

THE ELECTRONIC CONDUCTIVITY OF COMPACT LEAD DIOXIDE SAMPLES WITH VARIOUS STOICHIOMETRIC COMPOSITIONS

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Summary

The specific electronic conductivity, σ_e , of compact lead dioxide samples, deposited electrolytically, has been measured as a function of the stoichiometry of the oxide. The measurements were carried out using a four-point a.c. method. The various stoichiometric compositions of the oxide samples were obtained by equilibrating them with $\text{Pb}(\text{ClO}_4)_2/\text{HClO}_4$ solutions of different pH values. Lead dioxide in equilibrium with a very acid electrolyte, corresponding to a very small deviation from the ideal stoichiometric composition of the oxide, has a specific electronic conductivity $\sigma_e = 0.59 \times 10^4 \Omega^{-1} \text{cm}^{-1}$. The conductivity increases by about 30% up to the maximum deviation from ideal stoichiometry.

Zusammenfassung

Die spezifische elektronische Leitfähigkeit σ_e kompakter, elektrolytisch abgeschiedener Bleidioxidproben wurde als Funktion der Stöchiometrie des Oxids gemessen. Die Messungen wurden mit einer Vierpunkt-Wechselstrom-Methode ausgeführt. Die verschiedenen stöchiometrischen Zusammensetzungen der Oxidproben wurden dadurch eingestellt, dass die Proben mit $\text{Pb}(\text{ClO}_4)_2/\text{HClO}_4$ Lösungen verschiedener pH-Werte ins Gleichgewicht gebracht wurden. Bleidioxid im Gleichgewicht mit einem sehr sauren Elektrolyten — entsprechend einer sehr kleinen Abweichung von der idealen stöchiometrischen Zusammensetzung des Oxids — hat eine spezifische elektronische Leitfähigkeit $\sigma_e = 0.59 \times 10^4 \Omega^{-1} \text{cm}^{-1}$. Die Leitfähigkeit erhöht sich um etwa 30% bis hin zur maximalen Abweichung von der idealen Stöchiometrie.

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Introduction

Lead dioxide is a compound with a variable stoichiometric composition, for which, in earlier papers [1, 2], the formula $\text{PbO}_{2-\delta}(x\text{H}_2\text{O})$ has been used. Fischer and Rickert [2] have considered in detail possible disorder models of lead dioxide. As disorder centres oxygen vacancies, interstitial protons and quasi-free electrons have been discussed.

It was the aim of the present work to measure the electronic conductivity of compact lead dioxide samples as a function of the deviation, δ , from the ideal stoichiometry. For this the stoichiometric composition of the oxide has been adjusted using a currentless electrochemical process.

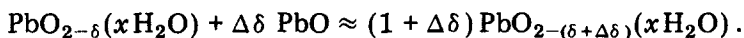
Investigations concerning the electronic conductivity of PbO_2 have been carried out by several authors with lead dioxide samples of different kinds, but none of these oxide samples was defined with regard to their stoichiometry. Kittel [3], Palmaer [4] and Thomas [5] have determined the specific electronic conductivity of PbO_2 ; the measured values were in the range 0.25×10^4 to $1.1 \times 10^4 \Omega^{-1} \text{cm}^{-1}$. Hall effect measurements [5] yielded Hall coefficients between -1.7 and $-3.7 \text{cm}^3 \text{A}^{-1} \text{s}^{-1}$ and electron concentrations between 10^{20} and 10^{21}cm^{-3} [5-7].

Based on n.m.r. investigations and measurements of the chemical shift of ^{207}Pb in lead dioxide, it was concluded that PbO_2 behaves as a metal with respect to the electrons [8, 9]. It is known, for a series of oxides [10], that they behave as metals in their electronic properties, *i.e.*, they have metallic conductivity. Mindt [6] has performed conductivity and Hall measurements with thin PbO_2 films. The samples were kept for several days in air. During this time a desorption of oxygen or an absorption of hydrogen was observed, related to an increase in the electron concentration from 5×10^{20} up to $8.7 \times 10^{20} \text{cm}^{-3}$ as well as to a decrease of the mobility by a factor of about three.

Adjustment of the stoichiometric composition of lead dioxide

If lead dioxide is in contact with an aqueous solution containing plumbous ions, and if the equilibrium between the oxide and the electrolyte has been established, the stoichiometric composition of $\text{PbO}_{2-\delta}(x\text{H}_2\text{O})$ is fixed by this equilibrium, and is determined by the pH value and by the Pb^{2+} concentration of the solution. This fact has been discussed in detail in earlier papers by Fischer and Rickert [2] and by Pohl and Rickert [11]. When changing the pH value and/or the Pb^{2+} concentration, a currentless adjustment of the stoichiometry of lead dioxide to the new composition of the electrolyte takes place by incorporation of PbO and/or $\text{Pb}(\text{OH})_2$ from the solution into the $\text{PbO}_{2-\delta}(x\text{H}_2\text{O})$, or by the removal of PbO and/or $\text{Pb}(\text{OH})_2$ from the oxide to the electrolyte.

Regarding the reaction between lead dioxide and PbO , the quantity, δ , in $\text{PbO}_{2-\delta}(x\text{H}_2\text{O})$ is changed as shown in the following equation:



In the corresponding reaction with $\text{Pb}(\text{OH})_2$ the quantity δ is changed in the same way, but, furthermore, the amount of water, x , in the oxide is increased.

The exact relation between the composition of the solution and the stoichiometric composition of lead dioxide — especially between the pH value at given Pb^{2+} concentration and the deviation, δ , from the ideal stoichiometry of the oxide — may be taken from the work of Fischer and Rickert [2].

From this paper it follows that δ increases by about one order of magnitude if the proton concentration of a solution with constant Pb^{2+} concentration decreases by two orders of magnitude, corresponding to a change of the pH value by +2. The maximum deviation, δ_{max} , from the ideal stoichiometry was measured to be 1.6×10^{-2} [14].

Experimental technique and measuring equipment

The measuring equipment for the conductivity measurements is shown schematically in Fig. 1. The investigations [12] were carried out using a four-point a.c. method, *i.e.*, current supply and voltage tapplings were separated in order to exclude the influence of conductor and contact resistivities. The alternating current (frequency 4 kHz) was supplied by a galvanostat. It was applied to the oxide sample by two silver rods, by which the sample was held. The voltage drop was measured using two needle-shaped platinum probes, and a lock-in amplifier, which also controlled the galvanostat.

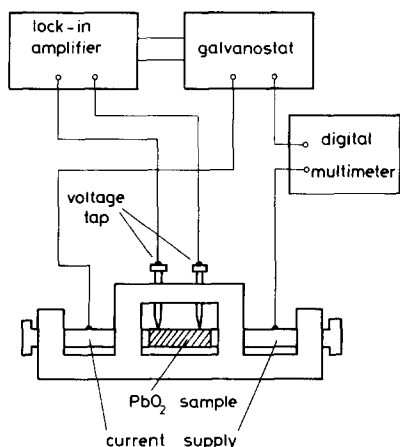


Fig. 1. Schematic representation of the measuring equipment for conductivity measurements.

The lead dioxide samples were prepared by electrolytic deposition onto a graphite base. The deposited compact oxide layer — being practically pure β - PbO_2 — was removed and then brought into the necessary geometry by abrasion.

The stoichiometry of the oxide samples was adjusted by keeping them, currentless, in $\text{Pb}(\text{ClO}_4)_2/\text{HClO}_4$ electrolytes of various pH values between -1 and 4.9 . The equilibrium restoration between an oxide sample and the solution was observed with the help of conductivity measurements, *i.e.*, the electronic conductivity of the sample was measured several times, at intervals of about 24 hours, until the value remained unchanged.

The above measurements were carried out with samples which had been removed from the solution, rinsed with distilled water and dried with filter paper. Following each measurement the sample was returned to the electrolyte.

It was the aim of this method to prepare the samples for conductivity measurements without changing their stoichiometric composition. It must be assumed from other measurements [12] that the stoichiometry of lead dioxide changes if the oxide is dried at elevated temperature. The direct contribution of the remaining moisture to the conductivity of the samples may be neglected because of the very high specific conductivity of the oxide.

Results and discussion

Figure 2 shows, by way of example, the results of conductivity measurements, representing the equilibrium restoration of a lead dioxide sample which had been taken from a $5 \times 10^{-3} \text{ M Pb}(\text{ClO}_4)_2$ solution with a very high HClO_4 concentration ($\text{pH} = -1$), and placed into an electrolyte having the same Pb^{2+} concentration but a much smaller acid concentration ($\text{pH} = 1.05$). From Fig. 2 it can be seen that during 200 h after the exchange

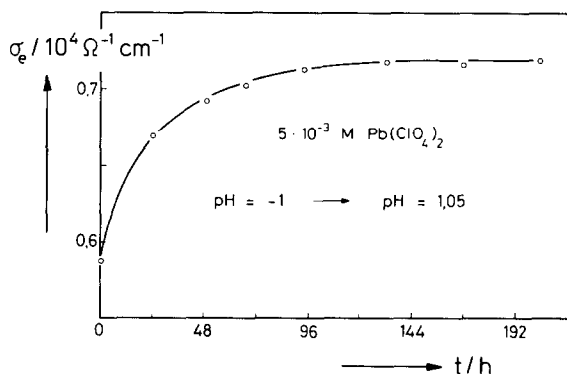


Fig. 2. Results of conductivity measurements, representing the equilibrium restoration of a PbO_2 sample after exchange of the electrolyte.

of the solution the specific conductivity of this oxide sample increased from $0.59 \times 10^4 \Omega^{-1} \text{ cm}^{-1}$ to $0.72 \times 10^4 \Omega^{-1} \text{ cm}^{-1}$.

Figure 3 shows the results of conductivity measurements which were carried out with the same lead dioxide sample, each after the equilibrium between the oxide and the electrolyte had been established. Lead dioxide in equilibrium with a $\text{Pb}(\text{ClO}_4)_2/\text{HClO}_4$ solution with a Pb^{2+} concentration of $5 \times 10^{-3} \text{ M}$ and $\text{pH} = -1$, corresponding to a very small deviation from the ideal stoichiometric composition of the oxide [2], has a specific electronic conductivity $\sigma_e = 0.59 \times 10^4 \Omega^{-1} \text{ cm}^{-1}$.

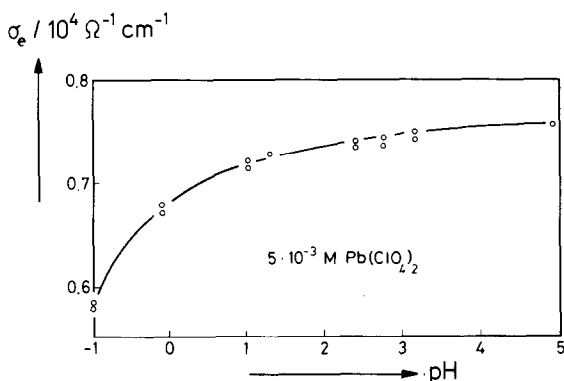


Fig. 3. Specific electronic conductivity, σ_e , of lead dioxide as a function of the pH of a $5 \times 10^{-3} \text{ M Pb}(\text{ClO}_4)_2$ solution.

The conductivity increases by about 30%, if the pH is changed by 6 units, corresponding to a change in δ of about three orders of magnitude [2]. A PbO_2 sample in equilibrium with an electrolyte with the same Pb^{2+} concentration but a pH value of 4.9, which corresponds to a value of δ near to the maximum deviation from the ideal stoichiometry, $\delta_{\text{max}} = 1.6 \times 10^{-2}$ [14], shows a conductivity of $\sigma_e = 0.76 \times 10^4 \Omega^{-1} \text{ cm}^{-1}$.

The quasi-free electrons inside the lead dioxide deviate in their behaviour from the Boltzmann approximation, because of their large concentration in the range between 10^{20} and 10^{21} cm^{-3} . They are highly degenerate, so that their behaviour may only be understood using Fermi-Dirac statistics [13].

The results of further measurements — *e.g.*, of the Hall coefficient of lead dioxide as a function of the stoichiometry — are necessary before a detailed discussion of the electronic behaviour of $\text{PbO}_{2-\delta} (x \text{ H}_2\text{O})$ becomes possible. The measurements indicate, however, that lead dioxide, even with a very small deviation from the ideal stoichiometry — *i.e.*, in equilibrium with a strongly acid solution — still exhibits a high conductivity. An alteration of the stoichiometry of the oxide up to the maximum deviation from its ideal value increases the specific conductivity by a factor of about 1.3.

Acknowledgment

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