

ELECTROCHEMICAL INVESTIGATIONS ON THE STATIONARY AND NON-STATIONARY BEHAVIOUR OF THE PbO_2 ELECTRODE

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Summary

The kinetic behaviour of the PbO_2 electrode is determined by three reactions (i) deposition/dissolution of lead dioxide, (ii) changes in the stoichiometry of the oxide, especially by incorporation/dissolution of hydrogen, (iii) anodic evolution of oxygen

Immediately following commencement of current flow the stoichiometry-changing reaction predominates, because, we postulate, the proton transfer across the PbO_2 /electrolyte phase boundary is almost uninhibited. Investigations of the kinetics of this reaction have therefore been carried out by means of current pulse measurements. Under appropriate conditions the current in the stationary state is used for PbO_2 deposition/dissolution only. Current-overvoltage curves for these reactions have been obtained from measurements with thin PbO_2 layers, where the stationary state was reached quickly.

Zusammenfassung

Das kinetische Verhalten der PbO_2 -Elektrode wird durch drei Reaktionen bestimmt. (i) Abscheidung/Auflösung von Bleidioxid; (ii) Änderungen der Stöchiometrie des Oxids, insbesondere durch Einbau/Ausbau von Wasserstoff, (iii) anodische Sauerstoffentwicklung.

Unmittelbar nach Beginn eines Stromflusses überwiegt die Stöchiometrieänderungsreaktion, da der Durchtritt von Protonen durch die Phasengrenze PbO_2 /Elektrolyt fast ungehemmt erfolgt. Deshalb sind Untersuchungen zur Kinetik dieser Reaktion mit Hilfe von Stromimpuls-Messungen ausgeführt worden. Unter geeigneten Bedingungen dient der Strom im stationären Zustand nur der PbO_2 -Abscheidung/Auflösung. Stromspannungs-

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kurven für diese Reaktionen wurden durch Messungen mit dünnen PbO_2 -Schichten erhalten, bei denen sich der stationäre Zustand schnell einstellte.

Introduction

If a constant anodic current is applied to a lead dioxide electrode in a perchloric acid electrolyte, a continuous rise in the electrode potential, ϵ_{PbO_2} , from its equilibrium value, $\epsilon_{\text{PbO}_2}^*$, to a stationary value (ϵ_{PbO_2})_{stat} is observed. The initial rise (during the first millisecond or less) is determined mainly by the charge of the double layer, during this period of time a substantial part of the net current is capacitive.

The subsequent potential increase is mainly determined by concentration changes on both sides of the PbO_2 /electrolyte phase boundary. For appropriate conditions — namely, acid electrolytes which are stirred well and current densities which are not too high — the concentration polarization arises almost completely from changes in the stoichiometric composition of the oxide electrode [1]. The main electrochemical reaction involves the dissolution of hydrogen from the oxide, since interstitial protons and quasi-free electrons are the main defects in PbO_2 [2 - 4]. The overvoltage, (ϵ_{PbO_2})_{stat} - $\epsilon_{\text{PbO}_2}^*$, which is measured in the stationary state, must be accepted as being due to changes of the hydrogen concentration in the solid state.

With increasing positive polarization further electrode reactions become evident, i.e., the anodic deposition of lead dioxide (where the electrolyte contains Pb^{2+} ions) and the evolution of oxygen. In the stationary state the stoichiometry changing reaction has come to rest, with regard to the proton transfer reaction the electrode is virtually in equilibrium. In the case of a relatively low overvoltage, and a sufficient Pb^{2+} concentration, the applied current is associated almost completely with the PbO_2 deposition reaction.

With regard to the deposition of the oxide components, lead and oxygen, the measured ϵ_{PbO_2} value has to be considered as a mixed potential. The quasi-equilibrium potentials of lead and oxygen are situated higher and lower than ϵ_{PbO_2} , resulting in a negative transfer overvoltage for lead and a positive one for oxygen, so that a cathodic lead and an anodic oxygen partial current become possible. This problem and the corresponding one for negative polarization of the PbO_2 electrode have been discussed in detail in previous papers [5, 6]. Two cases are of special interest when discussing current-overvoltage curves.

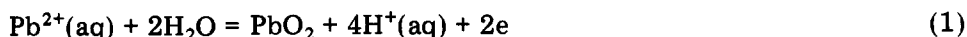
(1) The curve which describes the initial current-overvoltage behaviour of the PbO_2 electrode when negligible concentration polarizations have arisen. This would show the kinetic behaviour of the proton transfer across the oxide/electrolyte phase boundary.

(ii) The stationary current-overvoltage curve describing the rate of deposition and dissolution of PbO_2 as a function of the measured potential ϵ_{PbO_2} . From this a corresponding curve for the transfer of lead ions may be derived by making certain assumptions.

Theoretical considerations

The kinetic behaviour of the PbO_2 electrode can be described by the three reactions which are possible when the electrode is in contact with an acid Pb^{2+} electrolyte [1]:

(1) Anodic deposition or cathodic dissolution of lead dioxide according to the following equation (deposition from left to right; dissolution: from right to left)



This overall reaction may be divided into two partial reactions. For PbO_2 deposition we have the cathodic partial reaction

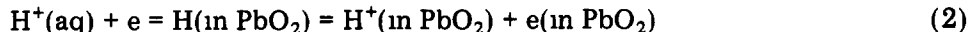


and the anodic partial reaction



This has been discussed in detail in previous papers [5, 6].

(ii) Changes in the stoichiometric composition of the lead dioxide. This reaction occurs particularly by cathodic incorporation of hydrogen into the oxide (eqn (2) from left to right) or by anodic dissolution out of it (eqn (2) from right to left):



(iii) Anodic evolution of gaseous oxygen:



During this process the PbO_2 electrode works as an inert electrode.

If a current is applied to the lead dioxide electrode, it is, in effect, divided into three parts, corresponding to the three reactions eqns. (1), (2) and (3). The net current density, i_{net} , is derived from the partial current densities i_{PbO_2} (PbO_2 deposition/dissolution, eqn. (1)), i_{H} (stoichiometry change, eqn (2)) and i_{O_2} (oxygen evolution, eqn. (3)).

$$i_{\text{net}} = i_{\text{PbO}_2} + i_{\text{H}} + i_{\text{O}_2} \quad (4)$$

Considering the partition of i_{net} , the following general statement can be made on the basis of the results of previous investigations [1, 7, 8]. Immediately after commencement of the current flow, i_{H} predominates because the transfer reaction of the protons across the PbO_2 /electrolyte phase boundary is almost uninhibited. The kinetics of reaction (2) is determined mainly by the preceding or the subsequent diffusion processes. Using a solution with a high concentration of H^+ ions or an appropriate buffer system, the diffusion of the protons within the oxide is rate-determining. The electrons, which have to diffuse together with the protons, are always in local equilibrium because of their high concentration and mobility [4, 9].

With continuous current flow an increasing change of the stoichiometry at the PbO_2 /electrolyte phase boundary occurs, which extends into the interior of the solid phase. This stoichiometry change is associated with an increasing deviation of the measured electrode potential ϵ_{PbO_2} from its equilibrium value $\epsilon_{\text{PbO}_2}^*$ (Fig 1) For applied current densities up to about 10 mA cm^{-2} the transfer overvoltage of reaction (2) is negligible; the course of the electrode potential ϵ_{PbO_2} is determined only by the stoichiometry change in the oxide near the PbO_2 /electrolyte phase boundary

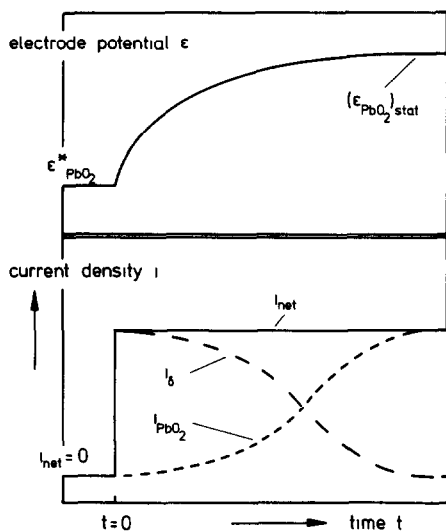


Fig 1 Schematic representation of the variations in the PbO_2 electrode potential and in the current densities i_{PbO_2} (PbO_2 deposition) and i_{δ} (stoichiometry change) with time for the case of a constant anodic net current density i_{net}

The driving force for reaction (1) and also reaction (3) becomes greater with increasing value of $\epsilon_{\text{PbO}_2} - \epsilon_{\text{PbO}_2}^*$. The theoretical conception underlying the connection between transfer and concentration overvoltages of the partial reactions (1a) and (1b) and the measured overvoltage $\epsilon_{\text{PbO}_2} - \epsilon_{\text{PbO}_2}^*$ has been discussed in detail in another paper [5]. If ϵ_{PbO_2} deviates from $\epsilon_{\text{PbO}_2}^*$ in a positive direction, increasing partial current densities i_{PbO_2} (PbO_2 deposition) and i_{O_2} (oxygen evolution) result, for the corresponding deviation in the negative sense, i_{PbO_2} (PbO_2 dissolution) becomes greater. If a constant current density, i_{net} , is applied to the electrode, i_{δ} has to decrease correspondingly because of eqn (4).

Depending on the thickness of the PbO_2 layer, a stationary state is eventually reached which is characterized as follows: i_{δ} is equal to zero, i_{PbO_2} is constant, and the stoichiometry of the oxide has changed completely to a new value.

These considerations give rise to the following equations: Immediately following commencement of a constant current flow (assuming that the

double layer is already charged) the following relation is a valid approximation

$$(i_{\text{net}})_{t_0} = i_{\delta} \quad (5)$$

For the stationary state we obtain from eqn. (4)

$$(i_{\text{net}})_{\text{stat}} = i_{\text{PbO}_2} + i_{\text{O}_2} \quad (6)$$

For the case of medium net current densities ($i_{\text{net}} < 10 \text{ mA cm}^{-2}$) and relatively high Pb^{2+} concentrations ($c_{\text{Pb}^{2+}} > 10^{-2} \text{ mol l}^{-1}$) i_{O_2} is smaller than i_{PbO_2} because of the high inhibition of reaction (3) [10, 11] and may be neglected. For this case eqns. (4) and (6) may be simplified

$$i_{\text{net}} = i_{\text{PbO}_2} + i_{\delta} \quad (4a)$$

$$(i_{\text{net}})_{\text{stat}} = i_{\text{PbO}_2} \quad (6a)$$

The variations of i_{PbO_2} and i_{δ} — corresponding to eqn. (4a) — are shown in a very schematic way in Fig. 1 for the period of time between commencement of the net current flow and the stationary state.

Experimental technique and measuring equipment

Stationary current–overvoltage curves of the PbO_2 deposition and dissolution

The stationary current–overvoltage curves have been measured using thin layer PbO_2 electrodes in $\text{Pb}(\text{ClO}_4)_2/\text{HClO}_4$ electrolytes with different pH values and different Pb^{2+} concentrations. The measurements have been carried out in such a manner, that lead dioxide layers on platinum electrodes were deposited anodically and dissolved cathodically with a constant current. Because of the thinness of the oxide layers, stationary overvoltages were measured after a short time compared with corresponding measurements for thick PbO_2 layers where the stationary state is only reached after minutes or hours.

The measuring equipment is shown schematically in Fig. 2. The measuring electrode (ME) was either a rotating platinum disc or a fixed platinum sheet, the reference electrode (RE) was a lead dioxide electrode in equilibrium with the electrolyte. The measurements were carried out at a temperature of 25°C (298 K). In the case of the fixed measuring electrode the solutions were well stirred.

At the beginning of each experiment the measuring electrode was covered with a thin lead layer which was anodically removed using a galvanostat. Subsequently, the whole platinum surface of the electrode was covered with a compact lead dioxide layer. If the PbO_2 deposition was carried out at a low current density, the electrode was initially covered with a PbO_2 film formed by a sequence of three overvoltage pulses ($\epsilon - \epsilon_{\text{PbO}_2}^* = 500 \text{ mV}$; duration 0.1 s ; frequency 0.3 s^{-1}) before the constant current flow was started.

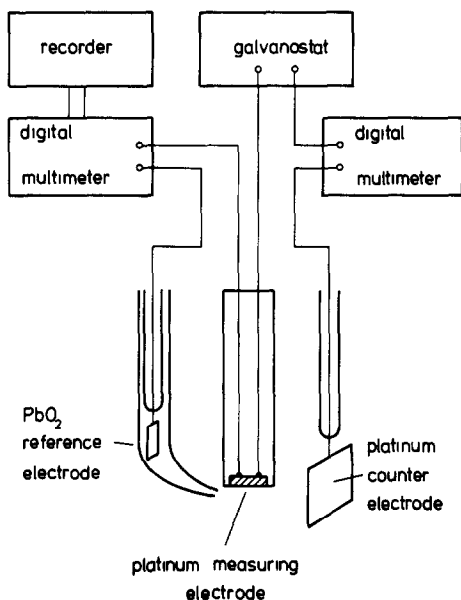


Fig 2 Schematic representation of the experimental set-up for stationary current-overvoltage measurements

After a certain period the current was interrupted for about one hundred seconds. A constant cathodic current was then applied to the measuring electrode, redissolving the oxide deposited on the platinum base. During this succession of anodic current, zero current and cathodic current periods, the electrode potential of the measuring electrode was measured against the reference electrode.

Current pulse measurements

The measurements were carried out using compact, disc-shaped lead dioxide electrodes which were prepared by anodic deposition from a solution of the composition $\text{Pb}(\text{NO}_3)_2$ (0.4 mol l^{-1}); concentrated HNO_3 (20 vol%), $\text{pH} = -0.3$ [1]. The oxide was deposited at room temperature onto a graphite disc substrate at a current density of 10 mA cm^{-2} . When the deposition was complete, the PbO_2 layer was removed from the graphite base and the samples formed into the required shapes. One sample was fitted with two contacts on one side, and another was fitted with one contact, as shown in Fig. 3. The two samples, together with their contacts, were cast into an acid-resistant polyester resin to form a single block containing the measuring electrode and the reference electrode.

The measuring equipment is shown schematically in Fig 3. Using a pulse galvanostat, short current pulses ($10 \mu\text{s} - 1 \text{ ms}$ and up to 350 mA cm^{-2}) were applied to the measuring electrode. The electrode potential of the measuring electrode was potentiostatically controlled up to the instant before commencement of the current pulse. The variation of the potential difference between measuring and reference electrodes, $U(\text{ME}/\text{RE})$, with time,

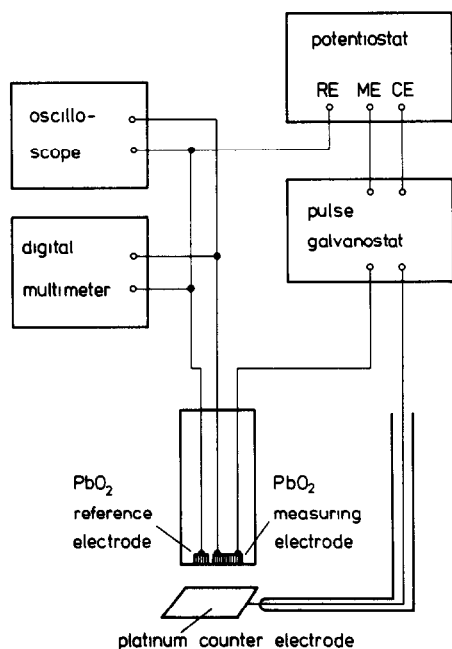


Fig 3 Schematic representation of the experimental set-up for current pulse measurements

before, during, and after the current pulse was recorded by a storage oscilloscope. The evaluation of pairs of faradaic current-overvoltage values from these curves is discussed in the following section

Evaluation of faradaic current-overvoltage pairs for the proton transfer across the PbO_2 /electrolyte interface

The potential behaviour of the PbO_2 electrode at the commencement of a current flow — when the faradaic current is associated almost completely with the transfer of protons across the oxide/electrolyte phase boundary — may be represented by the equivalent circuit shown in Fig. 4. In this circuit

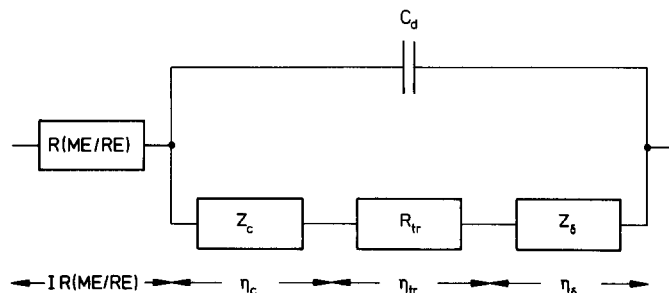


Fig 4 Equivalent circuit for the initial current-overpotential behaviour of the PbO_2 /electrolyte phase boundary (abbreviations are explained in the text)

the transfer resistance, corresponding to reaction eqn. (2), is denoted by the symbol R_{tr} , and η_{tr} is the corresponding transfer overvoltage. Z_c and Z_δ are complex impedances affecting the build up of the concentration overvoltages η_c and η_δ during continuous current flow. η_c is the overvoltage due to a changing H^+ concentration at the electrolyte side of the interface, η_δ denotes the overvoltage which arises from the changing stoichiometric composition of the oxide close to the surface

The potential difference, which is measured between the PbO_2 measuring electrode and the reference electrode when a current is flowing through the cell, is given by

$$U(\text{ME/RE}) = U^*(\text{ME/RE}) + IR(\text{ME/RE}) + \eta_c + \eta_{tr} + \eta_\delta \quad (7)$$

In this equation $U^*(\text{ME/RE})$ means the voltage $U(\text{ME/RE})$ for the case of zero current equilibrium; $U^*(\text{ME/RE})$ is equal to zero if a PbO_2 reference electrode is used. $IR(\text{ME/RE})$ denotes the loss in voltage arising from the part, $R(\text{ME/RE})$, of the electrolyte resistance between measuring and reference electrodes.

For an appropriate choice of the electrolyte and for a very short current pulse the concentration overvoltages η_c and η_δ are still small and may be neglected compared with η_{tr} . For this case a simplified equivalent circuit may be used as a basis (Fig. 5) A constant net current, I_{net} , which starts to flow at t_0 and which is interrupted at t_e , is divided into two parts, as shown on the left side of Fig 5: the capacitive part, I_c , charging the double layer with its capacity C_d , and the faradaic part I_{tr} flowing through R_{tr} and being connected with the electrochemical reaction eqn (2).

$$I_{net} = I_c + I_{tr} \quad (8)$$

For $t = t_0$ the faradaic part is still equal to zero

$$I_{net} = I_c \quad (\text{for } t = t_0) \quad (9)$$

After interruption of the net current at $t = t_e$, the double layer is discharged internally by a continuous flow of I_{tr} across R_{tr} (right side of Fig. 5) and the following expression is valid:

$$I_{tr} = -I_c \quad (\text{for } I_{net} = 0) \quad (10)$$

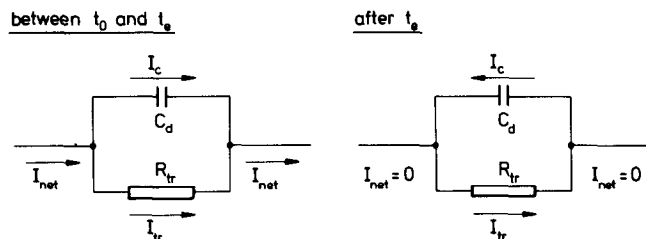


Fig 5 Simplified equivalent circuit (without the ohmic resistance of the electrolyte) Directions of the capacitive and the faradaic current for the cases with, and without, external current flow (abbreviations are explained in the text)

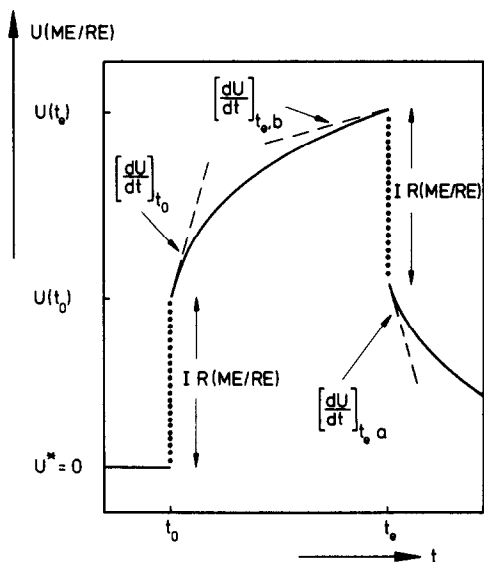


Fig 6 Schematic representation of the variation of the overvoltage of the PbO_2 electrode $U(\text{ME}/\text{RE})$ with time before, during, and after, a current pulse (abbreviations are explained in the text)

Figure 6 shows, schematically, the variation of $U(\text{ME}/\text{RE})$ with time before, during, and after, the current pulse. The rate of change of U with time t is determined by C_d and I_c and is given by.

$$\left(\frac{dU}{dt}\right)_t = \frac{I_c(t)}{C_d}; \quad I_c(t) = C_d \left(\frac{dU}{dt}\right)_t \quad (11)$$

Using eqns (9) and (11) the double-layer capacity of the electrode can be calculated.

$$\left(\frac{dU}{dt}\right)_{t_0} = \frac{I_{\text{net}}}{C_d}; \quad C_d = \frac{I_{\text{net}}}{(dU/dt)_{t_0}} \quad (12)$$

Assuming that C_d is constant between $U(t_0)$ and $U(t_e)$, the faradaic part of I_{net} may be calculated for each moment, t , between t_0 and t_e using eqns (8), (11) and (12):

$$I_{\text{tr}}(t) = I_{\text{net}} - C_d \left(\frac{dU}{dt}\right)_t \quad (13)$$

$$I_{\text{tr}}(t) = I_{\text{net}} \left[1 - \frac{(dU/dt)_t}{(dU/dt)_{t_0}} \right] \quad (\text{for } C_d = \text{const}) \quad (14)$$

Using these $I_{tr}(t)$ values and the corresponding $U(t)$ values a current-overvoltage curve for the incorporation/dissolution of hydrogen into or out of lead dioxide may be determined. If the approximation $C_d = \text{constant}$ is not used, e.g., for higher values of $U(t) - U(t_0)$, the partition of the net current may be calculated for the moment t_e using the rates of change of $U(\text{ME}/\text{RE})$ with time the instant before and the instant after interruption of the current, $(dU/dt)_{t_e, b}$ and $(dU/dt)_{t_e, a}$.

The points corresponding to these two slopes differ only by the ohmic voltage drop $IR(\text{ME}/\text{RE})$, as can be seen from Fig. 6; the overvoltage η_{tr} is equal for both points. The current across R_{tr} — i.e., the faradaic current of the proton transfer reaction —, therefore, is also the same immediately before and after interruption of the external circuit; it is denoted as $I_{tr}(t_e)$ and from eqns. (10) and (11) it follows that

$$I_{tr}(t_e) = -I_c(t_e, a) = -C_d \left(\frac{dU}{dt} \right)_{t_e, a} \quad (15)$$

where $I_c(t_e, a)$ = capacitive current the instant after interruption

For the partition of I_{net} at the moment t_e the following expression is obtained using eqns. (8), (11) and (15)

$$\begin{aligned} I_{net} &= I_c(t_e, b) + I_{tr}(t_e) \\ &= C_d \left[\left(\frac{dU}{dt} \right)_{t_e, b} - \left(\frac{dU}{dt} \right)_{t_e, a} \right] \end{aligned} \quad (16)$$

with $I_c(t_e, b)$ = capacitive current the instant before interruption. From eqns (15) and (16) one gets

$$I_{tr} = I_{net} \frac{-(dU/dt)_{t_e, a}}{(dU/dt)_{t_e, b} - (dU/dt)_{t_e, a}} \quad (17)$$

Using eqn. (17) I_{tr} can be calculated, without knowing C_d , from the rates of change of U the instant before and the instant after interruption. The corresponding η_{tr} value is given by $U(t_e) - IR(\text{ME}/\text{RE})$. From a series of such current pulse experiments with increasing durations the current-overvoltage curve can be obtained.

Results of the measurements and discussion

Stationary current-overvoltage curves of the PbO_2 deposition and dissolution

Figure 7 shows the variation of the electrode potential of the measuring electrode during a measuring cycle (as described earlier) with an anodic and a cathodic current density of 2 mA cm^{-2} using an electrolyte solution of composition $\text{Pb}(\text{ClO}_4)_2$, $c = 0.3 \text{ mol l}^{-1}$, HClO_4 , $\text{pH} = 1$.

The anodic current flow was started at $t = 0 \text{ s}$. When the initial lead covering had been completely dissolved from the platinum surface, the

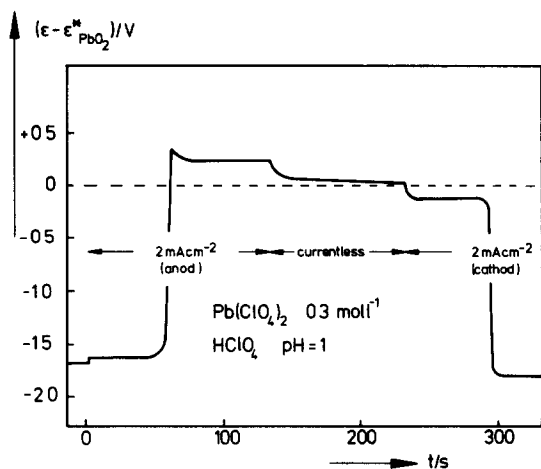


Fig 7 Variation of the measuring electrode potential during a measuring cycle with a constant anodic and a constant cathodic current density of 2 mA cm^{-2}

electrode potential increased within about 2 s from its early value near the equilibrium potential of the lead electrode to a value of $\epsilon - \epsilon_{PbO_2}^* = 350 \text{ mV}$, followed by a decrease to a stationary value of $(\epsilon_{PbO_2})_{stat} - \epsilon_{PbO_2}^* = 260 \text{ mV}$ within about 10 s. The initial potential peak may be understood as overvoltage for the formation of PbO_2 nuclei on the platinum surface.

Following the end of anodic current flow an overvoltage transient was observed corresponding to zero current stoichiometry relaxation of the oxide to its equilibrium value. With a cathodic load of the deposited PbO_2 layer the electrode potential reached the stationary value $(\epsilon_{PbO_2})_{stat} - \epsilon_{PbO_2}^* = -90 \text{ mV}$ after about 10 s. The end point of the PbO_2 dissolution was indicated by a sharp fall in the potential of the current loaded measuring electrode.

From such a measuring cycle two current density–overvoltage pairs were achieved: one pair of values for the stationary anodic deposition and one for the stationary cathodic dissolution of PbO_2 . From such values the stationary current density–overvoltage curves were derived. Further, the current efficiency of the PbO_2 deposition could be confirmed by comparing the time duration of anodic deposition with that of cathodic dissolution of the oxide. The anodic current density–overvoltage curves of Figs 8 and 10 correspond to current efficiencies between 95 and 100%.

Figures 8 and 9 show the results of measurements using $Pb(ClO_4)_2/HClO_4$ electrolytes with a Pb^{2+} concentration of 0.3 mol l^{-1} and pH values between 0 and 3. The Figures show that for a given current density the amount of $\epsilon_{PbO_2} - \epsilon_{PbO_2}^*$ (where $\epsilon_{PbO_2}^*$ denotes the PbO_2 equilibrium potential in the respective electrolytes) increases with increasing pH value, both in the cathodic and in the anodic case. If, for a given pH value, the amounts of the overvoltages for equal anodic and cathodic current densities are compared, the curves show that the deposition of PbO_2 occurs at much higher

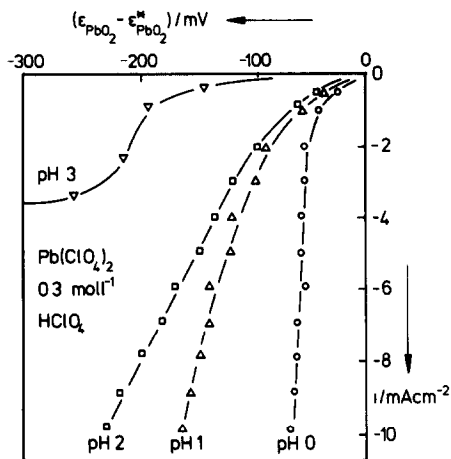
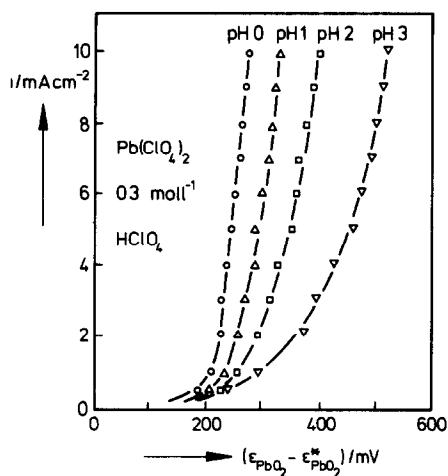


Fig 8 Stationary deposition of PbO_2 current density–overvoltage curves for $\text{Pb}(\text{ClO}_4)_2/\text{HClO}_4$ electrolytes ($c_{\text{Pb}^{2+}} = 0.3 \text{ mol l}^{-1}$) with various pH values (pH = 0, 1, 2 and 3)

Fig 9 Stationary dissolution of PbO_2 current density–overvoltage curves for $\text{Pb}(\text{ClO}_4)_2/\text{HClO}_4$ electrolytes ($c_{\text{Pb}^{2+}} = 0.3 \text{ mol l}^{-1}$) with various pH values (pH = 0, 1, 2 and 3)

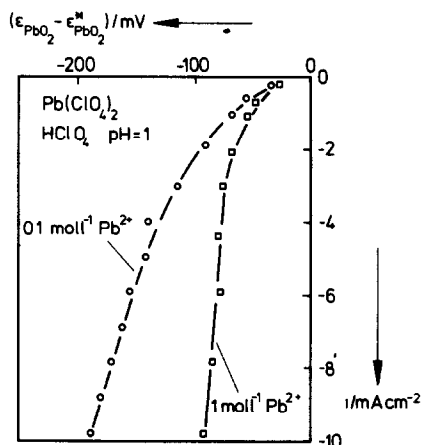
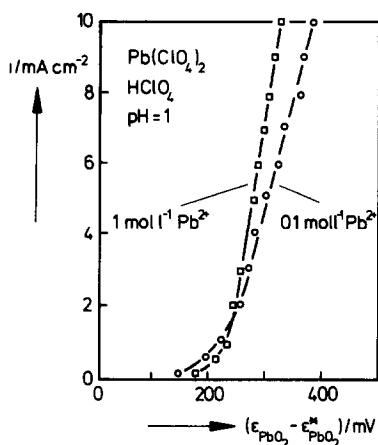


Fig 10 Stationary deposition of PbO_2 current density–overvoltage curves for $\text{Pb}(\text{ClO}_4)_2/\text{HClO}_4$ electrolytes (pH = 1) with the Pb^{2+} concentrations 0.1 mol l^{-1} and 1 mol l^{-1}

Fig 11 Stationary dissolution of PbO_2 current density–overvoltage curves for $\text{Pb}(\text{ClO}_4)_2/\text{HClO}_4$ electrolytes (pH = 1) with the Pb^{2+} concentrations 0.1 mol l^{-1} and 1 mol l^{-1}

overvoltages than the corresponding dissolution of the oxide. The same tendency is shown by Figs. 10 and 11, where the anodic and cathodic stationary current density–overvoltage curves are shown for two $\text{Pb}(\text{ClO}_4)_2/\text{HClO}_4$ electrolytes of the same pH value (pH = 1) but with different Pb^{2+} concentrations (1 mol l^{-1} and 0.1 mol l^{-1}).

Initial current–overvoltage curve of proton transfer

In order to optimize the proton concentrations on both sides of the phase boundary — *i.e.*, both in the oxide* and in the solution — and to delay the appearance of the concentration polarizations η_c and η_s , the lead acetate/acetic acid buffer system ($\text{Pb}(\text{CH}_3\text{COO})_2$, 1 mol l^{-1} , CH_3COOH , 1 mol l^{-1}) with a pH value of 3.8 was chosen as electrolyte for a first series of measurements. The results of these measurements are represented in Fig. 12 showing the current density–overvoltage curve for the incorporation and dissolution of hydrogen into or out of the PbO_2 electrode, respectively. From Fig. 12 an exchange current density i_0 , equal to 30 mA cm^{-2} and a symmetry factor of about 0.5, results. The double layer capacity of PbO_2 electrodes in this electrolyte was measured as about $60 \mu\text{F cm}^{-2}$ at the equilibrium potential $\epsilon_{\text{PbO}_2}^*$.

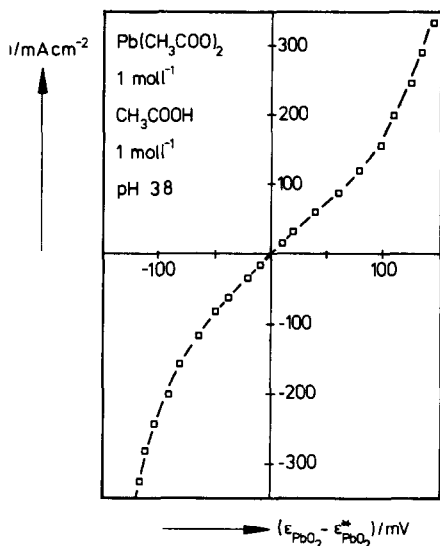


Fig. 12 Incorporation and dissolution of hydrogen into or out of PbO_2 current density–overvoltage curve for a lead acetate/acetic acid buffer electrolyte

Discussion

The current–overpotential curves confirm that there are two main processes occurring at the PbO_2 electrode at different rates. The stoichiometry changing reaction, which we have associated with a proton transfer across the interface, determines the initial kinetic behaviour of the oxide because the rate of transfer is high. Soon after the beginning of current flow the

*The concentration of interstitial protons in PbO_2 depends on the pH value of the electrolyte being in equilibrium with the oxide. The concentration in the solid phase increases with decreasing H^+ concentration in the solution [4, 12, 16]

transport rate and, hence, the overall reaction, becomes limited by diffusion processes, especially within the solid phase [17]

For potentiostatic conditions, *i.e.*, if a constant overpotential is applied to the electrode, an initial high current peak is observed which decreases rapidly to a much lower stationary value [1, 8]. The rate of this stationary reaction — the deposition or dissolution of PbO_2 — is much smaller than that of the initial reaction, as a comparison of the current–overvoltage curves demonstrates. Under galvanostatic conditions the stationary process becomes possible, because the first process has changed the oxide stoichiometry and through that has substantially increased the overvoltage.

From this it follows that each point of a stationary curve represents another stoichiometric composition of lead dioxide, in contrast to the current–overvoltage curve of the proton transfer reaction. Associated with the stoichiometry changes are the changes in the chemical potentials of lead and oxygen. Therefore quantities such as exchange current densities or symmetry factors cannot be obtained from these curves. Assuming that the transfer of lead is much more inhibited than is that of oxygen, the stationary current–overvoltage curves may be regarded as current–transfer overvoltage curves for the deposition or dissolution of Pb^{2+} ions into, or out of, lead dioxide. Then the axes have to be transformed according to the instructions $i = -i_{\text{Pb}^{2+}}$ (with $i_{\text{Pb}^{2+}}$ = lead partial current density) and $\epsilon_{\text{PbO}_2} - \epsilon_{\text{PbO}_2}^* = -\eta_{\text{Pb}^{2+}}$ (with $\eta_{\text{Pb}^{2+}}$ = transfer overvoltage of the Pb^{2+} ions). This problem has been discussed previously in detail [1, 5].

Finally, it should be noted that, although current–voltage curves measured with PbO_2 electrodes in $\text{Pb}(\text{ClO}_4)_2/\text{HClO}_4$, $\text{Pb}(\text{BF}_4)_2/\text{HBF}_4$ and $\text{Pb}(\text{NO}_3)_2/\text{HNO}_3$ electrolytes have already been published by various authors [13–15], these may not be compared with the curves of this paper. They were obtained either by current pulse measurements using much longer pulse durations, so that the measured overvoltage already includes a significant fraction due to stoichiometry changes, or by using potential sweep measurements, so that they have a “quasi-stationary” character. In this study we have made a unique *analysis* of the potential/time transients over the first 100 μs . The transients measured by us, however, are not claimed to differ significantly from those measured by other workers using the same measuring method and conditions.

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List of symbols

C_d	Capacity of the double layer
I_{net}	Net current

I_c	Capacitive part of the net current
I_{tr}	Faradaic part of the net current
$I_{tr}(t_e)$	Faradaic current immediately before and after interruption of the net current
$I_c(t_e, b)$	Capacitive current immediately before interruption of the net current
$I_c(t_e, a)$	Capacitive current immediately after interruption of the net current
$IR(\text{ME/RE})$	Voltage drop arising from $R(\text{ME/RE})$
i	Current density
i_0	Exchange current density
i_{net}	Net current density
i_{PbO_2}	Partial current density of PbO_2 deposition/dissolution
i_δ	Partial current density of stoichiometry change
i_{O_2}	Partial current density of oxygen evolution
$i_{\text{Pb}^{2+}}$	Lead partial current density
$(i_{net})_{t_0}$	Net current density immediately after the beginning of a current flow
$(i_{net})_{stat}$	Net current density in the stationary state
ME	Measuring electrode
RE	Reference electrode
R_{tr}	Transfer resistance
$R(\text{ME/RE})$	Part of the electrolyte resistance between ME and RE
t	Time
t_0	Time at which the current flow is started
t_e	Time at which the current flow is interrupted
U	Abbreviation for $U(\text{ME/RE})$
$U(\text{ME/RE})$	Potential difference between ME and RE
$U^*(\text{ME/RE})$	Potential difference between ME and RE for the case of currentless equilibrium
$U(t_0)$	$U(\text{ME/RE})$ at $t = t_0$
$U(t_e)$	$U(\text{ME/RE})$ at $t = t_e$
$\left(\frac{dU}{dt}\right)_t$	Rate of change of $U(\text{ME/RE})$ with time as a function of t
$\left(\frac{dU}{dt}\right)_{t_0}$	(dU/dt) at $t = t_0$
$\left(\frac{dU}{dt}\right)_{t_{e, b}}$	(dU/dt) the instant before interruption of the current
$\left(\frac{dU}{dt}\right)_{t_{e, a}}$	(dU/dt) the instant after interruption of the current

Z_c	Impedance affecting the build up of the concentration overvoltage η_c
Z_δ	Impedance affecting the build up of the stoichiometry change overvoltage η_δ
ϵ	Electrode potential
ϵ_{PbO_2}	Electrode potential of the PbO_2 electrode
$\epsilon_{\text{PbO}_2}^*$	Equilibrium electrode potential of the PbO_2 electrode
$(\epsilon_{\text{PbO}_2})_{\text{stat}}$	Electrode potential of the PbO_2 electrode in the stationary state
η_{tr}	Transfer overvoltage of the protons
η_c	Overvoltage due to changing H^+ concentration at the electrolyte side of the interface
η_δ	Overvoltage due to changing stoichiometry of PbO_2 close to the interface
$\eta_{\text{Pb}^{2+}}$	Transfer overvoltage of the Pb^{2+} ions

References

- 1 J P Pohl and H Rickert, in S Trasatti (ed), *Electrodes of Conductive Metallic Oxides*, Elsevier, Amsterdam, 1980, p 183
- 2 J P Pohl and H Rickert, *Z Phys Chem (NF)*, 112 (1978) 117
- 3 G L Schlechtriemen, *Z Phys Chem (NF)*, 130 (1982) 193
- 4 J P Pohl and G L Schlechtriemen, *J Appl Electrochem*, 14 (1984) 521
- 5 J P Pohl and H Rickert, in D H Collins (ed), *Power Sources 5*, Academic Press, London, 1974, p 15
- 6 J P Pohl and H Rickert, in D H Collins (ed), *Power Sources 6*, Academic Press, London, 1976, p 59
- 7 J P Pohl and H Rickert, *Z Phys Chem (NF)*, 95 (1975) 59
- 8 G P Papazov, J P Pohl and H Rickert, in J Thompson (ed), *Power Sources 7*, Academic Press, London, 1978, p 37
- 9 J P Pohl and W Schendler, *J Power Sources*, 6 (1981) 245
- 10 P Ruetschi, R T Angstadt and B D Cahan, *J Electrochem Soc*, 106 (1959) 547
- 11 D W Wabner, H P Fritz, D Missol, R Huss and F Hindelang, *Z Naturforsch*, B31 (1976) 39
- 12 W Fischer and H Rickert, *Ber Bunsenges Phys Chem*, 77 (1973) 975
- 13 N A Hampson, P C Jones and R F Phillips, *Can J Chem*, 45 (1967) 2045
- 14 N A Hampson, P C Jones and R F Phillips, *Can J Chem*, 46 (1968) 1325
- 15 F Beck and H Bohn, *Ber Bunsenges Phys Chem*, 79 (1975) 233
- 16 S Atlung and J P Pohl, *Electrochim Acta*, accepted for publication
- 17 R Munzberg and J P Pohl, *Z Phys Chem (NF)*, in press