

## ELECTROCHEMICAL INVESTIGATIONS ON THE KINETICS OF THE GROWTH OF PbO<sub>2</sub> LAYERS ON LEAD

JÜRGEN P. POHL and WILFRIED SCHENDLER\*

*Lehrstuhl für Physikalische Chemie I, Universität Dortmund, 4600 Dortmund 50 (F.R.G.)*

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### Summary

Potentiostatic polarization measurements of the growth of lead dioxide layers on lead electrodes in sulfuric acid solutions have been made. During an initial period a closed PbO<sub>2</sub> layer is formed anodically on the lead surface. Subsequent growth takes place according to a parabolic rate law with a "parabolic tarnishing constant",  $k_{\text{PbO}_2}$ , in the order of magnitude of  $10^{-11} \text{ cm}^2 \text{ s}^{-1}$ .

This is in agreement with the assumption that the rate-determining step of the growth reaction is the diffusion of oxygen (O<sup>2-</sup> ions and electrons) through the oxide layer from the PbO<sub>2</sub>/electrolyte interface, where oxygen is incorporated anodically into the solid phase, to the internal phase boundary, where the reaction with lead takes place. Using the fact that the chemical potentials of oxygen in the PbO<sub>2</sub> layer at the phase boundaries are fixed by the electrode potential and by the equilibrium with the internal neighbouring phase, respectively, a mean component diffusion coefficient,  $\bar{D}_{\text{O}^{2-}}(\text{PbO}_2)$ , of oxygen ions in lead dioxide has been calculated from  $k_{\text{PbO}_2}$ .  $\bar{D}_{\text{O}^{2-}}(\text{PbO}_2)$  is in the order of magnitude of  $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ .

### Zusammenfassung

Das Wachstum von Bleidioxid-Schichten auf Bleielektroden in schwefelsauren Lösungen wurde mit Hilfe potentiostatischer Polarisationsmessungen untersucht. Im Anschluss an eine Anfangsphase, in der eine geschlossene PbO<sub>2</sub>-Schicht anodisch auf der Bleioberfläche gebildet wird, läuft das nachfolgende Wachstum entsprechend einem parabolischen Geschwindigkeitsgesetz ab mit einer "parabolischen Anlaufkonstante",  $k_{\text{PbO}_2}$ , in der Größenordnung von  $10^{-11} \text{ cm}^2 \text{ s}^{-1}$ .

Dies ist in Übereinstimmung mit der Annahme, dass der geschwindigkeitsbestimmende Schritt der Wachstumsreaktion die Diffusion von Sauer-

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\*Present address: Mannesmann-Forschungsinstitut, 4100 Duisburg 25, F.R.G.

stoff — in der Form von  $O^{2-}$  Ionen und Elektronen — durch die Oxidschicht ist, und zwar von der Phasengrenze  $PbO_2$ /Elektrolyt, wo der Sauerstoff anodisch in die feste Phase eingebaut wird, bis zur inneren Phasengrenze, an der die Reaktion mit Blei stattfindet. Unter Verwendung der Tatsache, dass die chemischen Potentiale von Sauerstoff in der  $PbO_2$ -Schicht an den Phasengrenzen durch das Elektrodenpotential bzw. durch das Gleichgewicht mit der inneren Nachbarphase festgelegt sind, wurde aus  $k_{PbO_2}$  ein mittlerer Komponentendiffusionskoeffizient  $\bar{D}_{O^{2-}}(PbO_2)$  der Sauerstoffionen im Bleidioxid berechnet.  $\bar{D}_{O^{2-}}(PbO_2)$  liegt in der Grössenordnung von  $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ .

## Introduction

If a lead electrode in sulfuric acid solution is polarized anodically from its equilibrium potential  $e_{Pb}^0$  up to a potential which is sufficiently higher than the equilibrium potential  $e_{PbO_2}^0$  of a lead dioxide electrode in the same electrolyte, the formation of a surface layer of  $\beta$ - $PbO_2$  takes place [1 - 6].

The variations of the potential,  $e_{PbO_2}^0$ , of the lead dioxide electrode are shown in Fig. 1 as a function of the pH for cases when the  $Pb^{2+}$  concentrations are  $1 \text{ mol l}^{-1}$  and  $10^{-8} \text{ mol l}^{-1}$ . The potential,  $e_{O_2}^0$ , of an oxygen electrode with an oxygen partial pressure of 1 atm is also plotted [7].

If the lead dioxide electrode is in equilibrium with an electrolyte solution of the  $Pb^{2+}$  concentration  $c_{Pb^{2+}} = 1 \text{ mol l}^{-1}$  and the pH value is 3.73, then the chemical potential,  $\mu_O(PbO_2)$ , of oxygen in  $PbO_2$  corresponds to an oxygen partial pressure  $\rho_{O_2}$  of 1 atm.  $\mu_O(PbO_2)$  increases with decreasing pH value and decreasing  $Pb^{2+}$  concentration, respectively [8].

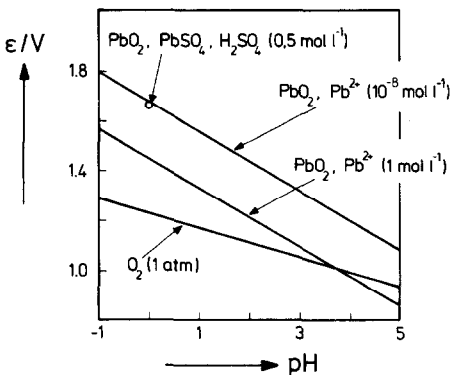


Fig. 1. Electrode potentials as a function of the pH value. (a) Oxygen electrode with  $\rho_{O_2} = 1 \text{ atm}$ ; (b) lead dioxide electrode with  $Pb^{2+}$  concentrations of  $1 \text{ mol l}^{-1}$  and  $10^{-8} \text{ mol l}^{-1}$ ; (c)  $PbO_2$  electrode in equilibrium with a sulfuric acid solution ( $0.5 \text{ mol l}^{-1}$ ) containing lead sulfate (single point).

Furthermore, Fig. 1 also shows the single value of the electrode potential of lead dioxide in equilibrium with a sulfuric acid solution of composition  $\text{H}_2\text{SO}_4$ ,  $c = 0.5 \text{ mol l}^{-1}$ ;  $\text{PbSO}_4$  (s). In this case the  $\text{Pb}^{2+}$  concentration is determined by the solubility product of lead sulfate ( $L_{\text{PbSO}_4} = 1.7 \times 10^{-8} \text{ mol}^2 \text{ l}^{-2}$  [8, 9]) and  $c_{\text{Pb}^{2+}} = 3.4 \times 10^{-8} \text{ mol l}^{-1}$  is calculated.

The anodic oxidation of lead in  $\text{H}_2\text{SO}_4$  electrolytes takes place according to the following overall electrode reaction:



This reaction is of great importance for the lead-acid battery and many papers have dealt with this [1 - 6, 9, 10].

Our measurements, which were carried out in connection with investigations on the disorder and the transport properties in lead dioxide, are concerned with the kinetics of the subsequent growth of the formed oxide layer in order to get information about the diffusion of oxygen in lead dioxide.

### Reaction mechanism of the growth of the $\text{PbO}_2$ surface layer on lead

In Fig. 2 the phase scheme lead/lead dioxide/electrolyte is shown. Three main anodic reactions can occur at the  $\text{PbO}_2$ /electrolyte phase boundary if the electrode is positively polarized.

(i) Incorporation of oxygen from water molecules into the solid oxide phase corresponding to the equation:



The anodic current density for this process is  $i_1$ .

(ii) The evolution of gaseous oxygen corresponding to:

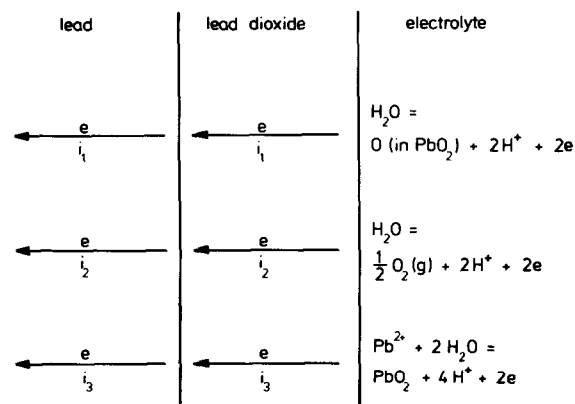
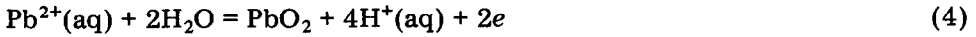


Fig. 2. Schematic representation of possible anodic reactions at the  $\text{PbO}_2$ /electrolyte interface during positive polarization.



In this case the  $\text{PbO}_2$  electrode works like an inert electrode. The current density for the reaction, eqn. (3), is  $i_2$ .

(iii) If  $\text{Pb}^{2+}$  ions are present in the solution, lead dioxide is deposited anodically onto the  $\text{PbO}_2$  surface:



The current density for this reaction of subsequent growth of the  $\text{PbO}_2$  layer by deposition of the oxide from the solution is  $i_3$ .

The net current density,  $i$ , is equal to the sum of the partial current densities:

$$i = i_1 + i_2 + i_3 \quad (5)$$

Using sulfuric acid electrolytes, the  $\text{Pb}^{2+}$  concentration in equilibrium with  $\text{PbSO}_4$  is very small because of the solubility product of lead sulfate. In this case, where the deposition of lead dioxide is diffusion controlled, the corresponding current density is negligible:

$$i_3 \cong 0 \quad (6)$$

Oxygen formed at the  $\text{PbO}_2$ /electrolyte phase boundary (eqn. (2)), may, in principle, combine with lead to form lead dioxide *via* two reaction paths (Fig. 3):

(i) Oxygen — incorporated into  $\text{PbO}_2$  at the external,  $\text{PbO}_2$ /electrolyte, phase boundary — is transported through the oxide layer to the internal,  $\text{PbO}_2$ /lead, phase boundary, where it reacts with the metal according to



For this, the transport of oxygen, in the form of oxygen ions and electrons — moving in different directions — has to be assumed.

(ii) Lead is transported from the internal, metal/oxide interface, through the  $\text{PbO}_2$  layer to the external phase boundary, where it reacts with oxygen to form lead dioxide. In this case the transport of  $\text{Pb}^{4+}$  ions and electrons is in the same direction and has to be taken into consideration.

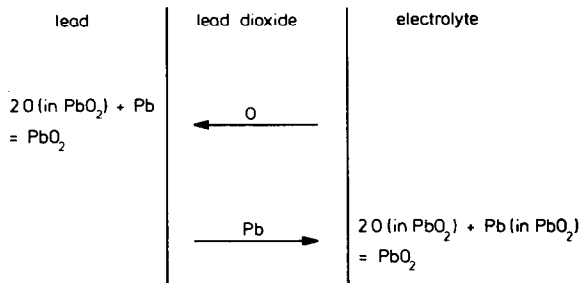


Fig. 3. Schematic representation of possible reactions for the formation of  $\text{PbO}_2$  on lead.

Investigations reported elsewhere [11, 19] eliminate the second potential mechanism and, therefore, it is the first mechanism, requiring the transport of oxygen ions, which is the most probable, with eqns. (2) and (7) controlling the process.

The rate of growth of the  $\text{PbO}_2$  layer is proportional to the partial current density  $i_1$ . From eqns. (2) and (7), and expressing the growth rate as the increase of the mole number,  $n_{\text{PbO}_2}$ , of the lead dioxide formed, we get:

$$\frac{dn_{\text{PbO}_2}}{dt} = \frac{A}{4F} i_1 \quad (8)$$

where  $t$  is the time,  $A$  the geometric surface area, and  $F$  is Faraday's constant.

The thickness,  $\Delta X$ , of the  $\text{PbO}_2$  layer is the following function of the mole number,  $n_{\text{PbO}_2}$ :

$$n_{\text{PbO}_2} = \frac{A \Delta X}{V_{\text{PbO}_2}} \quad (9)$$

where  $V_{\text{PbO}_2}$  is the molar volume of lead dioxide.

From eqns. (8) and (9), we can see that the rate of increase of the layer thickness is given by:

$$\frac{d\Delta X}{dt} = \frac{V_{\text{PbO}_2}}{4F} i_1 \quad (10)$$

Under potentiostatic conditions, *i.e.*, constant electrode potential, oxygen evolution (eqn. (3)) is controlled by a virtually constant partial current density,  $i_2$ , which is relatively small because of the high overpotential of the oxygen evolution at a lead dioxide surface [8 - 10, 12].

### Performance and results of the potentiostatic polarization measurements

Potentiostatic polarization measurements have been carried out to investigate the kinetics of the growth of the  $\text{PbO}_2$  layers on lead. The experimental set-up included a lead measuring electrode, a counter electrode, and a reference electrode (lead dioxide on platinum), which were arranged in sulfuric acid electrolytes of compositions:  $\text{H}_2\text{SO}_4$ ,  $c = 0.5 \text{ mol l}^{-1}$ ;  $\text{PbSO}_4(\text{s})$  and  $\text{H}_2\text{SO}_4$ ,  $c = 5 \text{ mol l}^{-1}$ ;  $\text{PbSO}_4(\text{s})$ . Using potentiostatic equipment, the potential of the measuring electrode could be changed as required, while the corresponding current was measured and recorded.

Figure 4, for example, shows the current-time transient for the case when the lead electrode — in a solution of composition  $\text{H}_2\text{SO}_4$ ,  $0.5 \text{ mol l}^{-1}$ ;  $\text{PbSO}_4(\text{s})$  — had been polarized suddenly at  $t = 0$  from its equilibrium potential  $\epsilon_{\text{Pb}}^0$  to a potential  $\epsilon = \epsilon_{\text{PbO}_2}^0 + 400 \text{ mV}$  (where  $\epsilon_{\text{PbO}_2}^0$  is the equilibrium potential of the lead dioxide electrode in the same electrolyte and equals  $903 \text{ mV}$  against a saturated mercury sulphate reference electrode ( $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ )). The current increased to an initial high peak followed by a second maximum and a slow decay to a nearly constant value.

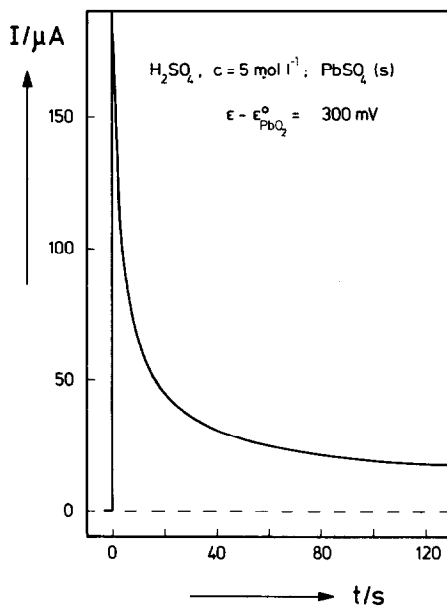
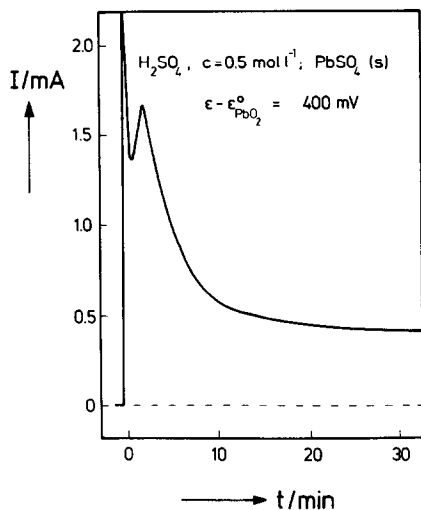


Fig. 4. Dependence of current  $I$  on time  $t$ , measured at a lead electrode ( $A = 0.15 \text{ cm}^2$ ) in sulfuric acid solution during positive potentiostatic polarization.

Fig. 5. Current-time transient, measured at a lead electrode ( $A = 0.01 \text{ cm}^2$ ) in sulfuric acid solution during positive potentiostatic polarization after an anodic current pre-impulse.

Current-time curves of this kind have been measured by other authors and are interpreted as follows [13]: During the first current peak a primary protective layer of lead sulfate is deposited followed by the formation of  $\text{PbO}_2$  nuclei, which grow together into a coherent oxide layer. Subsequently, this layer grows vertically to the surface of the substrate. Under potential conditions when no  $\text{PbO}_2$  nuclei are formed ( $\epsilon - \epsilon_{\text{PbO}_2}^o < 200 \text{ mV}$ ) only the first current peak is observed.

We have been particularly interested in the last part of the current-time transient, which is connected with the subsequent growth of the oxide layer, and have found that the current decays with  $t^{-1/2}$ \*

Further measurements have been performed after coating the lead surface with a very thin  $\text{PbO}_2$  film by applying a short and high anodic pre-impulse current to the electrode. This current pulse was followed immediately by the potentiostatic polarization of the measuring electrode. In this case the current decayed continuously after the initial peak. Such a curve is shown in Fig. 5 using an electrolyte of the composition  $\text{H}_2\text{SO}_4$ ,  $5 \text{ mol l}^{-1}$ ;  $\text{PbSO}_4(\text{s})$ .

\*Other authors [13] interpret this decay only as impingement and overlap of the growing  $\text{PbO}_2$  phase. This was one of the reasons for using an anodic current pre-pulse as described above.

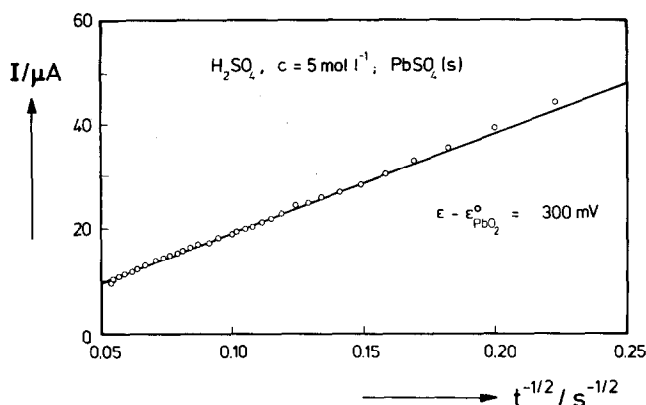


Fig. 6. Plot of the experimental values of current  $I$  (from Fig. 5) as a function of  $t^{-1/2}$ .

In Fig. 6 the individual values of the current used for Fig. 5 are plotted against  $t^{-1/2}$ . The linearity demonstrates the length of time over which the current is proportional to  $t^{-1/2}$ . During such measurements compact  $\text{PbO}_2$  layers of the order of  $1 \mu\text{m}$  thick were formed on the surface of the lead measuring electrode, as measured by cathodic dissolution of the layer and calculated using Faraday's Law. Electron microscopy confirmed the values.

### The rate law of the growth of the $\text{PbO}_2$ layers

While the  $\text{PbO}_2$  layer grows on the surface, the dependence of the net current density,  $i$ , on the reaction time,  $t$ , can be described by the relation:

$$i = Ct^{-1/2} + \text{const.} \quad (\text{for } \epsilon = \text{const.}) \quad (11)$$

As it has already been shown that  $i_2$  is a constant and  $i_3$  is zero and, as  $i$  is the sum of the partial currents (eqn. (5)),  $i_1$  is given by:

$$i_1 = Ct^{-1/2} \quad (\text{for } \epsilon = \text{const.}) \quad (12)$$

where  $C$  is the slope of the straight line  $i$  against  $t^{-1/2}$

Using this experimentally found relationship and inserting it into eqn. (10), we get:

$$\frac{d\Delta X}{dt} = \frac{V_{\text{PbO}_2} C}{4F} t^{-1/2} \quad (13)$$

A rate law of this kind is often stated in its integrated form as follows [14]:

$$\Delta X = (2kt)^{1/2} \quad (14)$$

It is therefore called the "parabolic rate law" of layer growth, and the quantity  $k$  is referred to as the "parabolic tarnishing constant".

The parabolic rate law was first established by Tammann [15] and Pilling and Bedworth [16]. Such a rate law is expected to hold (e.g., for

oxide or sulfide formation as a compact layer on a metal surface) when the growth rate is determined by diffusion processes of the ions and the electrons within the layer and the reactions at the internal and external phase boundaries are virtually in equilibrium [14]. From eqns. (13) and (14) the following expression for the parabolic tarnishing constant,  $k_{\text{PbO}_2}$ , for the growth of the  $\text{PbO}_2$  layer during anodic oxidation of lead is obtained:

$$k_{\text{PbO}_2} = \frac{V_{\text{PbO}_2}^2}{8F^2} C^2 \quad (15)$$

The potentiostatic polarization measurements with  $\text{H}_2\text{SO}_4$  electrolytes having concentrations of  $0.5 \text{ mol l}^{-1}$  and of  $5 \text{ mol l}^{-1}$  and with polarization voltages,  $\epsilon - \epsilon_{\text{PbO}_2}^0$ , between 240 and 400 mV yielded values of  $k_{\text{PbO}_2}$  in the order of magnitude of  $10^{-11} \text{ cm}^2 \text{ s}^{-1}$ . This is in general agreement with the results of measurements of Kabanov [11], where lead foils were oxidized from one side to the other in a sulfuric acid solution.

#### Calculation of the component diffusion coefficient of the oxygen ions in lead dioxide

As  $\text{PbO}_2$  exhibits a high electronic conductivity [17] and the mobility of the  $\text{Pb}^{4+}$  ions in lead dioxide is virtually equal to zero [18], it must be concluded that the diffusion of the oxygen ions through the oxide layer is the rate-determining step of the growth reaction\*. On this premise the component diffusion coefficient of the oxygen ions in  $\text{PbO}_2$  may be calculated from the parabolic tarnishing constant,  $k_{\text{PbO}_2}$ , according to the method of Wagner [14, 20].

For the case when the gradient of the chemical potential,  $\mu_{\text{O}^{2-}}$ , of the oxygen ions is only in the  $x$ -direction\*\* and when there is no electrical potential gradient the component diffusion coefficient,  $D_{\text{O}^{2-}}$ , of the oxygen ions is defined by the following equation [14]:

$$j_{\text{O}^{2-}} = -D_{\text{O}^{2-}} \frac{c_{\text{O}^{2-}}}{RT} \frac{d\mu_{\text{O}^{2-}}}{dx} \quad (16)$$

where  $j_{\text{O}^{2-}}$  is the particle flux of the  $\text{O}^{2-}$  ions,  $c_{\text{O}^{2-}}$  the concentration of the  $\text{O}^{2-}$  ions,  $R$  the gas constant and  $T$  the absolute temperature.

The chemical potential,  $\mu_{\text{O}^{2-}}$ , of the oxygen ions is related to the chemical potential,  $\mu_{\text{O}}$ , of oxygen and the chemical potential,  $\mu_{\text{e}}$ , of the electrons by the following expression:

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\*The protons in lead dioxide as main ionic disorder centres [8, 19] are of less interest in these investigations because they are, similar to the electrons, virtually always in complete local equilibrium.

\*\*The  $x$  direction is perpendicular to the electrode surface.



$$\mu_{O^{2-}} = 2\mu_e + \mu_O \quad (17)$$

For lead dioxide the approximation

$$\mu_e(\text{PbO}_2) = \text{const.} \quad (18)$$

will be assumed for the following discussion although this chemical potential of the electrons in  $\text{PbO}_2$ ,  $\mu_e(\text{PbO}_2)$ , is variable within certain limits, as has been shown by the results of Hall effect measurements [19, 21]. Nevertheless, the variations of  $\mu_e(\text{PbO}_2)$  are much smaller than the changes of the chemical potential of oxygen in lead dioxide,  $\mu_O(\text{PbO}_2)$ . Using the approximation of eqn. (18), the following relationship is obtained:

$$\frac{d\mu_{O^{2-}}(\text{PbO}_2)}{dx} = \frac{d\mu_O(\text{PbO}_2)}{dx} \quad (19)$$

Thus, the particle flux  $j_{O^{2-}}(\text{PbO}_2)$  of the  $O^{2-}$  ions in lead dioxide can be expressed as follows:

$$j_{O^{2-}}(\text{PbO}_2) = -D_{O^{2-}}(\text{PbO}_2) \frac{c_{O^{2-}}(\text{PbO}_2)}{RT} \frac{d\mu_O(\text{PbO}_2)}{dx} \quad (20)$$

In this equation  $D_{O^{2-}}(\text{PbO}_2)$  denotes the component diffusion coefficient and  $c_{O^{2-}}(\text{PbO}_2)$  the concentration of the  $O^{2-}$  ions in  $\text{PbO}_2$ .

Equation (20) indicates that a flux of  $O^{2-}$  ions takes place in the direction from the higher to the lower chemical potential of oxygen in lead dioxide. This is shown schematically in Fig. 7 for the case when the chemical potential,  $\mu_O^e(\text{PbO}_2)$ , of oxygen at the  $\text{PbO}_2$ /electrolyte external phase boundary is higher than the corresponding chemical potential,  $\mu_O^i(\text{PbO}_2)$ , at the internal phase boundary of lead dioxide.

$j_{O^{2-}}(\text{PbO}_2)$  may also be expressed using the differential gradient  $d\Delta X/dt$ , which describes the rate of growth of the  $\text{PbO}_2$  layer:

$$j_{O^{2-}}(\text{PbO}_2) = c_{O^{2-}}(\text{PbO}_2) \frac{d\Delta X}{dt} \quad (21)$$

From eqns. (14), (20) and (21) a relationship between  $k_{\text{PbO}_2}$  and  $D_{O^{2-}}(\text{PbO}_2)$  can be obtained:

$$\frac{k_{\text{PbO}_2}}{\Delta X} dx = - \frac{D_{O^{2-}}(\text{PbO}_2)}{RT} d\mu_O(\text{PbO}_2) \quad (22)$$

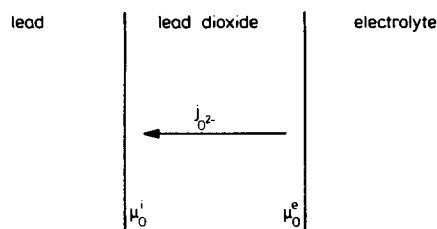


Fig. 7. Schematic representation of the flux of the  $O^{2-}$  ions through the  $\text{PbO}_2$  layer.

or after integration over the complete thickness,  $\Delta X$ , of the  $\text{PbO}_2$  layer:

$$k_{\text{PbO}_2} = - \frac{1}{RT} \int_{\mu_{\text{O}}^e(\text{PbO}_2)}^{\mu_{\text{O}}^i(\text{PbO}_2)} D_{\text{O}^{2-}(\text{PbO}_2)} d\mu_{\text{O}}(\text{PbO}_2) \quad (23)$$

One has to assume, on principle, that the diffusion coefficient of the oxygen ions depends on the chemical potential of oxygen (*i.e.*,  $D_{\text{O}^{2-}(\text{PbO}_2)}$  varies within the width of the oxide layer), and a mean diffusion coefficient,  $\bar{D}_{\text{O}^{2-}(\text{PbO}_2)}$ , has to be used as approximation instead in the case of lead dioxide. If the chemical potential,  $\mu$ , is related to the standard chemical potential,  $\mu^\circ$ , and the thermodynamic activity,  $a$ , according to the equation:

$$\mu = \mu^\circ + RT \ln a \quad (24)$$

the following relation between  $k_{\text{PbO}_2}$  and  $\bar{D}_{\text{O}^{2-}(\text{PbO}_2)}$  results from eqn. (23):

$$\bar{D}_{\text{O}^{2-}(\text{PbO}_2)} = \frac{k_{\text{PbO}_2}}{\ln[a_{\text{O}}^e(\text{PbO}_2)/a_{\text{O}}^i(\text{PbO}_2)]} \quad (25)$$

with  $a_{\text{O}}^e(\text{PbO}_2)$  equalling the activity of oxygen at the external phase boundary of the  $\text{PbO}_2$  layer, and  $a_{\text{O}}^i(\text{PbO}_2)$  the activity of oxygen at the internal phase boundary of the  $\text{PbO}_2$  layer.

The chemical potential of oxygen,  $\mu_{\text{O}}^e(\text{PbO}_2)$ , or the thermodynamic activity,  $a_{\text{O}}^e(\text{PbO}_2)$ , at the  $\text{PbO}_2$ /electrolyte phase boundary is fixed by the applied electrode potential  $\epsilon$ . As the transition polarization for the incorporation of oxygen generated according to eqn. (2) is negligible [8, 22], the oxygen activity may be calculated from the following equation\*, which results from treating the lead dioxide as an oxygen electrode [8, 23]:

$$\epsilon/V = 1.228 - 0.059 \text{ pH} + 0.0295 \log a_{\text{O}}^e(\text{PbO}_2) \quad (26)$$

As an example, a value of  $a_{\text{O}}^e(\text{PbO}_2) = 3 \times 10^{28}$  is obtained for the case of the electrolyte  $\text{H}_2\text{SO}_4$ ,  $0.5 \text{ mol l}^{-1}$ ;  $\text{PbSO}_4(\text{s})$  and  $\epsilon - \epsilon_{\text{PbO}_2}^\circ = 400 \text{ mV}$ .

The chemical potential  $\mu_{\text{O}}^i(\text{PbO}_2)$  or the thermodynamic activity  $a_{\text{O}}^i(\text{PbO}_2)$  of oxygen at the internal phase boundary is fixed by the local equilibrium between lead dioxide and the neighbouring phase. From a thermodynamic point of view it has to be assumed that between lead and lead dioxide there are further layers, however thin they may be, of lower oxides. If the equilibrium  $\text{PbO}_2/\text{Pb}_3\text{O}_4$  is considered, according to



the following relation holds for the chemical potential of oxygen:

$$\mu_{\text{O}}(\text{PbO}_2/\text{Pb}_3\text{O}_4) = \frac{1}{2}(3\mu_{\text{PbO}_2}^\circ - \mu_{\text{Pb}_3\text{O}_4}^\circ) \quad (28)$$

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\*To obtain this equation it has been assumed that  $a_{\text{O}}(\text{PbO}_2) = 1$  for  $p_{\text{O}_2} = 1 \text{ atm}$ . This assumption is arbitrary but does not influence the calculation of  $\bar{D}_{\text{O}^{2-}(\text{PbO}_2)}$ .

with  $\mu_{\text{PbO}_2}^\circ$  equalling the standard chemical potential of  $\text{PbO}_2$  and  $\mu_{\text{Pb}_3\text{O}_4}^\circ$  the standard chemical potential of  $\text{Pb}_3\text{O}_4$ .

Inserting the  $\mu^\circ$  values published by Pourbaix [7] into eqn. (28), the thermodynamic activity  $a_{\text{O}}(\text{PbO}_2/\text{Pb}_3\text{O}_4)$  of oxygen for the equilibrium  $\text{PbO}_2/\text{Pb}_3\text{O}_4$  may be calculated\*:

$$a_{\text{O}}(\text{PbO}_2/\text{Pb}_3\text{O}_4) = 4 \times 10^{-4} \quad (29)$$

If the numerical value of the oxygen activity is used for  $a_{\text{O}}^i(\text{PbO}_2)$ , the mean diffusion coefficient  $\bar{D}_{\text{O}^{2-}}(\text{PbO}_2)$  of oxygen in  $\text{PbO}_2$  is of the order of  $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ . If other possible equilibria at the internal phase boundary are assumed, one obtains other values for  $a_{\text{O}}^i(\text{PbO}_2)$ . The factor  $\ln[a_{\text{O}}^e(\text{PbO}_2)/a_{\text{O}}^i(\text{PbO}_2)]$  is changed only little by this, however, and the numerical value of  $\bar{D}_{\text{O}^{2-}}$  remains in the same order of magnitude\*\*.

### Acknowledgement

The authors thank Prof. Dr Hans Rickert for his steady encouragement and many helpful discussions.

### List of symbols

$A$	Geometric surface of the electrode
$a$	Thermodynamic activity
$a_{\text{O}}(\text{PbO}_2)$	Activity of oxygen in $\text{PbO}_2$
$a_{\text{O}}^e(\text{PbO}_2)$	Activity of oxygen at the $\text{PbO}_2$ /electrolyte phase boundary
$a_{\text{O}}^i(\text{PbO}_2)$	Activity of oxygen at the $\text{PbO}_2$ /lead (or lower lead oxide) phase boundary
$a_{\text{O}}(\text{PbO}_2/\text{Pb}_3\text{O}_4)$	Activity of oxygen for the equilibrium $\text{PbO}_2/\text{Pb}_3\text{O}_4$
$C$	Constant (slope of the straight line $i$ against $t^{-1/2}$ )
$c$	Concentration
$c_{\text{Pb}^{2+}}$	$\text{Pb}^{2+}$ concentration
$c_{\text{O}^{2-}}$	Concentration of the oxygen ions
$c_{\text{O}^{2-}}(\text{PbO}_2)$	Concentration of oxygen ions in $\text{PbO}_2$
$D_{\text{O}^{2-}}$	Component diffusion coefficient of oxygen ions
$D_{\text{O}^{2-}}(\text{PbO}_2)$	Component diffusion coefficient of oxygen ions in $\text{PbO}_2$
$\bar{D}_{\text{O}^{2-}}(\text{PbO}_2)$	Mean component diffusion coefficient of oxygen ions in $\text{PbO}_2$
$F$	Faraday's constant
$i$	Net current density
$i_1$	Partial current density of incorporation of oxygen into $\text{PbO}_2$

\*With  $a_{\text{O}} = 1$  for  $p_{\text{O}_2} = 1 \text{ atm}$ .

\*\*This aspect of the study will be discussed in more detail elsewhere [24].

$i_2$	Partial current density of evolution of gaseous oxygen
$i_3$	Partial current density of $\text{PbO}_2$ deposition
$j_{\text{O}^{2-}}$	Particle flux of the oxygen ions
$j_{\text{O}^{2-}}(\text{PbO}_2)$	Particle flux of oxygen ions in $\text{PbO}_2$
$k$	Parabolic tarnishing constant
$k_{\text{PbO}_2}$	Parabolic tarnishing constant for the growth of $\text{PbO}_2$
$L_{\text{PbSO}_4}$	Solubility product of $\text{PbSO}_4$
$n_{\text{PbO}_2}$	Mole number of $\text{PbO}_2$
$p_{\text{O}_2}$	Oxygen partial pressure
$R$	Gas constant
$T$	Absolute temperature
$t$	Time
$V_{\text{PbO}_2}$	Molar volume of $\text{PbO}_2$
$\Delta X$	Thickness of the $\text{PbO}_2$ layer
$\epsilon$	Electrode potential
$\epsilon_{\text{Pb}}^\circ$	Equilibrium electrode potential of lead
$\epsilon_{\text{O}_2}^\circ$	Equilibrium electrode potential of oxygen
$\epsilon_{\text{PbO}_2}^\circ$	Equilibrium electrode potential of lead dioxide
$\mu$	Chemical potential
$\mu^\circ$	Standard chemical potential
$\mu_{\text{PbO}_2}^\circ$	Standard chemical potential of $\text{PbO}_2$
$\mu_{\text{Pb}_3\text{O}_4}^\circ$	Standard chemical potential of $\text{Pb}_3\text{O}_4$
$\mu_{\text{O}^{2-}}$	Chemical potential of oxygen ions
$\mu_e$	Chemical potential of electrons
$\mu_e(\text{PbO}_2)$	Chemical potential of the electrons in $\text{PbO}_2$
$\mu_{\text{O}}$	Chemical potential of oxygen
$\mu_{\text{O}}(\text{PbO}_2)$	Chemical potential of oxygen in $\text{PbO}_2$
$\mu_{\text{O}}^\circ(\text{PbO}_2)$	Chemical potential of oxygen at the $\text{PbO}_2$ /electrolyte phase boundary
$\mu_{\text{O}}^i(\text{PbO}_2)$	Chemical potential of oxygen at the $\text{PbO}_2$ /lead (or lower lead oxide) phase boundary
$\mu_{\text{O}}(\text{PbO}_2/\text{Pb}_3\text{O}_4)$	Chemical potential of oxygen for the equilibrium $\text{PbO}_2/\text{Pb}_3\text{O}_4$

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