Concentration, mobility and thermodynamic behaviour of the quasi-free electrons in lead dioxide

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By means of Hall-effect measurements, the concentration, c_e, of the quasi-free electrons in β-lead dioxide has been determined as a function of the equilibrium oxygen partial pressure, p_{O_2} in the oxide. For high values of p_{O_2}, corresponding to the equilibrium of PbO_2 with a very acid electrolyte, the electron concentration amounts to 5.7×10^{20} cm^{-3}. The concentration increases with decreasing oxygen partial pressure, i.e. increasing pH values of the electrolyte. For lead dioxide with an oxygen activity which corresponds to a partial pressure of the magnitude of 1 atm an upper value of c_e equal to 10.3×10^{20} cm^{-3} has been determined.

Furthermore, the results of conductivity measurements are reported. Using the values of the specific electronic conductivity, σ_e, and the c_e data, the drift mobility, u_e, of the electrons in PbO_2 has been calculated as a function of p_{O_2}. With the aid of Fermi–Dirac statistics the chemical potential, $\tilde{\mu}_e$, and the activity, a_e, of the electrons have been evaluated from the corresponding concentration values. According to the results of these calculations a disorder model of lead dioxide is confirmed, where protons on interstitial lattice sites and quasi-free electrons are the dominating disorder centres.

1. Introduction

Lead dioxide is of great practical importance: firstly, as the positive plate of the lead–acid battery and secondly, as an inert electrode for various anodic processes. On the other hand, lead dioxide has a fundamental theoretical significance as an example of an oxide electrode exhibiting high electronic conductivity [1, 2].

The fact that PbO_2 must be treated as a non-stoichiometric oxide of variable composition (within a small range) and the correspondingly changing chemical potential of oxygen has been emphasized in a paper by Fischer and Rickert [3].

To describe the chemical composition of lead dioxide, these authors have chosen the formula $PbO_{2-\delta}(x\,H_2O)$. The index δ indicates that there exists a variable deviation from the 'ideal stoichiometry' (i.e. $\delta = 0$) with a maximum value, δ_{max}, equal to 1.6×10^{-2} [4]. According to the formula given above '$x\,H_2O$' indicates that a variable amount of water is present within the bulk of the oxide in a 'dissolved' state.

Another way of representing the composition of lead dioxide is by the formula $PbO_{2-y}H_z$ [5]. This shows more clearly that oxygen ion vacancies and interstitial protons are considered as possible ionic defects [2, 3]. The relation between these two representations has been treated by Schlechtriemen [5].

A paper by Moseley *et al.* [6] favours a model in which β-PbO_2 is fully stoichiometric with respect to oxygen and contains a substantial amount of disordered hydrogen. Furthermore, a small deficiency of atoms on the lead atom sites is discussed. Occupancies of the sites of the lead atoms – relative to oxygen – between 99 (chemically prepared samples) and 97% (samples from the lead–acid battery) in β-PbO_2 have been calculated from neutron powder diffraction profiles by Hill [7]. An amount of about 0.1 mol incorporated hydrogen (per mol PbO_2) in the form of OH or H_2O is also assumed. The fact that the stoichiometry of the oxide may be changed, and together with that the concentration of at least

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one of the defects, is not discussed in these papers.

Besides the ionic defects in lead dioxide, one must also take into consideration the presence of quasi-free electrons as disorder centres if a correct treatment of the thermodynamic behaviour of this oxide is to be given.

The existence of quasi-free electrons has been substantiated by measurements of the electronic conductivity and the electron concentration of β-PbO$_2$, which are described below and elsewhere [5, 8].

Investigations on the conductivity and the concentration of the electrons in lead dioxide have been carried out by several other workers [9–13] using lead dioxide samples of different origin, but none of these samples was defined with regard to its stoichiometry or its chemical potential of oxygen.

In this paper the results of Hall-effect measurements are reported. These have been carried out to determine the concentration of the quasi-free electrons in thin compact PbO$_2$ layers in contact with defined electrolyte solutions. The results of conductivity measurements are also reported, these experiments having been performed in a similar way. Using these results and the corresponding values of the electron concentration, the mobility of the electrons in β-PbO$_2$ as a function of the chemical potential of oxygen is calculated.

Since the measured values of the electron concentrations are in the range between 10^{20} and 10^{21} cm^{-3}, the behaviour of the electrons cannot be described using the Boltzmann approximation. The electrons are strongly degenerate and show a marked deviation from ideal behaviour, so that for a correct thermodynamic treatment, involving the calculation of activities and chemical potentials, Fermi–Dirac statistics must be applied [2, 14].

2. Adjustment of the stoichiometric composition of lead dioxide

The following equation describes a reaction for the formation of lead dioxide which, in principle, is possible [15].

$$2Pb^{2+}(aq) + 2H_2O + O_2(g) = 2PbO_2 + 4H^+(aq) \tag{1}$$
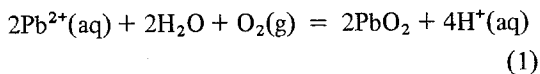
According to this equation, the following con-

nection between the chemical potential of oxygen in equilibrium with lead dioxide and the composition of the electrolyte solution can be derived:

$$\mu_{O_2} = \text{constant} + 4\mu_{H^+}(aq) - 2\mu_{Pb^{2+}}(aq) \tag{2}$$

An extended treatment of this point has been given in earlier papers [2, 3, 15].

The significance of Equation 2 lies in the fact that the chemical potential of oxygen, μ_{O_2}, is fixed by the chemical potential of hydrogen ions, $\mu_{H^+}(aq)$, and by the chemical potential of the lead ions, $\mu_{Pb^{2+}}(aq)$, which are present in the electrolyte phase which is in equilibrium with the oxide phase. In addition, assuming that equilibrium between lead dioxide and a gas phase has been established, if oxygen behaves ideally then the partial pressure of oxygen, p_{O_2}, is given by the following relation:

$$\log [p_{O_2}(\text{atm})] = \text{constant}' + 4 \log a_{H^+}(aq)$$
$$- 2 \log a_{Pb^{2+}}(aq) \tag{3}$$

where $a_{H^+}(aq)$ is the thermodynamic activity of the hydrogen ions in solution and $a_{Pb^{2+}}(aq)$ is the thermodynamic activity of the lead ions in solution.

The electrolyte solution used for the measurements had a fixed Pb^{2+} concentration of 4.8×10^{-3} mol l^{-1}. Inserting this value and that of the constant of Equation 3, containing the standard chemical potentials of Pb^{2+}(aq), H$_2$O, O$_2$(g), PbO$_2$ and H$^+$(aq), the following expression holds for the oxygen partial pressure:

$$\log [p_{O_2}(\text{atm})] = 19.67 - 4\,pH \tag{4}$$

The same relation is obtained if the equations for the electrode potentials of the oxygen electrode and lead dioxide electrode [16] given by

$$\epsilon_{O_2}(V) = 1.229 + 0.0148 \log [p_{O_2}(\text{atm})]$$
$$- 0.059\,pH \tag{5}$$

$$\epsilon_{PbO_2}(V) = 1.449 - 0.0295 \log a_{Pb^{2+}}(aq)$$
$$- 0.118\,pH \tag{6}$$

are set equal, due to the fact that the PbO$_2$ electrode can be treated as an oxygen electrode with variable oxygen partial pressure [2, 3, 17].

In Fig. 1 the variations of the electrode potentials of the oxygen electrode (p_{O_2} = 1 atm) and lead dioxide electrode ($c_{Pb^{2+}}(aq)$ = 4.8 × 10^{-3} mol l^{-1}) are plotted as a function of the pH of the
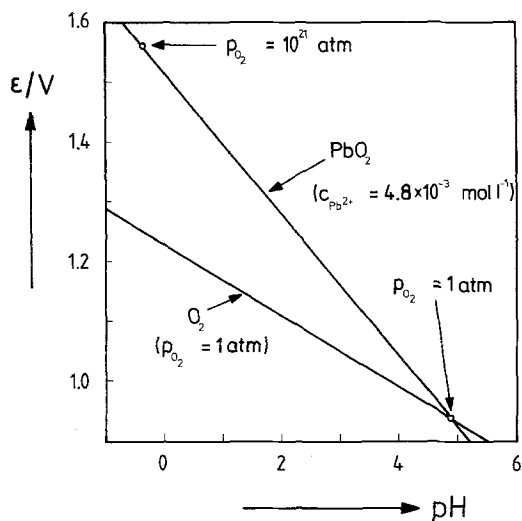
Fig. 1. Potential–pH diagram for the oxygen electrode ($p_{O_2} = 1$ atm) and the lead dioxide electrode ($c_{Pb^{2+}} = 4.8 \times 10^{-3}$ mol l^{-1}).

electrolyte solution at 298 K. As can be seen, the thermodynamic activity of oxygen in PbO$_2$ in equilibrium with an electrolyte with pH $= 4.9$ corresponds to a partial pressure of about 1 atm. The partial pressure of oxygen increases up to 10^{21} atm, corresponding to a pH value of -0.4. The measurements described in the following were carried out using electrolytes of pH values within these limits.

The equilibrium between lead dioxide and the gas phase given by

$$2O(\text{in PbO}_2) = O_2(g) \qquad (7)$$
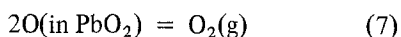
is not attained under the measurement conditions described below because of the extremely small reaction rate. On the other hand, the currentless reaction of the oxide with the electrolyte solution leads to an equilibrium between these phases within a few days [8].

As shown by Fischer and Rickert [3] the stoichiometric composition of the oxide depends on the chemical potential of oxygen in lead dioxide. Accordingly, PbO$_2$ samples with defined composition can be prepared by keeping them, currentless, in electrolyte solutions at given pH and Pb^{2+} concentration.

If, for example, a PbO$_2$ sample with a certain oxygen chemical potential is brought into contact with a solution corresponding to a smaller oxygen chemical potential of the oxide, the following

currentless reactions are possible without participation of Pb^{2+} ions:

(a) removal of oxygen corresponding to Equation 7,

(b) incorporation of hydrogen corresponding to the following reaction:

$$2H_2O = O_2(g) + 4H(\text{in PbO}_2) \qquad (8)$$
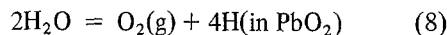
Both reactions result in a reduction of μ_{O_2}, but they are strongly inhibited [2].

If a sufficient amount of plumbous ions is present in the solution, the following reaction is favoured:

$$Pb^{2+}(aq) + 2H_2O = PbO_2 + 2H(\text{in PbO}_2)$$
$$+ 2H^+(aq) \qquad (9)$$
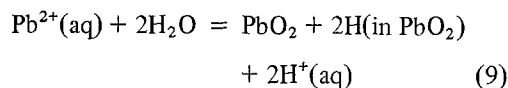
This means that hydrogen is incorporated into the oxide phase with simultaneous deposition of PbO$_2$, i.e. enlargement of the amount of lead dioxide. This currentless reaction may also be described as incorporation of 'Pb(OH)$_2$' into the oxide. The stoichiometry of lead dioxide is thus changed from a certain hydrogen content to a higher one associated with a decrease of the oxygen chemical potential [2, 3].

The alternative incorporation reaction of 'PbO' into the oxide, resulting in a production of oxygen vacancies with an enlargement of the amount of PbO$_2$, is of less importance, because it is shown by previous investigations [15, 18, 19] and by this paper, that interstitial protons are the main ionic defects of lead dioxide.

3. The PbO$_2$ sample in contact with an electrolyte solution

As will be described in detail below, the Hall-effect measurements have been carried out using disc-shaped lead dioxide samples. One surface of these discs was in contact with an electrolyte solution, while an electrical current entered at the other surface and left the oxide at opposite points close to the periphery of the sample (Fig. 2).

The transport of electrical charge (net current I) between these points may be achieved in two ways, in principle, namely, by an electronic current, $I_e(\text{PbO}_2)$, within the bulk of the oxide and by an ionic current, $I_{ion}(\text{ely})$, through the electrolyte.

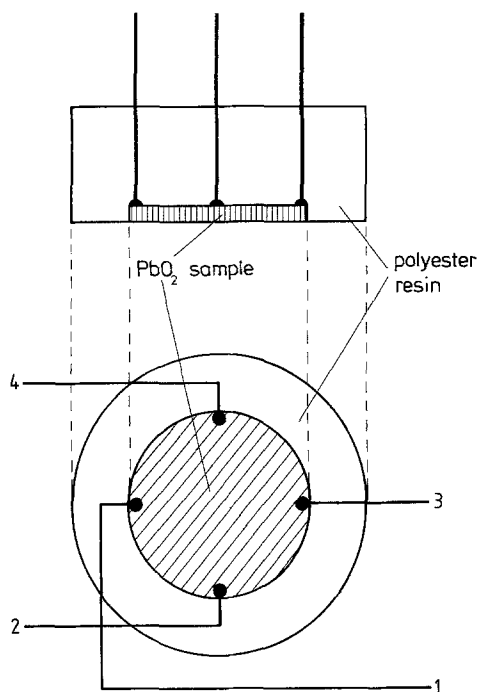$$I = I_e(\text{PbO}_2) + I_{ion}(\text{ely}) \qquad (10)$$

Fig. 2. Schematic representation of the PbO_2 sample for Hall-effect measurements.

The ionic charge transport in the solution is preceded and followed by electrochemical reactions at the phase boundary PbO_2/electrolyte. Accordingly, the total resistance R_{ion} for the ionic current contains three contributions:

$$R_{ion} = R_{cath} + R_{ely} + R_{anod} \qquad (11)$$

where R_{cath} is the resistance corresponding to the cathodic electrode reaction, R_{anod} is the resistance corresponding to the anodic electrode reaction and R_{ely} is the resistance corresponding to the transport reaction in the electrolyte.

Two processes should be discussed as the main electrode reactions:

(a) Hydrogen may be incorporated cathodically into the oxide or removed anodically. Thus, local changes of the stoichiometry will arise inside the PbO_2 sample, which are followed by diffusion processes in the solid phase.

(b) Lead dioxide may be dissolved cathodically or deposited anodically from the solution. By these processes the thickness of the sample is changed; it is increased in the area of the anodic electrode reaction and decreased in the area of the cathodic reaction.

If the values of the electronic resistance of the oxide sample, R_e, and of the ionic resistance, R_{ion}, become comparable, two consequences arise:

(a) The electronic current, I_e, through the solid conductors is smaller than the net current, I.

(b) If the current flows for a certain time, the sample will be changed with regard to its shape as well as to its stoichiometric composition.

This problem will be discussed principally and in detail in another paper [20].

In the present case of a PbO_2 sample in contact with an electrolyte, a calculation shows that the current applied to the sample flows almost completely as an electronic current through the oxide phase. The ionic current $I_{ion}(ely)$ may be neglected in comparison with $I_e(PbO_2)$, so that $I = I_e(PbO_2)$ holds with good approximation. This result depends on the very high electronic conductivity of lead dioxide [8] compared to the ionic conductivity of the electrolyte solution.

Therefore, noticeable changes of the thickness of the lead dioxide layer and of the stoichiometry of the sample are not to be expected and have not been observed.

4. Principle of the Hall-effect

The charge carriers moving in a current-carrying conductor are deflected from their original drift direction by the Lorentz force, which results from the presence of an external magnetic field at right angles to the direction of the current. Thus, an electric field arises, perpendicular to the direction of the current and that of the magnetic field, and a transverse voltage can be measured which is called the Hall voltage, U_H.

Using a conductor with a rectangular cross-section (Fig. 3), the following equation is valid [21]:

$$U_H = R_H \left(\frac{BI}{d} \right) \qquad (12)$$

where R_H is the Hall coefficient, B is the magnetic flux density, I is the sample current and d is the thickness of the sample.

Using the model of the free electron gas, an elementary treatment of the Hall-effect shows that, in the case of metals and degenerate n-semiconductors, R_H is associated with the concentration of the quasi-free electrons, c_e, by
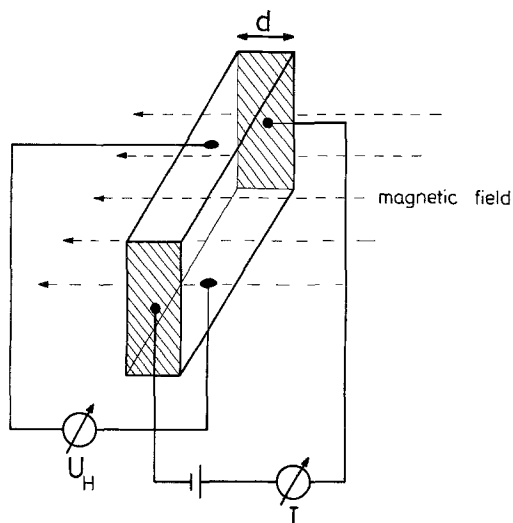
Fig. 3. Schematic representation of the experimental set-up for Hall-effect measurements using a conductor with a rectangular cross-section.

the following relation [21]:

$$R_H = -\frac{1}{c_e e} \qquad (13)$$

where e is the elementary charge.

From Equations 12 and 13 the following equation for the electron concentration results:

$$c_e = -\frac{BI}{edU_H} \qquad (14)$$

5. Experimental technique and measuring set-up

5.1. Preparation of the lead dioxide samples

By electrolytic deposition circular discs of β-lead dioxide with a diameter of 30 mm and a thickness of 2 mm have been prepared. A solution comprising of $Pb(NO_3)_2$ (0.4 mol l^{-1}) and HNO_3 (concn. 20 vol%, pH = $-$0.3) [2] was used as electrolyte for the anodic deposition. The oxide was deposited onto a graphite (DIABON R, Sigri) disc with suitable dimensions as substrate. The depositions were performed at room temperature with a current density of 10 mA cm^{-2}. At the beginning of the deposition, the graphite surface was covered almost completely and homogeneously by lead dioxide nuclei using a current density of 100 mA cm^{-2} for a short time. When deposition was completed, the PbO_2 layer was removed

from the graphite base and then brought into the necessary geometry by abrasion. By this method compact oxide discs of the size mentioned above were obtained, which were crack- and pore-free.

Each sample was supplied with four point contacts on one surface area as shown in Fig. 2. The samples, together with the contacts, were cast into an acid-resistant polyester resin (Palatal A 410, BASF) in such a way that the side of the PbO_2 disc bearing no contacts became the circular central part of the front surface of a lead dioxide–resin body of cylindrical geometry (Fig. 2). By further abrasion of this cylindrical body PbO_2 layers with thicknesses between 30 and 40 μm were achieved. The exact determination of the thicknesses was performed after the measurements had been completed. For this, the lead dioxide–resin bodies were sawn diagonally, and the thickness of the oxide layer measured using a microscope.

5.2. Adjustment of the stoichiometry of the samples

Various stoichiometric compositions of the oxide samples were achieved by keeping them currentless in $Pb(ClO_4)_2/HClO_4$ electrolytes ($c_{Pb(ClO_4)_2}$ = 4.8 × 10^{-3} mol l^{-1}) of certain pH values between $-$0.4 and 4.8 for a duration of about 20 days.

5.3. Hall-effect measurements

In order to conserve the adjusted stoichiometric composition of the oxide sample during measurements, the Hall-effect measurements were carried out with PbO_2 samples in contact with a thin electrolyte layer. The measuring equipment is shown schematically in Fig. 4.

Concerning the shape of the sample and the arrangement of the contacts, the method of van der Pauw [22] was used, by which Hall coefficients of samples with constant layer thicknesses but arbitrary shapes may be evaluated [23, 24].

The current flowing through the oxide layer was supplied by a precision galvanostat (Bank) and led into and out of the sample at the opposed contacts 1 and 3 (see Figs. 2 and 4). The Hall voltage between contacts 2 and 4 was measured with the help of a microvoltmeter (Keithley).
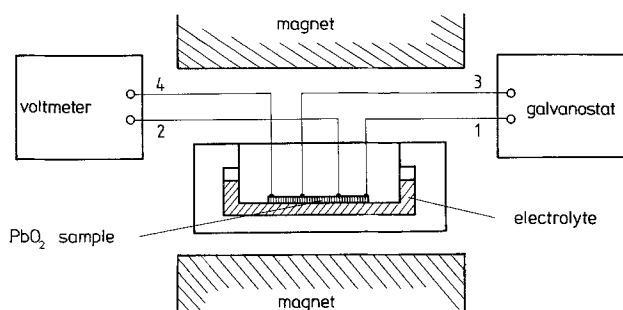
Fig. 4. Schematic representation of the measuring equipment for Hall-effect measurements with a PbO_2 sample in contact with an electrolyte solution.

The sample was then placed between the pole pieces of an electromagnet (Bruker) and the flux density of the magnetic field was evaluated to be $B = 1.68$ Tesla by means of a Hall probe (Siemens) and a special calibrating permanent magnet with defined field strength (Förster). The temporal fluctuations of the magnetic field amounted to a maximum of 1%. The measurements were carried out at room temperature.

6. Results of the Hall-effect measurements

The results of the measurements carried out with one of the samples are shown in Fig. 5. In this figure the Hall coefficient, R_H, divided by the layer thickness, d, is plotted vs the pH value of the solution in equilibrium with the PbO_2 layer. As can be seen from Equation 12, R_H/d is the quantity which can directly be determined from the
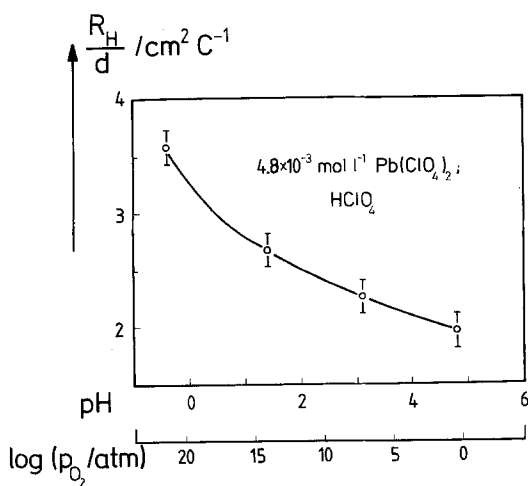
measurable quantities of the Hall voltage, U_H, sample current, I, and magnetic flux density, B.

The value of U_H is obtained following the procedure described in the ASTM-Standard F 76 [24]. Accordingly, the results of four voltage measurements between contacts 2 and 4 have been used, which follow from the two possible current directions and the two possible directions of the magnetic field.

Below the pH axis another abscissa is drawn where $\log [p_{O_2}(atm)]$ according to Equation 4 is plotted. p_{O_2} is the equilibrium partial pressure of oxygen in lead dioxide in contact with an electrolyte solution of Pb^{2+} concentration 4.8×10^{-3} $mol\,l^{-1}$ and the respective pH value.

In Fig. 6 the electron concentration c_e – the mean value for all samples – is plotted vs the pH values of the equilibrium electrolytes. It can be seen that the electron concentration in lead dioxide

Fig. 5. Hall coefficient, R_H, divided by the thickness of the PbO_2 layer, d, vs the pH value of the solution and vs the equilibrium partial pressure of oxygen (values for one sample).
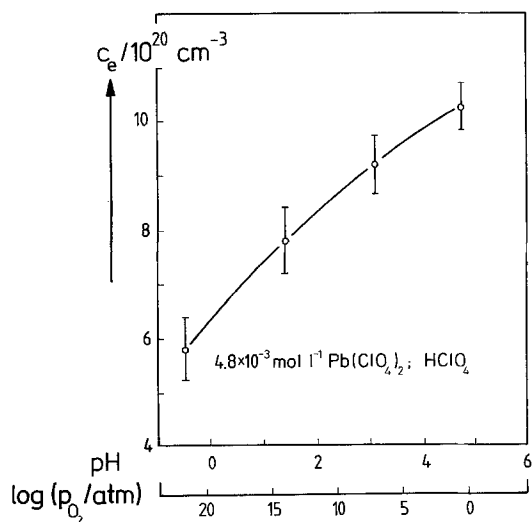

Fig. 6. Concentration, c_e, of the quasi-free electrons in PbO_2 as a function of the pH value and of the equilibrium partial pressure of oxygen.

in equilibrium with a highly acid solution (pH = − 0.4) amounts to 5.7×10^{20} cm^{-3}. The concentration of the quasi-free electrons increases with increasing pH value to an upper value of $c_e = 10.3 \times 10^{20}$ cm^{-3} (pH = 4.8).

In accordance with the conductivity measurements [8], these results show a quasi-metallic behaviour of the oxide within the whole range examined.

7. The electronic conductivity of lead dioxide

In a previous paper [8] the specific electronic conductivity, σ_e, of compact lead dioxide samples was measured as a function of the stoichiometry of the oxide. The various stoichiometric compositions of the samples were adjusted by equilibriating the latter with Pb(ClO$_4$)$_2$/HClO$_4$ solutions of a Pb^{2+} concentration equal to 5×10^{-3} mol l^{-1} but different pH values. The results of these measurements are shown in Fig. 7. Within the investigated range, the measured values of the electronic conductivity, σ_e, vary between 0.59×10^4 Ω^{-1} cm^{-1} (pH = − 1) and 0.76×10^4 Ω^{-1} cm^{-1} (pH = 4.9).

The results of these measurements may be compared directly with those of the Hall-effect measurements, although there is a small difference between the lead perchlorate concentrations of the electrolyte solutions used in both papers (5×10^{-3} mol l^{-1} and 4.8×10^{-3} mol l^{-1}).

At the same pH value, the equilibrium partial pressure of oxygen in lead dioxide in contact with the solution of the lower Pb^{2+} concentration is
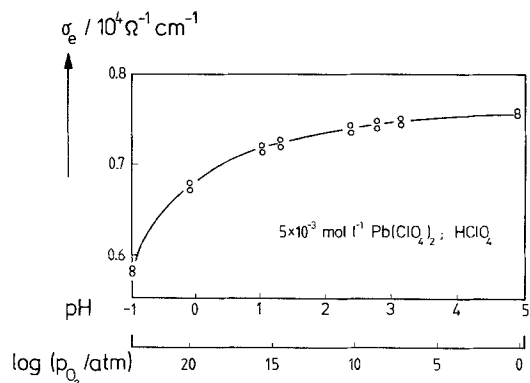
about 10% higher than the partial pressure corresponding to the other sample. The difference, δ, between the values of the samples amounts to about 1%. However, the effects of these deviations are much smaller than the limits of error for both measurements.

8. Discussion of the results of measurements

8.1. Mobility of the electrons

In Table 1, values of the electron concentration, c_e, and the specific conductivity, σ_e, are listed for various pH values of the electrolyte with practically the same Pb^{2+} concentration. The electronic conductivity is connected with the quantities: drift mobility, u_e; concentration, c_e; and elementary charge, e, according to the following equation [21]:

$$\sigma_e = e c_e u_e \qquad (15)$$

Thus

$$u_e = \frac{\sigma_e}{e c_e} \qquad (16)$$

Using this equation, values of u_e have been calculated which are also listed in Table 1 and plotted in Fig. 8 vs the pH of the electrolyte and vs log $[p_{O_2} (\text{atm})]$.

The mobility, u_e, of the electrons in lead dioxide varies between 70 (pH = − 0.4) and 46 cm^2 V^{-1} s^{-1} (pH = 4.8). The drift mobility decreases with increasing pH, i.e. with increasing density of the charge carriers, by about 35%. This reduction of the mobility with increasing electron concentration seems to be plausible because the concentration of the ionic disorder centres also rises in this direction [2, 3]. Due to this the probability of scattering processes of the quasi-free electrons at these defects is also increased.

8.2. The thermodynamic behaviour of the electrons

The measured electron concentration in PbO$_2$ – ranging between 5.7 and 10.3×10^{20} cm^{-3} – is so high that the thermodynamic behaviour of the electrons cannot be described using the Boltzmann approximation*. They are highly degenerate, i.e.

Fig. 7. Specific electronic conductivity, σ_e, of PbO$_2$ as a function of the pH value and of the equilibrium partial pressure of oxygen.

* The range of validity of the Boltzmann approximation for a special case may be seen from Fig. 9.

Table 1. Specific electronic conductivity, σ_e, electron concentration, c_e, and mobility, u_e, of the electrons in lead dioxide for various partial pressures of oxygen in equilibrium with the oxide

pH	p_{O_2}	σ_e $(\Omega^{-1}\,cm^{-1})$	c_e (cm^{-3})	u_e $(cm^2\,V^{-1}\,s^{-1})$
− 0.4	2×10^{21}	0.64×10^4	5.7×10^{20}	70
1.4	1×10^{14}	0.73×10^4	$7\,8 \times 10^{20}$	58
3.1	2×10^7	0.75×10^4	9.2×10^{20}	51
4.8	3	0.76×10^4	10.3×10^{20}	46

they have to be treated by applying Fermi–Dirac statistics [14, 21].

The treatment given in the following is based on the simplifying assumption that the actual density of states of the electrons in the conduction band of lead dioxide may approximately be described using a parabolic dependence on the energy. This means that the interaction between the quasi-free electrons and the ion cores of the lattice is taken into account by introducing a modified mass of the electrons – the so-called 'effective mass', m_e^* [14, 21].

According to Fermi–Dirac statistics the electron concentration, c_e, is given by the following relation [14]:

$$c_e = \frac{2}{(\pi)^{1/2}} N_C F_{1/2}\left(\frac{E_F - E_C}{kT}\right) \qquad (17)$$

The quantity N_C in Equation 17 is called the 'effective density of states'. Using the parabolic approximation for the density of states the following equation holds for N_C [14]:
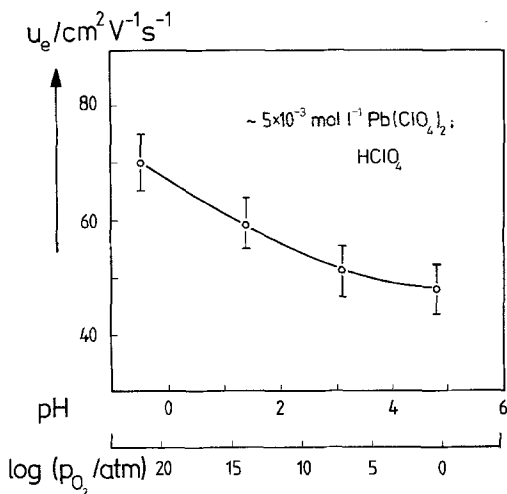
Fig. 8. Drift mobility, u_e, of the electrons in PbO$_2$ as a function of the pH value and of the equilibrium partial pressure of oxygen.

$$N_C = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2} \qquad (18)$$

where k is Boltzmann's constant, T is the temperature and h is Planck's constant.

The quantity $F_{1/2}[(E_F - E_C)/kT]$ in Equation 17 is known as the Fermi–Dirac integral 'one half'. E_F and E_C are the Fermi energy value and the energy value at the lower edge of the conduction band of one electron, respectively. Numerical values of $F_{1/2}$ may be taken from the tables [25] or may be calculated with the help of a suitable series expansion [26].

The argument of the Fermi–Dirac integral, which is sometimes also denoted by η, is connected to the chemical potential of the electrons, $\tilde{\mu}_e$, (referred to one particle) according to the relation [14]:

$$\eta = \frac{E_F - E_C}{kT} = \frac{\tilde{\mu}_e - \tilde{\mu}_e^0}{kT} + \ln\frac{c_e^0}{N_C} \qquad (19)$$

where $\tilde{\mu}_e^0$ denotes the chemical potential of the electrons in the standard state corresponding to the standard concentration c_e^0. It is stressed that all energy quantities in Equations 17–19 refer to one particle.

If the effective density of state is chosen as the standard concentration

$$c_e^0 = N_C \qquad (20)$$

and if in addition the following connection between $\tilde{\mu}_e$, $\tilde{\mu}_e^0$ and the thermodynamic activity, a_e, of the electrons is used

$$\tilde{\mu}_e = \tilde{\mu}_e^0 + kT \ln a_e \qquad (21)$$

for the argument, η, of the Fermi–Dirac integral $F_{1/2}$ applies

$$\eta = \ln a_e \qquad (22)$$

Using Equations 17 and 22 a fundamental relation between the concentration, c_e, and the activity,
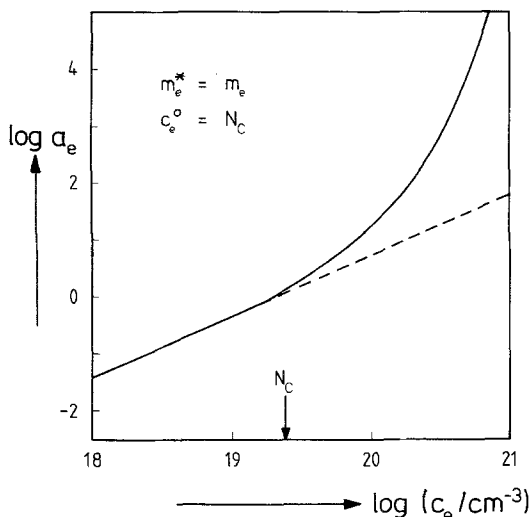
Fig. 9. Schematic representation of the relation between the electron activity, a_e, and the electron concentration, c_e, for the case $m_e^* = m_e$ and $c_e^0 = N_C$.

Fig. 10. Activity, a_e, of the electrons in PbO$_2$ as a function of the pH value and of the equilibrium partial pressure of oxygen.

a_e, of the electrons can be obtained. For the special case of $m_e = m_e^*$, this relation is sketched in Fig. 9, where $\log a_e$ is plotted vs $\log [c_e(\text{cm}^{-3})]$.

In the range of low electron concentrations ($c_e < N_C$), an approximately linear relation between a_e and c_e holds (range of validity of the Boltzmann approximation).

If electron concentrations are to be dealt with as they have been measured in the case of PbO$_2$, it can be seen that the activity, a_e, of the electrons increases much more strongly than the concentration, c_e, (range of degeneracy of the electrons). For a quantitative evaluation of the thermodynamic behaviour of the electrons in lead dioxide, a_e values must be calculated from the measured c_e values with the help of Equations 17 and 22. Accordingly, the value of the effective mass, m_e^*, has to be chosen. Assuming, as a first approximation, the effective mass, m_e^*, to be equal to the mass of the free electron, the variation of the activity, a_e, of the electrons in PbO$_2$ as a function of the pH value of the electrolyte (or as a function of the oxygen partial pressure p_{O_2}) is shown in Fig. 10.

To picture the variation of the chemical potential, $\tilde{\mu}_e$, of the electrons in PbO$_2$, the following connection between $\tilde{\mu}_e$, the electrochemical potential, $\tilde{\eta}_e$, of the electrons (identical with the Fermi energy, E_F) and the electrical potential, φ, is used:
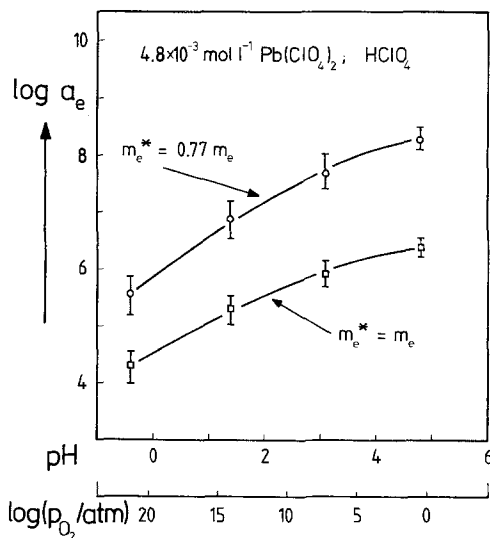
$$E_F = \tilde{\eta}_e = \tilde{\mu}_e - e\varphi \qquad (23)$$

Using Equation 20 also the following is obtained from Equation 19:

$$E_C = \tilde{\mu}_e^0 - e\varphi \qquad (24)$$

If the value of the electrical potential, φ, in lead dioxide is chosen to be zero, the lower edge of the conduction band, E_C, and the chemical standard potential of the electrons $\tilde{\mu}_e^0$ become equal. For this case the variation of the chemical potential, $\tilde{\mu}_e$, as a function of the pH value – or $\log [p_{O_2}(\text{atm})]$ – is sketched in Fig. 11. In addition, E_C has been taken as the zero point of the energy scale. As a conclusion, it follows from Figs. 10 and 11 that in the case of the approximation $m_e^* = m_e$ the values of a_e are considerably higher than unity, corresponding to chemical potentials $\tilde{\mu}_e$ lying at 0.25–0.40 eV above the standard value $\tilde{\mu}_e^0$. Within the investigated range the electron activity, a_e, increases by a factor of about 125:

$$\frac{a_e\,(\text{pH} = 4.8)}{a_e\,(\text{pH} = -0.4)} = 125 \qquad (25)$$

The corresponding concentration, c_e, increases by only a factor of about 1.8:

$$\frac{c_e\,(\text{pH} = 4.8)}{c_e\,(\text{pH} = -0.4)} = 1.8 \qquad (26)$$
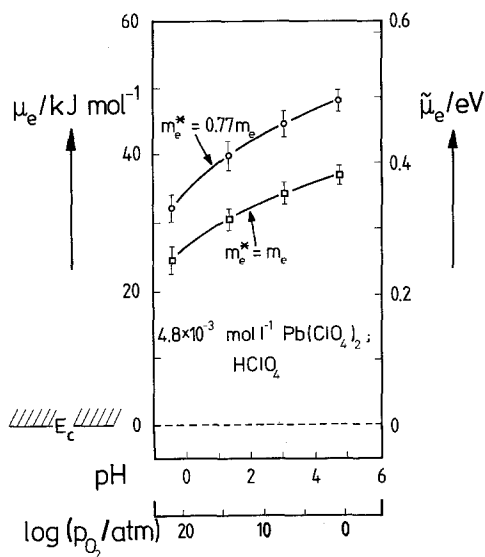
Fig. 11. Chemical potential, μ_e, (respectively, $\tilde{\mu}_e$) of the electrons in PbO_2 as a function of the pH value and of the equilibrium partial pressure of oxygen.

Table 2. Values of the Fermi–Dirac integral, $F_{1/2}$, of the argument, η, and of the electron activity, a_e, for different concentrations, c_e, of the quasi-free electrons in lead dioxide

c_e (cm^{-3})	$F_{1/2}(\eta)$[a]	η[a]	$\log a_e$[a,b]	a_e[a,b]
5.7×10^{20}	30.8	12.8	5.56	3.7×10^5
7.8×10^{20}	42.2	15.8	6.87	7.4×10^6
9.2×10^{20}	49.7	17.7	7.67	4.7×10^7
10.3×10^{20}	55.7	19.1	8.28	1.9×10^8

[a] For $m_e^* = 0.77 m_e$.   [b] With $c_e^0 = N_C$.

As has been discussed in detail in previous papers [2, 3], the assumption of a disorder model with interstitial protons and quasi-free electrons as main defects in lead dioxide leads to the following relation between the oxygen partial pressure, p_{O_2}, the deviation, δ, from the 'ideal stoichiometry' and the electron activity a_e:

$$p_{O_2} = \text{constant}''\delta^{-4}a_e^{-4} \tag{27}$$

Values of the quantity δ – proportional to the concentration, c_{H_i} of the interstitial protons if the mentioned disorder model is used – have been measured by Fischer and Rickert [3] as a function of the oxygen partial pressure. The results of these measurements can be summarized using the following proportionality:

$$\delta \sim p_{O_2}^{-1/8.4} \tag{28}$$

Assuming the validity of Equation 27 and using Equation 28 to substitute for the quantity δ, the following ratio of the activities a_e at pH values of − 0.4 and 4.8 has to be expected:

$$\frac{a_e \,(\text{pH} = 4.8)}{a_e \,(\text{pH} = -0.4)} = 530 \tag{29}$$

A value of the ratio of the electron activities which is in good agreement with this theoretical value may be calculated from the measured electron

concentrations if the following estimation of the effective mass of the electrons in lead dioxide is chosen:

$$m_e^* = 0.77 m_e \tag{30}$$

The values of $F_{1/2}(\eta)$, η, $\log a_e$ and a_e corresponding to this case are listed in Table 2. In addition, the corresponding variations of $\log a_e$ and $\tilde{\mu}_e$ are shown in Figs. 10 and 11. The values of a_e and $\tilde{\mu}_e$ are much higher in this case than for $m_e^* = m_e$ due to the influence of the lower effective mass of the electrons.

The estimation of m_e^* in PbO_2 given by Equation 30, which is based on the assumption that the disorder model involving protons and electrons as main defects is valid, is in good agreement with a value obtained from optical measurements [12], namely, $m_e^* = 0.8 m_e$.

To summarize the significance of the reported measurements, it can be said that the results support the above disorder model which was first discussed by Fischer and Rickert [3] and further substantiated by measurements concerning the permeation and diffusion of hydrogen in PbO_2 [18, 19]. In principle, a correct description of the microscopic behaviour of lead dioxide can be given using this disorder model.

Acknowledgement

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