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[21] Appl. No. **561,054**
[22] Filed **June 28, 1966**
[45] Patented **Dec. 28, 1971**
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[54] **CHEMICAL DEPOSITION FORMATION OF
ANODES**
7 Claims, No Drawings

[52] U.S. Cl. **117/227,
106/1, 117/130 R, 117/160 R, 117/230, 204/290
F, 252/472**
[51] Int. Cl. **B01k 3/04,
C23c 3/02, C23c 3/04**
[50] Field of Search **117/130,
160, 227, 50; 106/1; 252/472; 204/290 F; 148/18,
20.6; 136/120 FC**

[56]

References Cited

UNITED STATES PATENTS

2,719,797	10/1955	Rosenblatt et al.	117/65
2,166,076	7/1939	Rosenblatt	106/1 X
2,787,540	4/1957	Appell	252/472 X
2,999,767	9/1961	Clay, Jr. et al.	106/1 X
3,177,131	4/1965	Angell et al.	204/290 X
3,294,578	12/1966	Popeck	106/1 X

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ABSTRACT: Compositions and method for chemical deposition of platinum group metals on a base structure and to novel electrodes produced by the said method. The invention relates particularly, but not exclusively, to electrodes for use in the electrolysis of salt solutions.

CHEMICAL DEPOSITION FORMATION OF ANODES

PRIOR ART

Naturally occurring waters such as brackish, hard, and sea waters and other industrial solutions contain varying quantities of salts such as chlorides, sulfates, bicarbonates, carbonates and small quantities of nitrates, fluorides, etc. When a direct current is passed through such waters, the products of electrolysis are usually strongly corrosive and exert a strong chemical attack on the electrode material necessitating careful selection of the composition of such electrodes. For example, graphite electrodes have been successfully used in solutions containing high concentrations of chloride anions because the carbon is sufficiently resistant to anodic chlorine gas for the anode to last many months. On the other hand, carbon electrodes are not nearly as valuable in sulfate-containing solutions owing to the generation of oxygen which attacks the carbon. In pure sulfate solutions, lead anodes may be used because a protective film of insoluble lead oxide forms at the surface of the electrode which nevertheless continues to conduct electricity. Furthermore, the formation of lead oxide ceases shortly after the start of an electrolysis. On the other hand, lead electrodes are not nearly as valuable in chloride-containing solutions because the chlorine gas which forms at the anode attacks the lead forming soluble lead chloride which is not retained as a protective coating. Numerous materials have been tried and found unsatisfactory for various reasons usually attributable to chemical reaction with electrolysis products.

OBJECTS OF THE INVENTION

It is an object of the invention to provide novel compositions for chemideposition of platinum metals on a base metal.

It is another object of the invention to provide a novel chemideposition method for forming a platinum metal coating on a base metal.

It is an additional object of the invention to provide novel platinum metal coated anodes having a low anode potential and low wear rate.

These and other objects and advantages of the invention will become obvious from the following detailed description.

THE INVENTION

The novel compositions of the invention for the chemideposition of a platinum metal on a base structure are comprised of a solution of a soluble platinum group metal compound and preferably a thickening agent in an organic solvent and containing at least one component in the composition having a radical selected from the group consisting of $-\text{NH}_3$, $-\text{NH}_2$, $-\text{NH}$, and $-\text{NH}$. Platinum group metal includes ruthenium, rhodium, palladium, osmium, iridium and platinum and alloys of 2 or more of the said metals. Platinum is the preferred metal and is used as representative of the class.

The composition of the base upon which the platinum group metal is to be applied will vary depending upon the use of the coating. Examples of suitable bases are nonmetallic bases such as glass, carbon, etc., and metallic bases such as stainless steel, iron, nickel, titanium, tantalum, alloys thereof, etc. If the said structures are to be used as electrodes for the electrolysis of solutions such as sodium chloride brines to produce chlorine and caustic soda, the base structure is preferably a valve metal such as titanium or tantalum. The said electrodes may have any convenient form such as plate, expanded mesh, etc.

Examples of suitable soluble salts of the platinum group metals are diammonium dinitrite salts such as $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$, $\text{Ir}(\text{NH}_3)_3(\text{NO}_2)_3$, etc., ammonium salts such as ammonium chloroplatinate $(\text{NH}_4)_2\text{PtCl}_6$, ammonium chloroiridate $(\text{NH}_4)_2\text{IrCl}_6$, hexammineplatinum (IV) chloride $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$, chloropentammineplatinum (IV) chloride $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$, dichlorotetrammineplatinum (IV) chloride $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$, trichlorotriammineplatinum (IV) chloride $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$, tetrachlorodiammineplatinum (cis and trans isomers)

$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$, tetrammineplatinum (II) chloride $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$, chlorotrammineplatinum (II) chloride $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$, dichlorodiammineplatinum (cis and trans isomers) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$ and alkali metal salts such as potassium hexachloroplatinate (IV) $[\text{PtCl}_6]\text{K}_2$, potassium trichloroammineplatiniate (II) $[\text{Pt}(\text{NH}_3)\text{Cl}_3]\text{K}$, and potassium tetrachloroplatinate (II) $[\text{PtCl}_4]\text{K}_2$.

Examples of suitable organic solvents for the compositions of the invention are lower aliphatic carboxylic acid amides such as formamide, acetamide, dimethylformamide, etc.; lower alkyl amines such as butyl amine, diethylamine, etc. Particularly preferred as the solvent is formamide.

The components of the compositions of the invention having a radical selected from the group consisting of $-\text{NH}_3$, $-\text{NH}_2$, $-\text{NH}$, and $-\text{NH}$ may be the soluble platinum group compound, the organic solvent, the thickening agent or an added compound or any combination thereof. Examples of suitable added components are ammonium salts such as ammonium chloride, ammonium iodide, ammonium hydroxide; lower alkyl quaternary ammonium salts such as tetramethyl ammonium hydroxide, butyl trimethyl ammonium hydroxide, tetramethyl ammonium chloride, etc.; hydrazine and its derivatives such as hydrazine chloride, hydrazine hydrate and organic derivatives such as methyl hydrazine, phenyl hydrazine, etc. Particularly preferred are ammonium halides. The additional components are usually 0.05 to 0.5 percent of the total weight of the composition.

The thickening agent may be any suitable compound to increase the viscosity of the compositions of the invention so the compositions will not run off the base structure to be coated but will adhere thereto when applied by brush or other suitable means. Usually 20 to 25 percent of thickening agent in the composition is adequate although the thickening agent may be omitted. Examples of suitable thickening agents are polyethyleneoxy polyamines such as Polyrad 1110 A of Hercules Powder Company, quaternary ammonium compounds; polymeric aliphatic hydrocarbons such as polyisobutylene; polystyrene and alkyl styrenepolymers; polymers of long chain alkyl acrylates and polyesters, etc.

The amount of soluble platinum group metal compound present in the composition is kept near its saturation point in the organic solvent. Under such conditions, the platinum group metal content can be about 1.5 to 2.5 percent by weight of the composition.

The method of the invention for forming a platinum group metal coating on a base comprises applying a solution of a soluble platinum metal compound and a thickening agent in an organic solvent and containing at least one component in the composition having a radical selected from the group consisting of NH_3 , $-\text{NH}_2$, $-\text{NH}$, and $-\text{NH}$ to the base, by brushing, spraying, dipping or the like, heating the coated base to a temperature above 350°C . for a period of time to form a continuous, adherent coating of the platinum group metal on the base and cooling the said coated base in air. Temperatures as high as 650°C . may be used but temperatures below 600°C . are preferred since tests have shown that the best results are obtained at lower temperatures.

The electrodes produced by the novel coating method of the invention are particularly useful as anodes for the electrolysis of sodium chloride brines in mercury cathode cells and diaphragm cells as they will operate for longer periods of time at voltage values below passivation and at lower wear rates than platinum group metal coated anodes produced by electrolysis or other chemideposition methods. Wear rate is determined by the amount of the platinum group metal lost per ton of chlorine produced.

Passivity of platinum or platinum coated anodes in electrolysis of brines has been a problem. Passivity refers to the rapid rise in potential in the said anodes after being used for some time at sufficiently high current density under chlorine discharge. This rise in potential indicates that the anodic oxidation of the dissolved chlorine ion to molecular chlorine gas will proceed only at a high overvoltage because of the

diminished catalytic activity of the electrode surface due to the buildup of a less active platinum oxide layer.

The following theoretical discussion of the excellent properties of the anodes of the invention is not intended to limit the scope of the invention in any fashion. The presence of the N—H groups in any form in the liquid chemideposition coating composition are believed to promote the formation of a continuous and highly adherent layer of valve metal nitride on a valve metal substrum. The formation of a highly adherent layer of platinum metal is also likely to be promoted by the reducing action of the N—H groups which hinders the formation of an intermediate layer of valve metal oxide.

In the following examples there are described several preferred embodiments to illustrate the invention. However, it should be understood that the invention is not intended to be limited to the specific embodiments.

EXAMPLE I

A liquid coating composition of 750 ml./l. of formamide, 250 ml./l. of Polyrad 1110 A, 28 gm./l. of $(\text{NH}_4)_2\text{PtCl}_6$, g./l. of $(\text{NH}_4)_2\text{IrCl}_6$ and 5 g./l. of ammonium chloride was applied by brush in four coatings to strips of titanium which had been etched in an azeotropic hydrogen chloride solution (20 percent) at reflux temperatures for 40 minutes. After each of the first three coatings, the coated strips were placed in an oven at 400° C. swept with a forced air draft for 5 to 10 minutes and after the last coating, the strips were subjected to heating in the oven as indicated in table I.

TABLE I

Sample	Thickness of 60% Pt—40% Ir Coating in g./m. ²	°C.	Heating Time in Hours
A	20	550	1.5
B	20	600	1.5
C	20	650	2.0
D	10	650	2.0

The said samples were operated in plant scale horizontal mercury cells for prolonged periods of time and demonstrated low wear rates (less than 0.25 g./ton of chlorine) and voltages in the active state at 4.0 asi. For example, sample C was operated for 85 days in such a cell at 4.0 asi. and voltages remained in the active range. At the end of two 42 day periods, wear rates of 0.24 and 0.08 g./ton were obtained giving an average wear rate of 0.16 g. of platinum per ton chlorine. Sample B was still operating after 212 days and the wear rate after 41 days was 0.01 g. of platinum per ton of chlorine.

EXAMPLE II

Strips of titanium were etched in an azeotropic hydrogen chloride solution (20 percent) at reflux temperatures for 40 minutes. One titanium strip was then given a liquid coating of a solution of 17.5 g. of $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ per liter of 3 parts of formamide and 1 part of Polyrad 1110 A. Another titanium strip was given a liquid coating of a solution of 8.55 g. (as Pt) of $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ and 2.15 g. (as Ir) of $\text{Ir}(\text{NH}_3)_3(\text{NO}_2)_6$ per liter of 3 parts of formamide and 1 part of Polyrad 1110 A. The said coatings were applied four times as in Example I and the amount of the liquid coatings corresponded to a platinum group metal thickness of 20 gm./m.². For each coating, the strips were dried by infrared radiation and then held in an oven at 400° C. in the presence of ammonium phosphate for one-half hour and subsequently cooled in air.

The anode potential at 1 A./cm.² for each strip was determined for the electrolysis of a concentrated sodium chloride brine saturated with chlorine gas at 70° C. and the results ob-

tained after continuous operation at 1 A./cm.² for 8 hours are summarized in table II.

TABLE II

Strip Coating	Anode Potential at 1 A./cm. ² in Volts
Platinum	1.8
80% Platinum—20% Iridium	1.5

EXAMPLE III

Preetched strips of expanded titanium metal were given a liquid coating of a solution of 400 ml./l. of formamide, 200 ml./l. of Polyrad, 400 ml./l. of hydrazine hydrate, 0.5 g./l. of ammonium chloride, 40.7 g./l. of $(\text{NH}_4)_2\text{PtCl}_6$ and 4.6 g./l. of $(\text{NH}_4)_2\text{IrCl}_6$, the latter two quantities corresponding to 1 part of Ir over 9 parts of Pt, that is to a ratio of 10 percent Ir and 90 percent Pt in the final deposit of noble metal. The coating was applied in eight subsequent coatings totaling to a noble metal amount of 20 g./m.². After each of the first seven coatings the samples were submitted to a heat treatment at 400° C. for 5 to 10 minutes in an oven swept with a forced air draft; the final heat treatment after applying the eighth coating differed from the former ones in that it was carried out at 500° C. for 30 to 90 minutes, followed by cooling in air. The results obtained for anodic operation under same conditions as in example II are summarized in table III.

TABLE III

Initial Potential (NHE)	
at 1 A./cm. ²	1.35 v.
Noble metal coating	
Wear rate per kg. Cl ₂ produced	Less than 0.3 mg.
Passivation time	More than 5,000 hours

EXAMPLE IV

Strips of titanium samples were etched as formerly described. They were then given a liquid coating of a solution of 400 ml./l. of formamide, 200 ml./l. of Polyrad, 400 ml./l. of hydrazine hydrate, 0.5 g./l. of ammonium chloride, 36 g./l. of $(\text{NH}_4)_2\text{Pt}$, 15.1 g./l. of $(\text{NH}_4)_3\text{RhCl}_6$; the latter two quantities correspond to 2 parts of Rh over 8 parts of Pt, that is to a composition of 20 percent Rh and 80 percent Pt in the final deposit of noble metal. The coating was applied in eight subsequent coatings so as to deposit a total amount of noble metal equivalent to 20 g./m.². Intermediate and final heat treatments were applied in the same way as described in example III. The results obtained for anodic operation under same conditions as in example II are summarized in table IV.

TABLE IV

Initial potential (NHE)	
at 1 A./cm. ²	1.41 v.

Various modifications of the compositions, method and anodes of the invention may be made without departing from the spirit or scope thereof.

What is claimed is:

1. A method of forming a coating containing a platinum group metal on a valve metal electrode base comprising applying to the valve metal base a coating composition consisting essentially of a solution of at least one soluble platinum group

metal compound selected from the group consisting of diammonium dinitrate salts, ammonium salts and alkali metal salts thereof in an organic solvent selected from the group consisting of lower aliphatic carboxylic acid amides and lower alkyl amines, the platinum group metal content being about 1.25 to 2.5 percent by weight of the composition, heating the coated valve metal base at a temperature above 350° C. for a period of time to form a continuous, adherent coating of the platinum group metal on the valve metal base and cooling the coated valve metal base in air.

2. The method of claim 1 wherein the heating temperature is 400° to 600° C.

3. The method of claim 1 wherein the platinum group metal is 60 to 100 percent platinum and 40 to 0 percent iridium.

4. The method of claim 1 wherein the coating composition is applied in a series of applications with an intermediate heating after each coating.

5. A method of forming a coating containing a platinum group metal on a valve metal anode base comprising applying a coating composition comprising a solution of at least one

platinum group metal ammonium compound and 0.05 to 0.5 percent by weight of an ammonium halide dissolved in formamide, the platinum group metal content being about 1.25 to 2.5 percent by weight of the composition to the valve metal base in a series of applications with intermediate heating up to 600° C. after each coating, applying a final coating of the coating composition to the valve metal base, heating the coated base at 350° to 650° C. to form a continuous, adherent coating of the platinum group metal on the valve metal anode base and cooling the coated base in air to form an anode suitable for electrolysis of brines.

6. The method of claim 1 wherein the organic solvent is formamide.

7. The method of claim 1 wherein the coating composition contains 0.05 percent to 0.5 percent by weight of the total composition of a component selected from the group consisting of ammonium salts, lower alkyl quaternary ammonium salts, hydrazine and organic hydrazines.

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