

Preparation and Use of Ti/PbO₂ Anodes for the Oxidation of Cr(III)

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Cr(VI) solutions are widely used for the oxidation of organic compounds. In such processes, the resulting Cr(III) solutions often contain sulfuric acid and must be recycled due to environmental considerations. For that purpose, one can use lead dioxide electrodes, the PbO₂ layer being formed *in situ* on lead or a lead alloy (1). Other substrates have been proposed in the literature : titanium (2) or ceramic materials composed of Magnéli phase titanium oxides called Ebonex® (3).

Lead substrates do not give rise to “dimensionally stable anodes” and have poor performances. The electrochemical deposition of PbO₂ on Ebonex® substrates leads to good adherence coatings, but it is difficult to obtain cheap large electrodes. At last, it is difficult to prepare adherent PbO₂ coatings on titanium substrates. It is the reason why it is often necessary to deposit an intermediate layer between the Ti substrate and the electroactive PbO₂.

In this paper, we describe the results obtained with electrodes obtained by electroplating a stable and compact PbO₂ layer on a Ti substrate. They were used as anodes for oxidizing Cr(III) in sulfuric acid solutions in the 0 - 2 pH-range.

The results are compared with those obtained with Pb/PbO₂ and Ebonex®/PbO₂ anodes working in the same experimental conditions.

PREPARATION OF THE ELECTRODES

Titanium foils (Goodfellow; purity: 99.6%; area: 4 cm²) were mechanically polished and rinsed in methanol.

First, a thin and compact platinum film was deposited by Metal Organic Chemical Vapor Deposition by the oxidative decomposition of (methylcyclopentadienyl) trimethylplatinum (4). That intermediate layer was prepared for avoiding passivation or corrosion of the Ti substrate during all the subsequent experiments. Second, an undercoating of α -PbO₂ was produced by electrodeposition from an alkaline lead bath (3.5 M NaOH saturated with litharge PbO; $\theta = 40^\circ\text{C}$). At last, the top coating (β -PbO₂) was deposited from an acid lead bath (30 wt% Pb(NO₃)₂ solution at pH = 2 containing HNO₃; $\theta = 65^\circ\text{C}$) (2).

For the other substrates, no platinum film was necessary; the PbO₂ film was deposited according to the procedure reported above.

ELECTROCHEMICAL OXIDATION OF Cr(III)

The oxidation of Cr(III) was carried out a two-compartment cell, under galvanostatic conditions ($j = 10 \text{ mA cm}^{-2}$), at 25°C during 24 hours.

The cathodic compartment was containing 0.5 M sulfuric acid and the anodic compartment was containing 0.1 M Cr(III) and H₂SO₄ at several concentrations (pH = 0, 1 or 2).

An anion-exchange membrane resistant in such a corrosive medium was used (IONAC MA-3475) as a separator.

The determination of the Cr(VI) amount in the anodic compartment was performed by an electroanalytical technique : a small amount of electrolyte was removed and diluted in 0.5 M sulfuric acid. The limiting diffusion current intensity obtained with a rotating disk electrode (RDE) was measured for determining the concentration of Cr(VI); the RDE was fitted with a gold disk and operated at a 3000 rpm rotation speed.

The current efficiency, ϕ , was calculated for the different experimental conditions (pH = 0,1 or 2 with the three substrates). The best results were obtained with Ti/PbO₂, at pH = 2 ($\phi = 0.93$); ϕ decreased for decreasing pH values. See Table 1.

The surface of these electrodes was studied after electrolysis by Scanning Electron Microscopy. The results showed that the PbO₂ layer deposited on Ti is quite stable after 24 h electrolysis.

REFERENCES

1. D. Pletcher and F.C. Walsh, Industrial Electrochemistry, 2nd edition, Chapman and Hall, London (1990), p. 279.
2. M. Ueda, A. Watanabe, T. Kameyama, Y. Matsumoto, M. Sekimoto and T. Shimamune, *J. Appl. Electrochim.* **25**, 817 (1995).
3. J.E. Graves, D. Pletcher, R.L. Clarke and F.C. Walsh, *J. Appl. Electrochim.*, **22**, 848 (1992).
4. O. Valet, P. Doppelt, P.K. Baumann, M. Schumacher, E. Balnois, F. Bonnet and H. Guillon, *Microelectronic Engineering*, **64**, 457 (2002).

Table 1: Current efficiency for the oxidation of Cr(III) on PbO₂ electrodes at several pH values. PbO₂ was deposited on three different substrates.

	pH = 0	pH = 1	pH = 2
Ti/PbO ₂	0.60	0.80	0.93
Ebonex®/PbO ₂	0.55	0.57	0.74
Pb/PbO ₂	0.21	0.44	0.56