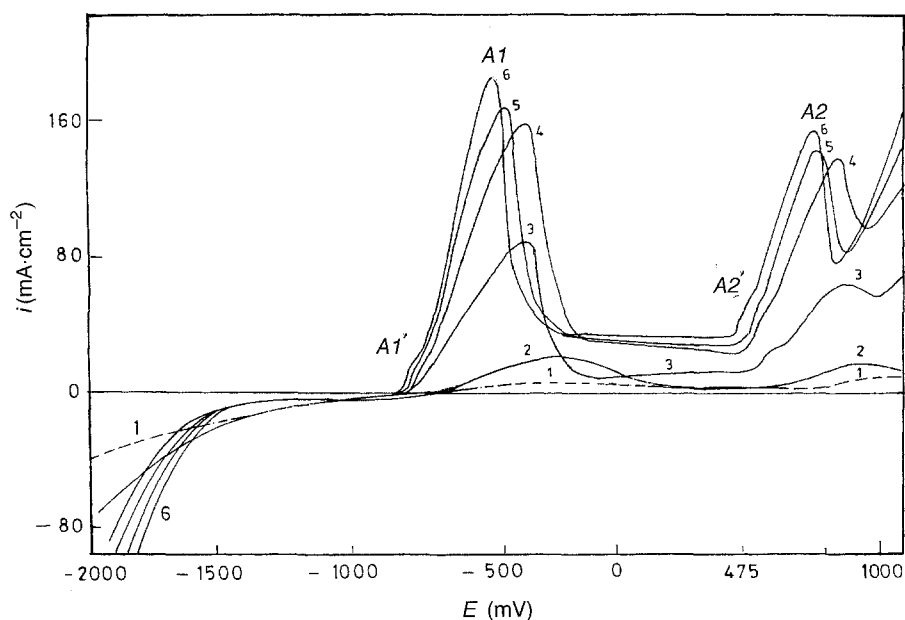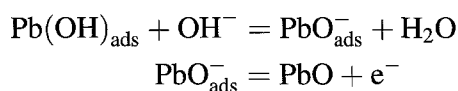
Fig. 1. Potentiodynamic polarization curves of Pb at 25°C and 100 mVs^{-1} at various NaOH concentrations; 1: 0.05, 2: 0.1, 3: 0.5, 4: 1.0; 5: 1.2, 6: 1.5 M NaOH

anism according to the reaction given below [10, 11]:

$$Pb(OH)_{ads} + OH^- = PbO^-_{ads} + H_2O$$

$$PbO^-_{ads} = PbO + e^-$$

The potential recorded practically coincides with the calculated value for a Pb/PbO electrode (-530 mV at $pH = 14$). The formed PbO film may undergo dissolution forming the soluble species $HPbO_2^-$:

$$PbO + OH^- = HPbO_2^-$$
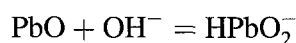
When the electrode surface is completely covered with a PbO layer, the anodic current density drops to a small i_{pass} ($\cong 35$ mA in 1.0 M NaOH) denoting the onset of passivation. The passivity region extends over a potential range of about 500 mV in 1.0 M NaOH (scan rate: 100 mVs^{-1}). Within the passive region, the values of i_{pass} is nearly constant and to some extent independent on the applied potential. This current is mainly consumed for growing of the passive layer. XRD analysis of the passive layers formed on the potentiodynamically polarized electrode surface in 1.0 M NaOH solutions starting from -2000 mV up to 400 mV at 100 mVs^{-1} showed that the films consist of PbO. However, on still increasing the applied potential i_{pass} increases sharply [2] at about 550 mV in 0.5 M NaOH forming the shoulder $A2'$ and then the peak $A2$ prior to oxygen evolution potential. The shoulder $A2'$ may be related to the electrooxidation of PbO to Pb_3O_4 according to the following reaction equilibrium potential of the system PbO/Pb_3O_4: 498 mV $vs.$ SCE; [12, 13]:

$$3PbO + 2OH^- = Pb_3O_4 + H_2O + 2e^-$$

However, this shoulder is apparently absent in dilute solutions ($<$ 0.5 M NaOH). The anodic peak can be correlated to the electrooxidation of PbO to PbO$_2$, since the threshold potential of this peak lies close to the equilibrium potential of the PbO/PbO$_2$ electrode in alkaline solution ($E = 592$ mV in $0.1M$ NAOH; [12]). Therefore, it may be suggested that the reaction leading to the formation of PbO$_2$ is

$$PbO + 4OH^- = PbO_2 + H_2O + 2e^-$$

in addition to the electrooxidation of Pb$_3$O$_4$ to PbO$_2$:

$$Pb_3O_4 + 4OH^- = 3PbO_2 + 2H_2O + 4e^-$$

The XRD pattern of the lead electrode potentiodynamically polarized from -2000 up to oxygen evolution potential with a scan rate of 100 mVs^{-1} in $1.0M$ NaOH at 25°C confirmed the existence of PbO and PbO$_2$.

Inspection of the data of Fig. 1 reveals that an increase in the concentration of NaOH increases the peak current densities i_{A1} and i_{A2} of peaks $A1$ and $A2$, respectively, and shifts their corresponding peak potentials E_{A1} and E_{A2} to more negative values. The heights of the shoulders $A1'$ and $A2'$ and the value of i_{pass} also increase with increasing alkali concentration. These results could be explained on the premise that the solubilities of lead oxides increase with increasing alkali concentration. In alkaline solutions, HPbO$_2^-$ and PbO$_3^{2-}$ are expected to form by a chemical dissolution of PbO and PbO$_2$, respectively [14]. The relations between i_{A1} and i_{A2} vs. log C_{NaOH} are given in Fig. 2.

The effect of the scan rate ν (20–400 mVs^{-1}) on the potentiodynamic polarization curves of the stationary Pb electrode in 1.0 M NaOH at 25°C was also investigated (Fig. 3). It is obvious that the intensities of i_{A1} and i_{A2} increase and their peak potentials E_{A1} and E_{A2} shift to more positive values with increasing scan rate. The plots of i_{A1} and i_{A2} against the square root of the scan rate are straight lines with positive intercepts indicating the amount of surface coverage
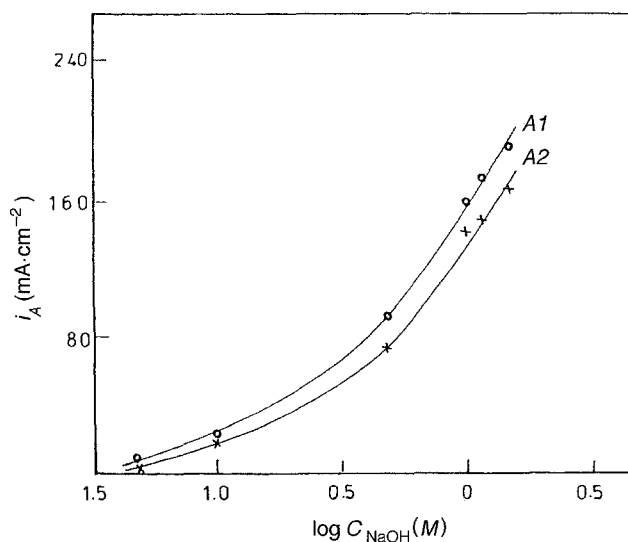

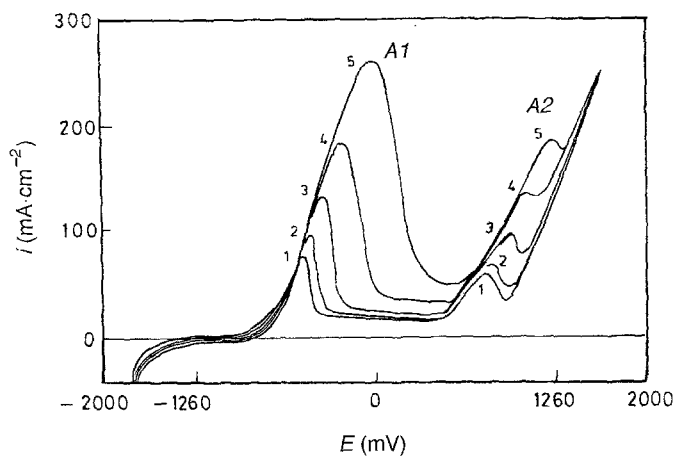Fig. 2. Relation between i_{A1} and i_{A2} vs. log C_{NaOH} at 25°C and 100 mVs^{-1}

Fig. 3. Potentiodynamic polarization curves of Pb at 25°C in 1.0 M NaOH at different scan rates; 1: 20, 2: 40, 3: 100, 4: 200; 5: 400 mVs^{-1}
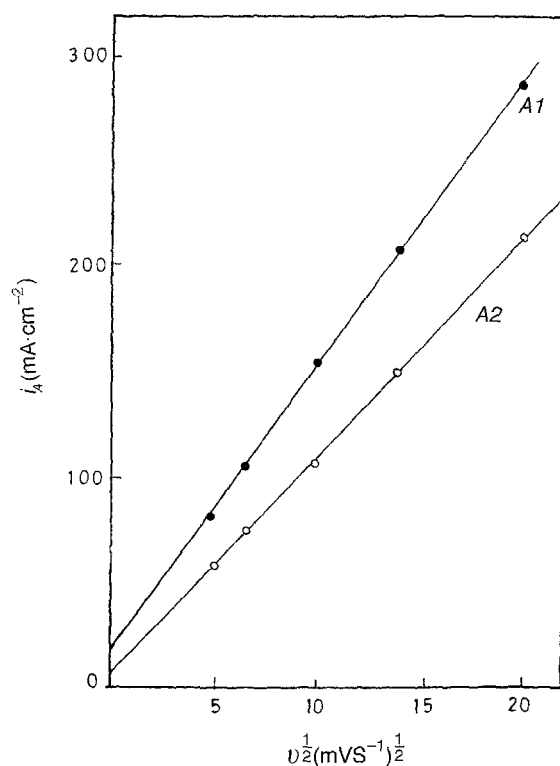

Fig. 4. Relation between i_{A1} and i_{A2} vs. $v^{1/2}$ for Pb in 1.0 M NaOH at 25°C

(Fig. 4). The results of Figs 1 and 3 may be considered as an indication that the formation of PbO (peak $A1$) and PbO$_2$ (peak $A2$) is controlled by diffusion transport of OH$^-$ ions through the surface films from the bulk of the electrolyte.

Figure 5 shows the influence of the temperature (25°C–64°C) on the E vs. i curve of a Pb electrode in 1.0 M NaOH at 100 mVs^{-1}. The general shape of the curve remains practically unaffected by changing the temperature. Increasing the temperature enhances the heights of the anodic peaks, particularly between 25°C and 40°C, and shifts their corresponding peak potentials to more negative values.
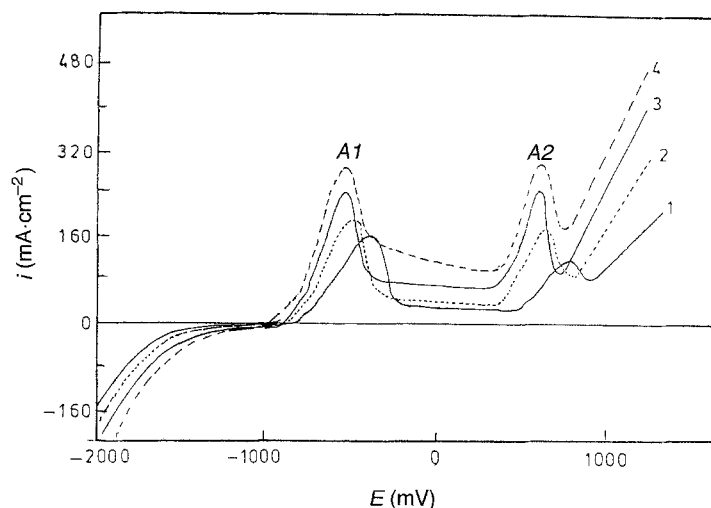
Fig. 5. Potentiodynamic polarization curves of Pb in 1.0 M NaOH at 100 mVs^{-1} and different temperatures; 1: 25, 2: 35, 3: 53, 4: 64°C
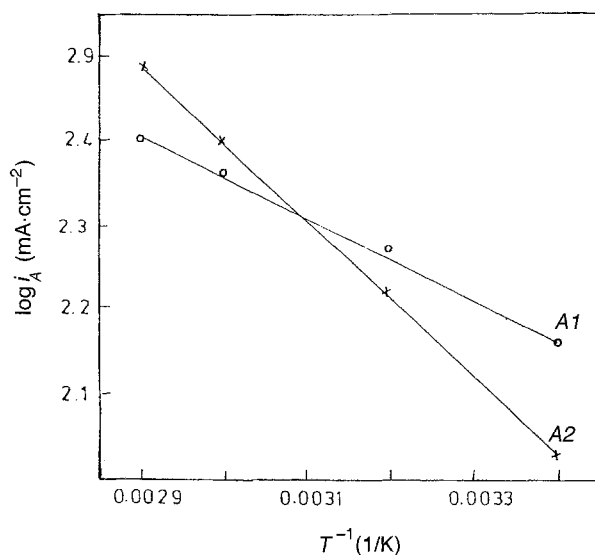

Fig. 6. Relation between $\log i_{A1}$ and i_{A2} vs. T^{-1} for Pb in 1.0 M NaOH at 100 mVs^{-1}

i_{pass} also increases with increasing temperature. These results could be interpreted in terms of increasing solubilities of lead oxides with rising temperature. In addition, an increase in temperature accelerates the transport of OH$^-$ ions and reaction products to and from the electrode. *Arrhenius* plots of $\log i_{A1}$ and $\log i_{A2}$ vs. T^{-1} are given in Fig. 6. From the slopes of the straight lines, apparent activation energy values of 1.685 KJ for $A1$ and 3.093 KJ for $A2$ are obtained.

Figure 7 shows cyclic voltammograms of a Pb electrode in 1.0 M NaOH at 25°C and 100 mVs^{-1}. The voltammograms started from −2000 mV and were reversed at various anodic potential limits. Inspection of the data reveals that if the anodic potential is reversed within the potential range of the shoulder $A1'$ (at −700

mV), the reverse scan retraces itself and does not display cathodic peaks. This result suggests that most of the $Pb(OH)_2$ film dissolves in the potential range of this shoulder. On the other hand, if the anodic potential is reversed at more positive potentials (at -650 mV), the reverse scan retraces only part of the forward scan and then yields a cathodic peak $C1$. Furthermore, when the reversal potential exceeds the potential of peak $A1$ (> -420 mV), a hysteresis between the forward and the reverse scan is observed within the potential region of $A1$. This hysteresis could be taken as indicative for the electrode surface becoming completely covered by a resistive film at potentials greater than E_{A1}. However, stepwise increasing the reversal potential limit within the peak $A1$ and the passive region yields only the cathodic peak $C1$ upon reverse scanning. Therefore, one can conclude that the cathodic peak $C1$ is due to the electroreduction of PbO to Pb. It is worth mentioning that the peak current density i_{C1} increases and its peak potential E_{C1} moves to more negative values as the potential limit becomes more positive. However, the voltammograms exhibit two cathodic peaks $C1$ and $C2$ if the anodic potential is reversed at values more positive than that of peak $A2$. The appearance of the more negative cathodic peak $C2$ may be correlated to the electroreduction of PbO_2 to Pb [10, 15]. *Briss* and *Shevelier* [10] observed the reduction peak $C2$, whereas *Centeno et al.* [15] did not, perhaps due to the slower scan rate used (0.5 mVs^{-1}). The electroreduction of PbO at a potential more positive than that for the electroreduction occurs first at the metal/inner film (PbO region) interface and then moves towards the outer film/solution interface PbO_2 region [10]. It is interesting to note that the appearance of the cathodic peak $C2$ is associated with a decrease in the charge consumed at the cathodic peak $C1$. Moreover, the charge consumed at $C2$
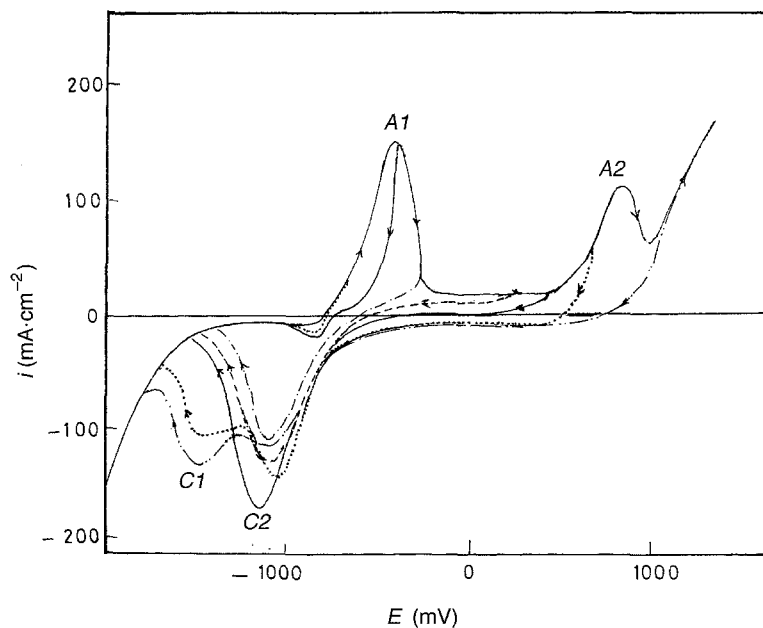

Fig. 7. Cyclic voltammograms of Pb in $1.0\ M$ NaOH at 25°C and 100 mVs^{-1} starting from -2000 mV and reversed at various anodic potentials
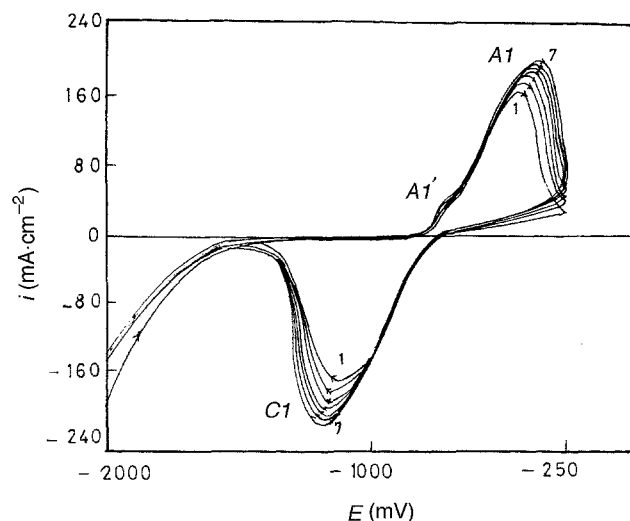
Fig. 8. Successive cycling voltam-
mograms of Pb in 1.0 M NaOH at
25°C and 100 mVs^{-1} between
−2000 and −250 mV (seven
cycles)

increases, whereas that consumed at $C1$ decreases with further increasing the
potential reversal limit. This result indicates that PbO_2 is formed by electrooxida-
tion of PbO and/or Pb_3O_4 to PbO_2 and not by direct oxidation of Pb to PbO_2.

Figure 8 represents typical cyclic voltammograms of a lead electrode in 1.0 M
NaOH at 25°C and 100 mVs^{-1} under the influence of successive cycling between
−2000 mV and −250 mV (the end of peak $A1$) without withdrawing the electrode
or changing the solution. The data reveal that the anodic charge Q_{A1} consumed at
$A1$ and the cathodic charge Q_{C1} consumed at its conjugate peak $C1$ (as represented
by the area of each peak) are similar. Nevertheless, the ratio Q_{C1}/Q_{A1} exceeds unity
by a small amount ($Q_{C1}/Q_{A1} \cong 1.013$), indicating that the extent of reduction is
greater than that of oxidation. The deviation of this ratio from unity could be due to
the electroreduction of some soluble species, likely a concurrent reaction beside
electroreduction of the PbO surface film. The data show that Q_{A1} and Q_{C1} increase,
but their ratios remain nearly constant with the number of cycles. This activation
may be due to progressive increase in the surface area of the electrode with
repetitive cycling, presumably as a result of increasing surface roughness. In ad-
dition, it is probable that soluble Pb(II)-species ($e.g.$ Pb(OH)$_3^-$ and HPbO$_2^-$), gener-
ated in the preceding sweeps, are reduced. It can be seen that the peak potential
difference ΔE_1 ($i.e.$, $E_{A1} - E_{C1}$) is about 400 mV, indicating an irreversible nature
of the processes. Moreover, the peak potential E_{A1} shifts to more positive values,
whereas E_{C1} moves in a more negative direction and consequently ΔE_1 increases
with increasing number of cycles. This change in ΔE_1 with cycling may also be
due to effects of changes in the surface roughness [16].

The cycling voltammograms plotted in Fig. 9 represent anodic and cathodic
contributions occurring on the Pb surface between hydrogen and oxygen evolution
potentials under the influence of successive cycling in 1.0 M NaOH at 25°C and
100 mVs^{-1}. It is obvious that the peak currents of the anodic and cathodic peaks
enhance with increasing number of cycles. The peak potential difference ΔE_2 ($i.e.$,
$E_{A2} - E_{C2}$) also increases with successive cycling. Furthermore, the multiplicity of
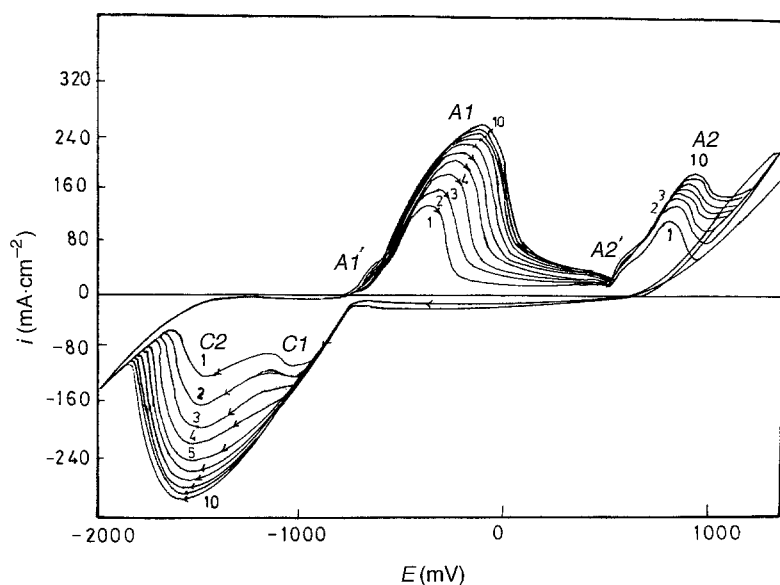the two cathodic peaks $C1$ and $C2$ decreases gradually with increasing number of

Fig. 9. Successive cycling voltammograms of Pb in 1.0 M NaOH at 25°C and 100 mVs^{-1} between −2000 and 1400 mV (ten cycles)

cycles, and after the seventh cycle, the two cathodic peaks coalesce with each other and appear as one cathodic peak.

Experimental

The working Pb electrodes consisted of discs (area 0.5 cm^2) cut from a rod supplied by Koch-Light (99.99% purity) and fixed in an araldite holder. These electrodes were pretreated by polishing with different grade emery papers (60 and 180) and by rinsing with distilled water, acetone, and doubly distilled water before immersion in the working solution. The counter electrode was a platinum wire (0.02 cm diameter, 0.5 cm length). The reference electrode was a saturated calomel electrode (SCE). In order to avoid contamination, the reference electrode was separated by an electrolyte bridge with *a* *Luggin* capillary tip filled with test solution. All solutions were freshly prepared using doubly distilled water and analytical grade chemicals.

Potentiodynamic and cyclic voltammetric measurements were carried out using an EG & G Potentiostat/Galvanostat Model 273. The E vs. i graphs were recorded with a series 2000 Omino-graphic X-Y recorder. The required temperature was adjusted within ±0.5°C by the help of an air thermostat.

X-ray diffraction (XRD) analysis of the passive films was carried out using a Philips diffracto-meter (30 KV, 20 mA) with a Fe filter and Co-K$_\alpha$ radiation.

References

[1] Elbs K, Forsell J (1920) Z Electrochem **8**: 760
[2] Glasstone F (1922) J Chem Soc **121**: 2091
[3] Jones P, Thirsk HR, Wyne-Jones WF (1956) Trans Faraday Soc **52**: 1003
[4] Popova SS, Fortunatov AV (1966) Sov Electrochem **2**: 413
[5] Popova SS, Fortunatov AV (1966) Sov Electrochem **2**: 626

[6] Tourky AR, Shalaby LA, Ashour S (1968) J Chem U.A.R. **11**: 177
 [7] Abd El Aal EE (1992) Corrosion **48**: 482
 [8] Ptitsyn MV, Zenin GS, Tikhanov KI (1977) Sov Electrochem **13**: 1144
 [9] Briss VI, Shevalier MT (1987) J Electrochem Soc **134**: 802
[10] Briss VI, Shevalier MT (1987) J Electrochem Soc **134**: 1595
[11] Briss VI, Shevalier MT (1990) J Electrochem Soc **137**: 2643
[12] Khairy EM, Abdul Azim AA, El Sobki KM (1966) J Electroanal Chem **11**: 282
[13] Abd El Aal EE (1991) Bull Soc Chim Fr **128**: 351
[14] Centeno B, Tascon MC, Vazquez MD, Batanero PS (1991) Electrochim Acta **36**: 227
[15] Veluchamy P, Sharon M, Minoura H, Ichihashi Y, Basavaswaran K (1993) J Electroanal Chem **344**: 73
[16] Abd El Halim AM, Fawzy MH, Abd El Rehim SS, Saty A (1992) Bull Chem Soc Jpn **65**: 1616