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(54) **Electrolytic refining method of copper and electrolytic copper**

(57) In an electrolytic refining method of copper, (1) electrolysis is operated by controlling the cathode potential at current density D_k of 330 A/m² or higher, and/or (2) electrolysis is operated by using an anion surfactant together with glue and thiourea as additives,

and/or (3) PR electrolysis is operated by adding an anion surfactant to the electrolyte solution by 0.001 g / t or more, and feeding inverting or reversing current continuously for 45 to 300 seconds, at 1/500 to 1/25 of continuous feeding time of positive current.

Description

1. Field of the Invention

[0001] The present invention relates to an electrolytic refining method of copper and electrolytic copper, and more particularly to an electrolytic refining method of copper capable of operating electrolytic refining process effectively by using high current density, and enhancing productivity and quality of electrolytic copper product by preventing anode passivation without spoiling economical merit, and electrolytic copper refined by this method.

2. Prior Art

[0002] It is the best cost saving measure to increase the current density in order to enhance productivity per unit facility in electrolytic refining. However, operation by high current density electrolysis is accompanied by various problems.

[0003] In copper electrolysis, the anode passivation determines the limiting current density. This anode passivation phenomenon occurs when the anode slime generated during copper electrolysis is stacked and left over on the anode surface to impede diffusion and convection of copper ions, and the copper ion concentration near the anode surface elevates to reach the saturation point, and a passive film of copper surface is formed on the anode surface. This phenomenon suppresses the productivity (expressed by the positive current density D_k per anode unit surface area), and in particular, in normal electrolysis (electrolysis by a specific direction of current), it has been considered to be limited around D_k 300 A/m².

[0004] Another problem is deposition of nodular, dendritic or granular copper due to local worsening of electrolytic condition by concentration polarization at the cathode side.

[0005] As preventive measures of anode passivation, hitherto, three methods have been known.

[0006] First is a method of decreasing the impurity content in the anode. By this method, generation of anode slime due to impurities is decreased, and it is effective to raise the limit point of D_k . However, at higher than current density 330 A/m², frequent shorting is caused by grains and nodules formed on the cathode (electrolytic copper) surface, and worsening of product quality tends to occur, and it seems to be limited at 330 A/m².

[0007] Second is a method of PR electrolysis (electrolysis by inverting or reversing the current direction periodically) instead of normal electrolysis. According to this method, elevation of copper ion concentration near the anode surface is suppressed, and it is effective to raise the limit point of D_k .

[0008] However, at current density of about 350 A/m² or higher, grains and wrinkles are likely to occur on the surface of product electrolytic copper formed on the cathode by electrodeposition. In the PR electrolysis, yet, since the copper depositing on the cathode is dissolved during inversion of electrolysis, the productivity is lowered in this period.

[0009] Third is a method of reinforcement of liquid circulation into the electrolytic tank, and by increasing the liquid circulation amount in the electrolytic tank, it encourages diffusion of copper ions and prevents passivation. In this case, it is effective to reinforce to such an extent that the slime may be washed away by convection of the liquid. However, to increase the liquid circulation flow, the energy cost increases, and to reinforce the liquid circulation enough to encourage diffusion, the facility of the electrolytic tank must be drastically modified.

[0010] If many grains and creases are formed, the electrolyte solution is captured in their gaps, and the impurity concentration of the product electrolytic copper is raised, and the purity is lowered. In particular, in the product electrolytic copper of high S concentration, wires are likely to be broken when re-melted into wires. Besides, sulfurous acid gas is generated to cause environmental problems.

[0011] Besides, when grains are grown to a large size, it causes shorting in electrolysis, or piling problems in transportation, and the cargo may collapse during transfer.

[0012] In the electrolytic bath used in electrolytic refining, aside from principal ingredients such as metallic salt and free acid, a small amount of organics or inorganics is added for the purpose of smoothing the surface of the product electrolytic copper (or merely called electrolytic copper) by depositing copper uniformly and finely on the cathode. They are collectively called additives. As additives, generally, glue and thiourea are widely used.

[0013] In the conventional normal electrolytic refining of copper, it is general to set the current density D_k at about 250 A/m², the contents of additives (per 1 ton of electrolytic copper) at 50 to 160 g/t for glue and 50 to 160 g/t for thiourea. These setting values are appropriate values obtained empirically.

[0014] In high current density electrolysis of current density D_k of more than 280 A/m², when glue and thiourea are added by setting the amount of additives at the conventional basis, the overpotential of the cathode climbs up, and the potential becomes base, and granular or acicular deposits are formed on the surface, which may roughen the electrodeposition. This electrodeposition roughening tendency is more obvious when the current is raised. As a result, the purity of electrolytic copper drops, and the impurity grade climbs. Accordingly, the contents of glue and thiourea must be decreased as the current density becomes higher, but when the glue content is decreased, on the other hand, the

slime floats and is accumulated on the electrolytic copper to become a nucleus of electrodeposition, and granular deposition is likely to take place. This is considered due to loss of slime settling action of glue which has been traditionally used as food flocculant.

[0015] Thus, the glue has two effects, the smoothing effect of cathode surface and the slime settling action, and if the current density is set higher in order to emphasize the smoothing effect of cathode surface, the amount of glue must be decreased, but the slime settling action becomes weaker and it cannot be decreased too much. To solve these contradictory problems, hitherto, in high current density operation, the balancing point of these two effects has been found by experience. This balance seems to be established at current density D_k of about 300 A/m² in normal electrolysis. In PR electrolysis, on the other hand, the current density D_k is higher than 330 A/m², and it is hard to keep balance, and the operation is more difficult.

[0016] Accordingly, in the conventional high current density electrolysis, the glue content is controlled within 80 to 100 g/t, but the impurity grade cannot be lowered sufficiently. That is, it is set so that the grade of S (sulfur) of electrolytic copper, that is the most difficult problem, may settle within the limiting range (15 ppm or less) of LME (London Metal Exchange) Standard, but in this range, whatever the content of glue may be, the electrolytic copper S grade settles at the high grade side of 10 to 15 ppm, and it cannot be set lower than 10 ppm. In this range, the cell voltage is not sufficiently low, and it has been demanded to improve the electrolytic power unit consumption by further decreasing the cell voltage.

[0017] Besides, among conventional preventive measures of anode passivation, the method of decreasing the impurity content of the anode is accompanied by increase of cost in the copper refining process for manufacturing the anode, and in the PR electrolysis method, the bath voltage elevates together with increase of current and the power consumption increases, and the loss due to inverting current has a large effect on production, and it is not only disadvantageous economically, but is poor in product quality due to many grains and nodules formed on the surface.

SUMMARY OF THE INVENTION

[0018] In the light of the problems of the prior arts, it is hence a first object of the invention to provide an electrolytic refining method of copper capable of obtaining an electrolytic copper of high quality in both purity (especially S grade) and surface state, by preventing formation of creases, grains and nodules on the electrodeposition surface in operation at current density of 330 A/m² or higher, and an electrolytic copper refined by this method.

[0019] It is a second object of the invention to provide an electrolytic refining method of copper capable of obtaining an electrolytic copper of high quality substantially decreased in the S concentration in the electrolytic copper, and achieving improvement of electric power unit consumption, in electrolytic operation at high current density including PR electrolysis, and an electrolytic copper refined by this method.

[0020] It is a third object of the invention to provide an electrolytic refining method of copper capable of enhancing the productivity by shortening the inverting or reversing time in PR electrolysis, preventing anode passivation economically and advantageously, and improving the quality, and an electrolytic copper refined by this method.

[0021] The means for achieving the first object (a first aspect of the invention) is described below.

[0022] In operation at current density of 200 to 260 A/m², grains and nodules could be suppressed in a range of glue of 50 to 160 g/t and thiourea of 50 to 160 g/t. In this range of additives, however, when the current density was increased to 330 A/m² or higher, the surface properties were impaired.

[0023] The present inventors considered the solving measures as follows. That is, to manufacture an electrolytic copper with favorable surface properties, it is considered preferable to electrolyze by holding the cathode potential (cathode overpotential) at a potential for inducing polycrystalline growth, on the basis of the current-potential curve shown in the characteristic diagram in Fig. 1. According to this idea, when the current or current density is raised, the cathode potential is shifted in the base (-) direction, to a potential for forming nodules, dendrites or whiskers. On the other hand, to electrolyze at a cathode potential for inducing polycrystalline growth at high current density, the potential must be shifted to the noble (+) direction, and it is found possible by reducing the overpotential by adjusting the contents of additives.

[0024] The inventors measured the cathode potential by varying the contents of additives in a range of current density of 330 A/m² or higher, and observed the surface properties of the obtained product electrolytic copper, and discovered that the surface properties are extremely improved, by decreasing the contents of additives as compared with conventional levels, as the cathode potential is shifted to a range for inducing polycrystalline growth, coinciding with the above proposed idea, and have come to reach the first aspect of the invention.

[0025] That is, the first aspect of the invention is an electrolytic refining method of copper characterized by electrolyzing by controlling the cathode potential at current density of 330 A/m² or higher. Electrolyzing by controlling the cathode potential means electrolyzing while keeping the cathode potential in an appropriate range in order to obtain an electrolytic copper improved in surface properties free from grains and nodules.

[0026] To control the cathode potential, it is preferred to measure the cathode potential, and adjust the contents of

additives, that is, glue and thiourea, so that the measured potential may settle within the specified range (the appropriate range).

[0027] Contents of additives are preferred to be 50 g/t or less for glue and 70 g/t or less for thiourea. According to this method, the cathode overpotential is lowered, and it leads to drop of voltage, so that it is possible to electrolyze at a far lower electric power than in the prior art.

[0028] The cathode potential is changed most significantly by variation of the contents of additives, but also varies with the copper concentration, sulfuric acid concentration and temperature of the electrolytic cell, and hence it is also preferred to adjust these electrolytic cell conditions so that the measured value of the cathode potential may settle within the specified range.

[0029] The first aspect of the invention also relates to an electrolytic copper with sulfur content of 10 ppm or less being electrolytically refined by controlling the cathode potential at current density of 330 A/m² or higher.

[0030] In the invention, the term "glue" is meant to include glue, gelatin, and a mixture of glue and gelatin.

[0031] Also in the invention, the unit "g/t" of contents of additives (glue, thiourea, anionic activator, etc.) refers to the gram mass per 1 ton of electrolytic copper.

[0032] The means for achieving the second object (a second aspect of the invention) is described below.

[0033] The present inventors intensively studied in order to achieve the second object, and expected that, if there is any other substance X having a slime settling effect than glue, the appropriate range of content of glue may be shifted to a smaller content side by adding it to the electrolyte solution, so that lowering of electrolytic copper S grade and reduction of electric power unit consumption might be achieved at once, and further accumulated investigations and experiments, and learned that a specific anion surfactant (of surface active agents, any one electrolytically dissociated in aqueous solution, of which main ingredient of surfactant becomes an anion) is ideal for such substance X, and have devised the second aspect of the invention.

[0034] That is, the second aspect of the invention is an electrolytic refining method of copper characterized by using an anion surfactant as additive, aside from glue and thiourea.

[0035] In the second aspect of the invention, the anionic activator is preferred to have 7 to 13 carbon atoms, preferably 8 to 12 carbon atoms, and most preferably 10 carbon atoms. The anion surfactant is preferably one or two or more type selected from the group consisting sulfonate, sulfate, phosphonate, and carboxylate. The anionic activator is preferred to be injected into the electrolyte solution continuously rather than intermittently. The anion surfactant in the electrolyte solution acts to adsorb the glue to the cathode side and itself to the anode side. The content of the anion surfactant is preferred to be 0.001 g/t or more.

[0036] The second aspect of the invention also relates to an electrolytic copper with sulfur content of 10 ppm or less being electrolytically refined by adding an anion surfactant, aside from glue and thiourea, as additives.

[0037] The means for achieving the third object (a third aspect of the invention) is described below.

[0038] The third aspect of the invention achieving the third object is an electrolytic refining method of copper characterized by adding an anion surfactant in the electrolyte solution by 0.001 g/t or more, and feeding the inverting current continuously for 45 to 300 seconds, at 1/500 to 1/25 of continuous feeding time of positive current, in PR electrolysis, or further by decreasing the contents of organic additives (that is, glue and thiourea) added to the electrolyte solution along with elevation of current, specifically 50 g/t or less of glue and 60 g/t or less of thiourea in electrolysis at D_k 300 A/m² or higher.

[0039] In the third aspect of the invention, it is preferred to use stainless steel as cathode material, and apply positive current in the first current feed.

[0040] The third aspect of the invention also relates to an electrolytic copper with sulfur content of 10 ppm or less being electrolytically refined in PR electrolysis by adding an anion surfactant in the electrolyte solution by 0.001 g/t or more, and feeding the inverting or reversing current continuously for 45 to 300 seconds, at 1/500 to 1/25 of continuous feeding time of positive current.

BRIEF DESCRIPTION OF THE DRAWINGS

[0041]

Fig. 1 is a characteristic diagram showing a current-potential curve.

Fig. 2 is a schematic diagram showing an example of measuring method of cathode potential (1: electrolytic cell, 2: cathode, 3: anode, 4: Ag/AgCl electrode, 5: potentiometer).

Fig. 3 is a graph showing an example of dependence of cathode potential measured in the method in Fig. 2 on the surface favorable region and additive contents.

DESCRIPTION OF THE INVENTION

[0042] In the first aspect of the invention, in electrolytic operation at current density of 330 A/m² or higher, it is the principle to operate by controlling the cathode potential. To control the cathode potential, for example, in a general method used in the electrochemical field as shown in Fig. 2, the cathode potential is measured, and the measured potential is controlled within a specified range. When measuring the cathode potential, it is important to keep the distance λ between the surface of a cathode 2 and the sensor of an Ag/AgCl electrode 4 as constant as possible (for example, within an range of about 1 to 2 mm). If the distance λ is changed slightly, the measured potential varies significantly. Measurement may be either continuous or intermittent.

[0043] In the cathode potential, there is a region in which the surface properties of the electrolytic copper are favorable (called surface favorable region). This surface favorable region, as expressed by the measured potential by the method in Fig. 2, corresponds to a range of -70 to -15 mV as shown in Fig. 3. Therefore, by measuring the cathode potential while controlling the distance λ within 1 to 2 mm in the method in Fig. 2, and controlling the measured potential within a range of -70 to -15 mV, preferably controlling at a constant value to coincide with the specific target provided in the range, it is possible to manufacture electrolytic copper free from wrinkle, grain or nodule in electrolytic operation at high current density.

[0044] The cathode potential corresponding to such surface favorable region has a region of a nearly specific value at current density of 330 A/m² or higher.

[0045] In the operation for such control of cathode potential, the content of the additive glue or thiourea, or both is important. Fig. 3 shows the relation between the cathode potential in the condition shown in the diagram and the contents of additives. As shown in Fig. 3, the cathode potential is shifted to the base (-) side along with the increase of glue content and/or thiourea content.

[0046] The contents of additives for maintaining the cathode potential in the surface favorable range vary with the current density and copper concentration, and an example is shown in Fig. 3. In the operation at current density of 330 A/m² or higher employed in the first aspect of the invention, if the glue is added by more than 50 g/t, the measured potential hardly settles within the surface favorable region, and it is preferred to add by 50 g/t or less, and preferably 1 to 50 g/t. If the thiourea is added by more than 70 g/t, the efficiency of electrolysis tends to decline, and it is preferred to added by 70 g/t or less, and preferably 60 g/t or less.

[0047] Both glue and thiourea act to shift the cathode potential in the base direction, and when one condition (either glue or thiourea) is fixed while measuring the cathode potential, the other can be adjusted, and there are numerous types of best combination of contents of additives.

[0048] In electrolytic refining of copper, the cathode potential varies also depending on the electrolytic cell conditions, in particular, copper concentration, sulfuric acid concentration, and temperature (cell temperature). Accordingly, it is preferred to adjust these electrolytic cell conditions so that the measured potential may settle within the surface favorable region. For such control, a preliminary experiment is conducted to determine the relation of the copper concentration, sulfuric acid concentration and cathode potential, for example, as shown in Table 1, and the relation of cell temperature and cathode potential, for example, as shown in Table 2, and on the basis of these results, one or two or more of the copper concentration, sulfuric acid concentration and cell temperature may be increased or decreased properly depending on the measured value of cathode potential, so that the measured potential may be kept within the surface favorable region. Additives are not limited to glue and thiourea, but other organic or inorganic additives having same effects may be used.

Table 1

Copper concentration (g/L)	Sulfuric acid concentration (g/L)	Cathode potential (mV vs Ag/AgCl)	Others
50	160	-50	Current density : 450 A/m ² Glue: 10g/t Thiourea: 30g/t Cell temperature: 60°C
50	190	-55	
50	200	-85	
45	190	-70	
40	190	-77	

Table 2

Cell temperature (°C)	Cathode potential (mV vs Ag/AgCl)	Others
55	-40	Current density: 450 A/m ² Copper concentration: 50g/L Sulfuric acid concentration : 190g/L Glue : 10g/t Thiourea: 30g/t
60	-15	
65	20	
70	50	

[0049] The first aspect of the invention is effective whether the method of electrolysis is normal electrolysis or PR electrolysis, but the PR electrolysis has a polarization preventive effect by inverting or reversing, and can be set at a higher current density without limitation as in normal electrolysis, and is hence applied in a wider range. When the current density is raised, meanwhile, if exceeding D_k 700 A/m², there was a tendency of worsening of properties of electrolytic copper surface.

[0050] The electrolytic copper of the first aspect of the invention is a product electrolytic copper refined by the refining method of the first aspect of the invention, and is an electrolytic copper having a high quality with S grade of 10 ppm or less, being free from problems such as wrinkle, grain or nodule on the surface.

[0051] In the second aspect of the invention, as the additives used in electrolysis of copper at high current density, aside from glue and thiourea, an anion surfactant for settling slime is used. The anion surfactant is a kind of surface active agent which is electrolytically dissociated in aqueous solution to transform the entity of the active agent into an anion.

[0052] As a result, since the role of settling the slime at the anode side can be converted from the glue to this anion surfactant, the content of the glue can be decreased and the cell voltage can be lowered, so that roughening of electrodeposition may be further lessened.

[0053] The anion surfactant for settling slime should preferably have about 10 carbon atoms. This kind of anion surfactant is electrolytically dissociated in an electrolyte solution, and produced anions are adsorbed on the anode surface by electric field, and are adsorbed to coat the slime before the slime peels off from the anode surface, that is, an adsorption layer is formed on the slime surface, and the slime particle surface is made anionic or hydrophobic to provide with adsorption property to the anode, and further by this anionic change, electric repulsion to the cathode or the product cathode (electrolytic copper) is applied to segregate the slime to the anode side, thereby preventing mixing of slime into the electrolytic copper.

[0054] This effect is maximum when the number of carbon atoms is 10, and is slightly decreased at 8 or 12 carbon atoms, and further decreased at 6 or less or 14 or more carbon atoms. The effect is confirmed in a range of 7 to 13 carbon atoms. This is considered because the hydrophobic property is too strong to form the film sufficiently at 14 or more carbon atoms, and the hydrophobic property is too weak at 6 or less carbon atoms, thereby lacking in the adsorption when the slime is separated from the anode.

[0055] By the addition of this anion surfactant, the two roles of the glue can be focused only on the effect on the cathode as hydrophobic cation (that is, the smoothing effect), and the content of the glue can be decreased substantially, and it can be adjusted to a proper amount depending on the electrolysis at high current density, and even in the electrolysis at a high current density of D_k of 360 A/m² or higher, an electrolytic copper of high quality not different from the quality in electrolysis at a low current density of D_k of 280 A/m² or lower can be produced. Incidentally, since the cathode (electrolytic copper) smoothing effect of the glue is attributable to the effect of hydrophobic cations, the glue may be replaced by, for example, a synthesized hydrophobic cationic substance.

[0056] Also by the addition of the anion surfactant, the cathode overvoltage can be lowered to a same level as in electrolysis at a low current density, and hence the voltage drops, and even in operation at a high current density, it is possible to operate at an electrolytic power of same level as in electrolysis at a low current density.

[0057] As the anion surfactant in the second aspect of the invention, it is preferred to use a substance having a hydrophilic radical not causing problems if decomposed, such as sulfonate, sulfate, phosphonate, and carboxylate. These substances may be used either alone, or in combination of two or more types. Examples of sulfonate include n-alkyl sodium sulfonate, examples of sulfate include n-alkyl sodium sulfate, examples of phosphonate include n-alkyl phosphate, and examples of carboxylate include n-sodium decanate and n-sodium octanate.

[0058] From the viewpoint of stabilization of cell composition, it is preferred to inject or drop the anion surfactant of the second aspect of the invention into the electrolyte solution continuously rather than intermittently. The point of injection or dropping is not particularly limited, including the circulation tank, head tank, and electrolytic tank in as a constituent element of electrolyte solution circulation system.

[0059] At current density D_k of 280 A/m² or higher, or in particular 300 A/m² or higher, if the content of the anion

surfactant is less than 0.001 g/t (in gram unit per 1 ton of electrolytic copper, same hereinafter), the effect for denaturing the slime surface is insufficient, and it is preferred to add by 0.001 g/t or more, preferably 1 g/t or more. However, if the content of the anion surfactant is increased too much, the effect levels off, and only the cost is increased, and it is preferred not to add more than 50 g/t.

[0060] According to the second aspect of the invention, because of such composition, it is possible to operate electrolysis for producing electrolytic copper of high quality at a high current density of 280 A/m² or higher (in particular, $D_k \geq 300$ A/m² in normal electrolysis generally employed in copper refining field, or $D_k \geq 330$ A/m² in PR electrolysis). Incidentally, when exceeding D_k of 900 A/m², a tendency of worsening of properties of electrolytic copper surface was observed.

[0061] The electrolytic copper of the second aspect of the invention is a product electrolytic copper refined by the refining method of the second aspect of the invention, and is an electrolytic copper having a high quality with S grade of 10 ppm or less, being free from problems such as wrinkle, grain or nodule on the surface.

[0062] In the third aspect of the invention, PR electrolysis is performed by adding the anion surfactant by 0.001 g/t or more in the electrolyte solution, and feeding the inverting or reversing current continuously for 45 to 300 seconds, at 1/500 to 1/25 of continuous feeding time of positive current. The anion surfactant usable in the third embodiment includes sulfonate, sulfate, phosphonate, and carboxylate, which may be used either alone or in combination.

[0063] When an anion surfactant is added to an aqueous solution of copper sulfate which is used as electrolyte solution, it is dissociated electrolytically in the solution, and the entity of the activating agent becomes anions, and the anions are attracted to the anode or the positive electrode, and are adsorbed on the anode surface, and when slime which is an undissolved portion due to anode dissolving (that is, anode slime, same hereinafter) peels off from the surface, an adsorption state is formed on the slime surface, and the anode slime is made negative electrically. The electrically negative anode slime receives an electrical attraction from the anode or positive electrode during feeding of positive current, but when an inverting or reversing current is fed, an electrical repulsion is received from the anode becoming a negative electrode, and a dissociation tendency from anode surface takes place.

[0064] By the electrical repulsion, during feeding of inverting or reversing current, the anode slime is separated from the anode surface, and is temporarily suspended in the solution, and then settles. When the slime in this process of suspending and settling is accumulated on the cathode, grains and nodules are formed on the surface, but since the slime surface is electrically negative, when the cathode returns to the normal negative electrode, the electric repulsion acts to prevent accumulation of slime. By this action and effect, passivation can be prevented, and deterioration of quality due to grains and nodules formed on the product can be prevented at the same time.

[0065] However, if the content of the anion surfactant is less than 0.001 g/t, the anode slime is not sufficiently negative electrically, and the dissociation tendency is not enough, and the anion surfactant must be added by 0.001 g/t or more. Preferably, it should be more than or equal to 3 g/t, or more preferably more than or equal to 10 g/t. However, if the content is increased too much, the dissociation tendency levels off, and only the cost is increased, and it is preferred not to add the anion surfactant by more than 30 g/t.

[0066] To prevent anode passivation, it is necessary to peel off the anode slime in the dissociation tendency sufficiently from the anode surface, and for this purpose it is effective to shake physically by liquid convection changes, by stopping or inverting the natural convection of electrolyte solution near the anode, together with electrical repulsion, before the anode slime is collected too much.

[0067] If the continuous feeding time of inverting current is less than 45 seconds, liquid convection changes are not sufficient, and physical shaking is not enough and scraping of anode slime is not promoted and it is not effective. If exceeding 300 seconds, on the other hand, the elution of copper from the cathode increases to spoil the productivity. Accordingly, the continuous feeding time of inverting or reversing current is required in a range of 45 to 300 seconds. Preferably, it should be 50 to 200 seconds, or more preferably 60 to 90 seconds.

[0068] In addition, if the continuous feeding time of inverting or reversing current is less than 1/500 that of positive current, the positive current feeding time becomes relatively long, and the anode slime is accumulated too much, and is hardly separated by physical shaking, and also the electrically negative effect is insufficient in the in-depth portion of the anode slime, and the adhesion inhibiting force to the cathode is weakened, and grains and nodules are increased. On the other hand, when exceeding 1/25, relatively, the positive current feeding time is shorter, and the electrodeposition amount of copper on the cathode is insufficient. Accordingly, the continuous feeding time of inverting or reversing current should be 1/500 to 1/25 that of positive current. Preferably, it should be 1/300 to 1/50, or more preferably 1/250 to 1/70.

[0069] When the inverting or reversing current density is in a range of 0.3 to 2.0 times of D_k , the effect is expected. If less than 0.5 times, however, it is accompanied by extension of inverting or reversing current feeding time, and the facility productivity is lowered, and the magnitude of liquid convection changes is slightly smaller. On the other hand, in a range of over 1.0 times, the inverting or reversing current feeding time can be shortened, but if exceeding 1.2 times, not only the magnitude of liquid convection changes is more likely to level off, but also an expensive rectifier for electrolysis is required, and the facility investment increases. Hence, the current density of inverting or reversing current

is preferred to be in a range of 0.5 to 1.2 times that of positive current.

[0070] Incidentally, during changeover from positive current to inverting current (or vice versa), there may be a power-cut (stoppage of electric power supply) time of about 20 seconds or less.

[0071] In electrolysis at a high current density of D_k of 300 A/m² or higher, in particular, 350 A/m² or higher, the cathode overpotential elevates, and the surface electrodeposition state tends to be inferior. To lessen this tendency, it is effective to decrease the content of organic additives in the electrolyte solution, and more specifically the glue should be 50 g/t or less and thiourea 60 g/t or less. Herein, lower limits of contents of glue and thiourea are not particularly specified.

[0072] In the conventional electrolysis, when the organic additives are decreased to the above range, the slime settling performance drops, and the suspending and floating slime increases and is likely to be accumulated on the cathode surface, and grains and nodules are more obvious, but in the invention, the added anion surfactant renders the slime negative electrically to repulse against the cathode surface, and further by appropriate inverting current feeding conditions, the slime is not collected but is separated from the anode surface by turning negative electrically, so that grains and nodules are hardly formed.

[0073] As described herein, according to the invention, by adding a proper amount of anion surfactant in the electrolyte solution, the anode slime is turned negative electrically, and the feeding condition of inverting current is optimized to induce liquid convection changes to shake physically, and hence the separating efficiency of anode slime is substantially improved, and the interference of diffusion and convection of copper ions due to slime is eliminated, and the resistance is lowered, and thereby the anode overpotential declines. As a result, by using an anode of ordinary copper grade, and without being accompanied by elevation of cell voltage, anode passivation can be prevented, and PR electrolysis at D_k of 360 A/m² or higher can be executed economically and advantageously. It is also the same in the PR electrolysis at a relatively low D_k (for example, about 280 A/m²).

[0074] Also in the third aspect of the invention, the cathode may be changed from the ordinary copper cathode to a stainless steel cathode. The stainless steel cathode is excellent in horizontality, and is small in occurrence of shorting and high in current efficiency, and is hence applied widely around the world in normal electrolysis. However, it has not been applied in PR electrolysis so far. This is because, in the conventional PR electrolysis, if the stainless steel cathode is anodized only for a moment, the stainless steel is dissolved, and pitting occurs on the surface, and stripping failure of electrolytic copper may occur. According to the third aspect of the invention, by feeding positive current in the first place, since a specific amount of copper can be continuously electrodeposited for a long time, when inverting or reversing the current, an electrodeposition layer of copper is already formed on the surface of the stainless steel cathode, so that the stainless steel is not dissolved.

[0075] Therefore, by using the stainless steel cathode in the third aspect of the invention, it is possible to operate electrolysis at D_k of 400 A/m² or higher, far higher than D_k of 330 A/m² as the limit of the conventional electrolysis using stainless steel cathode such as ISA method or KIDD method.

[0076] The electrolytic copper of the third aspect of the invention is a product electrolytic copper refined by the refining method of the third aspect of the invention, and is an electrolytic copper having a high quality with S grade of 10 ppm or less, being free from problems such as wrinkle, grain or nodule on the surface.

EXAMPLES

(1) Examples of the first aspect of the invention

[0077] (Example 1) In an electrolytic tank of 1200 mm long x 4850 mm wide x 1300 mm deep, 47 anodes measuring 990 mm long x 970 mm wide x 45 mm thick (weighing 370 kg), and 46 cathodes measuring 1022 long x 1022 mm wide x 0.7 mm thick (weighing 7 kg) were loaded, and PR electrolysis of copper was operated at current density of 450 A/m², in which the cathode potential was measured while keeping η constant as far as possible (in a range of 1 to 2 mm) in the method shown in Fig. 2, and the contents of glue and thiourea were adjusted so that the measured potential might coincide with the target determined within a surface favorable range (-70 to -15 mV).

[0078] The electrolytic cell conditions were basically copper concentration: 50 g/L, free sulfuric acid concentration: 190 g/L, cell temperature: 60°C, and circulation flow rate: 40 L/min, and if the measured potential could not be brought closer to the target by adjustment of contents of additives due to some cause, one or two or more of the copper concentration, sulfuric acid concentration and cell temperature were increased or decreased referring to the correspondence relationship determined in the preliminary experiment, and the measured potential was brought closer to the target.

[0079] (Example 2) Operated in the same conditions as in example 1, except that the target of measured potential was a different value in the surface favorable region.

[0080] (Example 3) Operated in the same conditions as in example 1, except that the current density was 330 A/m², and that the target of measured potential was a different value in the surface favorable region.

[0081] (Example 4) Operated in the same conditions as in example 3, except that the method of electrolysis was normal electrolysis, and that the target of measured potential was a different value in the surface favorable region.

[0082] (Comparative example 1) Operated in the same conditions as in example 1, except that the cathode potential was not measured and controlled, that the contents of glue and thiourea were appropriate values in operation at current density of 250 A/m², and that the electrolytic cell conditions were fixed at basic values.

[0083] (Comparative example 2) Operated in the same conditions as in comparative example 1, except that the method of electrolysis was normal electrolysis, and that the contents of glue and thiourea were appropriate values in operation at current density of 250 A/m² (however, different values from comparative example 1).

[0084] In examples 1 to 4 and comparative examples 1 and 2, contents of additives (median values in adjusting range in examples, and specific values in comparative examples), and S grade (same as concentration) and surface properties investigated in product electrolytic copper are shown in Table 3.

[0085] As shown in Table 3, whether in normal electrolysis or PR electrolysis, in comparative examples, the S concentration was higher than 10 ppm, and surface properties disclosed numerous acicular depositions and grains, but the examples were lowered in the S concentration to 6 ppm or less and were smooth in surface properties, and produced a high quality.

Table 3

	Electrolysis	Current density (A/m ²)	Content of additive (g/t)		Product electrolytic copper	
			Glue	Thiourea	S(ppm)	Surface properties
Example 1	PR	450	5	30	4	Favorable
Example 2	PR	450	10	30	5	Favorable
Example 3	PR	330	45	50	3	Favorable
Example 4	Normal	330	40	50	6	Favorable
Comparative example 1	PR	450	100	50	53	Grainy
Comparative example 2	Normal	330	100	80	20	deposition
(Note) In the case of PR electrolysis, current density is positive current density.						

(2) Examples of the second aspect of the invention

[0086] In an electrolytic tank of 1200 mm long x 4850 mm wide x 1300 mm deep, 47 anodes measuring 990 mm long x 970 mm wide x 45 mm thick (weighing 370 kg), and 46 cathodes measuring 1022 long x 1022 mm wide x 0.7 mm thick (weighing 7 kg) were loaded, and electrolytic refining of copper was operated in the conditions of solution by mixing additives in an aqueous solution of copper sulfate composed of copper concentration of 50 g/L and free sulfuric acid concentration of 190 g/L, circulation flow rate: 30 L/min, and cell temperature: 65°C, in which the current density D_k and contents of additives were varies as shown in Table 4, and the electrolytic copper S grade and cell voltage were investigated. Table 4 shows the result. Besides, there was no problem about the grade of other impurities such as As, Sb, Bi, Ni, Pb and Ag. Additives were injected or dropped continuously in the circulation tank communicating with the electrolytic tank. The injection or dropping amount per unit time was set so that the contents in Table 4 could be achieved.

[0087] As shown in Table 4, in the examples, the electrolytic copper S grade occupied the lower concentration side of the limit range (15 ppm or less) of the LME Standard. At the same current density D_k , those with S grade of 15 ppm or less were compared, the cell voltage was lower in the examples than in the comparative examples.

[0088] In the examples, n-alkyl sodium sulfate was used as the anion surfactant, but it has been confirmed that the same effects are obtained by using n-alkyl soda sulfonate, n-alkyl phosphate and n-sodium decanate.

Table 4

No.	Electrolysis	D_k (A/m ²)	Glue content (g/t)	Thiourea content (g/t)	n-Alkyl sodium sulfate	Anion surfactant		Electrolytic copper S grade (ppm)	Cell voltage (mV)	
						No. of carbons	Amount (g/t)			
1	PR	360	40	70	Added	10	25	4	338	Example
2	PR	360	40	70	Added	12	25	5	338	Example
3	PR	360	30	60	Added	10	25	2	326	Example
4	PR	360	120	90	Not added	-	-	16	365	Comparative example
5	PR	360	30	60	Not added	-	-	32	322	Comparative example
6	PR	450	10	30	Added	10	25	4	380	Example
7	PR	450	10	30	Not added	-	-	39	380	Comparative example
8	PR	450	120	90	Not added	-	-	41	380	Comparative example
9	PR	385	15	40	Added	10	25	4	290	Example
10	PR	385	15	40	Not added	-	-	39	335	Comparative example
11	Normal	330	40	70	Added	10	25	3	290	Example
12	Normal	330	40	70	Added	6	25	9	321	Example
13	Normal	330	40	70	Added	14	25	8	325	Example
14	Normal	330	80	70	Not added	-	-	12	335	Comparative example
15	Normal	330	40	70	Not added	-	-	18	290	Comparative example
16	Normal	280	80	60	Added	10	15	3	240	Example
17	Normal	280	80	60	Not added	-	-	10	262	Comparative example

(3) Examples of the third aspect of the invention

[0089] In an electrolytic tank of 1200 mm long x 4850 mm wide x 1300 mm deep, 47 anodes (copper grade 99.4%) measuring 990 mm long x 970 mm wide x 45 mm thick (weighing 370 kg), and 46 copper cathodes measuring 1022 long x 1022 mm wide x 0.7 mm thick (weighing 7 kg) were loaded, and PR electrolysis was operated in the conditions shown in Table 5, in the electrolyte solution by mixing additives in an aqueous solution of copper sulfate composed of copper concentration of 50 g/L and free sulfuric acid concentration of 190 g/L, circulation flow rate: 30 L/min, and cell temperature: 65°C. As the anion surfactant, n-alkyl sodium sulfate was used. Additives were injected or dropped continuously in the circulation tank communicating with the electrolytic tank. The injection or dropping amount per unit time was set so that the contents in Table 5 could be achieved. The inverting (or reversing) current density was 0.7 times of D_k . The operation was started by feeding positive current in the first place.

[0090] Table 5 shows the average cell voltage in each condition (average of momentary data of cell voltage), surface state of product (electrolytic copper), and the impurity sulfur (S) grade in electrolytic copper. As clear from Table 5, the average cell voltage is lower in examples than in comparative examples, and the S grade is lower along with decrease of grains and nodules.

Table 5

No.	Positive current density D_k (A/m ²)	Positive current continuous feed time τ_+ (s)	Inverting current continuous feed time τ_- (s)	τ_+ / τ_-	Contents of additives (g/l)			Average cell voltage (mV)	Product surface state	S grade (ppm)	Remarks
					Glue	Thiourea	Anion surfactant				
1	360	3000	60	1/50	30	60	25	335	No grains	2	Example
2	360	9000	60	1/150	30	60	20	340	No grains	3	Example
3	360	9000	60	1/150	30	60	10	338	No grains	3	Example
4	400	1800	60	1/30	10	30	20	372	No grains	2	Example
5	300	18000	60	1/300	50	60	25	280	No grains	3	Example
6	360	20	1	1/20	30	60	25	385	Many grains	18	Comparative example
7	360	50	1	1/50	30	60	25	390	Many grains	19	Comparative example
8	360	200	10	1/20	30	60	25	382	Some grains	10	Comparative example
9	400	20	1	1/20	10	30	20	398	Many grains	25	Comparative example
10	300	30	1	1/30	50	60	25	320	Some grains	6	Comparative example
11	360	600	30	1/20	30	60	25	378	Some grains	8	Comparative example
12	360	9000	60	1/150	100	70	-	390	Some grains	24	Comparative example
13	280	12000	60	1/200	60	75	10	259	No grains	2	Example
14	280	15000	60	1/250	60	75	20	265	No grains	2	Example
15	280	12000	60	1/200	100	75	-	305	Some grains	4	Comparative example
16	280	20	1	1/20	60	75	25	293	Some grains	7	Comparative example

[0091] Next, in an electrolytic tank of 1200 mm long x 4850 mm wide x 1300 mm deep, 47 anodes (copper grade 99.4%) measuring 990 mm long x 970 mm wide x 45 mm thick (weighing 370 kg), and 46 SUS304 stainless steel cathodes measuring 1152 long x 1047 mm wide x 3.2 mm thick (weighing 50 kg) with edges masked with resinous protectors were loaded, and electrolysis was operated in the conditions shown in Table 2, in an electrolyte solution by mixing additives in an aqueous solution of copper sulfate composed of copper concentration of 50 g/L and free sulfuric acid concentration of 190 g/L, circulation flow rate: 30 L/min, and cell temperature: 65°C. As the anion surfactant, n-alkyl sodium sulfate was used. Additives were continuously injected or dropped into the circulation tank communicating with the electrolytic tank. The injection or dropping amount per unit time was set so as to achieve the contents shown in Table 6. The inverting (or reversing) current density was 0.7 times of D_K . The operation was started by feeding positive current in the first place.

[0092] Table 6 shows the average cell voltage in each condition (average of momentary data of cell voltage), surface state of product (electrolytic copper), the impurity sulfur (S) grade in electrolytic copper, and stripping state. As clear from Table 6, the average cell voltage is lower in examples than in comparative examples, the S grade is lower along with decrease of grains and nodules, and the stripping state is superior.

Table 6

No.	Positive current density D_+ (A/m ²)	Positive current continuous feed time τ_+ (s)	Inverting current continuous feed time τ_- (s)	τ_+ / τ_-	Contents of additives (g/t)			Average cell voltage (mV)	Product surface state	S grade (ppm)	Scraping state	Remarks
17	360	9000	60	1/150	Glue	Thiourea	Anion surfactant	340	No grains	3	Good	Example
18	400	1800	60	1/30	10	30	20	372	No grains	4	Good	Example
19	400	20	1	1/20	10	30	20	398	Many grains	25	Poor	Comparative example

[0093] Thus, the invention brings about the following excellent effects.

(1) Copper can be electrolytically refined at high current density without worsening the purity or surface properties, and product electrolytic copper can be mass-produced.

(2) Both lowering of electrolytic copper S grade and improvement of electric power unit consumption can be achieved at the same time in electrolytic operation of copper at high current density.

(3) Anode passivation can be prevented without being accompanied by elevation of cell voltage, and electrolytic copper of high quality can be produced by electrolysis at high current density.

Claims

1. An electrolytic refining method of copper for electrolyzing by controlling the cathode potential at current density of 330 A/m² or higher.
2. The electrolytic refining method of copper of claim 1, wherein the cathode potential is measured, and contents of additives, glue and thiourea, are adjusted so that the measured potential may settle within a specified range.
3. The electrolytic refining method of copper of claim 2, wherein the contents of additives are 50 g/t or less for glue and 70 g/t or less for thiourea.
4. The electrolytic refining method of copper of any one of claims 1 to 3, wherein the cathode potential is measured, and the copper concentration, sulfuric acid concentration, and temperature of electrolytic cell are adjusted so that the measured potential may settle within a specified range.
5. An electrolytic copper with sulfur content of 10 ppm or less electrolytically refined by controlling the cathode potential at current density of 330 A/m² or higher.
6. An electrolytic refining method of copper, wherein an anion surfactant is used together with glue and thiourea as additives.
7. The electrolytic refining method of copper of claim 6, wherein the anion surfactant has 7 to 13 carbon atoms.
8. The electrolytic refining method of copper of claim 6 or 7, wherein the anion surfactant is one or two or more selected from the group consisting of sulfonate, sulfate, phosphonate, and carboxylate.
9. The electrolytic refining method of copper of any one of claims 6 to 8, wherein the anion surfactant is injected or dropped continuously into the electrolyte solution.
10. The electrolytic refining method of copper of any one of claims 6 to 9, wherein the content of the anion surfactant is 0.001 g/t or more.
11. An electrolytic copper with sulfur content of 10 ppm or less electrolytically refined by using an anion surfactant together with glue and thiourea as additives.
12. An electrolytic refining method of copper, wherein an anion surfactant is added to the electrolyte solution by 0.001 g /t or more, and PR electrolysis is operated by feeding inverting (or reversing) current continuously for 45 to 300 seconds, at 1/500 to 1/25 of continuous feeding time of positive current.
13. The electrolytic refining method of copper of claim 12, wherein glue is added by 50 g/t or less and thiourea by 60 g/t or less in electrolysis at current density D_k of 300 A/m² or higher.
14. The electrolytic refining method of copper of claim 12 or 13, wherein the cathode is made of stainless steel, and operation is started by first feeding positive current.
15. An electrolytic copper with sulfur content of 10 ppm or less electrolytically refined by PR electrolysis by adding an anion surfactant to the electrolyte solution by 0.001 g /t or more, and feeding inverting (or reversing) current continuously for 45 to 300 seconds, at 1/500 to 1/25 of continuous feeding time of positive current.

Fig. 1

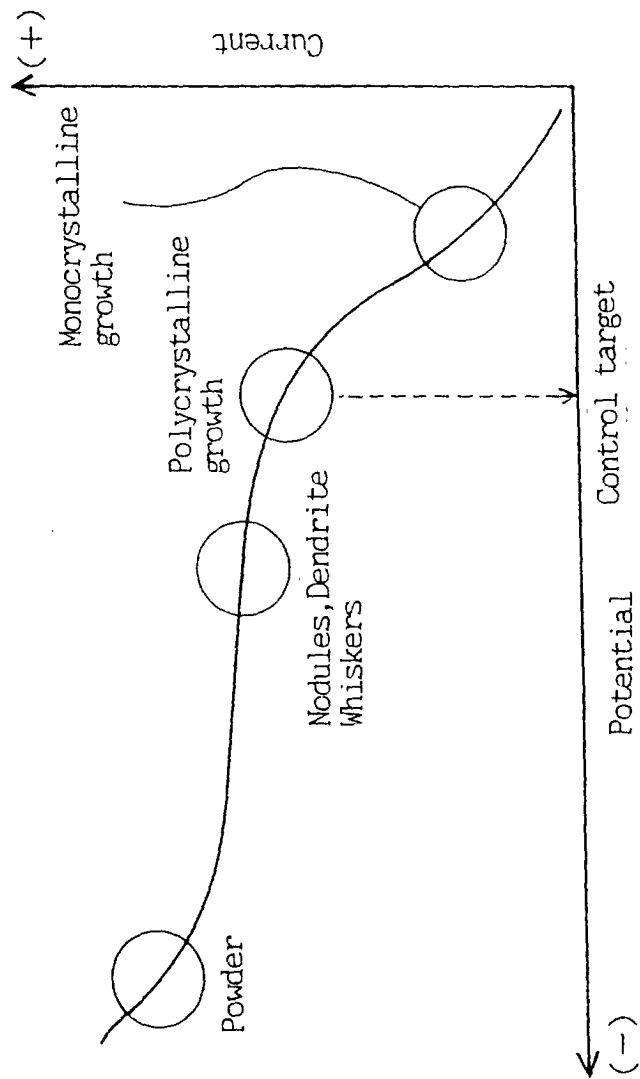


Fig. 2

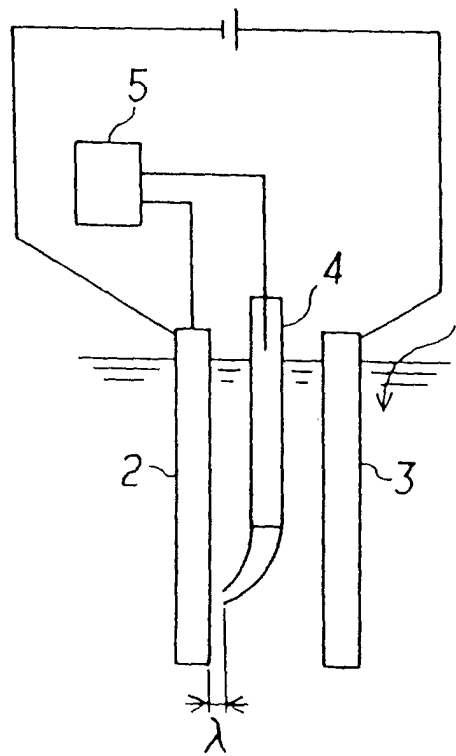
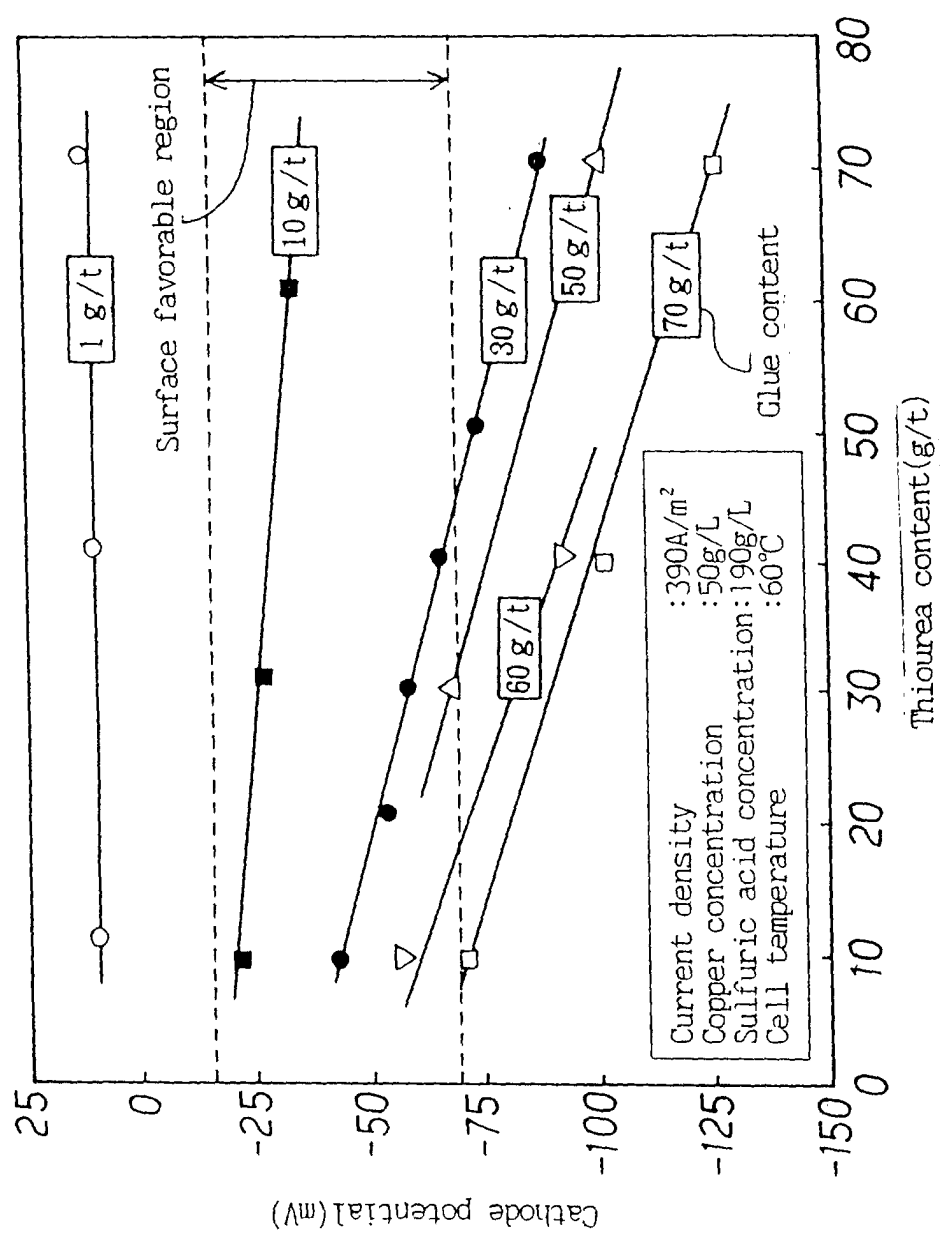


Fig. 3





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EUROPEAN SEARCH REPORT

Application Number
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