# The preparation and behaviour of Ti/Au/PbO$_2$ anodes

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Ti/Au/PbO$_2$ electrodes have been prepared and their stability in H$_2$SO$_4$ (2–12 mol dm$^{-3}$) has been studied. It has been found that incorporation of a gold layer between the Ti substrate and the PbO$_2$ decreases the resistance of the electrode. The corrosion of an electrode polarized anodically increases with H$_2$SO$_4$ concentration especially above 8 mol dm$^{-3}$ H$_2$SO$_4$.

## 1. Introduction

During recent years, there have been several studies on the preparation of Ti/PbO$_2$ anodes [1–3]. Such anodes are now available for commercial use [4].

Ti/PbO$_2$ anodes have two advantages over the graphite/PbO$_2$ ones usually used:

(a) The electrochemical stability of the titanium substrate permits its re-use at the end of the anode's life.

(b) A more compact cell can be constructed with Ti/PbO$_2$ anodes.

The main problem with this type of anode is the growth of TiO$_2$ between the titanium substrate and the deposited PbO$_2$, as TiO$_2$ has a high electric resistivity and a high potential barrier. The voltage loss in the bulk of the electrode is, therefore, high and its practical application is not good.

Wabner *et al.* [1] maintain that in 1 mol dm$^{-3}$ H$_2$SO$_4$ such anodes fail within 100 h or so, unless a special pre-treatment is applied to the titanium surface prior to coating. The pre-treatment is claimed to suppress the growth of TiO$_2$ between the titanium substrate and the deposited PbO$_2$.

In the present paper the titanium-supported PbO$_2$ electrode was modified by introducing an electroplated gold layer between the titanium and the PbO$_2$. Its stability and anodic polarization characteristics were examined in aqueous H$_2$SO$_4$ solutions [5]. Finally the electrode was used in the electrochemical oxidation of MnSO$_4$.

## 2. Experimental details

### 2.1. *Preparation of the electrodes*

The titanium was etched initially for 30 min in boiling 20% HCl then gold film was electroplated onto it from a citrate acid bath (Tecnor CF, Galvanotec, Suisse), followed by the deposition of PbO$_2$ from a plating bath of 350 g dm$^{-3}$ Pb(NO$_3$)$_2$ and 30 g dm$^{-3}$ Cu(NO$_3$)$_2$ at 65° C with a current density of 2.5 A dm$^{-2}$. The pH of the bath was maintained constant (at pH 3) by periodic addition of CuCO$_3$. Most studies have used electrodes containing 3.8 g Au m$^{-2}$ and 529 g PbO$_2$ m$^{-2}$.

### 2.2. *Measure of stability*

The electrochemical stability of the Ti/Au/PbO$_2$ electrode has been studied by measuring the weight loss of the test electrode (plates of 20 cm$^2$) polarized anodically under different conditions. A platinum plate was used as the counter electrode and the cell (50 cm$^3$) was stirred with a magnetic bar.

### 2.3. *Polarization measurements*

Steady-state current–potential curves were obtained at 20° C using a platinum sheet counter electrode and a mercury–mercurous sulphate (Hg/Hg$_2$SO$_4$) reference electrode.
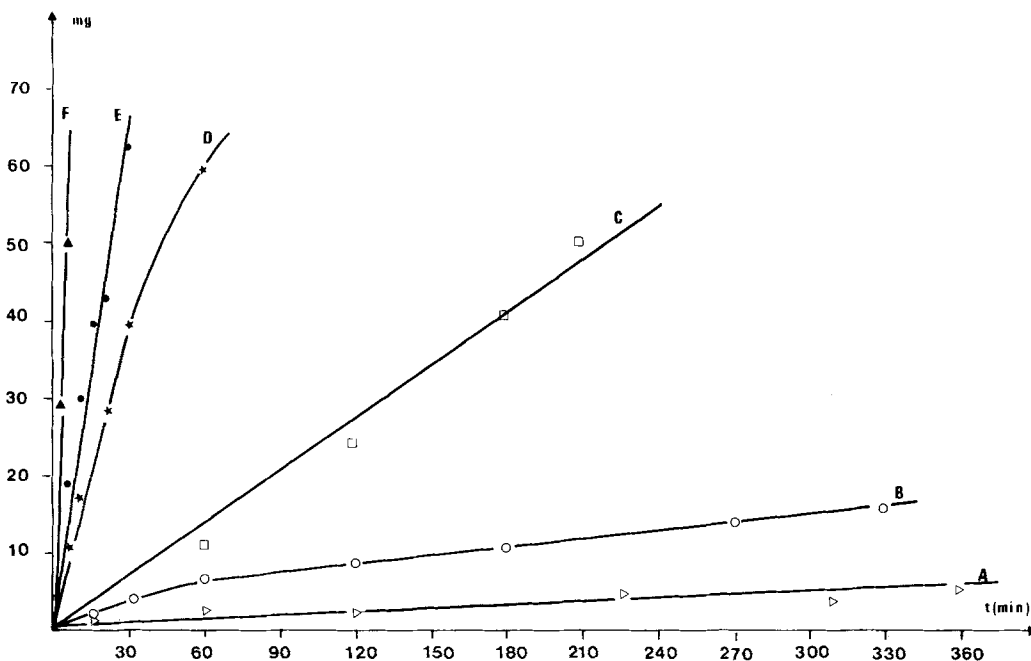
Fig. 1. Weight loss of the Ti/Au/PbO$_2$ electrode polarized anodically at 200 mA cm$^{-2}$ as a function of time. $T = 30°$ C. A = 2 mol dm$^{-3}$ H$_2$SO$_4$; B = 5 mol dm$^{-3}$ H$_2$SO$_4$; C = 7.5 mol dm$^{-3}$ H$_2$SO$_4$; D = 8.5 mol dm$^{-3}$ H$_2$SO$_4$; E = 9.0 mol dm$^{-3}$ H$_2$SO$_4$; F = 12.0 mol dm$^{-3}$ H$_2$SO$_4$.

## 2.4. Preparative electrolysis

The electrolytic cell consisted of a thermostatted cylindrical reactor (750 cm$^3$) without a diaphragm and stirred with a magnetic bar.

A titanium plate (10 cm × 6.2 cm × 0.25 cm) was coated with gold and PbO$_2$ as described previously and was used as the anode (130 cm$^2$). Four wires (stainless steel) placed around the anode were used as cathodes (18 cm$^2$).

The amount of manganic sulphate (or/and MnO$_2$) formed in the cell was determined by iodometric titration.

## 3. Results

### 3.1. Stability of the electrode

Many factors influence the electrochemical stability of the electrode in H$_2$SO$_4$ as is shown below.

*3.1.1. H$_2$SO$_4$ concentration.* The weight loss of the Ti/Au/PbO$_2$ electrode polarized anodically at 200 mA cm$^{-2}$ is shown in Fig. 1 as a function of time at different H$_2$SO$_4$ concentrations. The

average corrosion rate is shown as a function of the H$_2$SO$_4$ concentration in Fig. 2.

From these figures we can see that: (a) the corrosion of the electrode increases linearly with time for all H$_2$SO$_4$ concentrations; (b) the corrosion rate of the electrode increases rapidly above 8 mol dm$^{-3}$ H$_2$SO$_4$.

*3.1.2. Temperature.* The influence of temperature on the average corrosion rate of the electrode polarized anodically at 200 mA cm$^{-2}$ in 9 mol dm$^{-3}$ H$_2$SO$_4$ is shown in Fig. 3. This figure shows that the stability of the electrode increases with increasing temperature.

*3.1.3. Current density and quantity of electricity.* Figure 4 shows the weight loss of the electrode as a function of current density for two quantities of electricity. The corrosion of the electrode is independant of current density but increases with the quantity of electricity.

*3.1.4. Influence of metallic cations.* The presence of metallic cations as Co$^{2+}$, Mn$^{2+}$ in the electro-
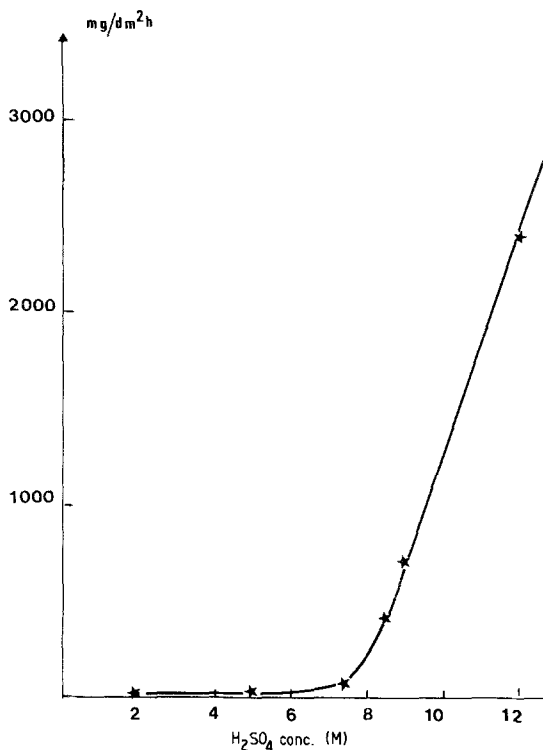
Fig. 2. Average corrosion rate of the Ti/Au/PbO$_2$ electrode polarized anodically at 200 mA cm$^{-2}$ as a function of H$_2$SO$_4$ concentration. $T = 30°$ C.

lyte decreases the corrosion rate of the electrode (Figs 5 and 8).

### 3.2. Anodic characteristics of the electrode

Figure 6 shows the current–potential curves obtained on Ti/PbO$_2$ and Ti/Au/PbO$_2$ containing different amounts of gold.

The resistance of the electrode (slope of the linear part of the $i$–$V$ curve) is high (1.38 $\Omega$ cm$^2$) in the absence of gold and decreases considerably (0.3–0.5 $\Omega$ cm$^2$) if gold is incorporated between the Ti and PbO$_2$.

### 3.3. Electrochemical oxidation of manganous sulphate

The variation of instantaneous current efficiency for manganous sulphate oxidation with the charge passed is shown in Fig. 7 at different H$_2$SO$_4$ concentrations using a Ti/Au/PbO$_2$ electrode. The corrosion rate of this electrode at different H$_2$SO$_4$ concentrations in the presence of manganous sulphate is shown in Fig. 8.
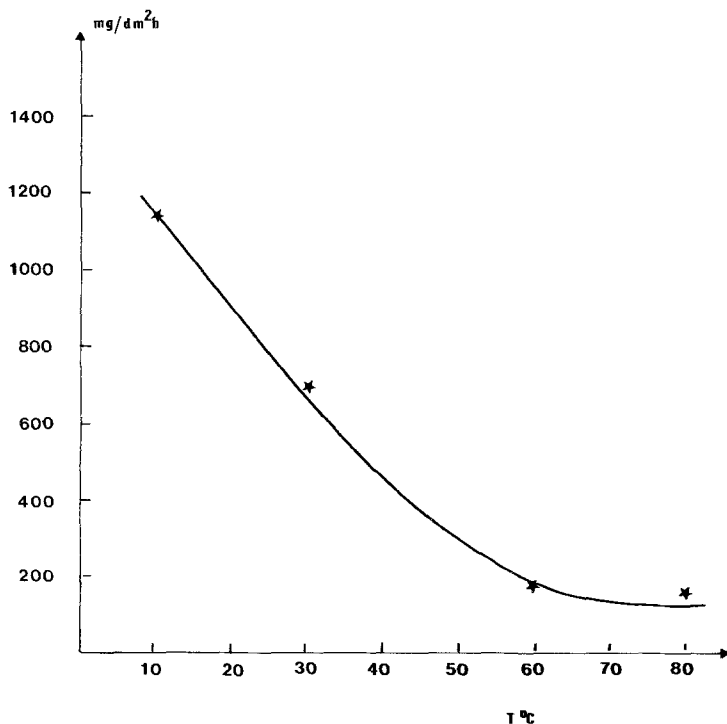


Fig. 3. Influence of temperature on the average corrosion rate of the Ti/Au/PbO$_2$ electrode polarized anodically at 200 mA cm$^{-2}$ in 9 mol dm$^{-3}$ H$_2$SO$_4$.
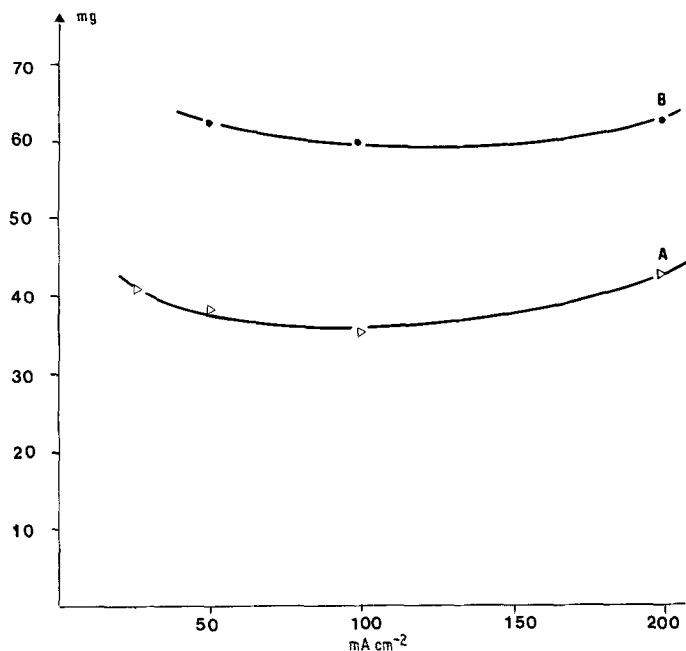
Fig. 4. Weight loss of the Ti/Au/PbO$_2$ electrode polarized anodically at different current densities in 9 mol dm$^{-3}$ H$_2$SO$_4$. $T = 20°$ C. A: quantity of electricity, 1 Ah; B: quantity of electricity, 2 Ah.

## 4. Discussion

### 4.1. *Influence of incorporated gold between the titanium and lead dioxide*

The formation of TiO$_2$ between the titanium substrate and PbO$_2$ is probably due to oxygen forma-tion, part of which is discharged on the active layer–electrode interface–leaving the electrode surface in the form of bubbles. A part of it is adsorbed on the surface and penetrates through the active oxide layer towards the titanium inter-face by diffusion or migration. Oxygen is then chemisorbed on to titanium foming TiO$_2$.

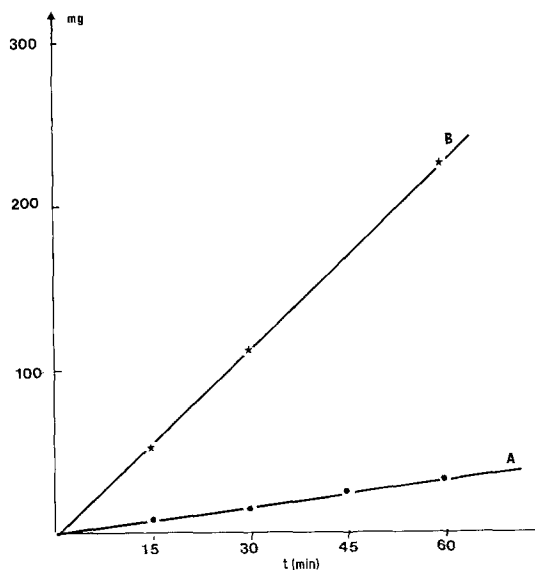Incorporation of a layer of precious metal (Au, Pt) between the titanium substrate and PbO$_2$



Fig. 5. Corrosion of the Ti/Au/PbO$_2$ electrode polarized anodically at 200 mA cm$^{-2}$. $T = 10°$ C. A = 9 mol dm$^{-3}$ H$_2$SO$_4$ + 0.714 mol dm$^{-3}$ CoSO$_4$ · 7 H$_2$O; B = 9 mol dm$^{-3}$ H$_2$SO$_4$. 9.1 g Au m$^{-2}$, 522.1 g PbO$_2$ m$^{-2}$.
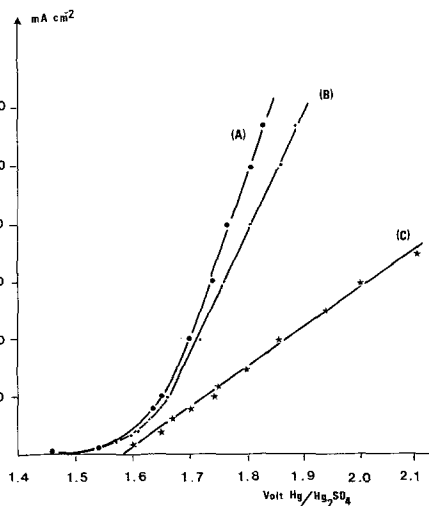


Fig. 6. Stationary polarization curves obtained in 2 mol dm$^{-3}$ H$_2$SO$_4$ at 20° C. (A) Ti/Au/PbO$_2$ (9.1 g Au m$^{-2}$, 522.1 g PbO$_2$ m$^{-2}$); (B) Ti/Au/PbO$_2$ (2.31 g Au m$^{-2}$, 532.75 g PbO$_2$ m$^{-2}$); (C) Ti/PbO$_2$.
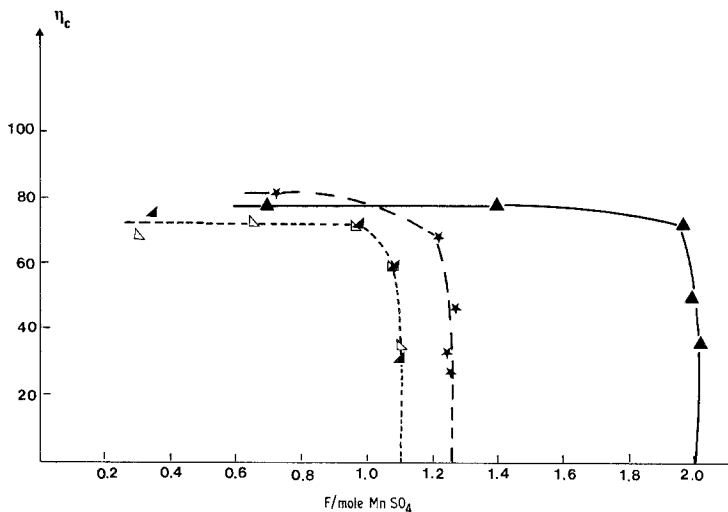
Fig. 7. Variation of instantaneous current efficiency for manganous sulphate oxidation with charge passed using a Ti/Au/PbO$_2$ electrode. 0.228 mol dm$^{-3}$ MnSO$_4 \cdot$H$_2$O; $T = 85°$ C; 50 mA cm$^{-2}$ current. ▲ 6.8 mol dm$^{-3}$ H$_2$SO$_4$; ★ 9.0 mol dm$^{-3}$ H$_2$SO$_4$; △10.8 mol dm$^{-3}$ H$_2$SO$_4$; ◢12.0 mol dm$^{-3}$ H$_2$SO$_4$.

decreases the penetration rate of adsorbed oxygen and thus the growth of TiO$_2$ is suppressed.

### 4.2. Corrosion of the lead dioxide electrode

The corrosion of the PbO$_2$ electrode polarized anodically in H$_2$SO$_4$ increases under conditions where the formation of H$_2$O$_2$ is favoured [6] as: high H$_2$SO$_4$ concentration; low temperature; and absence of metallic cations (Mn$^{2+}$, Co$^{2+}$, Fe$^{2+}$).



Fig. 8. Influence of H$_2$SO$_4$ concentration on the average corrosion rate of Ti/Au/PbO$_2$ polarized anodically at 50 mA cm$^{-2}$ in 0.228 mol dm$^{-3}$ MnSO$_4 \cdot$H$_2$O. $T = 85°$ C.

The stability of the PbO$_2$ electrode depends on the acid used as electrolyte, thus, in nitric and perchloric acids the corrosion of PbO$_2$ decreases considerably. For both these acids no H$_2$O$_2$ is formed by electrolysis at the electrode [7].

Taking these experimental facts in to consideration we can suppose that the corrosion of the PbO$_2$ electrode is due to the oxidation of H$_2$O$_2$ (formed in H$_2$SO$_4$ solution) by the PbO$_2$ film:

$$PbO_2 + H_2O_2 + H_2SO_4 \rightarrow PbSO_4 + 2\,H_2O + O_2.$$
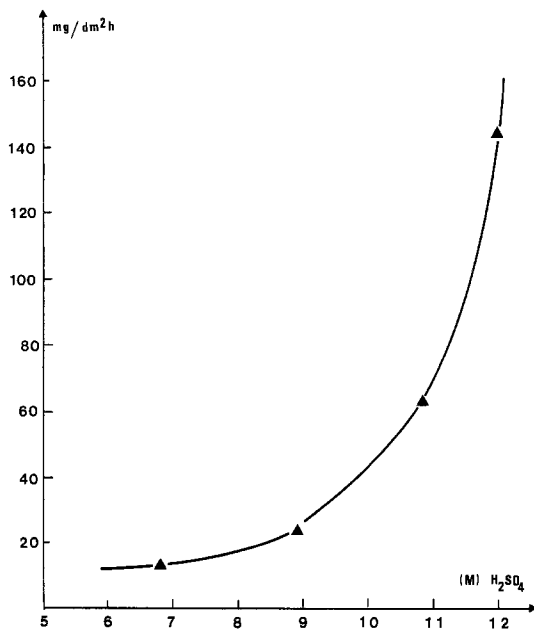$$(1)$$
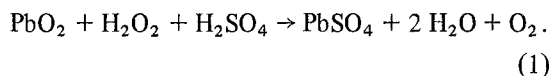
### 4.3. Electrochemical oxidation of manganous sulphate

The electrochemical reactions that may be involved in electrolysing MnSO$_4$ in H$_2$SO$_4$ are

$$Mn^{2+} \rightarrow Mn^{3+} + e \qquad E^0 = 1.51 \quad (2)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \qquad E^0 = 1.229. \quad (3)$$
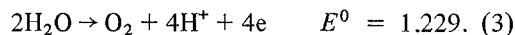
According to these potentials, oxygen evolution (Equation 3) should compete with the main reaction. However, oxygen evolution requires a considerable overvoltage on PbO$_2$ [8]. This explains the high yield of Mn$^{3+}$ (or/and MnO$_2$) obtained. The Mn$^{3+}$ formed electrochemically at the anode disproportionates to Mn$^{2+}$ and MnO$_2$.

$$2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+. \qquad (4)$$
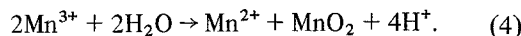
This reaction is favoured at low H$_2$SO$_4$ concentrations. Figure 7 shows that in 6.8 mol dm$^{-3}$ H$_2$SO$_4$, 2 F are used for each mole of MnSO$_4$

indicating that $MnO_2$ is the electrolysis product. At high $H_2SO_4$ concentrations(10.8–12 mol $dm^{-3}$) 1.1 F are used for each mole of $MnSO_4$ indicating that the main electrolysis product is $Mn_2(SO_4)_3$.

## References

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