

14. INSOLUBLE ANODES IN THE ELECTROWINNING OF COPPER*

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PROGRAMA DE ENGENHARIA METALÚRGICA E DE MATERIAIS

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by

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Introduction

Interest in the electrowinning of copper has increased in recent years primarily because of its application in the recovery of copper from electrolytes obtained from solvent extraction processing of dilute copper-containing solutions (1). The properties required of an anode for metal electrowinning can be generally defined as (a) Good electrical conductivity, (b) Low oxygen overpotential, (c) High corrosion resistance, (d) Mechanical strength. Whilst these properties are typically required of an anode for the electrowinning of copper, a process (2) has been described where depolarization of the oxygen evolution reaction is effected by the use of sulphur dioxide, with the reaction [2] replacing reaction [1] as the anodic reaction.



In this specific instance carbon, which is normally unable to meet requirement (c) in typical electrowinning environments, can serve satisfactorily as an anode. In general, however, the trend is to seek anode systems for copper electrowinning which have the increased corrosion resistance required for acceptable performance in the highly acid electrolytes produced by solvent extraction processing (3).

The alternative materials available for anodes for electrowinning are limited both by chemistry and economics and it is for this reason that lead and its various alloys with, for example, antimony and silver have had such general application. A technique for decreasing the corrosion of lead anodes by the addition of small amounts of cobalt to the electrolyte was developed many years ago (4). This technique is able to be used in the recovery of

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copper from solvent extraction solutions and enables low lead contamination of the cathode copper to be achieved. A study has recently been made of the inhibition of lead corrosion due to the presence of aqueous cobalt (5). On the basis of corrosion resistance, the platinum metals should be considered as alternatives to lead and lead dioxide as anode materials. Indeed, in recent years major advances have been made in the use of these metals, applied as coatings to various metal substrates, in the chlor-alkali industry. The economic advantages of using the precious metals in the form of thin coatings is obvious, provided the corrosion resistance of the composite is acceptable. In the chlorate industry where neutral halide electrolytes are used the rates of precious metal loss from titanium based platinum-iridium alloy coated anodes has been shown to be extremely low (6). Reports of the corrosion levels observed when platinum coated titanium is used in the electrowinning of copper from high strength sulphuric acid solutions are less encouraging (7).

A major question to be answered in the corrosion behaviour of precious metal coated anodes concerns the role of the substrate metal. The well known principal upon which the operation of these composite anodes is based, is that at their potentials of operation any exposed titanium metal should be protected by an oxide film (8). If the conditions of operation should be such as to lead to the destruction of this film, particularly in regions of porosity of the precious metal coating, then corrosion and undermining of the coating may occur.⁽⁹⁾ In addition to this mode of anode destruction a slow direct dissolution of the platinum metals may occur. In summary the degradation of precious metal coated electrodes may occur by the following mechanisms:

- Noble metal dissolution due to the presence of complexing anions or complexing organic additives.
- Noble metal dissolution due to local conditions of high activity.
- Pitting and breakdown of the titanium substrate due to the presence of aggressive anions.
- Accelerated corrosion of the titanium substrate due to local conditions of high acidity or alkalinity.

- Undermining of the coating due to oxidation of the substrate.
- Accelerated attack of the noble metal and the titanium substrate due to high local temperature.

Platinum coated titanium anodes have been utilized in electroplating of gold, rhodium, palladium, nickel, tin, chromium, and copper with service lifetimes depending on the particular condition of current density, temperature, and electrolyte composition (10,11). Fortunately, sulphate electrolytes are commonly employed, with a consequent lower possibility of corrosion of the noble metal or breakdown of the substrate (12). The onset of pitting in titanium occurs at very low potentials in solutions containing as little as .001 M I^- or Br^- (13). The presence of sulphate anions in chloride electrolytes has been shown to inhibit the breakdown of titanium (14,15). The use of substrate materials, superior to titanium in corrosion resistance, has been suggested. Tantalum, niobium, or titanium alloy substrates are possibilities. For the particular case of copper electroplating, Warne and Hayfield report that, for an electrodeposited platinum-titanium anode (50-60 gm./m.² loading) operating at 90 A/ft.² in 75-100 gpl H_2SO_4 and 50-57 gpl Cu at temperatures to 40°C, degradation occurred through coating undermining (10). Ives and Gilbert (16) recently reported rates of loss from massive platinum anodes of approximately 10 μ g/A hour at 40°C in 150 g/l sulphuric acid.

The present study is concerned with the behaviour of anodes of platinum-iridium alloy coatings on titanium in solutions of sulphuric acid and sulphuric acid and copper sulphate.

Experimental

Experiments with 70% platinum/30% iridium-coated titanium electrodes (prepared by a thermal decomposition method by Imperial Metal Industries Ltd. (17)) were conducted in neutral and acid chloride electrolytes, sulphuric acid solutions, and a simulated electrowinning electrolyte containing 2M H_2SO_4 + 0.5M $CuSO_4$. All experiments were made at 20°C, with

helium stirring in some cases, in cells constructed from Pyrex and Teflon in order to reduce possible contamination. Reference electrodes used, in conjunction with a Luggin capillary, included the saturated calomel, hydrogen, mercury/mercurous sulphate, and copper/copper sulphate electrodes. Potentiostatic and galvanostatic techniques were employed, with batch runs extending to times of 30 seconds to 28 days. In addition to monitoring the current vs. time or potential vs. time behaviour of the anodes, the change in the surface area of the electrodes was determined by means of an anodic charging technique, and the coating losses were established using an X-ray fluorescence method. Scanning electron microscopy was used to observe changes in surface morphology, a multichannel X-ray analyzer permitted the determination of the distribution of the elements over the electrode surfaces, and X-ray diffraction provided information concerning crystalline species on the anode surface.

Results

Experiments were conducted at anodic potentials between 1.8 and 2.0 volts (n.h.e.) or with anodic currents up to 350 mA/m.². Electrolysis in all systems revealed a "passivation" process occurred continuously over the period of a run, as observed by either a decay of the anodic current (potentiostatic runs) or an increase in the anode potential (galvanostatic runs). This "passivation" was rapid during the first few hours of polarization, followed by a slower, nearly-constant "rate" thereafter (Figure 1). This passivation was reversible, however, and repetition of experiments with the same anode gave similar results.

A marked difference in the change of the electrochemically active surface area of the anodes was noted between the sulphate- and chloride-containing electrolytes. In the former, decreases were so small as to be within the range of error for the method of determination (about 5%), even after 28 days service at 1900 mV (n.h.e.). In neutral or acid chloride systems, however, the surface area decreased rapidly within the first minute of polarization and become half the original value within an hour (Figure 2).

This surface area loss was irreversible, and several "activation" procedures failed to recover any portion of the initial area.

Scanning electron microscopy revealed that the appearance of anodes which had been used in various media showed little change from their new condition. However, localized attack was observed to occur after long polarization in 2M H₂SO₄ (Figure 3). The substrate is clearly exposed, as can be ascertained by comparison with the appearance of the uncoated titanium base (Figure 4). Operation in neutral chloride environment produces a rough, nodular growth in surface pits (Figure 5). Polarization in copper sulphate electrolyte produced a crystalline deposit on the electrode surface, which was identified as PbO₂ (Figure 6). The deposit was extremely adherent, and anodic polarization in copper-free 2M H₂SO₄ failed to significantly remove it. However, treatment for several minutes at open-circuit in 1N HCl solution removed the PbO₂, leaving a surface again characteristic of a new anode (visually, electrochemically and composition-wise).

Coating losses were determined for experiments performed in 2M H₂SO₄, with and without the addition of 0.5M CuSO₄ (Figure 7). Losses in 2M H₂SO₄ were small, and depended on the total time of electrolysis more than the magnitude of the applied current. For example, after 97 hours at 350 mA/in.², the coating loss was 2.4%. After 205 hours at 105 MA/in.², the loss was 5.0%. In copper sulphate-containing electrolytes, it was initially observed that the rate of loss of coating was apparently much higher - at least six times as much. However, discovery and subsequent removal of the PbO₂ surface deposit showed that the X-ray fluorescence method for determining coating thickness was giving erroneously low results when the PbO₂ deposit was present. After removal of the deposit, coating losses were found to be of the same order as in copper-free electrolyte.

Discussion

The rather complex results obtained indicate that the degradation of noble metal coated titanium anodes may be due to the simultaneous occurrence of several phenomena, depending on the system and the electrolysis conditions. In all cases, a slow passivation of the anodes was observed during use, which may affect the mechanism of direct dissolution of the noble metal itself. Initially, "active" dissolution may occur (especially in complexing media), followed by "passive" dissolution of surface noble metal oxides. The dissolution behaviour is likely to change with time, as the properties of the passive layers on noble metals change with potential.

Irreversible oxidation of the titanium substrate also occurs during anodic polarization, with the quality of the titanium oxide film dependent on the electrolyte system in question. In halide media, the electrochemically active surface area was significantly decreased, as opposed to the negligible effect in sulphate electrolytes. It is known that the breakdown voltage of TiO_2 films is significantly decreased in halide media, and that sulphate, conversely, inhibits titanium pitting, hence it is not unreasonable to expect different degrees of substrate attack, depending on the system in question. The morphology of the degradation of anodes, as observed by means of scanning electron microscopy, showed the formation of irregular masses of titanium oxide "nodules" in "pits" on the surface of anodes used in neutral chloride electrolytes. In sulphuric acid electrolytes, extended anodic electrolysis produced clean pits which exposed the titanium substrate beneath the noble metal coating, clearly suggesting that the loss of noble metal may occur through undermining. Undermining is also suggested in the case of chloride electrolytes, as the electrical isolation of the coating (as observed by the decrease of surface area of visually unaffected anodes) could indicate that a poorly-conducting film forms between the substrate and parts of the coating. No electrical isolation of the surface is observed in sulphate electrolytes.

Anodes used in the electrowinning of copper show similar behaviour to those used in sulphuric acid solution, having no apparent change in surface area, and similar corrosion rates. The appearance of the PbO_2 deposit on

the anode surfaces was traced to the presence of about 1 ppm of lead in the electrolyte. It is not unreasonable to expect the lead to migrate to the anode as an anionic complex. The PbO_2 crystals are most abundant at the platinum-rich sites (i.e. conducting sites) indicating that their appearance is indeed an electrochemical phenomenon. The behaviour of the PbO_2 -covered anodes is not significantly different from that of PbO_2 -free anodes, and hence it is not surprising that this phenomenon has not been reported previously. The masking of the true platinum values by this deposit may account for the reports of accelerated coating loss, in copper sulphate media, made by other authors. It is interesting to note that the production of a titanium-noble metal-lead dioxide anode has been described by Antonov and Stepanenko (18), whereby PbO_2 is deposited anodically over the noble metal coatings from a lead nitrate-containing solution.

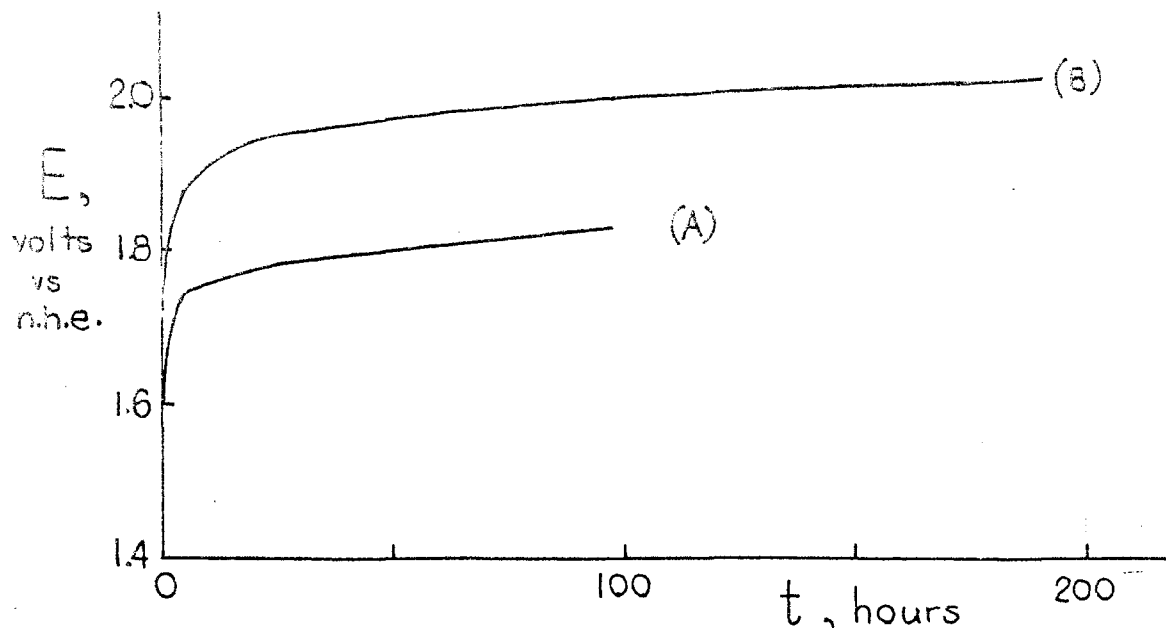


Figure 1 . Potential vs time curves for galvanostatic electrolysis at 350 mA/in^2 : (A) in $2 \text{ M H}_2\text{SO}_4$ (B) in $2 \text{ M H}_2\text{SO}_4 + .5 \text{ M CuSO}_4$

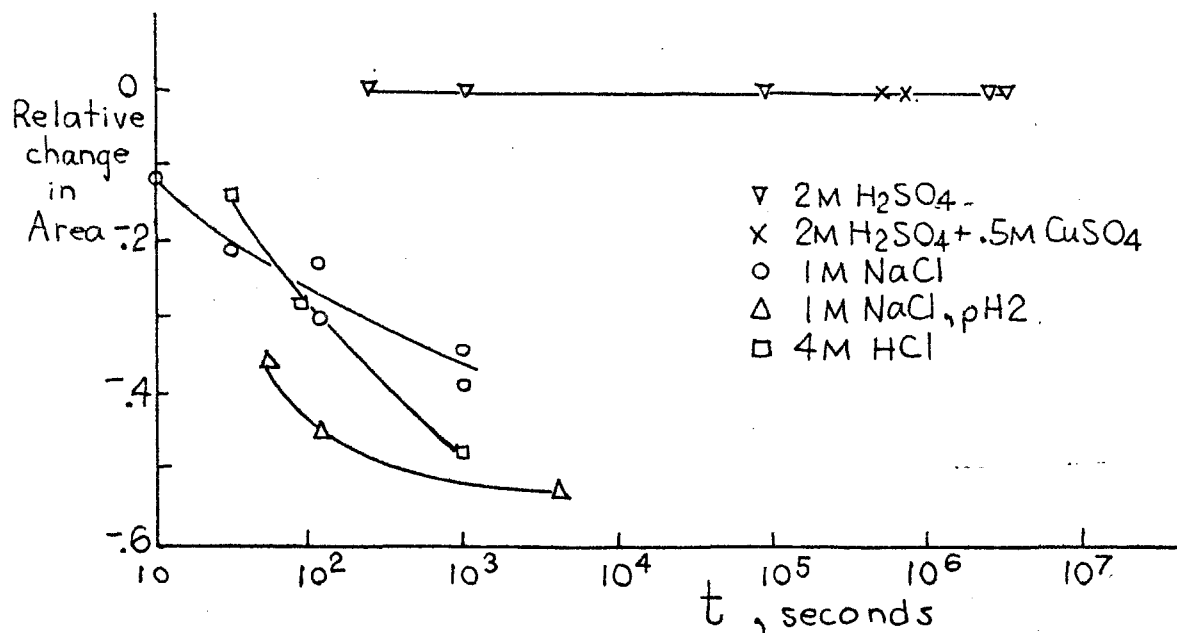


Figure 2 . Change of surface area vs time for potentiostatic polarization at 1800 mV (n.h.e.) in various electrolytes at 20° .

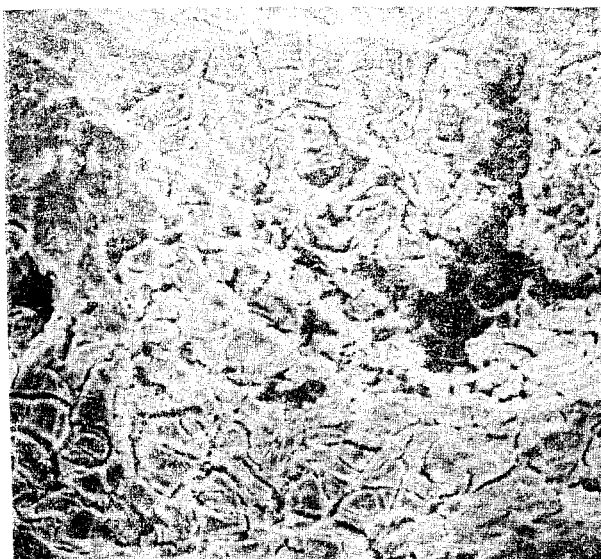


Figure 3: S.E.M. view of anode surface after 500 hr. at 1900 mv (n.h.e.) in 2M H₂SO₄. Final current density was 220 mA/in². (1000 x)

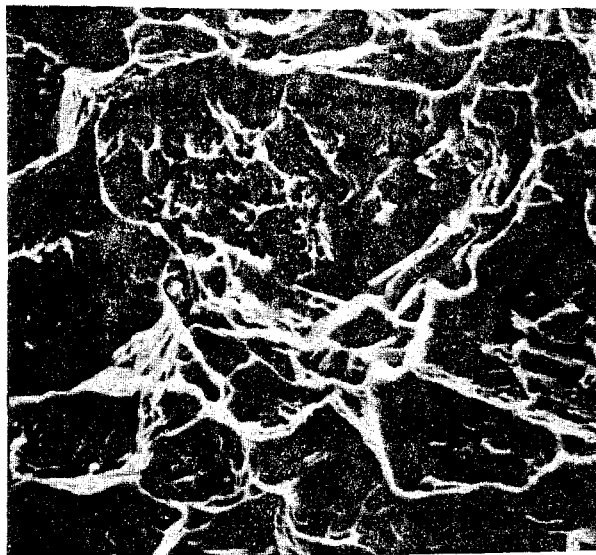


Figure 4: S.E.M. view of etched titanium substrate, prior to application of noble metal coating. (1000 x)



Figure 5: S.E.M. view of anode which was used in industrial preparation of chlorate. (1000 x)

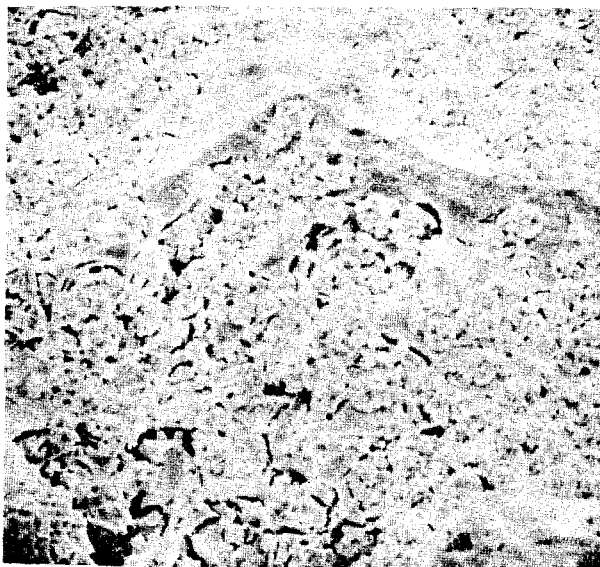


Figure 6: S.E.M. view of anode surface after 670 hr at 1800 mv (n.h.e.) in 2M H_2SO_4 + .5M CuSO_4 . Final current density was 25 mA/in². Surface deposit was identified as PbO_2 . (1000 x)

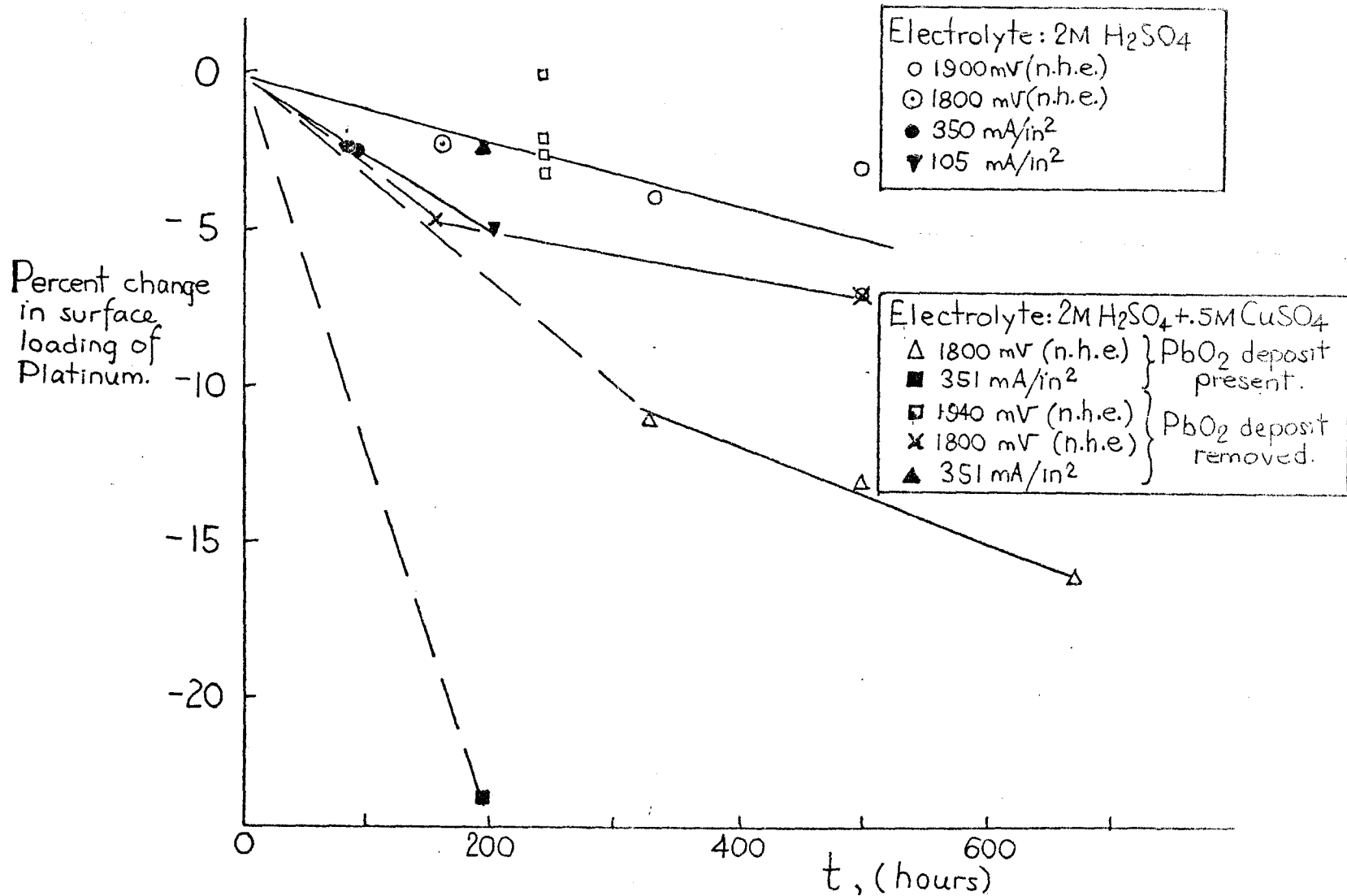


Figure 7. Change in platinum surface loading as a result of galvanostatic and potentiostatic electrolysis in 2M H₂SO₄, with and without the addition of 0.5M CuSO₄.

References

1. Nelson, R.R. and Brown, M.L., The Great Canadian Copper Leach, Liquid Ion Exchange Pilot Plant, in 'The Design of Metal Processing Processes', Proceedings A.I.M.E. Symposium, Chicago, 1967.
2. Pace, G.F. and Stauber, J.C., Direct Electrowinning of Copper from Synthetic Pregnant Leach Solutions Utilizing SO_2 and Graphite Anodes - Pilot Plant Results, C.I.M. Trans. LXXVII, Jan. 1974, 31-37.
3. Agers, D.W. and Dement, E.R., The Evaluation of New LIX Reagents for the Extraction of Copper and Suggestions for the Design of Commercial Mixer - Settler Plants, in 'Solvent Extraction in Metallurgical Processes', Antwerp, May 1972, 31-47.
4. Ray, M., et al., Trans. Electrochem. Soc. 73, 1938, 315
5. Hyvärinen, O., The Effect of Silver and Cobalt on the Oxygen Evolution at Lead Anodes.
6. Warren, I.H., et al., Metal Electrodes for Chlorate Cell Operation, presented at the Fourth Joint Chemical Engineering Conf. of C.S.C.R.E./A.I.C.R.E., Sept. 1933.
7. Hopkins, W.R., et al., Electrowinning of Copper from Solvent Extraction Electrolytes - Problems and Possibilities in International Symposium on Hydrometallurgy, A.I.M.E., Chicago, 1973, 127-154.
8. Cotton, J.B., Anodic Polarization of Titanium, Chem. Ind., London, 1958, 68-69.
9. Khodkevich, S.D., et al., Corrosion Resistance of the Titanium Base under a Platinum coating in relation to the pH of the Anolyte, Elektrokimiya, 6, 1970, 135-8.
10. Warne, M.A. and Hayfield, P.C.S., Durability of Titanium Anodes in Electroplating, Trans. Inst. Metal Finishing, 45, 1967, 83-92.
11. Haley, A.J., Use of Insoluble Auxiliary Anodes, Englehard Ind. Tech. Bull., 7, 1967, 157-64.
12. Juchniewicz, R., et al., Influence of Some Factors on Anodic Behaviour of Platinized Titanium, Zesz. Nauk. Politech. Gdansk., Chem., No. 20, 1970, 119-33.
13. Mikhcolova, L.A., et al., Electrochemical Behaviour of the Titanium Base of a Platinized Titanium Anode during Electrolysis of Natural Waters, Elektrokimiya, 9, 1973, 825-9.

14. Dugdale, I. and Cotton, J.B., The Anodic Polarization of Titanium in Halide Solutions, *Corr. Sci.*, 4, 1964, 397-411.
15. Cerny, M., Behaviour of Platinized Titanium Anodes in River Waters, *Proc. Fourth Int. Cong. Met. Corr.*, 1969, 721-3.
16. Ives, J.G. and Gilbert, J.R.B., Factors Affecting the Life of Noble Metal Treated Titanium Anodes, presented at A.I.M.E. Annual Conference, Dallas, Feb. 1974.
17. Angel, C.H. and Deriaz, M.G., *Brit. Pat.* 885,819.
18. Antonov, S.P. and Stepanenko, V.G., Production of Titanium-Palladium (rhodium, platinum)-lead dioxide-type Anodes and their Corrosion Resistance in Sulphate Solutions, *Korroz. Zashch. Metal.*, 1972, 67-71.