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Platinum-iridium catalyzed titanium anode. I. Properties and use in chlorate electrolysis

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The use of dimensionally stable titanium anodes activated with Pt, Ir or ruthenium oxide for electrolytic chlorate production has been investigated. Simultaneous measurements were made of the amount of noble metal at the surface and of electrode activity, as functions of time of electrolysis at constant current and temperature. After more than 400 days of operation, an electrode with 7 g m^{-2} of surface of noble metals exhibits good polarization characteristics as well as freedom from corrosion of the coating.

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1. Introduction

In recent years there has been a major shift in electrochemical industries from graphite electrodes to titanium based, dimensionally stable, anodes (DSA). Two types are available, differing in the material used to render the titanium surface conducting and for catalyzing the electrochemical reactions. The catalysts used are ruthenium oxide [1] and a platinum–iridium alloy [2].

At present, little data is available concerning the stability of these catalysts and their electrochemical properties [3].

This communication reports on some investigations of the properties and performance of platinum–iridium catalyzed titanium anodes prepared in the Institute of Chemistry, Technology and Metallurgy, Belgrade.

2. Experimental

2.1. *Preparation of electrodes*

The electrodes were prepared by coating titanium sheets (Tikrutan RT–12) 5 x 5 and 0·8 mm with platinum–iridium alloy (60:40 wt.%). The coating was achieved by painting with a solution of 2·13 mg cm^{-3} of the noble metals (as tetrachlorides) in a 3:1 vol.% mixture of butyl alcohol and methyloxybenzene (anisole). The samples were subsequently heated to 500 °C. The procedure was repeated as required to build up the catalyst deposit from 0·2–9 g m^{-2}. Thus, the electrodes have been investigated, coated with far smaller amounts of noble metal than when commercially available. For comparison, electrodes were also prepared with coatings of pure platinum and pure iridium.

The structure of the electrode surfaces was investigated by electron microprobe.

2.2. *Investigation of electrochemical properties*

The prepared electrodes were then used as anodes for the production of chlorate using concentrated brine (initially ca. 5 M NaCl) containing 3 g l^{-1} of chlorates. The pH of 6 was maintained. Steady-state polarization curves were taken for each electrode in the conventional manner. Electrodes were then submitted to prolonged electrolysis (up to 500 days) at a current density of 3 kA m^{-2} and 60° C except where otherwise stated. Potentials were measured with respect to SCE.

2.3. *Corrosion of the catalytic coating*

Each electrode was irradiated for 7·5 min with a neutron flux density of $4{\cdot}10^{12}$ m cm^{-2} s^{-1}.

After 28 days, the activity due to ^{192}Ir having a half-life of 74 days remained as a measure of the amount of iridium present over the period of investigation. The platinum content of some samples was determined spectroscopically.

3. Results

Typical polarization curves in the current density region of practical importance are shown in Fig. 1 for electrodes with different amounts of the noble metal alloy at the surface.

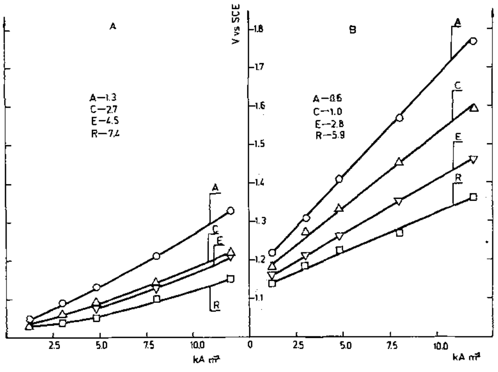

Fig. 1. Polarization characteristics of DSA. (A) at the beginning; (B) after 405 days of work.

Fig. 2. shows the dependence of electrode polarization at different current densities on the amount of alloy. This plot indicates that for the given method of preparation, polarization rises rather sharply when the alloy concentration falls below 1–2 g cm^{-2}, and most investigations were consequently performed with electrodes having more than 1 g cm^{-2} of catalyst.

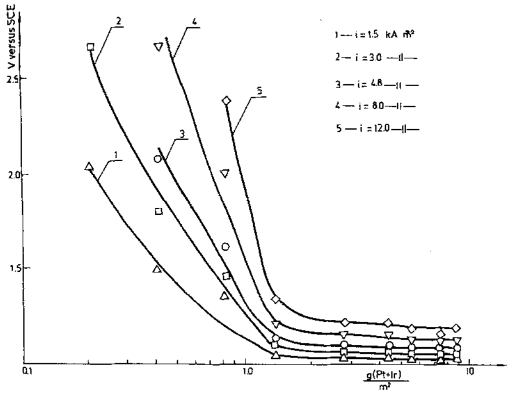

Fig. 2. Dependance of anodic polarization on the amount of noble metals.

Corrosion tests with electrodes containing pure platinum, pure iridium and platinum-iridium alloy coating showed (Fig. 3) that the alloy is much more stable than a pure platinum coating (which practically disappeared within 2 months) and considerably more stable than a pure iridium coating.

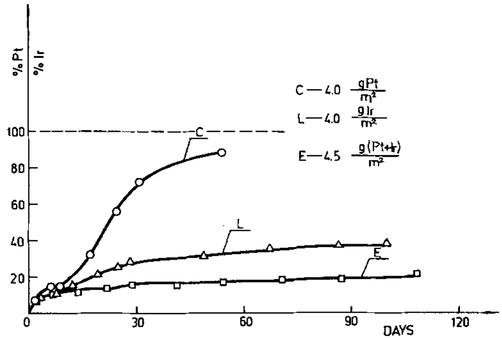

Fig. 3 Corrosion curves for Pt, Ir and (Pt + Ir) alloy.

Figs. 4a and b depict corrosion tests for electrodes having various amounts of alloy. Some were tested at 80 °C and current densities up to 9 kA m^{-2}. No definite conclusions were reached as to the effect of these changes.

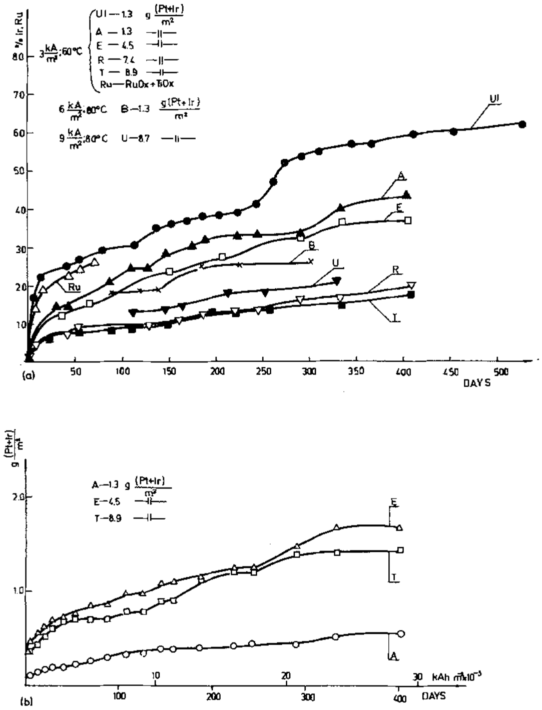

Fig. 4. Corrosion curves of noble metals. (a) percentes, referred to the initial amounts; (b) absolute values.

A commercial ruthenium oxide electrode (De Nora, Milan) was also investigated for corrosion of the coating under the same conditions. Fig. 4a shows that it was exhibiting behaviour typical of platinum-iridium coated electrodes with amounts of the alloy at the lower limit (about 1g m^{-2}).

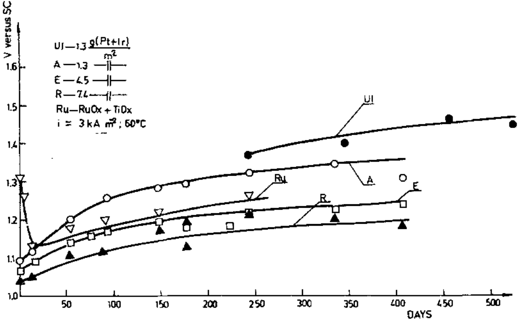

Fig. 5. Changes of potential with time.

The effect of corrosion of the coating on the polarization of the electrodes at the operating current density (3 kA m^{-2}) is shown in Fig. 5. A considerable increase in polarization (up to 0·2 V) occurs in a fairly reproducible manner at electrodes having less than about 1 g m^{-2} of alloy during the period of observation.

4. Discussion

Structural investigations revealed (Fig. 6) that the platinum-iridium alloy is deposited in a disperse form. The polarization curve of an electrode, having only 4 g m^{-2} of alloy is compared in Fig. 7 with those of other electrodes used in chlorate electrolysis.

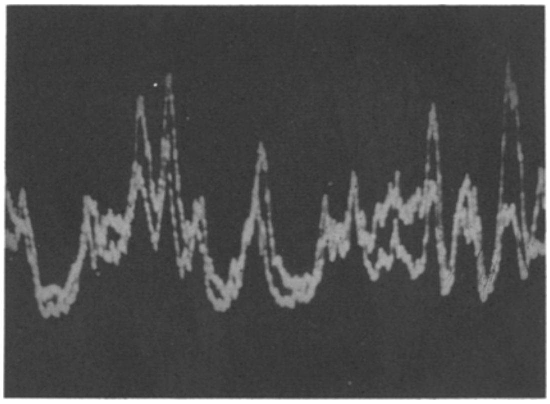

Fig. 6. Electron microprobe Pt and Ir distributions on the sample containing 4 g m^{-2} (Pt + Ir); Pt-upper curve; Ir-bottom curve (Lα line; SEM – 2, Manchester, England).

The comparison clearly demonstrates the advantages of this electrode over other electrodes including pure platinum, in terms of the energy consumption. At a comparable current density of for example 1 kA m^{-2}, conventional graphite electrodes have over 0·6 V greater polarization, or in other words require about 18% higher cell voltage than those which are Pt–Ir coated. This accounts for the conclusion that for graphite electrodes this current density is at the upper limit of reasonable cell operation, while for the Pt–Ir DSA this would be the lower limit at which to carry out electrolysis. Operation at up to 10 kA m^{-2} does not increase the energy consumption to any significant extent.

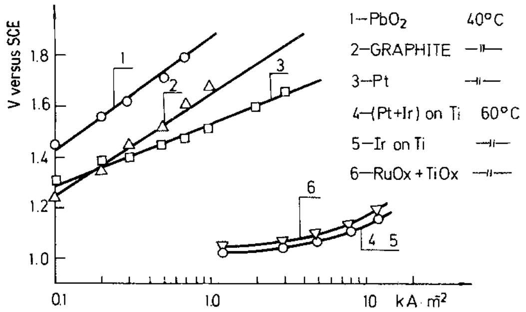

Fig. 7. Polarization curves for various anodic materials in chlorate electrolysis.

The polarization characteristics of the Pt–Ir DSA are comparable with those of the ruthenium oxide DSA. This indicates that the electrode process is controlled by factors other than activation of the charge transfer and probably by diffusion of the reactants. There would therefore be no point in attempting to achieve a further increase in electrocatalytic activity without improving the reactant transfer process.

A somewhat surprising result is the difference in behaviour between pure platinum and the alloy. This is in agreement with some published suggestions that the role of iridium may be to prevent the oxidation of platinum [5], and that bare platinum is a much better catalyst for oxidation of chloride than the oxidized surface. This is also found to be true for oxygen evolution [6].

The alloy is so efficient a catalyst for the process that in the entire range of current densities employed the process appears to be under diffusion control. Hence, the conclusion about the amount of the alloy below which the electrode properties worsen is probably associated with the method of electrode preparation. It is likely that even smaller amounts of the alloy could, under different conditions of preparation, such as might give rise to a higher degree of dispersion, produce efficient electrodes. However, 7 g m^{-2} of catalyst represents so small a portion of the cost that little would be gained by a further reduction. It is more important to examine the effect of catalyst content on the maintenance of the catalytic activity, i.e. the corrosion behaviour of the coating, as shown in Fig. 4. Fig. 4a and b show that different conclusions can be reached if the corrosion is considered in terms of percentage or absolute loss.

It should be noted that some electrodes exhibited a step-wise increase in the loss of catalyst with time. No definite conclusion is offered as to cause of this phenomenon, but it seems to be linked with the interruption of electrolysis with electrodes in the cell (current failure).

The amount of corroded metal as a function of amount initially present is a maximum at a catalyst content of about 5 g m^{-2}. This would favour the use of somewhat higher amounts of the alloy than would be necessary if only the polarization characteristics are considered. As seen in Fig. 1. and 5, these are related to the percentage loss of the catalyst and to the loss of catalytic activity of the coating. The relatively large increase in energy consumption with use in the case of electrodes with low catalyst content places a much heavier burden on the economics on the process. These facts favour the use of electrodes with intermediate catalyst contents (about 7 g m^{-2}). This catalyst content is still only about one third of that of commercially available Pt–Ir DSA.

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