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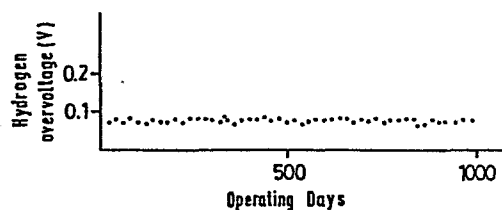
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(54) **A low hydrogen overvoltage cathode and method for producing the same.**

(57) Disclosed is a low hydrogen overvoltage cathode having a nickel or a nickel alloy coating layer containing electroconductive fine particles which hold a platinum group metal and/or an oxide thereof. Also disclosed is process for producing the same which comprises using a codeposit plating tank wherein an anode and an object to be plated of a non-perforated flat structure are positioned in parallel, supplying a dispersant slurry through one side to thus allow it to flow between the anode and the object, then removing the slurry through the opposite side, whereby codeposit plating is applied to only one surface of the object.

FIG.1



A LOW HYDROGEN OVERVOLTAGE CATHODE
AND METHOD FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the invention

The present invention generally relates to a low hydrogen overvoltage cathode for use in electrolysis of water or alkali metal halides and method for producing the same. More particularly, it relates to a low hydrogen overvoltage cathode having low hydrogen-generating electric potential and satisfactory durability specifically suitable for electrolysis of an aqueous alkali metal halide solution and production method thereof.

2. Description of prior art

In the electrolysis of water or an aqueous alkali metal halide solution using an asbestos diaphragm or an ion exchange membrane, punched mild steel plates, mild steel meshes and the like have been served as cathodes. These materials are advantageous in respect of cost, alkali-resistance, processability and the like, as compared with other materials. Moreover, mild steel shows hydrogen overvoltage of from 0.3 to 0.4 Volt, which is relatively low excepting platinum group metals.

Nonetheless, recently a rapid increase in energy cost accelerates the need of reducing more vastly hydrogen overvoltage of mild steel cathodes for use in hydrogen generation to thus lower energy cost and a variety of cathodes are proposed. Most of those improved cathodes employ iron group metals less expensive, easily processable and available as a cathode base, on the surface of which a coating of reducing hydrogen overvoltage is formed.

For example, there are known electrodes obtained by spray

coating an iron group cathode base with nickel or tungsten carbide powder (Patent non-examined Publication No. 32832 /77) , electrodes spray coated with cobalt and zirconium (No. 36582 /77) , electrodes comprising nickel and cobalt subjected to leaching treatment after spray coating (No. 36583 /77) , electrodes obtained by spray coating an electrode base with Raney-nickel and then leaching with alkali a sacrificial metal contained in the coating layer (No. 122887/80, electrodes obtained by spray coating of an alkali-resistant metal on a cathode base and depositing a platinum group metal on the surface thereof (Nos. 131189 /80, 158288/80) , electrodes obtained by forming an activated layer by plating method on a cathode base, e.g., electrodes obtained by dispersing a platinum group metal powder into nickel (No. 110983/79) or dispersing Raney-nickel into nickel (No. 112785/79) and so on.

These activated cathodes, however, involve disadvantages including such as insufficient durability or high cost. In particular, when exposed to high temperature and high concentrated caustic soda, those are far from satisfaction as cathodes for use in ion exchange membrane electrolysis. That is, in, for example, a process for forming Raney-nickel-containing nickel or a nickel alloy coating layer, when the content of electroconductive fine particles is small, e.g., approximately less than 20 %, the performance is insufficient while a firm coating layer with strong adhesion is obtained. Inversely, when electroconductive fine particles are contained in great amounts, e.g., in excess of 45 %, a highly activated coating layer is obtained but strength as well as adhesion is not satisfactory. Accordingly it is difficult to provide cathodes which are thoroughly satisfactory in

On the other hand, various methods for manufacturing low hydrogen overvoltage cathodes are proposed. As a structure of low hydrogen overvoltage cathode, a cathode base is at first considered. As a material for the cathode base, carbon steel, stainless steel, nickel and the like are known but carbon steel is normally used from economical consideration. On the cathode plate is an activated layer of low hydrogen overvoltage deposited. In this case, when corrosion of the base is feared during the course of operation at low hydrogen overvoltage, it is necessary to provide a protective layer of alkali-resistance between the base and the activated layer. As the protective layer, nickel-plating bodies, copper-plating bodies and the like are normally employed and as the activated layer, it is prevailing to employ those of alkali-resistant metals designed so as to have large surface. For example, there are included a method for electroplating a Raney alloy (Patent Examined Publication Nos. 4766 /53, 6611/56, Patent Non-examined Publication No. 25275 /79) , a method for codepositing Raney-nickel (Patent Non-examined Publication Nos. 68795/79, 112785/79) , a method for depositing a Raney alloy by spray coating, sintering and the like (Patent Non-examined Publication Nos. 3658 /77, 81484 /78, 79803 /80) , a method for spray coating of metals such as nickel (Patent Non-examined Publication Nos. 32832/77, 131189/80) , a method for depositing by electroplating a coating, a sacrificial component of which is leached during operation (Patent Non-examined Publication Nos. 115674 /78, 22161 /78, 102876/78 and 100987 /80) and the like.

Notwithstanding, those cathodes manufactured by the foregoing

methods are not always suited to industrial use in performance, i.e., those with low hydrogen overvoltage are inferior in durability for a prolonged period of time, while those with durability are high in hydrogen overvoltage.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a low hydrogen overvoltage cathode with low hydrogen overvoltage as well as adequate durability especially suited to electrolysis of an aqueous alkali halide solution, more specifically, to provide a low hydrogen overvoltage cathode having a nickel or a nickel alloy coating layer containing electroconductive fine particles (e.g., Raney-nickel etc) which contain a platinum group metal and/or an oxide thereof.

It is another object of the present invention to provide a method for producing the foregoing low hydrogen overvoltage cathode which comprises using a codeposit plating tank in which an anode and an object to be plated of a non-perforated flat structure are positioned in parallel with each other, introducing a dispersant slurry through one side of the tank to thus cause it flow in a space formed between the anode and the object, then removing the slurry through the opposite side, whereby codeposit plating is applied to only one surface of the object.

These and other objects of the present invention together with advantages thereof will become apparent to those skilled in the art from the detailed disclosure of the present invention as set forth hereinbelow.

BRIEF DESCRIPTION OF DRAWING

FIG. 1 and FIG. 2 are graphs showing the relationship between

operating days and hydrogen overvoltage in Examples 1 and 2, respectively.

FIG. 3 is a schematic representation illustrating an embodiment of a production method of the present invention.

FIG. 4 (X) is a schematic representation of a codeposit plating tank used in the present invention in which the surface to be plated is located to be substantially horizontal and to face upwardly, and FIG. 4 (Y) is a cross-sectional view taken on line A-A of FIG. 4 (X).

FIG. 5 (X) is a schematic representation of a codeposit plating tank used in the present invention in which two sheets of cathodes, the surfaces to be plated being located substantially vertical, are codeposit plated at a time and FIG. 5 (Y) is a cross-sectional view taken on line B-B of FIG. 5 (X).

DETAILED DESCRIPTION OF THE INVENTION

The present invention encompasses a low hydrogen overvoltage cathode having a nickel or a nickel alloy coating layer containing electroconductive fine particles which contain a platinum group metal and /or an oxide thereof, and method for producing the same which comprises using a codeposit plating tank in which an anode and an object to be plated of a non-perforated flat structure are positioned in parallel with each other, introducing a dispersant slurry through one side of the tank to thus cause it to flow in a space formed between the anode and the object, then removing the slurry through the opposite side, whereby codeposit plating is applied to only one surface of the object. The cathode of the present invention is coated in such a manner that electroconductive fine particles holding a platinum group metal and /or an oxide thereof are dispersed in nickel or a nickel alloy, and is capable of reducing hydrogen generation electric potential

by 200 to 300 mV as compared with conventional iron cathodes.

As a cathode base, iron, stainless steel, nickel and the like may be suitably used and further, iron coated with nickel, a nickel alloy such as Ni-Mo, Ni-W and the like may also be used.

As a coating layer, nickel or nickel alloys such as Ni-Mo, Ni-W and the like may be suitably used and further, a mixture of nickel and oxides thereof may also suitably be used.

As an active substance, a platinum group metal selected from the group consisting of platinum, ruthenium, iridium, rhodium, palladium and osmium, and an oxide thereof may be used singly or in combination of two or more.

Electroconductive fine particles should have electroconductivity and large surface area and be superior in resistance to caustic alkali, which may be exemplified by porous nickel particles synthesized by nickel formate or nickel carbonyl, carbon particles such as activated carbon, Raney-nickel, Raney-cobalt, Raney-silver and the like. When Raney-nickel alloy is employed, it is necessary to leach by a known manner after formation of the coating layer. For example, adequate activity is obtained by immersing the coating layer in a 10 to 30 % aqueous caustic soda solution at 40 to 60 °C for more than one hour.

As a process for allowing the electroconductive fine particles to hold the active substance, known techniques may be employed including such as chemical plating, displacement plating, electroplating, vapor deposition, a process for making alloys by hot melting and the like. The foregoing fine particles should desirably be as fine as possible, as are uniformly dispersed in nickel or a nickel alloy and supplied for coating. The particle size of the fine particles should preferably be

approximately 100 mesh-pass or less, more preferably 200 mesh-pass or less, through not limited in particular. An amount of 0.01 % or more of a platinum group metal and /or an oxide thereof to be held by the fine particles provides cathodes having an adequate activity. An amount exceeding 50% leads to economical disadvantage. The thickness of the coating layer is not specifically limited but should preferably be 800 μm or less, more preferably 400 μm or less, taking into consideration economy. With a view to keeping activity for a prolonged period of time, thickness should be at least 10 μm or more, more preferably 50 μm or more.

On the other hand, an extensive series of studies have been made by the present inventors on a method for obtaining low hydrogen overvoltage cathodes satisfying low hydrogen overvoltage and long-term durability, and the following conclusion has been derived.

That is, cathodes having less durability are caused by many vacant spaces present in the active portion or insufficiency of adhesion force among particles, i.e., shortage of mechanical strength, whereas cathodes having high hydrogen overvoltage are caused by lack of active area actually working or activity per unit area. Looking into prior arts from the above viewpoint, cathodes produced by electroplating containing a sacrificial component dissolving during the electrolysis, when containing the sacrificial component in great amounts to lower hydrogen overvoltage, deteriorate in mechanical strength, thereby being inferior in durability. A process for codeposit plating of Raney-nickel is characterized in that the mechanical strength of the active portion is great but it has been found through studies by the present inventors that it is still insufficient in long-term durability. That is, for

the purpose of minimizing hydrogen overvoltage, the content of Raney alloy in a codeposit plating coating layer has to be increased, but the increased content of Raney-nickel results in a decrease in the mechanical strength of the active portion.

A modified process of the foregoing Raney alloy codeposit plating method producing low hydrogen overvoltage cathodes is revealed by Patent Non-examined Publication No. 133387 /83. In this process, Raney alloy and a platinum group metal are admixed in powder, with which codeposit plating is made. However, it is not yet satisfactory though providing cathodes which are not only stronger in the mechanical strength, but smaller in hydrogen overvoltage, as compared with the codeposit plating using Raney alloy alone. That may be because uniform codeposit plating is difficult due to the differences in particle size, specific gravity and the like between the Raney alloy and the platinum group metals. The platinum group metals, different from Raney alloy, shows no activity when buried in a nickel matrix.

In light of the situation, the present inventors have repeated studies on a new codeposit plating method which makes use of both activities of Raney alloy and platinum group metals and have arrived at an idea of adding as a third component platinum group metals to the Raney alloy. That is, it has been discovered that cathodes with sufficient strength, long-term durability and satisfactorily low hydrogen overvoltage can be provided by employing a three-component alloy as a dispersant which is comprised of a first metal selected from the group consisting of nickel, cobalt and silver, a second metal selected from the group consisting of aluminum, magnesium, zinc and tin, and a third metal selected from the group consisting of platinum, palladium,

rhodium, ruthenium, iridium and osmium.

The method for producing low hydrogen overvoltage cathodes by codeposit plating of the three-component alloy is characterized by using a codeposit plating tank in which an anode and an object to be plated of a non-perforated flat structure are positioned in parallel with each other, supplying a dispersant slurry through one side of the tank to thus cause it to flow in a space formed between the anode and the object, then removing the slurry through the opposite side, more preferably, recirculating the removed slurry back to a codeposit plating bath storage tank, whereby codeposit plating is applied to only one surface of the object.

An apparatus for codeposit plating of Raney alloy is disclosed by, for example, Patent Non-examined Publication No. 104491 /80. According to the apparatus, however, it is impossible to perform codeposit plating uniformly and firmly, in cases where a cathode is a structure of a non-perforated flat plate and only one surface is subjected to codeposit plating. That is, in conventional Raney alloy codeposit plating, a dispersant slurry is flowed in a vertical way by the use of gas, a vibrating plate, a pump and the like. Notwithstanding, according to the study by the present inventors, a process for codeposit plating while flowing a dispersant slurry vertically involves a disadvantage that deposition of the dispersant onto an object to be plated is inferior. In an attempt to raise the deposition of the dispersant, processes of adding aluminium ions to a nickel plating bath or increasing the slurry concentration to 3 g/l or more have been proposed (Patent Non-examined Publication No. 31091 /83) . It is surmised that decreased deposition in the case of the dispersant slurry being flowed vertically is

attributable to rare colliding chances of dispersant particles against the object. Raney alloy is generally greater in density than a plating bath and therefore tends to precipitate.

The present invention has been completed on the thought that if a dispersant slurry is flowed horizontally rather than vertically, contacting and colliding chances between dispersant slurry particles and an object to be plated should be enhanced to thereby improve the deposition of the particles onto the object.

The cathode base usable for activated cathodes of the present invention may be in any form but a non-perforated flat plate may preferably be employed. In an electrolytic cell for use in the electrolysis of an aqueous alkali metal halide solution, providing as a separator a cation exchange membrane, in particular, operation is often carried out for saving energy cost by reducing an anode-cathode distance to 3 mm or less, often 2 mm or less. In those cases, non-perforated flat plate cathodes are capable of making uniform micro-distribution of current density over the cation exchange membrane and hence very desirable. Moreover, in the case of non-perforated flat plates, formation of a coating layer may be suitably achieved by conventional techniques including such as plasma spray coating, chemical plating, electroplating and the like, if it can be attained to deposit with good adhesion force on the cathode base electroconductive fine particles holding platinum group metals and /or oxides thereof together with nickel or nickel alloys.

In practicing the present invention, only the necessary area of the cathode base had best be subjected to the treatment, i.e., only the area approximately equal to the cation exchange membrane had best

be treated.

Further, in the case of a perforated cathode, electric current, during operation, is liable to concentrate in edges in the vicinity of perforations to thus cause ununiformity in current density over the cathode. For this reason, there are raised problems including partial corrosion of nickel or a nickel alloy served as a coating layer base. Therefore, it is preferred to apply the present technique to a cathode base of a flat structure having neither perforations nor edges.

The cathodes of the present invention obtained in such a manner as aforesaid are adapted for use as electrodes which generate hydrogen gas in, for example, the electrolysis of water, alkali metal halides and the like.

The method for producing low hydrogen overvoltage cathodes of the present invention will be explained by referring to the drawings illustrating embodiments.

FIG. 3 depicts a schematic representation showing an example in which codeposit plating is effected according to the present invention. In a codeposit plating bath storage tank (1), a dispersant is well stirred to give a uniform slurry concentration. A dispersant slurry (2) is supplied by a pump (3) to a codeposit plating tank (4) through one side, then removed through the other side. The removed dispersant slurry is returned back to the codeposit plating bath storage tank (1) and recirculated between the plating bath storage tank (1) and the plating tank (4). Although uniform codeposit plating is possible without recirculating the dispersant slurry between the plating bath storage tank (1) and the plating tank (4), it is preferred to effect recirculation since a large quantity of dispersant slurry is needed.

The codeposit plating tank (4) is equipped with a cathode (6) to be plated and an anode (5) , both being positioned in parallel with each other, to thus form a closed codeposit plating chamber (7) . The cathode (6) is, needlessly, located so that the surface to be plated faces to the inside of the chamber. As the anode (5) , any known anode for use in electroplating may be used and the shape is not specifically limited, including a flat plate, a perforated plate, a net, an aggregate of nickel tips and the like.

An amount of the dispersant contained in a codeposit plating coating in the present invention is variable according to the direction in which the object to be plated was placed, the concentration of the dispersant slurry, the average flow rate of the dispersant slurry within the codeposit plating chamber and the like.

FIG. 4 and FIG. 5 are schematic representations showing the direction in which the object to be plated are placed. In FIG. 4, the object is located horizontal and faces upward, as in the case of FIG. 3. In FIG. 5, the object is located vertical. A preferred embodiment is to locate the object substantially horizontal to face upward, as shown by FIG. 3 and FIG. 4. It is also considered to locate the object to face downward, but in this case the same plated object as in the case of FIG. 3 and FIG. 4 can not be obtained because of a decrease in a deposition-improving effect caused by gravity, unless the slurry concentration is higher than in the case of FIG. 3 and FIG. 4.

An embodiment of locating the objects as shown by FIG. 5 is useful when two sheets of cathodes are produced at one time. That is, by locating two objects so that the backsides of the objects are in contact with each other, two sheets of hydrogen overvoltage cathodes

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can be produced through one operation of codeposit plating. In FIG. 3, colliding chances between the dispersant particles and the object are somewhat reduced as compared with the cases in FIG. 3 and FIG. 4, and hence codeposit plating should desirably be made with a higher slurry concentration.

The dispersant slurry should be flowed substantially horizontal in the codeposit plating tank. "Substantially horizontal" means an extent within which an increase in deposition of the dispersant particles resulting from gravity is achievable, i.e., the angle between the horizontal surface and the slurry flowing line being within 45 degrees, more preferably 30 degrees, regardless of upward or downward direction, most preferably 0 degree. The dispersant slurry is normally supplied through one side of the tank and removed through the opposite other side, but it is possible for the purpose of uniformization, to flow it to a reverse direction during the operation by changing an inlet and an outlet. It is further desired to position dispersing plates at an inlet and an outlet to improve uniformization.

The slurry concentration should preferably be not less than 0.01 g/l and less than 3 g /l, more preferably not less than 0.05 g /l and less than 3 g /l. In the case of less than 0.01 g /l, only the plated object containing a dispersant in less amounts is obtained and thus showing high hydrogen overvoltage. In the case of not less than 3 g /l, the plated object contains a dispersant in greater amounts, which shows low initial hydrogen overvoltage but is poor in the mechanical strength, thus lacking in long-term durability. The average flow rate of the dispersant slurry within the codeposit plating chamber should preferably be 0.05 m /sec or more, more preferably less

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than 10 m /sec. In the case of less than 0.05 m /sec; local unbalance of the dispersant content becomes great and thus the plated object of a uniform composition is not obtained. In the case of 10 m /sec or more the dispersant content decreases and the obtained plated object possesses high hydrogen overvoltage, further, equipment cost and energy cost increase due to an increased amount of the dispersant slurry recirculated.

As a bath solution forming the dispersant slurry, a well-known nickel plating bath may be suitably employed, including such as watts bath, all nickel chloride bath, high nickel chloride bath and the like.

The particle size of the dispersant is not specifically limited, but should preferably be approximately 100-mesh pass or less, more preferably 200-mesh pass or less.

When the object to be plated is of great dimensions, it is separated into several parts and codeposit plated with requiring only some consideration.

The dispersant may be comprised of an optional combination of a first metal selected from the group consisting of nickel, cobalt and silver, a second metal selected from the group consisting of aluminium, magnesium, zinc and tin, and a third metal selected from the group consisting of platinum, palladium, rhodium, ruthenium, iridium and osmium. The second metal is leached by being immersed in an aqueous caustic alkali solution after codeposit plating, whereby a coating layer is made porous and thus activated. The content of the third metal is considered from both aspects of cost and activity, but should desirably be not higher than 50 weight %. In the case of less than 0.01 weight %, an effect of increasing activity is hardly expected.

As far as the changes in the dispersant slurry concentration are concerned, it is possible to start with an initial given concentration and end with a concentration lower than the initial concentration, or to keep the concentration constant from the beginning to the end by supplying the dispersant to the codeposit plating bath tank continuously or periodically, or to end with a higher concentration than the initial one.

Cathodes subjected to codeposit plating are stored for a prolonged period of time by being washed and dried. To use the cathodes as low hydrogen overvoltage cathodes, the second metals must be leached in an aqueous caustic alkali solution. This treatment may be made either before or after installing of the cathodes to an electrolytic cell, but the latter is preferred.

As cathodes used in the production of an aqueous alkali metal hydroxide solution by an ion exchange membrane process or an asbestos diaphragm process, expanded metals, perforated plates or net structure cathodes have been commonly employed. Notwithstanding, according to the study made by the present inventors, it has been made clear that cathodes of non-perforated flat plates, only one surface of which is codeposit plated provide the best results, when served as cathodes used in a horizontal type ion exchange membrane electrolytic cell. Moreover, it has been also discovered that even when an asbestos diaphragm electrolytic cell is retrofitted to an ion exchange membrane electrolytic cell, cells equipped with cathodes of non-perforated flat plates, only one surface of which is codeposit plated possess low cell voltage. The non-perforated flat plate structure has numerous merits including such as highly uniform current distribution, reduction of electric resistance,

high accuracy of dimensions on manufacturing and the like.

As stated above, the present invention is capable of production of epock-making cells equipped with low hydrogen overvoltage cathodes, upsetting knowledge of persons skilled in the art that cells with non-perforated flat plate cathodes show high cell voltage (e.g., Patent Non-examined Publication No. 174477 /82, "SODA AND CHLORINE", 32, 281, 1981), and therefore exceedingly valuable in the industry.

The present invention will be explained in more detail by way of Examples and Comparative Examples that follow, to which the invention is in no way limited.

EXAMPLE 1

Nickel particles having an average particle size of 8 μm were electroplated with ruthenium to be 4 weight %.

The obtained nickel particles containing ruthenium and nickel particles having an average particle size of 54 μm were admixed at the proportion of 3 : 7, with which sand blasted nickel plates of 4 cm $\times$ 4 cm were subjected to plasma spray coating to be 200 μm in thickness.

The foregoing test piece was served as a cathode, a DES (manufactured by Permelec Electrode Company) was served as an anode, "NAFION 901" (manufactured by E. I. Du Pont de Nemours & Co.) was served as a cation exchange membrane, an aqueous sodium chloride solution was electrolysed while controlling the catholyte concentration to 32 %, current density to 25 A /d m² and catholyte temperature to 90 °C. Hydrogen overvoltage was measured by a current interruptor method.

Hydrogen overvoltage of the cathode was 0.07 to 0.09 V and no

degradation in performance could be observed even after continuous 1000-day operation or more. In FIG. 1, a change in hydrogen overvoltage was depicted.

COMPARATIVE EXAMPLE 1

The same sand blasted nickel plates as in Example 1 were subjected to plasma spray coating with nickel particles of an 8 μm average particle size to be 200 μm in thickness.

The obtained 10 sheets of test pieces were supplied for the electrolysis under the same conditions as in Example 1. The test pieces showed initially hydrogen overvoltage of 0.08 to 0.09 V but each of them showed an abrupt increase after 50 to 150 days. The section was observed by an electron microscope and cracks could be seen in the inside of every test piece.

COMPARATIVE EXAMPLE 2

Nickel particles of a 54 μm average particle size were applied by plasma spray coating to the same test pieces as used in Comparative Example 1 and supplied for the electrolysis under the same conditions as in Example 1.

Hydrogen overvoltage was 0.15 V initially but increased to 0.23 V after 50-day operation.

EXAMPLE 2

A three-component-alloy Raney-nickel comprising 48.9 weight % of nickel, 50 weight % of aluminium and 1.1 weight % of platinum were pulverized and classified. The 200-mesh passed three-component Raney-nickel particles were dispersed⁺ in a plating bath containing 300 g /l of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 40 g /l of H_3BO_3 and aged with stirring for a hour.

+ in the concentration of 1 g/l

Nickel plate test pieces of 4 cm × 4 cm were immersed in the foregoing plating bath and plated with stirring at 50 °C for 90 minutes. As an anode, nickel was served and 0.48 A direct current was supplied. The content of Raney-nickel was 25.6 % and the thickness of a coating was 250 μm.

The obtained test pieces were leached at 80 °C for 2 hours by being immersed in a 20 % aqueous caustic soda solution. The activated test pieces were served as cathodes and the electrolysis was effected under the following conditions. Hydrogen overvoltage was measured by a current interruptor method.

Electrolysis conditions ;

Anolyte	NaCl	220 g / l
Catholyte	NaOH	30 %
Temperature		85 °C
Anode	insoluble anode	
Ion exchange membrane	"NAPION 901"	

The cathodes produced according to the foregoing manner showed hydrogen overvoltage ranging from 0.06 to 0.08 V and even after 800-day operation, a change in performance could not be recognized. A change in hydrogen overvoltage was shown in FIG. 2.

EXAMPLE 3

The test pieces were prepared in a similar fashion to that of Example 2 excepting that a three-component-alloy Raney-nickel comprising 45.7 weight % of nickel, 50 weight % of aluminium and 4.3 weight % of ruthenium was employed, and the electrolysis was carried out under the same conditions.

Hydrogen overvoltage was between 0.07 V and 0.08 V and even

after 750-day operation no degradation in performance was observed. During the period, operation was shut down five times for one week, respectively, degradation in performance could not be recognized before or after every shut-down.

EXAMPLE 4

The sand blasted test pieces of 4 cm $\times$ 4 cm were coated by plasma spray with the 200-mesh passed three-component-alloy particles obtained in Examples 2 and 3 to be 200 μ m in thickness.

Using the foregoing cathodes, the electrolysis was effected similarly to Example 2. The cathode using Al-Ni-Pt alloy showed 0.06 V hydrogen overvoltage, while the cathode using Al-Ni-Ru alloy showed 0.07 V. No degradation in performance was observed even after 650-day operation in respective case. During the period, operation was shut down 15 times for one week, respectively, a change in performance before or after every shut-down did not occur.

COMPARATIVE EXAMPLE 3

Codeposit plating was effected in a similar manner to that of Example 2, excepting that 200-mesh passed Raney-nickel comprising 50 weight % of nickel and 50 weight % of aluminium, and the electrolysis was conducted similarly to Example 2.

Hydrogen overvoltage was 0.10 V and increased to 0.18 V after 100-day operation. During the period, operation was shut down five times for one week, respectively, degradation of 0.01 V on an average was observed every shut-down.

EXAMPLE 5

Non-perforated flat plates of carbon steel, 660 mm $\times$ 2,000 mm, were degreased, washed with an acid, and chemical plated with nickel

to be 30 μ m in thickness.

Two sheets of the obtained flat plates were placed vertically so that the backs are in contact with each other, as shown by FIG. 5. Anodes formed by wrapping nickel tips for electroplating in a titanium mesh were arranged in parallel and the non-perforated flat plates and the anodes were secured to hard rubber-lined iron frames to thus form two codeposit plating chambers.

On the other hand, in a codeposit plating bath storage tank having the inside capacity of 1.8 m³, a Raney alloy dispersant slurry (Al : Ni : Ru = 50 wt% : 45 wt % : 5 wt%, Particle size : 200 - mesh pass) was dispersed in a nickel plating bath (NiCl₂ · 6H₂O 300 g /l, H₃BO₃ 38 g /l, PH 2 ~2.5) to prepare 1.5 m³ codeposit plating bath containing the slurry concentration of 2 g /l.

The codeposit plating bath was removed with stirring by a pump and supplied into the codeposit plating chambers through one side to flow in a horizontal way. Codeposit plating was carried out under the conditions ; temperature 50 °C, current density 3 A /d m², time 90 minutes and average flow rate of the slurry within the chamber 1.0 m /sec. A plating coating thus obtained was hard and uniform in thickness.

From the resultant flat plates, only one surfaces of which were codeposit plated, 26 sheets of cathodes were made under the same conditions and installed to an asbestos diaphragm electrolytic cell (H-4 type, manufactured by Hooker Chem. Corp. Inc.) . After assembling of the cell, the cathodes were subjected to leaching treatment by being immersed in a 25 % aqueous NaOH solution for three hours. As a cation exchange membrane "NAFION 901" was used. Cell voltage was 3.4 V

under the conditions ; temperature 90 °C, current density 23.5 A /d m² and NaOH concentration 32 %. Hydrogen overvoltage was 0.07 V.

EXAMPLE 6

A cathode bottom plate (carbon steel) , 1800 mm × 11,000 mm, used in a mercury electrolytic cell was polished smooth and then chemical plated with nickel to be 30 μm in thickness.

The obtained plate was separated into six parts in a longitudinal way, by which the codeposit plating tank is formed substantially horizontal to allow the surface to be plated to face upward, as illustrated by FIG. 3 and FIG. 4.

Each part was codeposit plated in the same manner and the same conditions as in Example 5. A plating coating was hard and was approximately uniform in thickness in every part.

Using this cathode, a cell was assembled and leaching treatment was performed under the same conditions as in Example 5. "NAFION 901" was positioned and the electrolysis was effected. Cell voltage was 3.45 V under the conditions ; temperature 90 °C, current density 50 A /d m² and NaOH 32 %, and hydrogen overvoltage was 0.10 V.

WHAT WE CLAIM IS :

1. A low hydrogen overvoltage cathode having a nickel or a nickel alloy coating layer containing electroconductive fine particles which contain a platinum group metal and/or an oxide thereof.
2. The low hydrogen overvoltage cathode of Claim 1, wherein said electroconductive fine particles comprise nickel.
3. The low hydrogen overvoltage cathode of Claim 1, wherein said electroconductive fine particles comprise carbon.
4. The low hydrogen overvoltage cathode of Claim 1, wherein said electroconductive fine particles comprise Raney-nickel.
5. The low hydrogen overvoltage cathode of Claim 1, wherein said electroconductive fine particles comprise Raney-cobalt.
6. The low hydrogen overvoltage cathode of Claim 1, wherein said electroconductive fine particles comprise Raney-silver.
7. The low hydrogen overvoltage cathode of Claim 1, wherein said platinum group metal comprises at least one selected from the group consisting of platinum, ruthenium, iridium, rhodium, palladium and osmium.
8. The low hydrogen overvoltage cathode of Claim 1, wherein said coating layer is formed by plasma spray method.
9. The low hydrogen overvoltage cathode of Claim 1, wherein said coating layer is formed by electroplating method.
10. The low hydrogen overvoltage cathode of Claim 1, wherein a cathode base is selected from the group consisting of iron, nickel, chromium, stainless steel and an alloy of foregoing.
11. The low hydrogen overvoltage electrode of Claim 1, wherein an electrode structure comprises a non-perforated plate structure.

12. A method for producing a low hydrogen overvoltage cathode which comprises using a codeposit plating tank in which an anode and an object to be plated of a non-perforated flat structure are positioned in parallel with each other, supplying a dispersant slurry through one side of the tank to thus allow it to flow in a space formed between the anode and the object, then removing the slurry through the opposite side, whereby codeposit plating is applied to only one surface of the object.

13. The method of Claim 12, wherein said dispersant slurry removed is recirculated back to the tank.

14. The method of Claim 12, said dispersant comprises an alloy of a first metal selected from the group consisting of nickel, cobalt and silver, a second metal selected from the group consisting of aluminium, magnesium, zinc and tin, and third metal selected from the group consisting of platinum, palladium, rhodium, ruthenium, iridium and osmium.

15. The method of Claim 12, wherein a solution forming said dispersant slurry is a nickel plating bath.

16. The method of Claim 12, wherein the concentration of said dispersant slurry is not less than 0.01 g /l and less than 3 g /l.

17. The method of Claim 12, wherein the average flow rate of said dispersant slurry in the tank is not less than 0.05 m/sec and less than 10 m/sec.

18. The method of Claim 12, wherein said dispersant slurry flows in the tank in the substantially horizontal way.

FIG.1

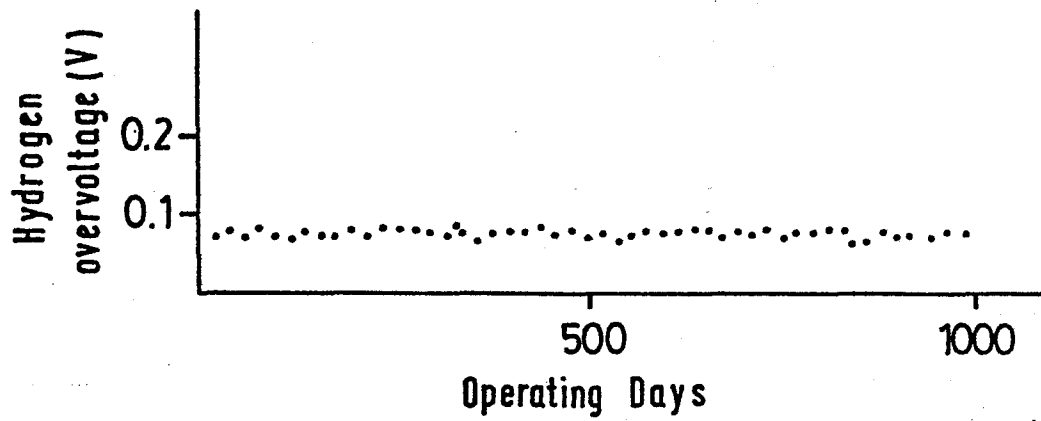


FIG.2

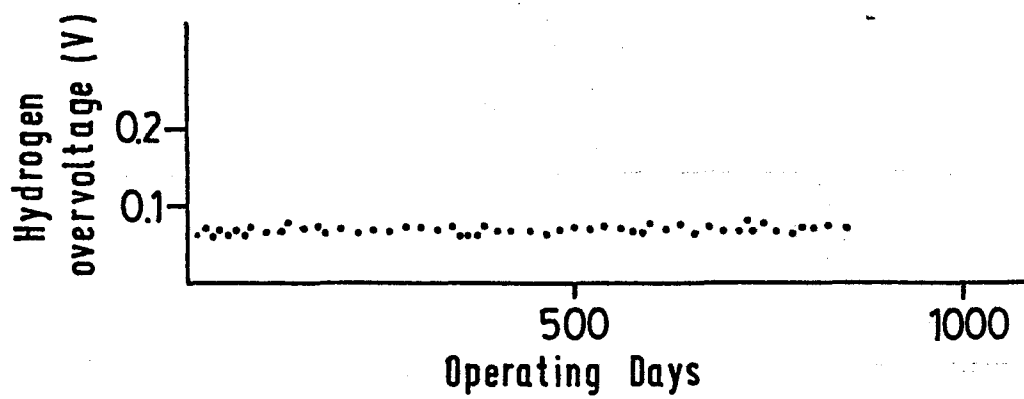


FIG.3

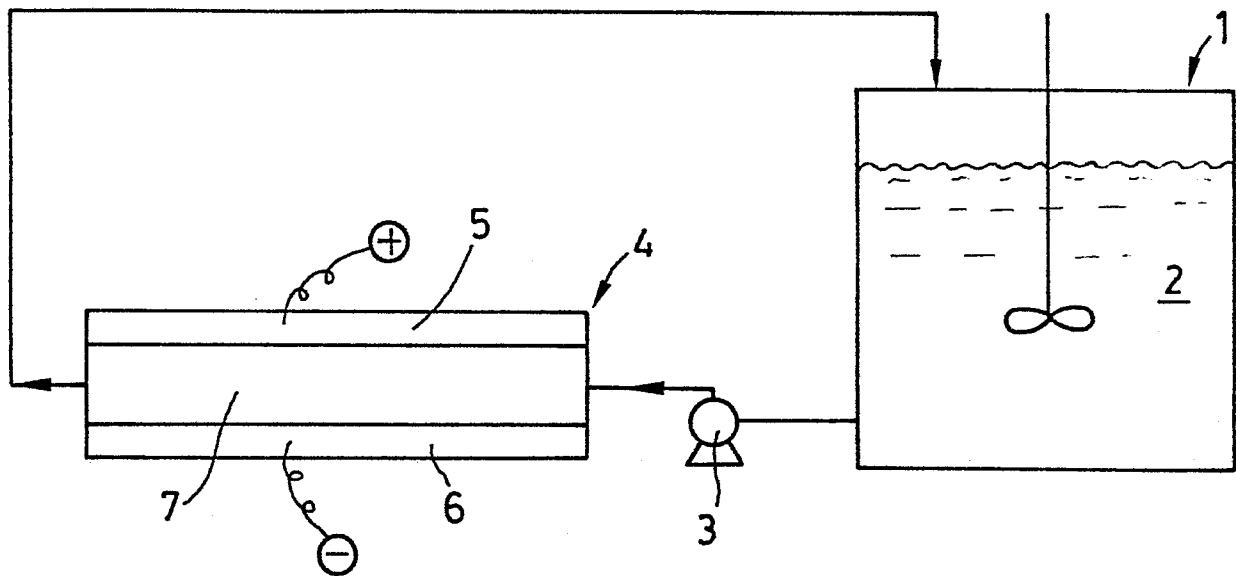
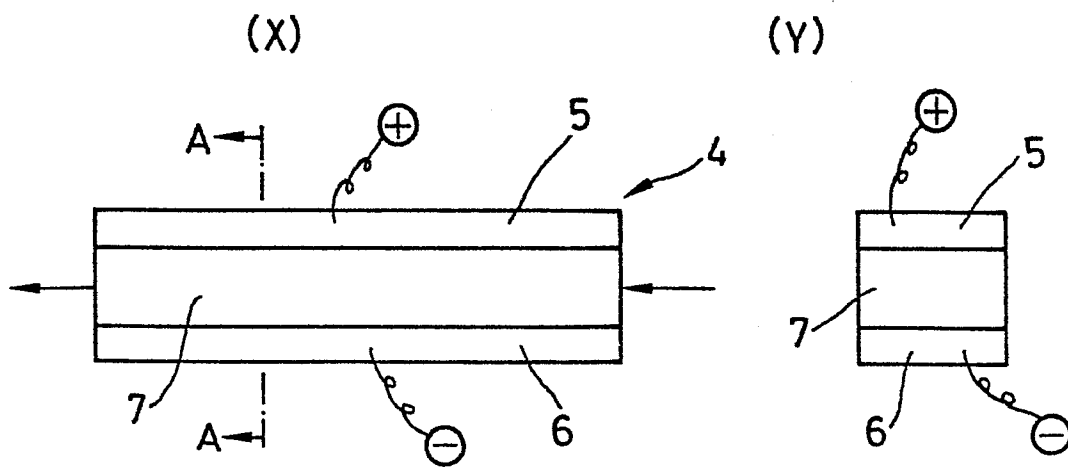


FIG.4



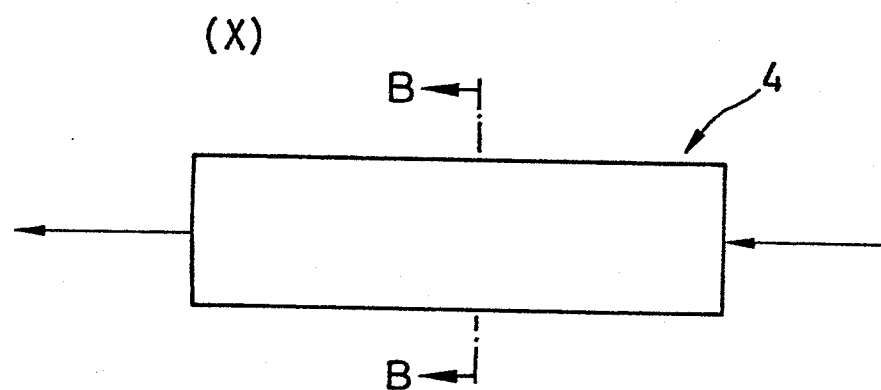
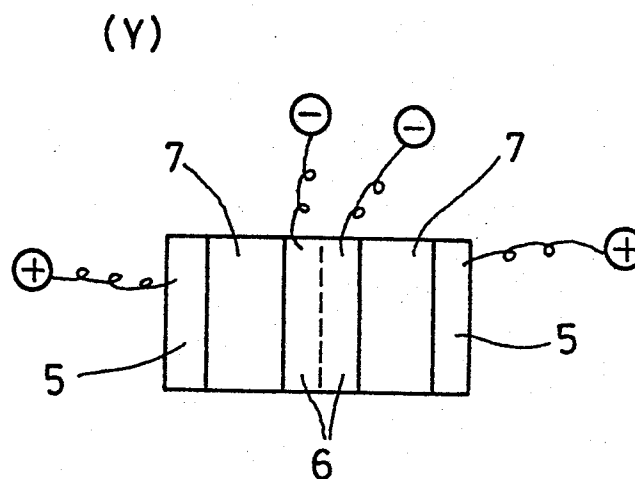


FIG. 5





DOCUMENTS CONSIDERED TO BE RELEVANT			EP 84106905.7
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 2)
A	DE - A1 - 3 116 032 (JOHNSON, MATTHEY & CO., LTD.) * Pages 12,14-16; examples * --	1,2,7,9-11	C 25 B 11/08 C 25 D 5/08// C 25 B 1/04 C 25 B 1/46
A	GB - A - 991 231 (BROWN, BOVERI & COMPANY LIMITED) * Page 2, lines 5-42 * --	1,4,7	
A	US - A - 4 331 517 (THOMAS A. RECH-LICZ) * Claims 1,6-8 * ----	1,12,14,15	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 2)
			C 25 B C 25 D
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 27-08-1984	Examiner HEIN
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			