A Comparative Study of Lead Oxide Modified Graphite Paste Electrodes and Solid Graphite Electrodes with Mechanically Immobilized Lead Oxides

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The cyclic voltammetry of red PbO, α-PbO₂, β-PbO₂ and BaPbO₃ was studied with two different types of electrodes in acidic and alkaline media. In one case, microcrystalline particles of lead oxides were mechanically immobilized on the surface of paraffin-impregnated graphite rod electrodes (PIGE), while in the other case, lead oxides were added to a paste of graphite and silicone oil. The overall behaviour of lead oxides in both electrodes is very similar to the well-known behaviour of electrodes made of lead oxide powders. The results show that the binder does not effect the overall electrochemistry of lead oxides. Moreover, the electrochemical reactions are more reversible for the paste electrode than in the case of the PIGE.

Key words: mechanical immobilization, modified graphite paste electrode, cyclic voltammetry, lead oxides.

INTRODUCTION

Numerous publications demonstrate the widespread applicability of the mechanical attachment of a solid compound to the surface of a suitable solid...
electrode (abrasive transfer technique)\textsuperscript{1–9} and modified graphite paste electrodes\textsuperscript{10–20} in the field of electrochemical analysis,\textsuperscript{10} for the solution of some physicochemical problems\textsuperscript{16–20} and for studying the electrochemistry of compounds which can be synthesized in large quantities and therefore can easily be characterized by other analytical or physical methods.\textsuperscript{1–9,14,15} Such characterisation cannot always be done when the compounds are synthesized as thin films on solid electrode surfaces. The electrochemical behaviour of solids at the surface of these two kinds of electrodes may be either identical or significantly different. In the first case, the solid is transferred onto the electrode surface by using mechanical immobilization.\textsuperscript{1–3} Even if the substance is very carefully prepared, it will be unevenly distributed on the electrode surface in the form of separate agglomerates. In the second case, the substance is introduced into the volume of the graphite paste electrode by evenly distributing the particles in the graphite paste. Because of the roughness of this electrode, the electrode reaction can to some extent proceed into the paste and larger amounts of substance can be involved. The second reason for differing results may be the presence of oil in the graphite paste as a binder between the graphite and sample particles. The oil of the paste electrodes may inhibit the electrochemical reactions, leading to a certain additional overpotential of reactions. Recently,\textsuperscript{21} we have shown that the overall behaviour of Prussian blue in both electrodes is very similar to the well-known behaviour of electrodes with an electrochemically synthesized Prussian blue film. Nevertheless, the binder affects the electrochemistry of Prussian blue to a certain extent. Differences have been observed for the modified paste electrode, particularly in acidic solutions. It is interesting to perform such comparative studies with other solids, for example, with oxide compounds as their electrochemistry has been sufficiently studied with graphite paste electrodes.\textsuperscript{10–12,22,23}

Here, the possibilities of both electrodes for the study of the behaviour of red PbO, α-PbO\textsubscript{2}, β-PbO\textsubscript{2}, and BaPbO\textsubscript{3} in acidic and alkaline media are examined. These studies are a necessary step towards electrochemically investigating phase stability, determining the degree of the oxidation of elements and assessing the electronic properties of such phases as, for example, Bi\textsubscript{2–x}Pb\textsubscript{x}Sr\textsubscript{2}Ca\textsubscript{2}CuO\textsubscript{8+δ}\textsuperscript{18} Bi\textsubscript{2–x}Pb\textsubscript{x}BaLaCuO\textsubscript{6+δ}\textsuperscript{20} and other cuprates. Literature data on the electrochemical behaviour of PbO are rather rare while the standard potentials of several different oxides are available.\textsuperscript{24} Without referring to other sources, Brainina and coauthors\textsuperscript{11} wrote that the oxidation of yellow PbO proceeds at +0.6 V whereas the oxidation of red PbO does so only at +1.2 V in 0.1 M NaOH solution. They suggested using this effect for the identification of these phases in mixtures. Other authors\textsuperscript{23} studied the electrochemical behaviour of PbO and PbO\textsubscript{2} in graphite paste electrodes prepared from graphite powder and where the aqueous electrolyte 0.1 M
NaOH was used as a binder. Unfortunately, the authors\textsuperscript{23} did not mention which modifications of lead oxides have been studied. There are many data about the electrochemistry of both modifications of lead dioxide in strongly alkaline and sulfuric acid solutions\textsuperscript{29,30} and of $\alpha$-PbO$_2$ in neutral media.\textsuperscript{31} No data on the electrochemical behaviour of BaPbO$_3$ are available.

**EXPERIMENTAL**

*Equipment*

All measurements were made with an Autolab (ECO-Chemie, Utrecht, Netherlands), an electrode stand VA 633 (Metrohm, Herisau, Switzerland), and a 386 personal computer. The reference electrode (Metrohm, Switzerland) was an Ag/AgCl electrode with 3 mol l$^{-1}$ KCl ($E = 0.208$ V vs. SHE). All measurements were performed in solutions, which were thoroughly deaerated with high-purity nitrogen for at least 10 min. The voltammograms were recorded at $22 \pm 1 ^\circ$C.

*Chemicals*

BaPbO$_3$ was prepared from high-purity powders of BaCO$_3$ and PbO$_2$ by conventional solid state procedure. Temperatures of 500–780 $^\circ$C were used for the thermotreatment of compressed tablets. Subsequent annealing was accomplished within a range of 530–1120 $^\circ$C. The phase purity of BaPbO$_3$ was controlled by X-ray analysis (Philips APD 1700, Cu-K$\alpha$ radiation). The data obtained by a full chemical analysis of samples showed this phase to have a barium deficit, and the composition of the phase was found to be $\text{Ba}_{0.80 \pm 0.03}\text{PbO}_{3.10 \pm 0.02}$. The structure is of rhombic perovskite type having the following unit cell parameters: $a = 6.024$, $b = 6.065$ and $c = 8.506$ Å. $\beta$-PbO$_2$ and $\alpha$-PbO$_2$ were prepared according to what has been described in Ref. 29, p. 681, and in Ref. 32, respectively. X-ray diffraction pattern showed that the synthesized samples are single-phase systems. The following chemicals (Merck) were used: yellow and red PbO, Pb$_3$O$_4$, NaClO$_3$, NaNO$_3$ and HNO$_3$. The electrolyte solutions were prepared from HCl (Merck, analytical grade) and KOH (Merck, analytical grade) using twice distilled ion-exchanged water. The graphite paste electrodes were made from graphite powder (Merck, Germany) and silicone oil (NM 500, Nünchritz, Germany).

*Electrode Preparation*

**Abrasive Transfer Technique**

A few milligrams of the solid compound were placed on a spot on a clean glazed porcelain tile. The lower circular surface of a paraffin-impregnated graphite rod electrode (PIGE) was gently rubbed on the compound spot to transfer the sample onto the electrode surface. The PIGEs were made by impregnating graphite rods with melted paraffin (m.p. 65 $^\circ$C) under vacuum. The graphite rods were the usual type of electrodes for spectrometric emission analysis with a diameter of 5 mm. Detailed descriptions of PIGEs and the abrasive transfer technique are published elsewhere.\textsuperscript{1}
Modified Graphite Paste Electrodes

The finely powdered solid compound was mixed with graphite powder in a ratio of $(5 \times 10^{-5} \text{ to } 5 \times 10^{-4})$ mol to 1 g graphite paste. This powder mixture was transferred to an agate mortar and mixed thoroughly for 1–2 min with 2–3% (mass fractions, $w$) of silicone oil. The homogeneous paste was filled into the electrode holder, which was an impregnated graphite rod enclosed in a Teflon tube several millimetres longer than the rod and forming a cup. The cup was filled with the paste, and the electrode surface was smoothed on the flat surface of a glazed tile or a glass plate. The diameter of the electrode surface was 5 mm. A suitable check of the homogeneity of the paste was the reproducibility of the peak currents obtained for a number of renewed electrodes.

RESULTS AND DISCUSSIONS

The background current of a graphite paste electrode and a PIGE in contact with 0.1 M HCl and 1 M NaOH exhibits some differences (see also Ref. 21). The cathodic range of the paste electrode is smaller in acid solution while the anodic range is smaller in alkaline solutions. Probably, the simple reason is that the true surface area of the paste electrode is much larger because of its roughness. The currents are equivalent in the potential range from 0.9 to –1.0 V for 0.1 M HCl and from 0.5 to –1.2 V for 1 M NaOH.

The Electrochemical Behaviour of Lead Oxides in Contact with a Hydrochloric Acid Electrolyte

In the synthesis of several copper-bismuth high-temperature superconductors, lead oxides are added to stabilize the structure. In combination with other physical and physicochemical methods, solid state voltammetry can help to elucidate the role of lead in the formation of the high-temperature superconducting phase. Thus, the questions arises what is the limit of solubility of lead oxides in the system and what is the oxidation state of lead in this phase. These problems have been studied for copper and bismuth in 123, 2201 and 2221 phases.16–20 From the specific composition of the copper and bismuth containing ceramics, it follows that the most suitable electrolyte is a weakly acidic solution of hydrochloric acid. For these studies, it is very important to know the voltammetric behaviour of the pure phases that constitute the complex system. Unfortunately, there are only insufficient literature data available concerning the linear sweep voltammetry of lead oxides with hydrochloric acid solutions as electrolyte.
Red PbO

From a thermodynamic point of view in acidic electrolytes, the reduction of PbO can be described as

\[ \text{PbO}_{\text{red}} + 2\text{H}^+ + 2\text{e}^- = \text{Pb}^0 + \text{H}_2\text{O} \]

\[ E^0 = +0.040 \text{ V vs. Ag/AgCl} \] (1)

At pH = 1, the formal potential of this reaction is -0.019 V vs. Ag/AgCl. Figure 1 shows typical cyclic voltammograms of red PbO at the PIGE and at the paste electrode in 0.1 M HCl. The reduction of PbO proceeds at one single peak C at the paste electrode. At the PIGE, the signal of PbO reduction exhibits a more complicate form and is less reproducible. As a rule, one observes at the descending part of the peak a shoulder (Figure 1b) or a second peak C2 (Figure 1a, dark line). The potential of peak C \( E_{p(C)} \) depends on the charge that is consumed during reduction. Figure 2a shows that \( E_{p(C)} \) shifts from \(-0.630 \pm 0.02\) V to \(-0.680 \pm 0.01\) V for the paste electrode and from \(-0.680 \pm 0.04\) to \(-0.730 \pm 0.03\) V for the PIGE, when the charge increases from 0.1 to 1.2 mC. The slope of the dependence of \( E_{p(C)} \) on \( Q \) is the

![Figure 1. Typical cyclic voltammograms of red PbO dispersed in the graphite paste electrode and immobilized at the PIGE surface. Scan rate: 100 mV s\(^{-1}\); electrolyte: 0.1 M HCl; starting potential: 1.0 V.](image)
same for the paste electrode as for the PIGE, but the absolute values are about 50 mV more negative for the PIGE (Figure 2a). The peaks are also much broader on the PIGE especially for charges above 4.5 mC (Figure 2b). In both cases the dependence of the half-width of the peak on $Q$ exhibits two parts with different slopes. This indicates that the mechanism changes with increasing charge, i.e. with an increasing amount of reacting PbO. For the PIGE and the graphite paste electrode, the reduction appears at more negative potentials as compared to the formal potential of reaction (1). This shift of the reduction is not only due to a mass-transport effect but it is certainly also the result of irreversibility. Two anodic signals ($A_1$ and $A_2$) appear in the cyclic voltammograms for the dissolution of elementary lead. They are observed at both electrodes. No response indicating a subsequent oxidation of Pb$^{2+}$ to Pb$^{4+}$ is observed.

Until now there are no mathematical models available which sufficiently describe the electrochemical conversions of solid compounds. Only limited features of the electrochemical processes can be studied so far. Thus, it

Figure 2. Plot of (a) potential and (b) half-width of peak C versus the amount of charge consumed during reduction of PbO dispersed in the graphite paste electrode (–○–) and immobilized on the PIGE (–●–). Conditions as in Figure 1.
is possible to estimate the role of diffusion in electrochemical processes by measuring the dependence of the peak current on the scan rate $v$. Under certain conditions, information can be obtained from plots of peak currents ($I_p$) and peak potentials ($E_p$) versus the logarithm of the scan rate, which says whether there are parallel or follow-up reactions present, and it is possible to determine the effective transfer coefficients $\alpha_n$ and $\beta_n$. Figures

Figure 3. Plot of peak currents of C, A1 and A2 versus scan rate (a), and versus square root of the scan rate (b) for electrochemical conversions of PbO dispersed in the graphite paste electrode. Electrolyte: 0.1 M HCl; concentration of PbO in the graphite paste: $5 \times 10^{-5} \text{ mol g}^{-1}$; starting potential: 1.0 V.
3 and 4 show such plots for the peaks C, A₁ and A₂ at the graphite paste electrode. The linear dependence of the peak current on the square root of the scan rate (Figure 3) indicates a diffusion character of the observed signals. The fact that two linear parts are present in the plot of $E_{p(C)}$ vs. the log $v$ with slopes of 60 mV and 120 mV, resp., indicates the presence of two competing electrode reactions (Figure 4a, curve C). Based on the equations $dE_p / d \log v = 0.059 / an$ or $\beta n$, the effective transfer coefficients can be cal-

![Graph](image-url)

Figure 4. Plot of (a) peak potentials, (b) half-width, and (c) peak currents of peaks C, A₁ and A₂ versus logarithm of scan rate for the electrochemical conversions of PbO dispersed in the graphite paste electrode. Electrolyte: 0.1 M HCl; concentration of PbO in the graphite paste: $5 \times 10^{-5}$ mol g⁻¹; starting potential: 1.0 V. On top is given the plot of peak currents versus logarithm of scan rate.
culated for the cathodic and the anodic processes. With respect to curve C, the effective transfer coefficient for the first step of the PbO reduction is near to 1 for scan rates below 50 mV s\(^{-1}\). For scan rates above 50 mV s\(^{-1}\), signal C is due to another reaction for which the effective coefficient is 0.5. Based on these results, we suggest that reaction (1) is accompanied by the following reactions:

\[
PbO_{\text{red}} + 2H^+ \rightarrow Pb^{2+}_{(gr.)} + H_2O \quad (2)
\]

and

\[
Pb^{2+}_{(gr.)} + 2e^- \rightarrow Pb^o_{(gr.)} \quad E^o = -0.334 \text{ V (vs. Ag/AgCl)} \quad (3)
\]

((gr.) indicates that the species is confined to the graphite surface).

Reaction (3) occurs at the graphite/electrolyte interface, whereas the reaction (1) occurs in the solid phase and may be written as:

\[
PbO + 2H^+_{(PbO)} + 2e^- = Pb^o_{(PbO)} + H_2O \quad (4)
\]

(The subscript (PbO) indicates the locus of the species).

Obviously, this reaction is slow and determines the electrochemical reduction of PbO in the presence of weakly acid solutions. Therefore, the half-width \(W_{1/2}\) of peak C will increase by more than 100 mV, if the scan rate increases from 5 to 100 mV s\(^{-1}\) (Figure 4b, curve C). With this interpretation one can well understand that the electrochemical dissolution of elementary lead proceeds along two different pathways:

\[
Pb^o_{(gr.)} = Pb^{2+} + 2e^- \quad \text{(peaks A\textsubscript{1})} \quad \text{and} \quad Pb^o_{(PbO)} = Pb^{2+} + 2e^- \quad \text{(peak A\textsubscript{2})}
\]

In both cases, elementary lead in its stable cubic modification is dissolved in the electrode process. In a previous \textit{in-situ} X-ray electrochemical study,\(^{34}\) it has been shown that cubic lead is formed in a topotactic solid-state electrochemical reduction of PbO. Peak A\textsubscript{1} is identical with the anodic dissolution peak of lead after preliminary cathodic plating from a Pb\(^{2+}\) solution. The reason for the appearance of peak A\textsubscript{2} at potentials which are more positive than those of A\textsubscript{1} can be as follows: Pb which is formed in a topotactic solid-state electrochemical reduction of PbO will be situated at such places where the PbO was present, and it might not be as well-crystallized as that deposited from solution. Pb that has been plated from a solution will be situated at the most active centres of the graphite surface, and it will be more ideally crystallized. This makes it understandable that the resistance of the lead-graphite interface can differ remarkably. The resistance of the
interface will be higher for the lead formed from PbO and it will be smaller or even negligible for the lead deposited from a solution. This model is consistent with the behaviour of the voltammetric peaks. Peak A₂ is very broad and is situated at more positive potentials. $E_p$ and $W_{1/2}$ of A₁ and A₂ depend linearly on the scan rate (Figure 4, curves A₁ and A₂). All parameters of peak A₁ are similar to the stripping peak for the reversible reaction: Pb$^{2+}$ + 2e$^-$ ↔ Pb⁰ at impregnated graphite electrodes.¹⁰⁻¹² For this peak, the slope of $E_p = f(\log v)$ is 26 mV (Figure 4a, curve A₁). The half-width of the peak slightly changes with the scan rate and it never exceeds 45 mV (Figure 4b, curve A₁). In case of A₂, there arises the question why the slope of $E_p = f(\log v)$ is only 56 mV although the peak is so broad (Figure 4b, curve A₂). Peak A₂ is more pronounced when the PbO is mechanically attached to a PIGE than in the case of its incorporation in a graphite paste electrode (Figure 1a, dark curve, and 1b). We suppose that the chemical reaction is faster at the PIGE than at the paste electrode. Additionally, the adsorption capacity of the PIGE is smaller than that of the paste electrode. At the PIGE, the dissolved Pb$^{2+}$ ions can easily escape the reaction (3) by diffusion. Then the reaction (4) will dominate. As the PbO is present at the PIGE in the form of larger agglomerates of particles, the ohmic resistance at the graphite-lead interface may also exceed the one in the case of paste electrodes.

$\alpha$-PbO$_2$ and $\beta$-PbO$_2$

For the following electrochemical reactions of PbO$_2$, the respective thermodynamic data are presented:

$$\text{PbO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{OH}^-$$

$$E_f = 1.747 - 0.059 \log a_{\text{OH}^-} - 0.0295 \log a_{\text{Pb}^{2+}} \quad (5)$$

$$3\text{PbO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{Pb}_3\text{O}_4 + 2\text{H}_2\text{O}$$

$$E_f = 1.014 - 0.059 \text{pH} \quad (6)$$

$$\text{PbO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{PbO} + \text{H}_2\text{O}$$

$$E_f = 0.899 - 0.059 \text{pH} \quad (7)$$

$$\text{PbO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{PbO} + 2\text{OH}^-$$

$$E_f = 0.040 - 0.059 \log a_{\text{OH}^-} \quad (8)$$
\[
PbO_2 + 4H^+ + 4e^- \rightarrow Pb^0 + 2H_2O \quad E_f = 0.458 - 0.059 \text{pH} \tag{9}
\]

At pH = 1, the formal potentials of these reactions are 1.747 – 0.0295 \log a_{\text{Pb}^{2+}}, 0.955, 0.840, 0.807 and 0.399 V, respectively.

Reactions (7) and (8) belong to the same reaction, the one formulated for an acidic solution and the other for an alkaline solution, but for a certain pH the formal potentials of both reactions must be identical. The difference of 33 mV in the formal potentials is due to different literature sources.

Figure 5 shows the cyclic voltammograms of the electrochemical conversion of \(\alpha\)- and \(\beta\)-PbO\(_2\) at the graphite paste electrode and at the PIGE using 0.1 M HCl as electrolyte. The voltammograms were recorded in the potential range from 1.4 to –1.5 V at a scan rate of 100 mV s\(^{-1}\). From this figure, it follows that both modifications can be reduced in consecutive steps to Pb\(^{2+}\) and Pb\(^0\):

\[
Pb^{4+} + 2e^- \rightarrow Pb^{2+} \text{ (peak C}_1\text{)} + 2e^- \rightarrow Pb^0 \text{ (peak C}_2\text{)} - e^- \rightarrow Pb^{2+} \text{ (peak A)} \tag{10}
\]

For both electrodes, the potentials of the first signal (peak C\(_1\)) are identical and they are determined only by the structure of PbO\(_2\). For the orthorhombic \(\alpha\)-PbO\(_2\), the potential of peak C\(_1\) is about 50 mV more positive than for the tetragonal \(\beta\)-PbO\(_2\) (Figures 5a and 5b). The standard potential of the \(\alpha\)-PbO\(_2\) electrode is only 7–8 mV more positive than that of the \(\beta\)-PbO\(_2\) electrode in sulfuric acid solution.\(^{29}\) With an increasing amount of consumed electric charge, the potential of peak C\(_1\) shifts only slightly by 2.5 mV/mC (Figure 6a). The peak potential fluctuates between + 0.95 and + 0.85 V, depending on the modification of PbO\(_2\) and also depending on the amounts of substance on the electrode surface. A comparison of these potentials with the formal potentials of reactions (5) to (9) shows that these processes may be involved in peak C\(_1\). The question which of these reactions is of main significance has to be studied in further experiments.

We propose that in weakly hydrochloric acid both hydrogen ions and water molecules participate in the electrode process with the generation of both Pb\(^{2+}\) ions and PbO or Pb\(_3\)O\(_4\) in the pre-electrode layer. The half-width \(W_{1/2}\) of peak C\(_1\), in contradiction to its potential, already depends on the type of electrode that is used. Peak C\(_1\) is always significantly broader for the PIGE than for the paste electrode (Figures 7a and 7b, curve C\(_1\)). \(W_{1/2}\) also depends on the structure of the PbO\(_2\). Peak C\(_1\) is about 70 mV broader for the \(\beta\)-PbO\(_2\) than for \(\alpha\)-PbO\(_2\) (Figures 7c and 7d, curve C\(_1\)). These figures
show that the $W_{1/2}$ of peak $C_1$ is always significantly smaller in case of the graphite paste electrode than in case of the PIGE, and it is smaller for $\alpha$-PbO$_2$ than for $\beta$-PbO$_2$ at both electrodes. This means that the electrode process is more reversible at the paste electrode than at the PIGE, and the electrode process is more reversible for $\alpha$-PbO$_2$ than for $\beta$-PbO$_2$. 

Figure 5. Typical cyclic voltammograms of (a) $\alpha$-PbO$_2$ and (b) $\beta$-PbO$_2$ dispersed in graphite paste electrode (...) and immobilized on the PIGE (---). Scan rate: 100 mV s$^{-1}$; electrolyte: 0.1 M HCl; concentrations of PbO$_2$ in the graphite paste: (...) $2.0 \times 10^{-4}$ mol g$^{-1}$; (---) $0.8 \times 10^{-4}$ mol g$^{-1}$; starting potential: 1.4 V.
The next step in the reduction of PbO$_2$ (peak C$_2$) depends in a complex way on the type of the electrode used and also on the structure of PbO$_2$. α-PbO$_2$ yields identical peak potentials for both electrodes (Figure 5a), which are determined by the amount of PbO$_2$ at the electrode surface (Figure 6b). The half-widths of the peaks (250 to 280 mV) depend only slightly on the amount of charge in case of the paste electrode. In case of the PIGE, the half-widths increase from 250 to 380 mV when the amount of charge increases from 10 to 34 mC (Figure 7b, curves C$_2$). For β-PbO$_2$, the line of $E_p$ values of C$_2$ versus the amount of charge is situated about 85 mV more positive than the same line for α-PbO$_2$ (Figure 6b), and the shape of the peaks is very much determined by the amount of the substance at the electrode surface (Figure 5b). Peak C$_2$ is much sharper for β-PbO$_2$ than for α-PbO$_2$, if the concentration of the substance in the paste is equal or less than $8 \times 10^{-5}$ mol g$^{-1}$ (Figure 5b, curve ---), but the values $W_{1/2}$ of β-PbO$_2$ will exceed those of α-PbO$_2$, if the concentration of the substance in the paste is higher than $2.5 \times 10^{-4}$ mol g$^{-1}$ (Figures 5b and 6d, curve C$_2$). This becomes visible only when the graphite paste electrode is used. Because of the complex form of peak C$_2$ when the PIGE is used (Figure 5b, curve −), the measurement of the consumed charge is not correct. Therefore, these data are not given in Figures 6 and 7. Figure 5b shows, however, that the second step of the reduction of β-PbO$_2$ at the PIGE proceeds with an overpotential of about 100 mV as compared to the reduction of this compound at the graphite paste electrode.
Much more significant differences occur in the oxidation of cathodic reaction products (peak A). For α-PbO₂ (Figure 5a), in this oxidation, there is one particular signal, which is sharper in case of the paste electrode. Additionally, it is situated at more negative potentials in case of the paste electrode than of the PIGE. For β-PbO₂, peak A (Figure 5b) is usually divided into two badly separated peaks. This is especially typical of the PIGE. Signal A had a fully symmetric form when the amount of the β-PbO₂ in the graphite paste was reduced to amounts of less than $1 \times 10^{-4}$ mol g⁻¹ graphite powder (curve ---, Figure 5b).
From scheme (10), it follows that the areas below peaks C₁, C₂ and A should be equal. In Table I, the areas below peaks C₁, C₂ and A are compared. The Table shows that the area below peak C₁ is 2.5 times smaller than the area below peak C₂ (for α-PbO₂). For the graphite paste electrode, the areas below peaks C₁ and C₂ are roughly equal to each other, i.e. for all concentrations of α-PbO₂ in the graphite paste. Q(C₁)/Q(C₂) values will be always smaller than 1, if the solution is stirred during the experiment. This will also apply to β-PbO₂, if the concentration of the compound in the paste is smaller than 1 × 10⁻⁴ mol g⁻¹. The ratio Q(C₂)/Q(A) will be always near to 1, if the ratio Q(C₁)/Q(C₂) is equal or higher than 1.

All this indicates that the processes that we observe are more complicated than the simple reactions (5) to (9). Obviously, in case of the PIGE, at peak C₁, there is not the entire amount of PbO₂ consumed but only a certain part of it (reactions which are similar to (7) – (8) may proceed only partially). As Q(C₁)/Q(C₂) will be always smaller than 1, if the solution is stirred, reactions as formulated in Eq. (5) will take place. Such reactions preferably occur with α-PbO₂. The presence of chloride ions in the electrolyte shifts the formal potential of such reactions to more negative potentials. Because of

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<th>Table I</th>
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<tr>
<td>The ratio between the charges consumed in the stepwise reduction of PbO₂ and the following oxidation of the cathodic reaction products (n = 5, P = 0.95)</td>
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<tr>
<td>PIGE</td>
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<tr>
<td>α-PbO₂</td>
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<td>Q(C₁)/Q(C₂)</td>
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<tr>
<td>0.33 ± 0.12</td>
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<td>β-PbO₂</td>
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<td>Q(C₁)/Q(C₂)</td>
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<td>It is not correctly determined</td>
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<td>Graphite paste electrode</td>
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<td>Concentration &gt; 1 × 10⁻⁴ mol g⁻¹</td>
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<td>α-PbO₂</td>
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<td>1.08 ± 0.09</td>
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<td>β-PbO₂</td>
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<td>Q(C₁)/Q(C₂)</td>
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<td>0.75 ± 0.05</td>
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<td>Concentration &lt; 1 × 10⁻⁴ mol g⁻¹</td>
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<td>α-PbO₂</td>
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<td>β-PbO₂</td>
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</tbody>
</table>
the rough surface of the graphite paste electrode and its large adsorption capacity, the soluble products of the reaction cannot easily disappear from the electrode surface during the experiment, and one observes a well-developed response of the reduction of $\text{Pb}^{2+}_{\text{(gr.)}}$ to $\text{Pb}^0_{\text{(gr.)}}$ (peak C$_2$). In this case, $Q(C_1)/Q(C_2)$ almost equals 1. Peak A has characteristics, which are similar to the anodic stripping peak of lead in 0.1 M HCl.$^{10–12}$ For larger amounts of $\beta$-PbO$_2$ and in case of the PIGE, the processes of successive reduction are more complicated. Because of larger agglomerates of the substance on the electrode surface, the solution reaction (5) has not enough time to be completed, and the solid-state reactions (7) to (8) occur at the electrolyte/PbO$_2$/graphite interface. Most probably, the reaction of PbO$_2$ leads to the formation of layers of lower oxides, which are known to be poor conductors.$^{35}$ When PbO$_2$ is reduced at $–1.5$ V vs. Ag/AgCl in contact with a neutral electrolyte and when, at a later time, the lead is oxidised during an anodic scan, one observes an almost ohmic line at negative potentials, and the entire oxidation peak exhibits a strong ohmic distortion (Figure 8). The formation of poorly conducting films of lower lead oxides will stop the further reduction. The reduction process can be formulated as follows:

$$\text{PbO}_2 + 2x\text{H}^+ + 2xe^- \rightarrow \text{PbO}_{2-x_{\text{solid}}} + x\text{H}_2\text{O} \text{ (peak C}_1\text{)}$$

(11)

At peak C$_2$, the lower lead oxides, including PbO, are reduced to metallic lead. It is possible that the reduction also includes that of dissolved Pb$^{2+}$ ions:

![Figure 8. Typical anodic voltammograms of lead, which was obtained by the reduction of PbO$_2$ mechanically attached to a PIGE. Reduction potential: $–1.5$ V; electrolyte: 0.1 M KNO$_3$.](image)
\[ \text{Pb}^{2+}_{(\text{gr.})} + \text{PbO}_{2-x}^{(\text{solid})} + 2(2-x)\text{H}^+ + (2(2-x)+2)e^- \rightarrow \]
\[ \text{Pb}^0_{(\text{gr.})} + \text{Pb}^0_{(\text{solid})} + (2-x)\text{H}_2\text{O} \]  

(12)

From this, it follows that the ratio of charges \( Q(C_1)/Q(C_2) \) is smaller than 1 and that the ratio \( Q(C_2)/Q(A) \) is always higher than 1. Just this can be observed in experiments. The fact that the half-width of signal \( C_2 \) is larger and more strongly depending on the amount of consumed charge in case of the PIGE \( (dW_{1/2}/dQ = 6 \text{ mV/mC}) \), Figure 7b, curve \(-\text{■—} \) than in case of the graphite paste electrode \( (dW_{1/2}/dQ = 1 \text{ mV/mC}) \), Figure 7b, curve \(-\text{□—} \) can be easily explained by the fact that a nonconducting film will affect the measurement more strongly when a PIGE electrode is used than in case of a graphite paste electrode where insulating particles are very effectively embedded in the graphite. This also influences the shape of the anodic signal \( A \). A certain amount of lead is present at the electrode surface in close contact with the graphite. This lead is oxidized at the sharp and more negative part of \( A \). This part of the signal is identical with the usual anodic stripping signal of lead after plating Pb from solutions. The broad shoulder of \( A \) at more positive potentials is most probably due to the oxidation of lead which was formed in a solid-state reduction of PbO\(_2\) and which does not so well adhere to the graphite particles. Obviously, the signal, which is obtained when lead is plated from a solution, is observed in case of \( \alpha\text{-PbO}_2 \) (Figure 5a, curve \( \cdots \) ) and also in case of small amounts of \( \beta\text{-PbO}_2 \) (Figure 5b, curve \( \text{---} \) ) in the graphite paste electrode. As is the case with PbO, no response of a further oxidation \( (\text{Pb}^{2+} \rightarrow \text{Pb}^{4+}) \) has been ever observed in a hydrochloric acid electrolyte.

**BaPbO\(_3\)**

Figure 9 shows typical cyclic voltammograms of the electrochemical conversion of BaPbO\(_3\) at the PIGE (a) and at the graphite paste electrode (b) in 0.1 M HCl. The voltammograms were recorded in the potential range from 1.2 to \(-1.5 \text{ V} \) at a scan rate of 100 mV s\(^{-1}\). It is generally assumed that the oxidation state of lead is 4+ in the BaPbO\(_3\) phase. In this connection, we expected that the voltammetry of this phase will resemble the voltammetry of PbO\(_2\). Unlike in case of PbO\(_2\), where the reduction of the studied substance occurs in two subsequent steps (peak \( C_1 \) and \( C_2 \), Figure 5), we observed four peaks \( (C_0, C_1, C_2, C_3) \) in this case. The anodic signals \( A_1 \) and \( A_2 \) are practically identical with those of PbO (Figure 1). The first two signals \( (C_0 \) and \( C_1 \) ) vanish during the following cycles, both in case of the PIGE (Figure 9a) and the graphite paste electrode (Figure 9b). Peak \( C_3 \) also vanishes when the PIGE is used and significantly decreases in case of the graphite paste.
electrode. Signal $A_1$ only occurs in the second cycle but decreases in the third cycle, peak $A_2$ also decreases, and peak $A_3$ is never observed when BaPbO$_3$ is studied using the PIGE. Under the same experimental conditions, but using the graphite paste electrode, peak $A_1$ does not change,

![Image of cyclic voltammograms](image)

Figure 9. Typical cyclic voltammograms of BaPbO$_3$ (a) immobilized at the PIGE surface and (b) dispersed in a graphite paste electrode. Scan rate: 100 mV s$^{-1}$; electrolyte: 0.1 M HCl; starting potential: 1.2 V.
whereas peak $A_2$ decreases and becomes broader. Peak $A_3$ occurs in the first cycle only. All observed signals are better developed in case of the graphite paste electrode than in case of the PIGE. Figure 10 shows cyclic voltammo-

![Cyclic voltammograms](image)

Figure 10. Typical cyclic voltammograms of BaPbO$_3$ (a) immobilized at the PIGE surface and (b) dispersed in a graphite paste electrode recorded in range potential from 1.2 to $-0.4 \text{ V}$ (---) and from 1.2 to 0.2 V (---). Scan rate: 100 mV s$^{-1}$; electrolyte: 0.1 M HCl; starting potential: 1.2 V.
grams of BaPbO$_3$ recorded in a limited potential range from 1.2 V to –0.4 V and from 1.2 V to 0.2 V to exclude the interference of products of peaks C$_2$ and C$_3$ in the elucidation of peaks C$_0$ and C$_1$. Peak C$_1$ was not present in the voltammetry of PbO$_2$. As can be seen from Figure 10, there is no separate anodic signal indicative of an oxidation of cathodic reaction products of C$_1$. There is one anodic peak A$_3$ that corresponds to the cathodic peaks C$_0$. Peak A$_3$ never occurs when the solution is stirred. Therefore, it is assumed that peak C$_0$ corresponds to a reduction of Pb$^{4+}$ in the electrode layer after a preliminary chemical reaction of the type:

$$\text{BaPbO}_3 + 6\text{H}^+ \rightarrow \text{Ba}^{2+} + \text{Pb}^{4+}_{(\text{gr.})} + 3\text{H}_2\text{O} \quad (13)$$

$$\text{Pb}^{4+}_{(\text{gr.})} + 2e^- \rightarrow \text{Pb}^{2+}_{(\text{gr.})} \quad \text{(peak C}_0) \quad (14)$$

Then peak C$_1$ may correspond to the solid-phase reaction:

$$\text{BaPbO}_3 + 2\text{H}^+ + 2e^- \rightarrow \text{BaPbO}_2 + \text{H}_2\text{O} \quad (15)$$

The limited rate of transport of H$^+$-ions in the solid phase may cause a retardation of the following electrochemical oxidation of BaPbO$_2$. In addition, in contrast to BaPbO$_3$, which has metallic conductivity,$^{36, 37}$ BaPbO$_2$ is dielectric. The formation of a poorly conducting film may stop the further reduction and subsequent oxidation. Therefore, the Pb$^{2+}$ ions from reaction (14) may be crucial only for peak A$_3$. As can be seen from Figure 9, only an insignificant part of the entire BaPbO$_3$ is reduced in the course of reactions (13–15). Probably, these reactions are only confined to a surface layer. The electrochemical conversion of the bulk phase of BaPbO$_3$ occurs at peaks C$_2$ and C$_3$. Metallic lead is the product of these electrochemical reactions. Shape and position of A$_1$ and A$_2$ are indicative of this. The ratio of the areas below peaks C$_2$ and C$_3$ to the areas below peaks A$_1$ and A$_2$, i.e. $Q(C_1 + C_2) / Q(A_1 + A_2)$, is equal to 2, within the limits of experimental error $\pm 0.15$ for $n = 5$ and $P = 0.95$. This indicates that four electrons are involved in the reduction of BaPbO$_3$. Studying the features of the phase formation and properties of BaPbO$_3$, the authors$^{36}$ have shown that the samples are microinhomogeneous. They change both their structure and morphology in the thermotreatment process. The lead ions are present in two oxidation states, Pb$^{4+}$ and Pb$^{2+}$. We think that all these features influence the electrochemistry of BaPbO$_3$. Only thin surface layers ($\approx 50$ $\mu$m)$^{36}$ take part in the reduction at peaks C$_0$ and C$_1$ (13–15). The bulk of BaPbO$_3$ is stepwise reduced at peaks C$_2$ and C$_3$:
Peak C₂,

\[
\text{BaPb}^{IV}_{1-x}\text{Pb}^{II}_x\text{O}_3 + 4xH^+ + 4xe^- \rightarrow \\
\text{BaPb}^{IV}_{1-2x}\text{Pb}^{II}_{2x}\text{O}_{3-2x} + 2xH_2O
\]  

(16)

and peak C₃,

\[
\text{BaPb}^{IV}_{1-2x}\text{Pb}^{II}_{2x}\text{O}_{3-2x} + 4(1+x)H^+ + 4(1+x)e^- \rightarrow \\
\text{Ba(OH)}_2 + \text{Pb}^0 + (1+2x)H_2O
\]

(17)

where \(x\) is a hole with a 2⁺ charge.

The anodic signals A₁ and A₂ correspond to the cathodic peaks C₂ and C₃. The solid phase BaPbO₃ will be gradually consumed during the subsequent cycles, if the graphite paste electrode is used (Figure 9b), but signal C₃ will vanish already after the first cycle if the PIGE is used (Figure 9a). The cyclic voltammograms are very similar to those of PbO (Figure 1) because in this case signal C₂ is due to the reduction of PbO as a product of the electrode reaction which is responsible for the arising of peaks A₁ and A₂. Because of the complex shape of the voltammograms, we could not study the dependence of \(E_p(C₁)\) on \(Q\).

### Electrochemical Behaviour of Lead Oxides in Contact with an Alkaline Electrolyte

There is information available about the voltammetric behaviour of PbO, \(^{11}\) PbO and PbO₂, \(^{23}\) α- and β-PbO₂ \(^{29}\) in 0.1 M NaOH \(^{11,23}\) and 4.7 M NaOH \(^{21,22}\) aqueous solutions. 1 M aqueous NaOH solution was used as a supporting electrolyte in our work. We think that such a concentration is more acceptable for the experiments since it is not as high as in Refs. 29 and 30 but eliminates the possibility of hydrolysis in the electrode layer as it is possible in Ref. 11 and 23.

### PbO

Figure 11 shows typical cyclic voltammograms of red PbO at the PIGE and at the graphite paste electrode in the potential range 1.0 V and -1.5 V (starting at -0.4 V). With both electrodes the reduction of PbO proceeds practically at the same peak (C₁) potential and shifts to more negative values with increasing amounts of PbO at the surface of the electrode (Figure 12a). In case of the PIGE, the ascending part of the reduction signal is usually
complicated by the occurrence of the shoulder C. This is very similar to what has been described\textsuperscript{23} for the graphite paste electrode with the 0.1 M NaOH solution as binder. The authors\textsuperscript{23} suppose that signal C corresponds to the reduction of a small amount of HPbO\textsubscript{2} formed by the chemically dissolution of PbO according to

\[ \text{PbO} + \text{OH}^- \rightarrow \text{HPbO}_2^- \]  \hspace{1cm} (18)

\[ \text{HPbO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Pb}^0 + 3\text{OH}^- \]  \hspace{1cm} (19)

whereas peak C\textsubscript{1} is most probably due to the electrochemically induced\textsuperscript{34} solid-state reduction of PbO:

\[ \text{PbO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Pb}^0 + 2\text{OH}^- \]  \hspace{1cm} (20)
In case of the graphite paste electrode with the organic binder, the reaction (18) is inhibited and practically all PbO is reduced via reaction (20). The voltammograms following the first cycle (Figure 13) indicate that the share of the reactions (18) and (19) increases with time. The increase in the peak currents of all peaks is possibly caused by the introduction of increasing amounts of the paste into the electrode reaction because of an increasing roughening\textsuperscript{21} of the paste surface which itself is caused by the oxygen evolution occurring at potentials more positive than 0.9 V. This can also be derived from the increasing background current at positive potentials (see Figures 11 and 13a). The opposite effect is observed in case of the PIGE, \textit{i.e.}
all peaks decrease after cycling (Figure 13b). Sometimes the descending part of peak C₁ is also complicated when the paste electrode is used. Possibly, the partial overlapping of signal C and peak C₁ causes the half-width of the peak to increase more, with increasing amounts of PbO in case of the PIGE as compared to the graphite paste electrode (Figure 14a). In contrast to the hydrochloric acid solution, we observe two steps of electrochemical oxidation of metallic lead (Pb⁰ → Pb^{2+} → Pb^{4+}, peaks A₁ and A₂) when 1 M NaOH is used as a supporting electrolyte. The potential and half-width of these peaks do not depend on the electrode used (Figures 12b, 12c and 14b). Apparently, the anodic peak A₁ is due to the following reaction:
The resulting ions $\text{HPbO}_2^-$ are further oxidized according to:

$$\text{HPbO}_2^- + 3\text{OH}^- - 2\text{e}^- \rightarrow \text{PbO}_3^{2-} + 2\text{H}_2\text{O} \quad \text{(peak A}_2\text{)}$$  \hspace{1cm} (22)
soluble products only. Peak C₂ occurs already in the second cycle when a graphite paste electrode is used with an electrolytic binder.²³ In principle, our results are identical with the results reported in Reference 23. A small shift of the reduction potentials to more negative values and a shift of the oxidation potentials to more positive values in our experiments is due to an increased concentration of the electrolyte. But \( W_{1/2} \) (< 200 mV) is always smaller in our case than it has been observed (> 270 mV) in Ref. 23. This means that the electrochemical conversions of PbO are more reversible at the PIGE and at the graphite paste electrode with the oil as a binder than those at the carbon paste electrode having an electrolytic binder.

\( \alpha\text{-PbO}_2 \) and \( \beta\text{-PbO}_2 \)

Centeno et al.²³ studied the voltammetry of lead dioxide in graphite paste electrodes with an electrolyte binder (0.1 M NaOH) and discussed the mechanism of some reactions. Unfortunately, there is no information about the modification of PbO₂, which has been studied by them. Chartier and Poisson³¹ have studied the cathodic reaction of \( \alpha\text{-} \) and \( \beta\text{-PbO}_2 \) electrodes in alkaline electrolytes and found that the mechanism of reduction differs for the two polymorphs. For \( \beta\text{-PbO}_2 \), it has been suggested that the electrode reaction mechanism consists of two processes: (a) a dissolution reaction:

\[
\alpha\text{-PbO}_2 + H_2O + 2e^- \rightarrow HPbO_2^- + OH^- \tag{23}
\]

and (b) a solid-phase reaction:

\[
\beta\text{-PbO}_2 + H_2O + 2e^- \rightarrow PbO + 2OH^- \tag{24}
\]

For \( \alpha\text{-PbO}_2 \), they suggested that the reduction process occurs exclusively in the solid phase but they were unable to give an exact mechanism. Carr and Hampson²⁹,³⁰ concluded that the adsorption of electrode products is involved in the electrode reaction of \( \alpha\text{-PbO}_2 \). They proposed the following sequence of reactions:

\[
\alpha\text{-PbO}_2 + H_2O + 2e^- \rightarrow PbO_{ads} + 2OH^- \tag{25}
\]

\[
PbO_{ads} \rightarrow PbO_{aq}
\]

\[
PbO_{aq} + OH^- + H_2O \rightarrow Pb(OH)_3^- 
\]
where PbO$\text{ads}$ and PbO$\text{aq}$ represent PbO adsorbed at the interphase and dissolved in solution, respectively. A further reduction to Pb$^\circ$ has not been discussed by the authors.\textsuperscript{29}

The cyclic voltammograms of both modifications of PbO$_2$ were recorded from 1.0 V to –1.5 V at a scan rate of 100 mV s$^{-1}$ (see Figure 15). As in the case of hydrochloric acid, two cathodic peaks (C$_1$ and C$_2$) occur but the separation of peaks C$_1$ and C$_2$ is better. In principle, this effect has been also observed by Centeno et al.\textsuperscript{23} but these authors have not paid attention to the difference in peak sizes and describe these peaks with the following reactions:

\[
PbO_2 + 2\text{OH}^- \rightarrow \text{PbO}_3^{2-} + \text{H}_2\text{O}
\]

\[
\text{PbO}_3^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HPbO}_2^- + 3\text{OH}^- \quad (\text{peak C}_1)
\]

(26)

and the subsequent reduction process:

\[
\text{HPbO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Pb}^\circ(\text{s}) + 3\text{OH}^- \quad (\text{peak C}_2)
\]

(27)

There are no differences in the peak potentials of peak C$_1$ of $\alpha$- and $\beta$-PbO$_2$ for both the PIGE and the graphite paste electrode (Figure 16a) when the amount of PbO$_2$ is very small (< 2 mC). These peak potentials are less positive than those for the graphite paste electrode with an electrolytic binder (0.1 M NaOH),\textsuperscript{23} but more negative than those for the electrode with lead dioxide electrodeposited onto platinum.\textsuperscript{29,30} The difference in the peak potentials of C$_1$ occurs for $\alpha$- and $\beta$-PbO$_2$ when the amount of reacting PbO$_2$ at the electrode surface ranges from 2.5 to 10 mC. In this case, the potential of peak C$_1$ of $\alpha$-PbO$_2$ shifts from – 0.12 to –0.15 V while that of $\beta$-PbO$_2$ shifts from – 0.12 to –0.22 V (Figure 16a) with a confidence range of ±0.02 V ($n = 5, P = 0.95$). At the lead dioxide electrode, the difference between $E_p(\alpha\text{-PbO}_2)$ and $E_p(\beta\text{-PbO}_2)$ reaches 0.12 V in 4.7 M NaOH.\textsuperscript{29} The half-width of peak C$_1$ depends on the electrode used (Figure 17a). $W_{1/2}$ is always smaller for the PIGE than for the graphite paste electrode. There are no differences in the half-width of $\alpha$- and $\beta$-PbO$_2$ peaks when the PIGE is used (Figure 17a). When the graphite paste electrode is used under the same conditions, the half-width of peak C$_1$ is much bigger, especially for higher amounts of $\alpha$-PbO$_2$ (Figure 17a). In case of $\beta$-PbO$_2$, the half-width of peak C$_1$ slightly depends on the amount of reacting PbO$_2$, and independently of Q, the difference between the half-widths of the PIGE and the graphite paste electrode remains practically constant (about 40 mV). Besides, when the solution is
stirred, signal $C_1$ decreases to a constant value for both electrodes. Under the same conditions, peak $C_1$ remains practically constant for $\alpha$-PbO$_2$. It seems that in our case the first step of the electrochemical reduction mecha-

Figure 15. Typical cyclic voltammograms of (a) $\alpha$-PbO$_2$ and (b) $\beta$-PbO$_2$ dispersed in the graphite paste electrode (---) and immobilized at the PIGE surface (—). Scan rate: 100 mV $s^{-1}$; electrolyte: 1 M NaOH; starting potential: 1.0 V.
Mechanism of $\alpha$- and $\beta$-PbO$_2$ is not different from the mechanism suggested for the reduction of lead dioxides deposited onto platinum.\textsuperscript{21} The reduction process of $\alpha$-PbO$_2$ occurs exclusively in the solid phase according to scheme (25). For $\beta$-PbO$_2$, the electrode reaction mechanism consists of (a) a dissolution reaction (23) or (26) and (b) a solid-phase reaction (24).

The second step of PbO$_2$ reduction (peak C$_2$, Figure 15) occurs at potentials below $-1.05$ V for the graphite paste electrode, and below $-1.17$ V for the PIGE (Figure 16c). This peak is narrower for the paste electrode than for the PIGE (Figure 17b). There are no differences between the peak potentials and half-widths of $\alpha$- and $\beta$-PbO$_2$. The slope of a plot of $E_p$ vs. $Q$ is the same for both electrodes ($11 \pm 1$ mV/mC), which is also true of peak C$_1$ in case of PbO reduction (Figure 12a). In contradiction to PbO, where the ratio $Q(C_1)/Q(A)$ was about 1, for PbO$_2$ the ratio $Q(C_2)/Q(A_1)$ is $1.9 \pm 0.2$. This indicates that the main part of PbO$_2$ is reduced in a 4e$^-$ step at peak C$_2$. The
potential and half-width of the anodic peak A₁ neither depend on the kind of electrode nor on the structural modification of PbO₂ (Figures 16b and 17c). Though, for the PIGE, there is a larger difference between the charges of peak A₁ and A₂, these two peaks have almost equal charges in case of the graphite paste electrode (Figure 15). The potential of peak A₂, which corre-

![Figure 17](image_url)

**Figure 17.** Plot of half-width of peaks versus the amount of consumed charge of (a) C₁, (b) C₂ and (c) A₁ for the electrochemical conversions of α-PbO₂ (○, •) and β-PbO₂ (○, ●) dispersed in the graphite paste electrode (○, ●) and immobilized at the PIGE surface (○, ●) in contact with a 1 M NaOH electrolyte. Experimental conditions as in Figure 15.
sponds to the further oxidation of Pb$^{2+}$, is almost independent of the experimental conditions. It is necessary to note that at low scan rates (5–10 mV s$^{-1}$) and with a low concentration of PbO$_2$ in the paste ($1 \times 10^{-4}$ mol g$^{-1}$), a linear relationship between $I_p(C_2)$ and $\sqrt{v}$ passing through the origin is observed for both lead dioxides. This indicates that diffusion is limiting the currents. The authors$^{29}$ observed the same plot of $I_p$ vs. $\sqrt{v}$ and explained this by the diffusion of OH$^-$ ions in the solution toward the electrode surface. They have calculated the diffusion coefficient of OH$^-$ ions for the reduction of $\alpha$-PbO$_2$ in alkaline solution. The obtained value of $10^{-7}$ cm$^2$ s$^{-1}$ is too small to be the true diffusion coefficient of the OH$^-$ ions in aqueous solution. These data can be interpreted by a possible diffusion of OH$^-$ ions through a PbO layer or, more probably, of H$^+$ only, at the electrode surface at peak C1. At higher scan rates and/or higher concentrations of PbO$_2$, a linear relationship between $I_p$ and $\sqrt{v}$ is also observed but it does not pass through the origin. In this case the current limitation can be due to the diffusion of ions in a film of PbO formed at the electrode surface at the peak C1. A tentative explanation of the observed effects can be formulated as follows:

\begin{equation}
\{2\text{PbO}_2\}\text{PbO} + 3\text{OH}^- \rightarrow \text{HPbO}_2^- + \{\text{PbO}_3^{2-}\} + \text{H}_2\text{O} \tag{28}
\end{equation}

\begin{equation}
\{\text{PbO}_3^{2-}\} + 3\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{Pb}^0 + 6\text{OH}^- \tag{29}
\end{equation}

\begin{equation}
\text{HPbO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Pb}^0 + 3\text{OH}^- \tag{30}
\end{equation}

where $\{\text{PbO}_2\}\text{PbO}$ denotes the bulk phase $\{\text{PbO}_2\}$ covered by a surface layer of PbO which has been formed at C1. Lamache and Bauer$^{15}$ have suggested that an electrochemically induced dissolution of a solid is well possible in the case of carbon paste electrodes and approached these reactions theoretically. From a thermodynamic point of view, reaction (29) may occur (Ref. 24, p. 232) at potentials more negative than the reaction of the solid-state reduction of PbO under the same conditions. May be that this is the reason why peak C$_2$ of PbO$_2$ is more negative than peak C$_1$ of PbO. For such reactions as (28–30), a direct interaction with ions of the electrolyte is necessary, and the amount of these ions in the electrode surface layer will be increased when the true surface of the electrode is roughened. Therefore, the peak potential of C$_2$ is more positive in case of the graphite paste electrode than in case of the PIGE. Because of the multistep nature of the overall reaction, the half-width of peak C$_2$ (Figure 17b) is considerably bigger for PbO$_2$ than for PbO (Figure 14b) although the number of electrons involved in the reduction is 4 for PbO$_2$ and 2 for PbO. It should be noted that the $W_{1/2}$ of C$_2$
(≤ 350 mV for the PIGE and ≤ 250 mV for the graphite paste electrode) and the \( W_{1/2} \) of the same peak in Ref. 19 (350 mV) are comparable. Peaks \( A_1 \) and \( A_2 \) cannot be distinguished from those of PbO in alkaline electrolytes.

**BaPbO\(_3\)**

Cyclic voltammograms of barium metaplumbate (Figure 18) show that the reduction of this phase also occurs at two peaks, \( C_1 \) and \( C_2 \). But in this case \( E_p(C_1) \) is shifted to more negative and \( E_p(C_2) \) to more positive potentials than for PbO\(_2\). The potentials of the anodic peaks \( A_1 \) and \( A_2 \) (≈ 0.6 V) are fully identical with the peaks of PbO and PbO\(_2\). After the anodic signal \( A_2 \), peak \( A_3 \) (0.8 V) is always observed when a graphite paste electrode is

\[
\begin{align*}
&\text{Figure 18. Typical cyclic voltammograms of BaPbO}\(_3\) dispersed in the graphite paste electrode (---) and immobilized at the PIGE surface (--). Scan rate: 100 mV s\(^{-1}\); electrolyte: 1 M NaOH; starting potential: 1.0 V.}
\end{align*}
\]
used. Peak A₃ will be only present, if the voltammograms are recorded in the potential range from 1 V to –0.4 V, i.e. when peaks C₂ and A₁ are not recorded (Figure 19). Under the same experimental conditions, signal A₃ will not occur, if a PIGE is used. Obviously, peak C₁ corresponds to the reduction process

$$\text{BaPbO}_3 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Ba(OH)}_2 + \text{HPbO}_2^- + \text{OH}^-$$  \hspace{1cm} (31)

It is possible that the very rough surface of the graphite paste electrode may serve as a trap for the HPbO₂⁻ ions, and we observe the oxidation peak of this ion as signal A₃. It seems that a well-polished surface of the PIGE is not well suited for the accumulation of HPbO₂⁻ ions on the electrode surface. It is possible that these ions diffuse away from the electrode layer and do not take part in a subsequent oxidation. The peak potential of C₁ does not depend on the kind of electrode used. A linear relationship between $E_p$ and $Q$ is observed with a slope of 2.5 mV/mC for both the PIGE and the graphite paste electrode (Figure 20a). Within the limits of experimental error (± 0.3), this is the same slope as it has been observed in the case of α- and β-PbO₂ on the graphite paste electrode (Figure 17a). Unlike PbO₂, the

Figure 19. Typical cyclic voltammograms of BaPbO₃ dispersed in the graphite paste electrode (---) and immobilized at the PIGE surface (—). Scan rate: 50 mV s⁻¹; electrolyte: 1 M NaOH; starting potential: 1.0 V.
barium metaplumbate yields a plot of $E_p$ vs. $Q$, which is situated at potentials which are about 120 mV more negative. The peak will be practically symmetrical and narrower, if a PIGE is used, especially for $Q > 10$ mC (Figure 21a). The following peak C$_2$ is also symmetrical and narrower for BaPbO$_3$ than for PbO$_2$ at the PIGE. If the graphite paste electrode is used, peak C$_2$ will be narrower for BaPbO$_3$ than for PbO$_2$, but the descending part of peak C$_2$ is partly obscured by the discharge of the supporting electrolyte. Therefore, an exact calculation of the area below the peak is not possible. For this reason, we determined the charge, which is consumed in the electrode reaction by extrapolation of the descending part of peak C$_2$ to the background current (see the dotted line for peak C$_2$ in Figure 18). The plot of $E_p(C_2)$ vs. $Q$ has the same slope (15 ± 1 mV/mC) for both electrodes. This slope is only 4 mV/mC larger than the slope of the same plots for PbO (Figure 12a) and PbO$_2$ (Figure 16c). Unlike for PbO$_2$ and PbO, in the present case, the cathodic peak, which is responsible for peak A$_1$ occurs at more

![Figure 20](image_url)

Figure 20. Plot of peak potentials versus the amount of consumed charge of (a) C$_1$, (b) A$_1$ and (c) C$_2$ for the electrochemical conversions of BaPbO$_3$ dispersed in the graphite paste electrode (−o−) and immobilized at the PIGE surface (−●−). Experimental conditions as in Figure 18.
positive potentials. For example, the difference between the peak potentials of C2 of PbO2 and BaPbO3 will amount to 100 mV, if a graphite paste electrode is used, and to 120 mV, if a PIGE is used. A comparison of the charges of peaks C1 and C2 shows that, as in the case of PbO2, only a small part (< 0.1 of it) takes part in the reaction (31). Almost all BaPbO3 is reduced at peak C2 to elementary lead, the oxidation of which is observed as peak A1. The parameters of this oxidation process (Figures 20b and 21b) are fully identical with those, which have been observed in case of PbO and PbO2. A comparison of the areas below peak C2 and A1 shows that the ratio $Q(C_2)/Q(A_1)$ is always significantly bigger than 2 for both the PIGE (2.56 ± 0.05) and the graphite paste electrode (2.35 ± 0.12). This strange re-

![Figure 21. Plot of half-width of peaks versus the amount of consumed charge of (a) C1, (b) A1 and (c) C2 for the electrochemical conversions of BaPbO3 dispersed in the graphite paste electrode (---) and immobilized at the PIGE surface (—). Experimental conditions as in Figure 18.](image-url)
sult can be understood, if we take into account that the real composition of the studied phase is Ba$_{0.8}$PbO$_{3.1}$ and not BaPbO$_3$:

$$\text{Ba}_{0.8}\text{PbO}_{3.1} + 1.6\text{OH}^- + 4.6\text{e}^- \rightarrow 0.8\text{Ba(OH)}_2 + \text{Pb}^0 + 3.1\text{O}^{2-} \quad (32)$$

Thus, the reduction of Ba$_{0.8}$PbO$_{3.1}$ requires 4.6 and not 4.0 electrons. This means that the expected ratio for $Q(C_2)/Q(A_1)$ should be 2.3, which is near to the experimental value. The observed deficit of barium and the surplus of oxygen are not unusual. On the contrary, it is very difficult to obtain a stoichiometric phase. It has been shown$^{36}$ that samples of barium metaplumbate are microheterogeneous and that the ratio of Ba/Pb changes from 0.80 to 0.97. The amount of oxygen ranges between 2.9 and 3.8. Apparently, the nonstoichiometry is the reason for the metallic conductivity, which is not typical of oxides with a perovskite structure. The specific resistance of Ba$_2$PbO$_{3+x}$ ranges between 15–300$^{36}$ or 200–600 $\mu\Omega$ cm$^{37}$ and depends on the temperature of the thermotreatment, i.e. on the nonstoichiometry of the samples. For the oxide compound with the nonstoichiometric composition, it is typical that the holes are located at the oxygen, and it is possible that the generation of O$^-$ takes place.$^{20}$ For our sample, the ionic composition can be given as Ba$_{0.81}$Pb$_{0.48}^{IV}$Pb$_{0.57}^{II}$O$_{1.36}^{II}$O$_{1.72}$. The presence of O$^-$ and of Pb$^{4+}$ and Pb$^{2+}$ (the authors of Ref. 36 confirmed this by RFES) may be the reason for the observed shape of the voltamograms of BaPbO$_3$ (Figure 18) and for all observed experimental data. Thus, the presence of oxygen, which easily accepts electrons, may shift the reduction potentials to more positive values than for PbO or PbO$_2$. The peak will be narrower because the reduction is not divided into several steps as in the case of PbO$_2$.

**CONCLUSIONS**

This study was primarily aimed at elucidating the differences and similarities which are observed in the voltammetry of solid materials when they are incorporated into a graphite paste electrode and mechanically immobilized at the surface of a graphite electrode. The most striking result is that the presence of an organic binder (paraffin oil) in the paste electrodes does not inhibit the electrode processes as one could expect. The second interesting result is that the paste electrode seems to keep the educts and products of the electrode reaction so much more effectively at the electrode surface that the chemical reversibility of the voltammetric systems is better than in case of solid particles, which are immobilized at the surface of the electrode. In the latter case, the chemical and electrochemical dissolution of the small
amounts of immobilized particles result in a more pronounced loss of substance during the electrochemical transitions, most probably due to an effective diffusion of dissolved products into the adjacent solution.

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SAŽETAK

Usporedba elektrodâ od oksidâ olova u grafitnoj pasti i vezanih na čvrsti grafit

Nina Zakharchuk, Stefan Meyer, Britta Lange i Fritz Scholz

Za usporedbeno proučavanje elektroda od crvenog PbO, α-PbO2, β-PbO2, i BaPbO3 priredenih na dva različita načina primijenjena je ciklička voltammetrija. U prvom su slučaju mikrokristalne čestice oksida olova imobilizirane na površini štapićaste grafitne elektrode impregnirane parafinom (PIGE), a u drugom su slučaju oksidi olova dodani pasti pripravljenoj od grafa i silikonskog ulja. Tako pripremljene elektrode ponašaju se slično dobro poznatim elektrodama pripravljencima od praškastih oksida olova. Također je utvrđeno da su elektrokemijske reakcije na elektrodama od paste silikona i grafa reverzibilnije nego PIGE.