JOURNAL OF APPLIED ELECTROCHEMISTRY **25** (1995) 817–822

Performance characteristics of a new type of lead dioxide-coated titanium anode

M. UEDA, A. WATANABE, T. KAMEYAMA

National Institute of Materials and Chemical Research, Higashi 1-1, Tsukuba, 305, Japan

Y. MATSUMOTO, M. SEKIMOTO, T. SHIMAMUNE

Permelec Electrode Ltd, Endo 2023-15, Fujisawa, 252, Japan

Received 26 October 1994; revised 30 January 1995

A new type of PbO_2-coated metal anode, useful for electrochemical processing requiring the use of high-overpotential anodes, was prepared by applying to a titanium substrate an undercoating of Ti–Ta oxides, then covering the undercoating with an intermediate coating of stress-free α-PbO_2 deposit, and finally covering the intermediate coating with a Ta_2O_5 particle-admixed β-PbO_2 deposit. The anode thus produced was found to be superior to the anodized Pb or platinized Ti anode in respect of oxygen overvoltage, and corrosion resistance, even in solutions containing organic solvents. The possibility for use in chromium plating is also indicated.

1. Introduction

Lead dioxide (PbO_2) occurs in two different crystallographic forms; α-form (orthorhombic or columbite structure) and β-form (tetragonal or rutile structure). Alpha-PbO_2 can be produced by electrodeposition from an alkaline lead bath and β-PbO_2 can be produced by electrodeposition from an acid lead bath. Unless otherwise noted, the term 'PbO_2' used in applied electrochemistry usually refers to the β-form.

PbO_2 has long been known to be a high-overpotential anode material, and as such the dioxide has been frequently used in the electrochemical oxidation of compounds. For more information about the properties and some preparative applications of PbO_2 anodes, reference should be made to a review paper by Carr and Hampson [1]. In this connection, it must be added that the feasibility of electrolytic production of ozone with the use of PbO_2 anodes has been indicated by Thanos *et al.* [2].

We have recently developed a new type of PbO_2-coated titanium (PbO_2/Ti) anode [3] for use in electrochemical processing requiring the use of high-overpotential anodes. The new type of anode was found to have some advantages over conventional metal anodes.

This paper deals with performance characteristics of the PbO_2/Ti anode in relation to anode potential, corrosion resistance and Cr-plating.

2. Experimental details

2.1. *Electrodes*

2.1.1. Preparation of the PbO_2/Ti anode. The PbO_2/Ti anode was produced by applying to a titanium substrate an electroconductive undercoating consisting mainly of Ti–Ta oxides, then covering the undercoating with an intermediate coating consisting of a stress-free α-PbO_2 deposit [4], and finally covering the intermediate coating with a top coating consisting of a mixture of β-PbO_2 deposit and Ta_2O_5 particles.

The undercoating was produced by the thermal decomposition of the precursor, which preferably included thermally decomposable compounds of Ti and Ta. Such an undercoating is necessary for protecting the substrate from passivation. The undercoating must have high oxygen overvoltage. Oxygen evolution on it may break down the coatings.

The stress-free intermediate coating was produced by electrodeposition from an alkaline lead bath. This coating plays the role of binder. In the absence of this coating, the top coating cannot be firmly held by the undercoating.

The top coating was produced by electrolytic codeposition from an acid lead bath containing suspended fine Ta_2O_5 particles, since the incorporation of the particles was found to result in a coating with a low and reproducible internal stress [3]. If β-PbO_2 alone is deposited, the internal stress in the deposit changes as deposition progresses, and hence, approximately with the deposit thickness [5].

2.1.2. Application of coatings. The substrates used were 100 mm square sheets of expanded titanium mesh (1.5 mm thick, mesh size 12.5 mm × 5.6 mm) and of titanium plate (3 mm thick), which were roughened by sand-blasting, then degreased, and finally chemically etched.

For producing the undercoating, two coating solutions were used: solution A and solution B.

0021-891X

Table 1. Conditions of electrodeposition of both intermediate and top coatings

	Intermediate coating	*Top coating*
Cell	Undivided	Undivided
Bath composition	Note 1	Note 2
Bath temperature/K	313	343
Counter electrode	Note 3	Note 3
Current density/A dm^{-2}	1.1	4.0
Coating thickness/mm	0.1	0.7

Note 1: 3.5 M aqueous NaOH saturated with litharge (PbO).

Note 2: an aqueous solution of Pb $(NO_3)_2$ (30 wt %) in which Ta_2O_5 particles passed through 345 mesh screen were suspended in the proportion of 5 g dm^{-3}; pH 0–2.

Note 3: Pt plate cathode same in the nominal working area as the anode.

Solution A contained three main ingredients, $TiCl_4$, $TaCl_5$ and HCl, each present in a concentration of 0.13 mol dm^{-3} (M). Solution B contained a thermally decomposable compound of platinum (0.13 M) besides the above-noted three ingredients (each present in the aforesaid concentration). In the first step, solution A was applied to the substrate by brushing; the substrate was then dried at 313 K for 15 min, and subsequently heated at 793 K in air for 10 min. Several more coats of solution A were applied in the same way. In the second step, a few coats of solution B were applied to the coated substrate in the same way as in the first step, in order to increase electric conductivity of the coating. The undercoating produced in this study was about 1 μm thick.

Thereafter, both intermediate and top coatings were applied electrolytically under the conditions shown in Table 1.

2.1.3. Preparation of other types of anode. Three types of anode were also used: (i) platinized titanium (Pt/Ti) anode with a 3 μm thick platinum coating (made to order by a company); (ii) iridium oxide-coated titanium (IrO_2/Ti) anode with a coating thickness of about 1 μm (coating by the procedure given in [6]); and (iii) anodized lead (PbO_2/Pb) anode. The substrates used in the first two anodes were the same as specified in Section 2.1.2.

2.1.4. Preparation of anode samples. The original 100 mm square PbO_2/Ti anode, of which the substrate was titanium mesh or plate, was carefully cut into narrow strips of the desired size for tests. The plate anode had a better defined working (or exposed) area than the mesh anode, which resembles commercial anodes in shape. Both longitudinal sides of the strip showed a section of the metal core. Hence, in some experiments, both sides were insulated. Hereafter, such strips will be called simply 'protected samples'; if the sides were not insulated, such strips will be called 'unprotected samples'. In the case of the PbO_2/Pb anode, which was a strip of lead sheet, the back and the longitudinal sides, as well as the side at the end, were coated with corrosion-resistant ceramic paint.

The nominal working area was adjusted by coating the upper portion of the sample with a polyfluoroethylene insulation tape.

2.1.5. Counter-electrodes (cathodes). The counter electrode used in anode potential measurement was a rod of pure platinum, 2 mm in diameter, while the counter electrode used in corrosion resistance tests was a strip of pure platinum sheet of the same working area as the unprotected samples of coated titanium anode. The counter electrode used in the chromium plating test was a piece of copper plate with a working area of 0.10 dm^2, which was two-thirds of the nominal working area of the protected sample used.

2.2. *Tests of the PbO_2/Ti anode*

2.2.1. Anode potential measurement. Protected samples of three types of coated titanium plate anodes and a sample of PbO_2/Pb anode, each with a working area of 10 mm × 10 mm, were used. Before potential measurement, the protected sample of each coated titanium anode was conditioned at a current density of 50 A dm^{-2} in 1.53 M H_2SO_4 at 333 K for 30 min, while the sample of PbO_2/Pb anode was conditioned in the same acid for 90 min under the same conditions of current density and temperature.

Anode potential was measured against a mercury/mercurous sulfate reference electrode, at various current densities in the range 1 to 100 A dm^{-2} in the same acid and at the same temperature as above. Only the steady-state potential was recorded as the potential relative to the standard hydrogen electrode (SHE).

2.2.2. Corrosion resistance test of the PbO_2/Ti anode. The unprotected sample with the titanium mesh was cut into the following shape: 14 mm wide by 100 mm long. The sample was tested at anode current densities of 50, 100, and 200 A dm^{-2} in 1.53 M H_2SO_4 at 333 K. The test was continued for 2000 h. In the course of this test, the sample was occasionally removed from the electrolyte, then washed with water, and subsequently dried in air. Thereafter, the unprotected side was examined under a stereomicroscope.

The wear rate was calculated from the loss in weight of the sample at the end of a 2000 h run.

2.2.3. Test for durability of the PbO_2/Ti anode. In this test, the operation period during which the anode functioned without causing an abrupt and serious increase in the cell voltage was taken as the lifetime of the anode.

The protected sample of PbO_2/Ti anode had a nominal working area of 20 mm × 40 mm and the platinum cathode used had a working area of 14 mm × 50 mm. The electrolyte solution selected

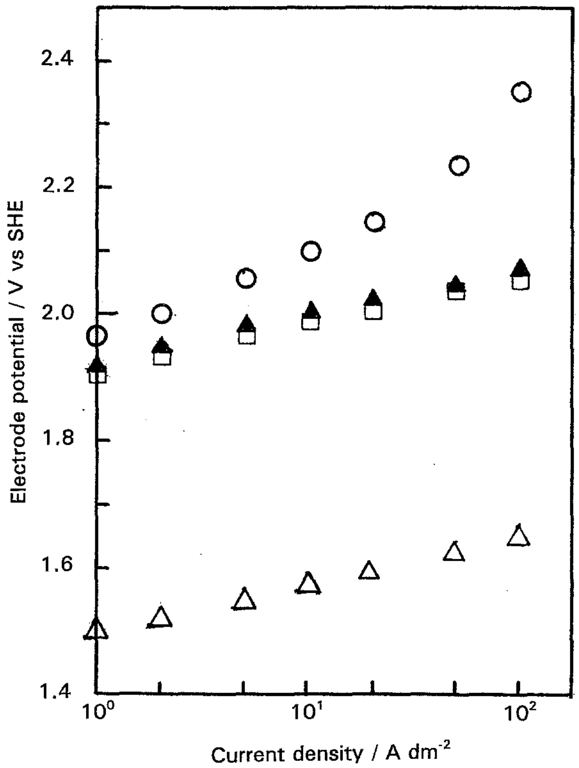

Fig. 1. Electrode potentials of four types of anode at various current densities in 1.53 M H_2SO_4 at 333 K. Key: (○) PbO_2/Ti; (▲) PbO_2/Pb; (□) Pt/Ti; (△) IrO_2/Ti.

was a 7.30 M solution of acetonitrile (CH_3CN) in 1.02 M aqueous H_2SO_4, because platinum anodes had been known to undergo marked dissolution when used in electrolysis of acid solutions containing CH_3CN. The test was conducted in the solution at 313 K, with the anode current density held at 50 A dm^{-2} and the makeup solution fed at a rate of 0.10 dm^3 A^{-1} h^{-1}. During the run, the cell voltage was measured continually until the voltage increased abruptly beyond 2 V above the initial.

For purposes of comparison, the protected sample of Pt/Ti anode was tested, not only in the same solution according to the above scheme, but also in 1.53 M H_2SO_4 at 333 K at anode current densities of 50, 100 and 200 A dm^{-2}.

2.2.4. Test for applicability to chromium plating. The test was conducted at a cathode current density of 30 A dm^{-2} in a chromium plating bath at 333 K. The bath comprised 3.00 M CrO_3, 41 mM H_2SO_4, and an additive concentration of 120 cm^3 dm^{-3}. The volume of the bath was 2.5 dm^3. The cathode was renewed after 12 h and an amount of CrO_3 equivalent to the chromium deposited was added after 48 h.

The total chromium concentration was determined by inductively-coupled plasma-emission spectrometry at a wavelength of 267.716 nm and the Cr(VI) concentration was determined by iodometry [7]. The Cr(III) concentration was then obtained by difference.

3. Results and discussion

3.1. *Anode potential and oxygen overvoltage*

Electrode potential is plotted against current density in Fig. 1 for the four types of anode studied. The PbO_2/Ti anode showed the greatest potential of all the types of anode tested over the current density range up to 100 A dm^{-2}. Therefore, the PbO_2/Ti anode was considered to be superior to the others in respect of oxygen overvoltage.

The PbO_2/Pb anode gave a potential somewhat lower than that of the PbO_2/Ti anode, though the

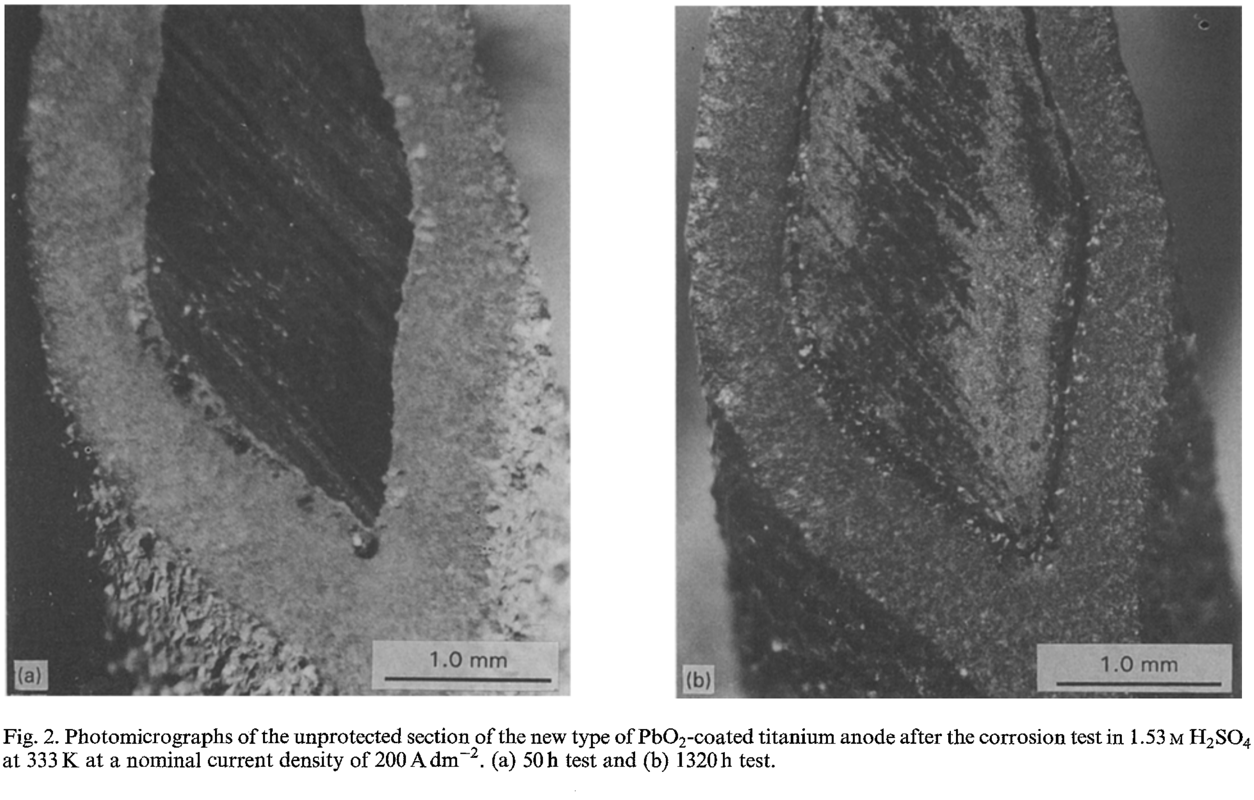

Fig. 2. Photomicrographs of the unprotected section of the new type of PbO_2-coated titanium anode after the corrosion test in 1.53 M H_2SO_4 at 333 K at a nominal current density of 200 A dm^{-2}. (a) 50 h test and (b) 1320 h test.

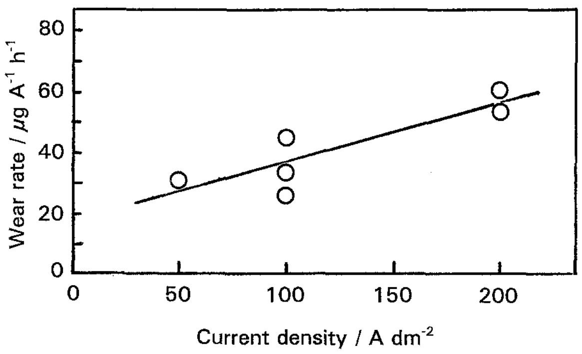

Fig. 3. Wear rate of the new type of PbO_2-coated titanium anode as a function of current density in the electrolysis of aqeous 1.53 M H_2SO_4 at 333 K.

surface of the anodized lead electrode had been known to consist of β-PbO_2. It appears that the lead oxide matrix in the surface of the PbO_2/Pb anode was responsible for the low electrode potential.

3.2. *Corrosion resistance and wear rate in aqueous H_2SO_4*

Figure 2 shows two photomicrographs of unprotected sections of the PbO_2/Ti anode tested at 200 A dm^{-2}. Micrograph (a) shows the section exposed to 1.53 M aqueous H_2SO_4 for 50 h of electrolysis and micrograph (b) shows the section exposed to the same acid for 1320 h. Because of the insufficient magnifying power of the microscope used, the 1 μm thick undercoating is not visible.

From micrograph (a), it appears that the unprotected sections of top and intermediate coating layers were scarcely corroded during 50 h of electrolysis. However, further prolonged exposure, as shown in micrograph (b), has resulted in slight corrosion only in the section of the intermediate coating layer.

The wear rate for the unprotected samples in the same acid is plotted against current density in Fig. 3. The straight line through the points is the regression line obtained by the least square method. The wear rate increases with current density.

3.3. *Lifetime of the PbO_2/Ti anode*

As mentioned earlier, the lifetime was defined in terms of cell voltage. Figure 4 represents the variation of cell voltage observed in two experiments with the protected samples in a solution of CH_3CN in aqueous H_2SO_4. A similar observation made with a protected sample of Pt/Ti anode is also indicated in Fig. 4 for the purpose of comparison. According to the definition of lifetime, it follows that the lifetime of the PbO_2/Ti anode is between 1.6 and 2.8 years, whereas the lifetime of the Pt/Ti anode is as short as 1 day.

The thickness of the top coating of the PbO_2/Ti anode after the lifetime at 200 A dm^{-2} in H_2SO_4 without CH_3CN was about one half of the initial. The lifetimes of the anode at 50 and 100 A dm^{-2} is then estimated from the wear rate given in Fig. 3, by assuming that the anode functions until one half of the initial thickness of the top coating is worn out. The lifetimes are shown in Fig. 5, as a function of anode current density. The lifetimes represented in Fig. 4 are again shown in Fig. 5 for the purpose of comparison. The lifetime curves for the two types of anode are similar in trend, indicating that the lower the current density, the longer the lifetime.

It must be noted that the filled circles and filled squares represent the anode lifetimes in a 7.3 M solution of CH_3CN in 1.02 M aqueous H_2SO_4 at 313 K, while the open circles and open squares represent the lifetimes in 1.53 M aqueous H_2SO_4 at 333 K without

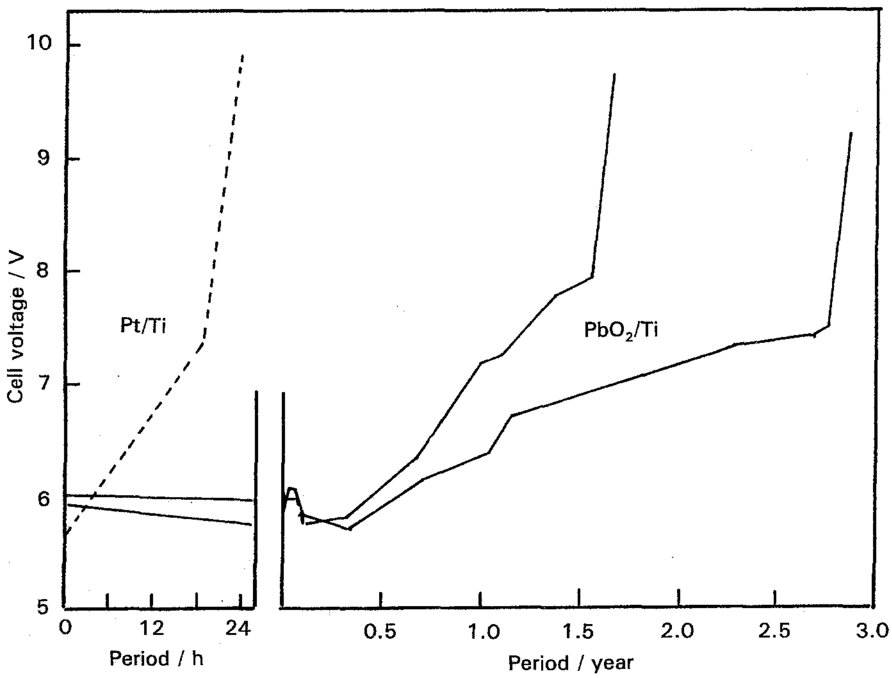

Fig. 4. Variation of the cell voltage during the electrolysis of 7.30 M solution of CH_3CN in aqeous 1.02 M H_2SO_4 at 313 K with platinized titanium anode or the new type of PbO_2-coated titanium anode at a current density of 50 A dm^{-2}.

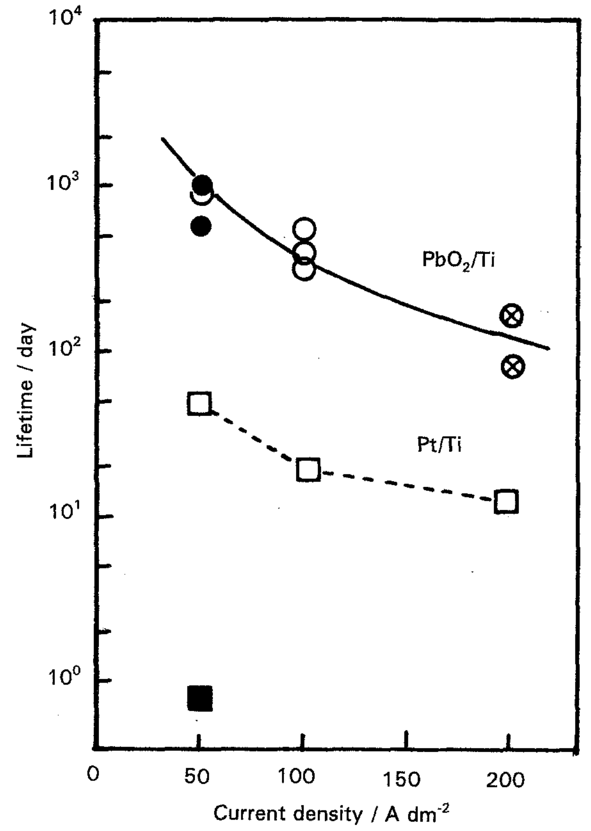

Fig. 5. Comparison of two types of anode in their lifetime at various current densities in different electrolytes. (○, ⊗ and □), in 1.53 M H_2SO_4 at 333 K. (● and ■), in a 7.30 M solution of CH_3CN in 1.02 M H_2SO_4 at 313 K. Note: the open circles represent the values estimated from Fig. 3.

CH_3CN. In the case of the PbO_2/Ti anode, the difference between the lifetime in H_2SO_4 solution and the lifetime at the same current density of 50 A dm^{-2} in acid CH_3CN solution is well within the limits of experimental error. On the other hand, in the case of the Pt/Ti anode, the difference between the lifetimes in different solutions is greater, though the tests were made under somewhat different conditions of acid concentration and temperature, suggesting that the anode was corroded by the dissolved organic material.

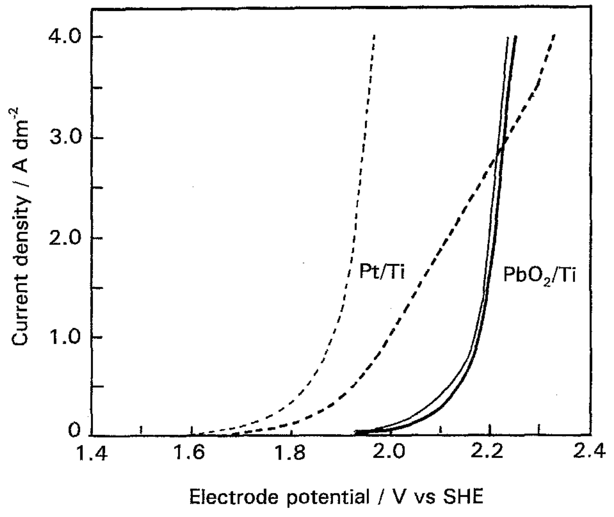

Fig. 6. Current–potential curves on two types of anode at sweep rate of 2 mV s^{-1} in different electrolytes at 323 K. Key: (thin curves): in 1.53 M H_2SO_4; (thick curves): in a 1.00 M solution of CH_3CN in 1.02 M H_2SO_4.

As to the short lifetime of platinum coating in CH_3CN-containing acid solution, it was suspected that the potential of the Pt/Ti anode was nobler than that without CH_3CN [8]. This agrees with the results of linear-sweep voltammetric studies of electrode materials at slightly higher temperature. The results are shown in Fig. 6. It is likely that such a noble potential facilitated the dissolution of platinum [8]. In contrast to the Pt/Ti anode, the potential of the PbO_2/Ti anode was not affected by the addition of CH_3CN as can be seen from the voltammogram of Fig. 6. The wear rate of the PbO_2/Ti anode was almost independent of whether or not the solution contained the organic solvent.

3.4. *Applicability of the PbO_2/Ti anode to chromium plating*

The variation of Cr(III) concentration observed in the chromium plating bath during operation with the PbO_2/Ti anode is shown in Fig. 7, together with the variation during operation with the IrO_2/Ti anode. Evidently, when the PbO_2/Ti anode was used, the Cr(III) concentration remained almost constant at 1.2 g dm^{-3} during a prolonged period of operation. On the other hand, when the IrO_2/Ti anode was used, the concentration increased steadily with time, up to about 16 g dm^{-3} in the same period of operation.

The two different phenomena may be explained as follows. In the course of two-step cathodic reduction of Cr(VI) ions to the metallic state, some of the

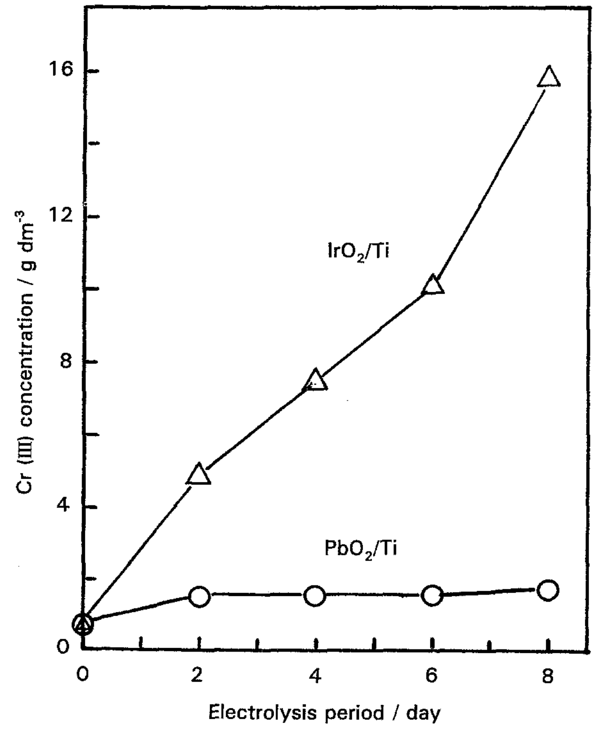

Fig. 7. Variation of Cr(III) concentration in a chromium plating bath during a prolonged period of operation at 333 K. Initial bath composition: Cr(VI) conc.: 3.00 M; H_2SO_4 conc.: 41 mM; additive: 120 cm^3 dm^{-3}.

Cr(III) ions formed escape from the cathode and are anodically oxidized to Cr(VI) ions. If the anodic oxidation reaction is slower than the cathodic formation of Cr(III) ions, the latter ions accumulate in the solution. This is the case with the IrO_2/Ti anode. However, if anodic oxidation is faster than the cathodic formation of Cr(III) ions, the latter ions cannot remain at high concentrations in the bulk of solution. This is the case with the PbO_2/Ti anode. The faster anodic oxidation in this latter case occurs by 'an indirect electrochemical reaction' [9], or by 'any specific electrode catalytic activity' [1].

Further tests on a commercial scale yielded similar results. In the plating operation with the PbO_2/Ti anode, the Cr(III) in the bath decreased to $1.2\,g\,dm^{-3}$ in 10 days, whereas in the operation with the IrO_2/Ti anode, the concentration increased to $6.5\,g\,dm^{-3}$ in 14 days. The concentrations were outside the optimal concentration range, $2–5\,g\,dm^{-3}$. On the other hand, when both types of anode were used simultaneously, with the ratio of the working area of the PbO_2/Ti anode to the working area of the IrO_2/Ti anode held at 1/0.8, the Cr(III) concentration remained in the range, $2–3\,g\,dm^{-3}$, during 24 days of plating. The simultaneous use of both types of anode may result in efficient chromium plating.

4. Conclusion

A new type of PbO_2-coated metal anode, useful in electrochemical processing requiring the use of high-overpotential anodes, was prepared by applying pyrolytically, to a titanium substrate, an undercoating consisting of platinum-occluding Ti–Ta mixed oxides, then covering the undercoating electrolytically with an intermediate coating consisting of stress-free α-PbO_2, and finally electrolytically covering the intermediate coating with a top coating consisting of a mixture of β-PbO_2 and Ta_2O_5 particles. The anode thus prepared was found to be superior to other types of anode tested in respect of oxygen overvoltage. It was superior to platinized titanium anode in corrosion resistance even in solutions containing organic solvent. Tests in a chromium-plating bath indicated the possibility of application as an anode for controlling the Cr(III) concentration in the bath, with the result of facilitating the efficient anodic oxidation of Cr(III).

Acknowledgement

The authors wish to acknowledge the useful discussion and criticisms extended by H. Takahashi.

References

[1] J. P. Carr and N. A. Hampson, *Chem. Rev.* **72** (1972) 679.
[2] J. C. G. Thanos, H. P. Fritz and D. Wabner, *J. Appl. Electrochem.* **14** (1984) 389.
[3] A. Watanabe, M. Ueda, T. Shimamune, M. Sekimoto, T. Kameyama and K. Fukuda, *Denki Kagaku oyobi Kogyo Butsuri Kagaku* **57** (1989) 139.
[4] A. Fukasawa and M. Ueda, *ibid.* **44** (1976) 646.
[5] For example: K. S. A. Gnanasekaran, K. C. Narasimham and H. V. K. Udupa, *Electrochim. Acta* **15** (1970) 1615.
[6] R. T. Atanososki, B. Ž. Nikolić, M. M. Jakšić and A. R. Despić, *J. Appl. Electrochem.* **5** (1975) 155.
[7] I. M. Kolthoff and P. J. Elving (eds), 'Treatise on Analytical Chemistry', Part II, vol. 8, Interscience, New York (1963) p. 330.
[8] M. Takahashi, Abstracts for the 53rd Meeting of Denki Kagaku Kyoukai (1986) p. 32.
[9] J. Mizuguchi, *J. Electrochem. Soc. Japan* **17** (1949) 294.