

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

Publication number:

0 407 355 A1

(12)

EUROPEAN PATENT APPLICATION

(21)

Application number: **90830250.8**

(51)

Int. Cl.⁵: **C25D 17/10**

(22)

Date of filing: **01.06.90**

(30)

Priority: **07.06.89 JP 142980/89**

(43)

Date of publication of application:
09.01.91 Bulletin 91/02

(64)

Designated Contracting States:
DE FR GB IT

(71)

Applicant: **Permelec Electrode Ltd**
No. 1159 Ishikawa
Fujisawa-shi Kanagawa(JP)

(72)

Inventor: **Matsumoto, Yukiei**
519-5 Takakura
Fujisawa-shi, Kanagawa(JP)
Inventor: **Hayashi, Takanobu**
6-11, Rinkan 1-chome
Yamato-shi, Kanagawa(JP)
Inventor: **Suganuma, Yoshiaki**
1739 Ishikawa
Fujisawa-shi, Kanagawa(JP)

(74)

Representative: **Pellegrini, Alberto et al**
c/o Società Italiana Brevetti S.p.A., Via
Cavour, 9
I-21100 Varese(IT)

(54)

Insoluble electrode for electroplating and process for producing the same.

(57)

An insoluble electrode for electroplating and a process for producing the same are disclosed, the electrode comprising a base having coated thereon an electrode active substance containing a platinum metal or an oxide thereof, said base comprising an anticorrosion-metal plate having joined thereon a porous anticorrosion-metal sheet. The insoluble electrode has improved durability even when used at a high current density.

EP 0 407 355 A1

INSOLUBLE ELECTRODE FOR ELECTROPLATING AND PROCESS FOR PRODUCING THE SAME

FIELD OF THE INVENTION

5 This invention relates to an electrode for electroplating and a process for producing the same. More particularly, it relates to an electrode having excellent durability as an anode for continuous plating of a steel plate which is conducted at a high current density, and a process for producing such an electrode.

BACKGROUND OF THE INVENTION

10

A demand for surface-treated steel sheeting has recently been increasing in various fields, such as automobiles and appliances. With this demand, the electroplating technique used for continuously coating the surface of a steel band has become increasingly important.

15 A conventional electroplating technique using a soluble electrode as an anode has been replaced with a process of using an insoluble electrode, as described in JP-B-53-18167 (the term "JP-B" as used herein means an "examined published Japanese patent application") and JP-A-56-47597 (the term "JP-A" as used herein means an "unexamined published Japanese patent application").

20 Use of an insoluble electrode in electroplating is expected to bring about various advantages, such as (1) a possibility of plating with various alloys, (2) improvement of productivity by increasing anode current density and increasing line speed, (3) improvement of quality by leveling current distribution, and (4) reduction in frequency of anode exchange.

25 Known insoluble electrodes include lead electrodes, lead alloy electrodes, and platinum-plated electrodes. However, lead or lead alloy electrodes to be used for lead or lead alloy electroplating have insufficient insolubility, so that lead is gradually dissolved out, resulting in deterioration of plated product quality or formation of a large quantity of sludge. It is therefore necessary to use a large amount of an adsorbent for removing the dissolved lead ion.

Further, the platinum coating of platinum-plated electrodes easily falls off upon use at a high current density, making the electrode useless in a short time.

30

SUMMARY OF THE INVENTION

35 An object of this invention is to provide an insoluble electrode for electroplating which is free from the above-described disadvantages associated with conventional insoluble electrodes for electroplating, that is, which has sufficient durability even when used at a high current density.

Another object of this invention is to provide a process for producing the above-described insoluble electrode for electroplating.

40 The present invention provides an insoluble electrode for electroplating comprising a base having coated thereon an electrode active substance containing a platinum metal or an oxide thereof, said base comprising an anticorrosion-metal plate having joined thereon a porous anticorrosion-metal sheet.

45

DETAILED DESCRIPTION OF THE INVENTION

50 The base of the electrode according to the present invention comprises an anticorrosion-metal plate having joined thereon a porous anticorrosion-metal sheet. The anticorrosion-metal which can be used in the present invention is not particularly limited in kind, as long as it is usable as an electrode base. Suitable anticorrosion-metals include Ti, Ta, Nb, Zr, and alloys thereof, in view of their excellent anticorrosion properties and sufficient mechanical strength.

The material of the porous anticorrosion metal sheet and that of the metal plate are usually the same, but may be different.

The metal plate, which is usually a non-porous flat plate but may be a curved plate, should have a

sufficient thickness to maintain mechanical strength of the electrode and for electricity to sufficiently pass.

The porous metal sheet which is joined to the metal plate functions to permit a large quantity of a gas evolved from the anode, such as oxygen, to escape, thereby preventing retention of bubbles. The porous metal sheet also functions to greatly increase the electrode surface area, to thereby reduce electrolytic voltage. Suitable porous metal sheets providing this effect include expanded metal, punched metal, wire sheet, and wire cord fabric, each having a porosity of from 5 to 90%. Metallic fiber laminated sheets, metallic fiber cloth, wire rolls, metallic felt, and porous sintered bodies of metals are also employable. If desired, taking strength and electricity quantity into consideration, a plurality of such porous sheets may be laminated.

To assure electrical conduction between the metal plate and the porous sheet, joining of the metal plate and the porous sheet is carried out by bolting, welding, or like technique. Taking it into consideration that a large electric current passes through the joining area, a welded joint having a small electrical resistance is preferred. An increase in electrolytic voltage and heat generation can be suppressed by forming a sufficient number or amount of welded joining area.

The above-described base comprising the metal plate having joined thereon the porous metal sheet is then coated with an electrode active substance. Prior to coating, the base can be subjected to a surface treatment, such as nitriding treatment, boriding treatment, or carbonization treatment, to further improve anticorrosion properties.

Further, in order to prevent passivation of the electrode and to improve durability, an intermediate layer comprising a conductive oxide containing an oxide of at least one metal selected from the group consisting of Ti, Zr, Nb, Sn, Sb, and Ta may be provided on the base. Such an intermediate layer can be formed by various means, such as those employable for coating of an electrode active substance on the base as hereinafter described. In particular, a pyrolysis method comprising applying a solution of a salt of the metallic component for the intermediate layer onto the base and calcining the salt to form an oxide layer is preferred.

Electrode active substances containing a platinum metal or an oxide thereof exhibit excellent electrochemical characteristics and chemical resistance for use in insoluble electrodes for electroplating. Specific examples of suitable electrode active substances include at least one platinum metal, e.g., Ru, Rh, Pd, Ir, and Pt, platinum metal alloys, and platinum metal oxides. Composite substances comprising such a platinum metal, alloy or oxide and at least one of base metals, e.g., Ti, Zr, Nb, Ta, and Sn, or an oxide thereof may also be used. This being the case, the content of the platinum metal component in the composite substance is preferably 10% by weight or more, based on the elemental platinum content, to ensure satisfactory electrode activity.

Methods for coating the electrode active substance on the base are not particularly restricted, and include various known methods for electrode coating, such as those described in JP-B-48-3954. A suitable method is a pyrolysis method in which a solution of the above-described electrode active substance metallic component or a salt thereof in an appropriate solvent is applied to the base by coating or dipping, and then calcined by heating in an oxidative, neutral or reductive atmosphere to form a coating layer. If desired, the coating procedure can be repeated to obtain a desired coating thickness.

The thus produced electrode of the present invention, when used for continuous plating on a steel plate, etc., exhibits higher anticorrosion and electrode activity than conventional insoluble electrodes, even at a high current density. Hence, it withstands use in various corrosive electrolytic solutions, thereby enjoying various advantages accompanying use of an insoluble electrode as set forth above.

Since the electrode of the present invention has a composite structure in which a porous metal sheet is joined to a metal plate, it is possible to pass a higher electric current as compared with smooth plate electrodes, and bubbles generated on the electrode can satisfactorily escape. Further, since the bubbles, if any remains on the electrode, have a small thickness, an increase in electrolytic voltage due to resistance of the bubbles can be inhibited. Thus, the electrode of the invention brings about marked improvements in productivity of a plated steel plate and economy due to increased line speed, saving of electric power, and the like.

While the present invention has been described chiefly with respect to particular use for electroplating on a steel plate, the insoluble electrode according to the present invention is also applicable to other organic or inorganic electrolysis, surface treatment of metals, electrolytic winning, and the like.

The present invention is now illustrated in greater detail by way of Examples, but it should be understood that the present invention is not limited thereto.

EXAMPLE 1

An expanded metal sheet made of pure titanium having a thickness of 0.1 mm, 0.3 mm, or 0.5 mm and a porosity of 50% was joined by welding to a commercially available titanium plate having a size of 100 mm x 100 mm x 5 mm (t) to prepare three kinds of bases. After degreasing with acetone, each base was washed successively with a pure oxalic acid solution and pure water, and then dried.

For comparison, the same titanium plate having thereon no expanded metal was degreased, washed and dried in the same manner as described above to prepare a comparative base.

A butanol solution containing iridium chloride and tantalum chloride at a molar ratio of 6/4 was coated on each of the bases with a brush, dried, and calcined in air at 550 °C to prepare an electrode. The coating, drying and calcination operations were repeated until the iridium content in the coat reached 0.3 mg/cm².

Electrolysis was carried out in a model zinc plating bath described below in a non-mobile phase, using each of the resulting electrodes as an anode and mild steel sheet as a cathode, and the electrolytic voltage (bath voltage) was measured.

Model Zinc Plating Bath:

Na₂SO₄: 100 g/l

(NH₄)₂SO₄: 100 g/l

pH: 1.2

Temperature: 60 °C

Current Density: 200 A/cm²

Further, in order to evaluate electrode durability, electrolysis was carried out in a 1M sulfuric acid aqueous solution at a current density of 2 A/cm² using the electrode as an anode and a platinum plate as a cathode. The time required for the bath voltage to reach 10 V was taken as durability.

The results of these tests are shown in Table 1 below.

TABLE 1

Run No.	Thickness of Porous Sheet	Electrolytic Voltage	Durability
	(mm)	(V)	(hr)
1	0.1	7.1	149.3
2	0.3	6.8	168.2
3	0.5	6.9	152.8
Comparison	-	7.4	69.8

It is apparent from the results in Table 1 that the electrode according to the present invention using a base comprising a titanium plate having joined thereon a titanium expanded metal porous sheet reduces electrolytic voltage and has a greatly improved durability.

EXAMPLE 2

A punched metal sheet made of titanium having a thickness of 0.5 mm, a pore diameter of 2 mm, and a porosity of 50% was joined to a titanium plate or a Ti-3Ta alloy (Ti-based alloy containing 3 wt% Ta, hereinafter the same) plate to prepare a Ti or Ti-3Ta base (Samples 1 and 3).

The same punching metal sheet was joined to a titanium plate, and the surface of the Ti plate was subjected to a nitriding treatment to form a 3 μm thick nitride layer to prepare a TiN/Ti base (Sample 5).

An intermediate layer of a metallic oxide shown in Table 2 below was formed on a Ti or Ti-3Ta sheet to a thickness of 3 μm to prepare a Ti or Ti-3Ta base (Samples 2 and 4).

An electrode active substance shown in Table 2 was coated on each of the bases to a thickness of 0.3 mg-Pt/cm² to prepare an electrode, and durability of the resulting electrode was evaluated in the same manner as in Example 1.

For comparison, electrodes were prepared in the same manner as for Samples 1 to 5, except that the base had no punched metal sheet, and evaluated in the same manner as in Example 1.

The results obtained are shown in Table 2.

TABLE 2

Sample No.	Base	Intermediate Layer	Electrode Active Substance	Example	Comparison
1	Ti	-	IrO ₂	128.1	30.4
2	Ti	Nb ₂ O ₅	RuO ₂ -IrO ₂ -SnO ₂	182.4	29.6
3	Ti-3Ta	-	Pt-RuO ₂ -IrO ₂ -SnO ₂ -Sb ₂ O ₃	109.8	23.1
4	Ti-3Ta	SnO ₂ -Sb ₂ O ₃	Pt-Ir	76.6	20.3
5	TiN/Ti	-	Pt	32.7	11.2

It is apparent from the results in Table 2 that the electrode of the present invention using a base having a titanium punching metal porous sheet has an extended durability.

As described above, the insoluble electrode for electroplating according to the present invention, which comprises an anticorrosion-metal composite plate base having coated thereon an electrode active substance containing a platinum metal or an oxide thereof, exhibits excellent durability and makes it possible to reduce electrolytic voltage. Because of the composite structure of the base comprising a basic metal plate having joined thereon a porous metal sheet, the electrode permits operations at high current density and prevents an increase in voltage due to evolution of gases, thereby greatly improving productivity and saving electric power in electroplating.

In addition, the durability of the electrode can be further enhanced by treating the surface of the base by nitriding, boriding, or carbonizing, or by providing an intermediate layer comprising a conductive oxide on the surface of the base.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. An insoluble electrode for electroplating comprising a base having coated thereon an electrode active substance containing a platinum metal or an oxide thereof, said base comprising an anticorrosion-metal plate having joined thereon a porous anticorrosion-metal sheet.
2. An insoluble electrode as in claim 1, wherein the anticorrosion-metal is selected from Ti, Ta, Nb, and Zr, and alloys thereof.
3. An insoluble electrode as in claim 1, wherein the base has a nitrided, borided, or carbonized surface.
4. An insoluble electrode as in claim 1, wherein the electrode further comprises a conductive intermediate layer containing an oxide of at least one metal selected from the group consisting of Ti, Zr, Nb, Sn, Sb, and Ta provided between the base and the electrode active substance.
5. An insoluble electrode as in claim 1, wherein said porous anticorrosion metal sheet has a porosity of from 5 to 90%.
6. An insoluble electrode as in claim 1, wherein the electrode active substance contains the platinum metal or an oxide thereof in an amount such that the content of platinum is 10% by weight or more.
7. A process for producing an insoluble electrode for electroplating which comprises electroconductively joining a porous anticorrosion-metal sheet on an anticorrosion-metal plate to prepare an electrode base, and coating the base with an electrode active substance containing a platinum metal or an oxide thereof.
8. A process for producing an insoluble electrode as in claim 7, wherein the process further includes forming an intermediate conductive layer containing a metal oxide on the surface of the electrode base prior to the coating of the electrode active substance.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 83 0250

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 271 924 (PERMELEC S.p.A.) * Page 3, lines 53-54 * ---	1,2,5,6 ,7	C 25 D 17/10
A	PATENT ABSTRACTS OF JAPAN, vol. 13, no. 414 (C-635)[3762], 13th September 1989; & JP-A-1 150 000 (NIPPON STEEL CORP.) 13-06-1989 -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 25 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 07-09-1990	Examiner NGUYEN THE NGHIEP
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	