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(54) ELECTRICALLY CONDUCTIVE DIAMOND ELECTRODE, AND SULFURIC ACID ELECTROLYSIS METHOD AND SULFURIC ACID ELECTROLYSIS APPARATUS EACH UTILIZING SAME

(57) The present invention provides an electrically conductive diamond electrode comprising an electrically conductive substrate and an electrically conductive diamond layer coated on the surface of the electrically conductive substrate, featuring that:
1) the thickness of the electrically conductive diamond layer is 1~25μm,
2) the potential window fulfills Equation (1) and
3) the ratio (A/B) of the diamond component A and the non-diamond component B by the Raman spectroscopic analysis fulfills Equation (2).

$$2.1\mathrm{V} \leqq \text{potential window} \leqq 3.5\mathrm{V} \quad \cdots (1)$$

$$1.5 < A/B \leqq 6.5 \quad \cdots (2)$$

A:Intensity at the wave number 1300cm^{-1} by the Raman spectroscopic analysis
B:
Intensity at the wave number 1500cm^{-1} by the Raman spectroscopic analysis.

The present invention intends to provide an electrically conductive diamond electrode with a high durability as electrode, which achieves a high current efficiency of oxidizing agent at a low cell voltage by controlling the thickness of the electrically conductive diamond layer and crystallinity of the electrically conductive diamond, a sulfuric acid electrolysis method and an electrolysis apparatus of sulfuric acid applying the electrically conductive diamond electrode.

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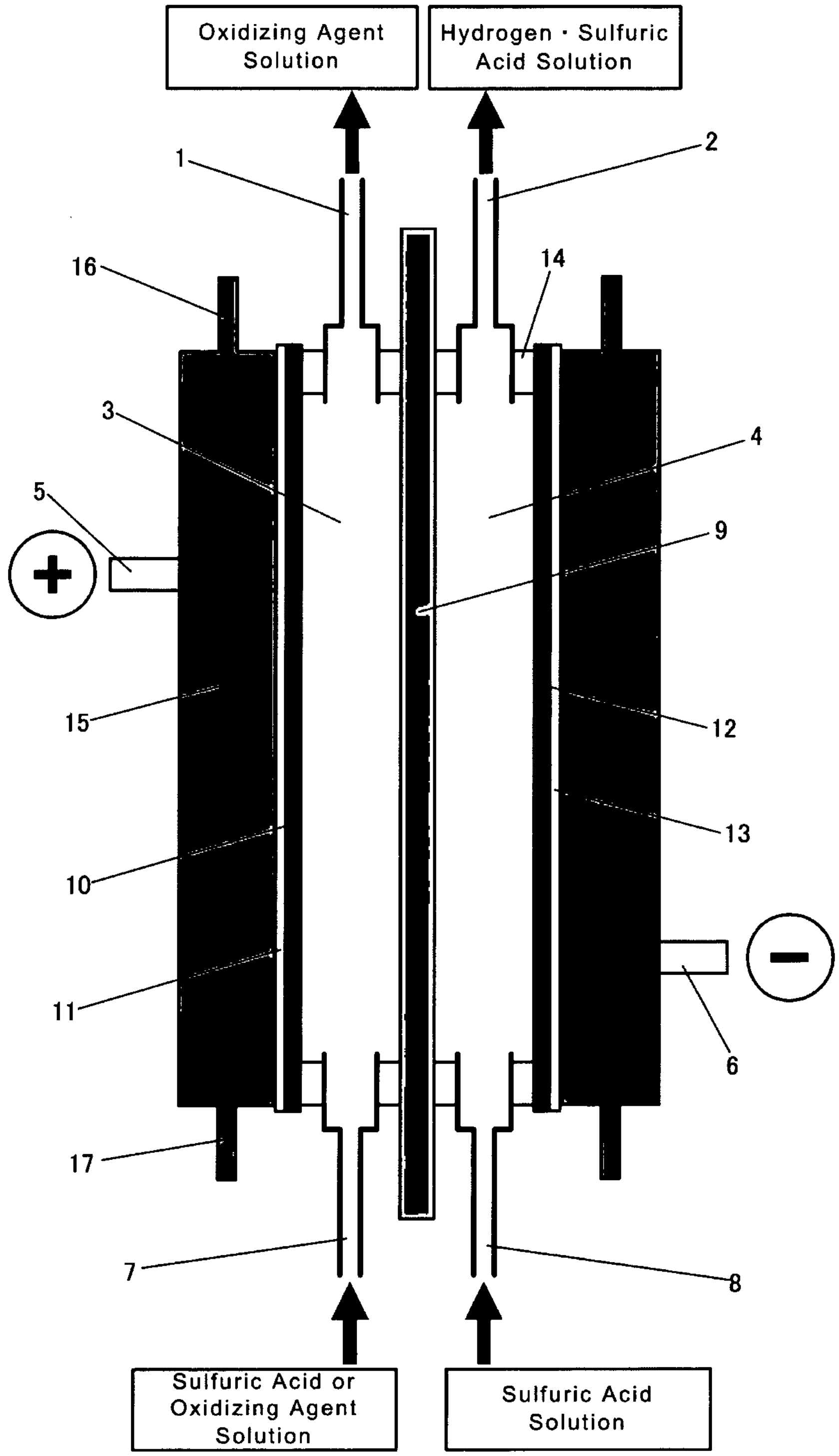
【Fig.1】


Oxidizing Agent Solution
Hydrogen · Sulfuric Acid Solution
1
2
16
14
3
4
5
+
9
15
12
13
10
11
−
6
17
7
8
Sulfuric Acid or Oxidizing Agent Solution
Sulfuric Acid Solution

Description

[Technical Field]

[0001] The present invention relates to an electrically conductive diamond electrode, and a sulfuric acid electrolysis method and a sulfuric acid electrolysis apparatus each utilizing same which stably form oxidizing agent through direct electrolysis of sulfuric acid applying the electrically conductive diamond electrode.

[Background Art]

[0002] Persulfuric acid and persulfate have been used in various manufacturing and inspection processes as chemical agents, such as pre-treatment agent for electrolytic metal plating, etching agent, oxidizing agent in chemical and mechanical polishing treatment for semiconductor device manufacturing, oxidizing agent for organic substance in wet analyses, and cleaning agent for silicon wafer. These chemicals of persulfuric acid and persulfate, which are called "oxidizing agent", are known to be formed by electrolysis of sulfuric acid, and have been electrolytically manufactured in an industrial scale.

[0003] In the present invention, the "oxidizing agent" indicates persulfuric acid which names generically peroxodisulfuric acid and peroxomonosulfuric acid and hydrogen peroxide. When the "oxidizing agent", which is an electrolysis product, is used for cleaning or surface treatment of components, a method to produce a chemical solution with a high concentration is required, since in most cases, the higher the total concentration is, the higher the effect obtained from it becomes. For the production of these solutions, electrolysis process is applied, where it is effective for high productivity to maintain the electric power consumption rate calculated from cell voltage, electrolytic current and current efficiency to be low and to keep a high current efficiency stably over time in order to save energy required for the production. To achieve it, required is a manufacturing method of a highly durable electrode for long life and for production of clean electrolyte free from pollution from the electrode.

[0004] PTL 1 discloses a sulfuric acid electrolysis method for manufacturing persulfuric acid through electrolysis of concentrated sulfuric acid applying an electrically conductive diamond anode and a cleaning method to rinse silicon wafer work piece applying produced persulfuric acid. This electrically conductive diamond electrode is superior in efficiency of electrolytic oxidation of sulfuric acid to persulfuric acid because it has a larger overvoltage of oxygen generation compared with a platinum electrode so far used widely as electrode to form persulfate. Also, the electrically conductive diamond electrode features chemically stable property and a long life as electrode.

[0005] The electrically conductive diamond electrode has a higher current efficiency of persulfuric acid and a higher durability, compared with other electrode catalysts (Pt, PbO_2, etc.), and can produce clean electrolyte free from pollution from the electrode. The application of the electrically conductive diamond electrode is being promoted in the areas, such as manufacturing cleaning solution for semiconductor wafer.

[0006] However, PTL 1 only discloses a method relating to a sulfuric acid electrolysis method applying an electrically conductive diamond anode to produce persulfuric acid through electrolysis of concentrated sulfuric acid, in which cleaning solution containing persulfuric acid is formed by electrolyzing concentrated sulfuric acid, the cleaning solution is supplied to the materials to be rinsed such as silicon water with resist, the used cleaning solution with decreased concentration of persulfuric acid is recovered for successive electrolysis, and the same cleaning solution with increased concentration of persulfuric acid is used cyclically for cleaning, without disclosing the relation between the crystallinity of the electrically conductive diamond electrode and the Raman spectrometry property · potential window, and the relation between the crystallinity of the electrically conductive diamond electrode and the productivity in terms of the current efficiency, cell voltage, etc. of persulfuric acid like peroxodisulfuric acid or the oxidizing agent in the cleaning solution.

[0007] PTL 2 discloses the methods to maintain a high strength of the diamond by prescribing the diamond layer thickness and to enhance abrasion resistance of the diamond by prescribing the peak intensity ratio of Raman spectrometry, as polycrystalline diamond for tools. Further, it is specified that the diamond described in PTL 2 should have a layer thickness of 50μm or more and the peak ratio of the diamond carbon and non-diamond carbon (non-diamond carbon/diamond carbon) by Raman spectroscopic analysis being within a range of 2.0 or less. This diamond, however, is not an electrode for electrolysis, and there is no disclosure about the correlation between the crystallinity of the electrically conductive diamond electrode and the potential window as one of properties of electrolysis, or about the relation of the crystallinity with productivity in terms of current efficiency or cell voltage of persulfuric acid as peroxodisulfuric acid or oxidizing agent in the cleaning solution

[0008] PTL 3 discloses an electrically conductive diamond electrode having an electrically conductive layer of electrically conductive diamond-like carbon as an electrode for the electrolysis for an ozone water production apparatus. The electrically conductive layer described in PTL 3 has the ratio of the integrated intensity Int <1340> of the peak present at $1340cm^{-1} \pm 20cm^{-1}$ to the integrated intensity Int <1580> of the peak present at $1580cm^{-1} \pm 20cm^{-1}$ in Raman spectroscopic analysis which satisfies the following equation. Thus, an ozone water production apparatus producing ozone water at a high current efficiency, while maintaining durability of electrode is disclosed.

$$\mathrm{Int}\ \langle 1340\rangle / \mathrm{Int}\ \langle 1580\rangle = 0.5 \sim 1.5$$

[0009] However, PTL 3 explicitly describes that diamond-like carbon indicates amorphous hard carbon, different in structure from an electrically conductive diamond having a crystalline structure.

[0010] PTL 3 applying diamond-like carbon as electrode gives no disclosure about the relation between the crystallinity of the electrically conductive diamond electrode and the Raman spectrometry property · potential window, and the relation between the crystallinity of the electrically conductive diamond electrode and the productivity in terms of current efficiency, cell voltage, etc. of persulfuric acid like peroxodisulfuric acid and the oxidizing agent in the cleaning solution.

[0011] The methods described in PTL 1~3 do not disclose explicitly the correlation of the crystallinity of the electrically conductive diamond electrode with the Raman spectrometry property and the potential window. Moreover, it has been proven that the electrically conductive diamond electrode featuring a high current efficiency of oxidizing agent at a low cell voltage cannot be manufactured by those methods.

[Citation List]

[Patent Literature]

[0012]

PTL 1: JP2006-278838(A)
PTL 2: JPHei2- 232106(A)
PTL 3: JP2008 - 266718(A)

[Summary of the Invention]

[Technical Problem]

[0013] The present invention aims to solve the problems of the conventional technologies and to provide an electrically conductive diamond electrode featuring a high durability as electrode and a high current efficiency of oxidizing agent at a low cell voltage, an electrolysis method of sulfuric acid and an electrolysis apparatus for sulfuric acid, applying the electrically conductive diamond electrode.

[0014] Inventors of the present invention have found from their extensive studies to solve the problems that the crystallinity of the electrically conductive diamond has a close relationship with electrolysis performance including durability of electrode, cell voltage and current efficiency of oxidizing agent, and have succeeded in achieving aimed electrolysis performance by evaluating the crystallinity from the thickness of the electrically conductive diamond layer, the range of the potential window and the peak intensity ratio of the Raman spectrometry.

[Solution to Problem]

[0015] In order to solve the afore-mentioned problems, the present invention provides an electrically conductive diamond electrode comprising an electrically conductive substrate and an electrically conductive diamond layer coated on the surface of the electrically conductive substrate, featuring that:

1) the thickness of the electrically conductive diamond layer is in the range of 1~25μm,
2) the potential window fulfills Equation (1) and
3) the ratio (A/B) of the diamond component A and non-diamond component B by the Raman spectroscopic analysis fulfills Equation (2).

$$2.1\mathrm{V} \leqq \text{potential window} \leqq 3.5\mathrm{V} \quad \cdots (1)$$

$$1.5 < A/B \leqq 6.5 \quad \cdots (2)$$

A: Intensity at the wave number 1300cm^{-1} by the Raman spectroscopic analysis

B: Intensity at the wave number 1500cm^{-1} by the Raman spectroscopic analysis

[0016] As the second solution to solve the afore-mentioned problems, the present invention provides the electrode applying the electrically conductive diamond layer containing boron in the range of 1000~6000 ppm.

[0017] As the third solution to solve the afore-mentioned problems, the present invention provides the electrode applying the silicon substrate as an electrically conductive substrate.

[0018] As the fourth solution to solve the afore-mentioned problems, the present invention provides a sulfuric acid electrolysis method in which an anode compartment is separated from a cathode compartment by a diaphragm, an electrically conductive diamond anode is installed in the anode compartment, a cathode is installed in the cathode compartment, electrolyte containing sulfate ion is supplied respectively to the anode compartment and the cathode compartment from the outside, and oxidizing agent is formed in the anode electrolyte in the anode compartment by electrolysis, wherein a special electrically conductive diamond electrode is applied as electrically conductive diamond electrode and the concentration of sulfate ion in the electrolyte containing sulfate ion is in the range of 2~14 mol/l.

[0019] As the fifth solution to solve the afore-mentioned problems, the present invention provides a sulfuric acid electrolysis method wherein the concentration of acid in the electrolyte containing sulfate ion under the afore-mentioned electrolysis conditions is in the range of 4~28 mol/l.

[0020] As the sixth solution to solve the afore-mentioned problems, the present invention provides a sulfuric acid electrolysis apparatus in which an anode compartment is separated from a cathode compartment by a diaphragm, an electrically conductive diamond anode is installed in the anode compartment, a cathode is installed in the cathode compartment, electrolyte containing sulfate ion is supplied respectively to the anode compartment and the cathode compartment from the outside, and oxidizing agent is formed in the anode electrolyte in the anode compartment by electrolysis, wherein the afore-mentioned electrically conductive diamond electrode is applied and a fluororesin type cation exchange membrane or a hydrophilically treated porous fluororesin membrane is applied as diaphragm.

[0021] As the seventh solution to solve the afore-mentioned problems, the present invention provides a sulfuric acid electrolysis method in which an anode compartment is separated from a cathode compartment by a diaphragm, an electrically conductive diamond anode is installed in the anode compartment, a cathode is installed in the cathode compartment, electrolyte containing sulfate ion is supplied respectively to the anode compartment and the cathode compartment from the outside, and oxidizing agent is formed in the anode electrolyte in the anode compartment by electrolysis, wherein the afore-mentioned electrically conductive diamond electrode is applied as electrically conductive diamond electrode and the electrolyte containing sulfate ion is electrolyzed on a condition to satisfy Equation (3) and Equation (4) :

$$100 \leqq X \leqq 10000 \quad \cdots (3)$$

$$25 < Y < 250 \quad \cdots (4)$$

X=current /anolyte volume (A/l)
Y=current density (A/dm^2)

[0022] As the eighth solution to solve the afore-mentioned problems, the present invention provides a sulfuric acid electrolysis method by which a solution containing sulfate ion is electrolyzed on the afore-mentioned electrolysis condition to satisfy Equation (5) :

$$18000 \leqq Z \leqq 1080000 \quad \cdots (5)$$

Z= electric charge per unit volume (C/l) = current value × electrolysis time / anolyte volume (A・s/l)

[Advantageous Effects of Invention]

[0023] An electrically conductive diamond electrode, and a sulfuric acid electrolysis method and a sulfuric acid electrolysis apparatus applying the electrically conductive diamond electrode by the present invention can manufacture a solution of oxidizing agent with a high concentration at a low cell voltage and at a high current efficiency using an electrode with a high durability, which have not been achieved by the conventional technology.

[Brief Description of Drawings]

[0024]

[Fig. 1]
An overall view of an example of the electrolysis cell applied to the sulfuric acid electrolysis method and the sulfuric acid electrolysis apparatus by the present invention.
[Fig. 2-1]
An overall view of an example of the sulfuric acid electrolysis method and the sulfuric acid electrolysis apparatus by the present invention.
[Fig. 2-2]
An overall view of another example of the sulfuric acid electrolysis method and the sulfuric acid electrolysis apparatus by the present invention.

[Description of Embodiments]

[0025] The present invention has found that a close relationship exists between the crystallinity of the electrically conductive diamond electrode and the durability of the electrode, cell voltage, concentration of oxidizing agent of the produced oxidizing agent solution of oxidizing agent, and current efficiency, when sulfuric acid is electrolyzed by an electrolysis cell in which the electrically conductive diamond electrode is incorporated.

[0026] Diamond is a cubic crystal in which each constituent carbon atom connects by SP3 hybrid orbital and an insulator with a large band gap. The electrically conductive diamond in the present invention indicates a diamond provided with conductivity by doping impurities with different valency from carbon. From a viewpoint of raising conductivity, the concentration of impurities should be high, but if it is too high, crystallinity collapses and the electrode looks as if soot attaches to and durability becomes poor.

[0027] The crystallinity in the present invention represents a regularity of crystal sequence or the content of impurities other than carbon. More specifically, crystallinity becomes low when there are many components of non-diamond, graphite, and amorphous diamond, when the electrically conductive diamond layer is thin, when the particle size of electrically conductive diamond is small and when there is much content of the impurity elements other than carbon.

[0028] As shown in the examples to be described in the latter part, the results of many experiments conducted by the inventors of the present invention have revealed that both of the thickness of electrically conductive diamond layer and the ratio (A/B) of diamond component A and non-diamond component B by the Raman spectroscopic analysis are the factors which represent crystallinity, and by specifying these, it becomes possible to obtain an electrically conductive diamond electrode, a sulfuric acid electrolysis method and a sulfuric acid electrolysis apparatus with the electrically conductive diamond electrode applied, which achieve high durability as electrode, electrolysis at a low cell voltage, high current efficiency of oxidizing agent and production of highly concentrated oxidizing agent solution

[0029] The present invention constitutes an electrically conductive diamond electrode which features that the thickness of the electrically conductive diamond layer is in the range of 1~25μm, the potential window fulfills Equation (1), and the ratio (A/B) of the diamond component A and non-diamond component B by the Raman spectroscopic analysis fulfills Equation (2).

$$2.1\text{V} \leqq \text{potential window} \leqq 3.5\text{V} \quad \cdots (1)$$

$$1.5 < A/B \leqq 6.5 \quad \cdots (2)$$

A=Intensity at the wave number 1300cm^{-1} in the Raman spectroscopic analysis
B= Intensity at the wave number 1500cm^{-1} in the Raman spectroscopic analysis

[0030] The following explains the reasons for restricting the thickness of the electrically conductive diamond layer of the electrically conductive diamond electrode. The thickness of the electrically conductive diamond layer preferably is in the range of 1~25μm, more preferably 1~15μm. The thinner the electrically conductive diamond layer is, the shorter the production time of above electrically conductive diamond layer becomes and the lower the crystallinity of the electrically conductive diamond becomes. If crystallinity becomes low, the current efficiency of oxidizing agent becomes high, and the cell voltage becomes low. However, the layer becomes too thin, thinner than 1μm, the substrate can be exposed by corrosion of the matrix, and the layer peels off during electrolysis, showing poor durability of electrode. If the layer becomes too thick, thicker than 25μm, the crystallinity becomes high and the durability of the electrode enhances without exposure of the substrate and penetration of electrolyte to the matrix, but the current efficiency of the oxidizing agent is low and the cell voltage is high, and therefore, the layer thickness of the electrically conductive diamond electrode by the present invention is preferably in the range of 1~25μm

[0031] The following explains the reasons for restricting the potential window. The potential window in the present invention indicates the electric potential region where generation of neither hydrogen nor oxygen occurs in water electrolysis reactions.

When the potential window is wide, the crystallinity of electrically conductive diamond layer becomes high and the durability of electrode enhances. However, if the width of potential window is greater than 3.5V, the current efficiency of oxidizing agent decreases and the cell voltage increases. On the other hand, if the width of the potential window is narrower than 2.1 V, the durability of the electrode deteriorates.

[0032] In addition, when the peak intensity ratio A/B by the Raman spectrometry is large, the crystallinity of electrically conductive diamond layer becomes high and the durability of electrode enhances. However, when the peak intensity ratio A/B by the Raman spectrometry is larger than 6.5, the current efficiency of oxidizing agent lowers and the cell voltage increases. Whereas, when the peak intensity ratio A/B by the Raman spectrometry is small, the crystallinity of electrically conductive diamond layer decreases, the efficiency of oxidizing agent increases and the cell voltage decreases. However, the durability of the electrode decreases when the peak intensity ratio A/B by the Raman spectrometry is 1.5 or less.

[0033] The electrically conductive diamond layer contains boron in the range of preferably 1000~6000 ppm, more preferably 3000~5000 ppm.

The higher the boron concentration is, the lower the crystallinity becomes, the cell voltage decreases, the current efficiency of oxidizing agent becomes high, leading to a desirable electrode. However, if the boron concentration becomes too high, more than 6000 ppm, the electrode looks as if soot attaches to and the durability of electrode decreases. Then, the electrically conductive diamond electrode by the present inventions should contain boron in the range of 1000~6000 ppm.

[0034] As an electrically conductive substrate, there is no specific restriction and such materials as tantalum, tungsten, titanium and niobium are applicable. In particular, a silicon substrate provides an electrode with superior adhesion. Also, there is no restriction to the shape of the electrically conductive substrate, allowing plate, rod, pipe or spherical type. The electrically conductive substrate can contain impurities, such as boron and carbon.

[0035] The following explains, in detail, one embodiment of the sulfuric acid electrolysis method and the sulfuric acid electrolysis apparatus by the present invention in reference to figures.

[0036] Fig.1 shows one example of the electrolysis cell used for the sulfuric acid electrolysis method and the sulfuric acid electrolysis apparatus by the present invention.

The electrolysis cell is divided by the porous PTFE diaphragm 9 into the anode compartment 3 accommodating the electrically conductive diamond anode 10 filled with electrolyte containing sulfate ion and the cathode compartment 4 accommodating the electrically conductive diamond cathode 12 filled with sulfuric acid solution with the same concentration as that in the anode compartment 3. To the anode compartment 3, the anolyte inlet 7 is connected, through which sulfuric acid which is anolyte is supplied to the anode compartment 3. To the cathode compartment 4, the catholyte inlet 8 is connected, through which catholyte is supplied to the cathode compartment 4. The oxidizing agent solution formed in the anode compartment 3 is discharged from the anolyte outlet 1. Hydrogen and sulfuric acid solution formed in the cathode compartment 4 are discharged from the catholyte outlet 2. Other components include the anode power supply terminal 5, the cathode power supply terminal 6, the electrically conductive substrate 11 of the electrically conductive diamond anode 10, the electrically conductive substrate 13 of the electrically conductive diamond cathode 12, the sealing material 14 of the electrolysis cell, the cooling jacket 15, the cooling water outlet 16 and the cooling water inlet 17.

[0037] The electrically conductive diamond anode 10 and the electrically conductive diamond cathode 12 by the present invention comprise the electrically conductive diamond layer coated on the surfaces of the electrically conductive substrates 11, 13.

The coating method of the electrically conductive diamond layer is not necessarily limited. Typical methods optionally applicable include the hot filament CVD method, the microwave plasma CVD method and the DC arc jet plasma CVD method.

As the cathode, a cathode made of platinum and others can be used instead of the electrically conductive diamond cathode 12.

[0038] The electrolyte containing sulfate ion (HSO_4^- or SO_4^{2-}) for the present invention should contain sulfate ion in the range of 2~14 mol/l, more preferably 3~9 mol/l. If the concentration of sulfate ion (HSO_4^- or SO_4^{2-}) is smaller than 2 mol/l, the current efficiency of oxidizing agent decreases because of reduced reactant. If the concentration of sulfate ion is larger than 14 mol/l, the viscosity of electrolyte increases, gas liberation becomes poor, the bubble fraction increases

and the conductivity of electrolyte decreases, leading to the increase of cell voltage.
For this reason the present invention specifies the concentration of sulfate ion in the electrolyte containing sulfate ion to the range of 2~14 mol/l.

[0039] The acid (H^+) concentration of the electrolyte containing sulfate ion for the present invention is in the range of 4~28 mol/l, more preferably 6~18 mol/l. If the acid (H^+) concentration is smaller than 4 mol/l, the conductivity of electrolyte is low and the cell voltage increases. On the other hand if the acid concentration (H^+) is larger than 28 mol/l, the current efficiency of oxidizing agent decreases.
For this reason the present invention specifies the acid concentration to the range of 4~28 mol/l.

[0040] In the sulfuric acid electrolysis method by the present invention, the electrically conductive diamond electrode is applied and the electrolysis of the electrolyte containing sulfate ion is conducted under the conditions which satisfy X=current /anolyte volume (A/l) being $100 \leqq X \leqq 10000$, more preferably $300 \leqq X \leqq 6000$ and Y=current density (A/dm^2) being $25<Y<250$, preferably $50 \leqq Y \leqq 200$.
The present invention has found that If X is smaller than 100, the current efficiency of oxidizing agent decreases. On the other hand, if X is larger than 10000, the cell is filled with generated gas and the cell voltage increases.
Moreover, in the sulfuric acid electrolysis method by the present invention, if the current density Y (A/dm^2) is 25 or below, the current efficiency of oxidizing agent decreases. On the other hand, if Y is 250 or more, heat generates remarkably and proper temperature control of the electrolyte becomes difficult. In addition, gas liberation becomes poor, the bubble fraction increases and the conductivity of electrolyte decreases, leading to the increase of cell voltage.
For this reason the present invention specifies the range to $100 \leqq X \leqq 10000$ and $25<Y<250$.

[0041] Further, in the sulfuric acid electrolysis method by the present invention, the electrically conductive diamond electrode is applied and it is desirable to conduct the electrolysis of the electrolyte containing sulfate ion under the conditions which satisfy Z= electric charge per unit volume (C/l) = current value × electrolysis time/anolyte volume (A · s/l) being $18000 \leqq Z \leqq 1080000$, more preferably $100000 \leqq Z \leqq 800000$.
If Z is smaller than 18000, the concentration of oxidizing agent decreases. On the other hand, if Z is larger than 1080000, the current efficiency of oxidizing agent decreases. Then, the range is specified to $18000 \leqq Z \leqq 1080000$.

[0042] In the present invention, the porous PTFE diaphragm 9 separates the anode compartment 3 from the cathode compartment 4 and let conductivity be generated by ion exchange action or moving of electrolyte between the anode compartment 3 and the cathode compartment 4 through apertures in the diaphragm. The constitution materials are not limited in particular, but in view of durability, it is desirable to use a diaphragm comprising fluororesin type cation exchange membrane or hydrophilically treated porous fluororesin type membrane. In the present invention, if diaphragm is not provided, the oxidizing agent is electrolytically reduced at the cathode and the concentration of oxidizing agent decreases. For this reason, it is desirable to provide the porous PTFE diaphragm 9.

[0043] In the present invention, the constitution materials for the parts which are in contact with sulfuric acid electrolyte, such as the electrolysis cell of sulfuric acid, the piping, a pump and the gas-liquid separation tank are not limited in particular, but desirable are such materials as fluororesin like PTFE and PFA, glass and quartz, having resistivity to sulfuric acid.

[0044] The electrolyte containing sulfate ion in the present invention may include impurities other than sulfate ion. Electrolyte comprising sulfuric acid or sulfates like ammonium sulfate and water is desirable in view of high current efficiency in the production of persulfuric acid. Whereas, it is not desirable to include organic substance because it reacts with oxidizing agent formed by the electrolysis, which will be a cause for decreasing the concentration of the oxidizing agent of the electrolyte. In case that the oxidizing agent is used for the washing material in the production of semiconductor device, it is preferable not to include metal ion because metal adversely affects the device as an impurity.

[0045] In the present invention, it is preferable to control the electrolysis temperature to the range of 0-50 degrees Celsius. The lower the temperature is, the higher the current efficiency of the oxidizing agent becomes. On the other hand, if it is too low, the viscosity of electrolyte increases, gas liberation becomes poor, the bubble fraction increases and the conductivity of electrolyte decreases, leading to the increase of cell voltage. Therefore, it is desirable to maintain the electrolysis temperature within the range of 0-50 degrees Celsius.

[0046] In the present invention, circulation of electrolyte is optional. In view of effective cooling of the electrolyte, circulation is preferable. In case that circulation of electrolyte is performed, the anolyte volume means the sum of the anolyte on the anode side within the circulation apparatus including electrolysis cell, piping, gas-liquid separation tank, and pumps. The present invention include the case of "one-pass", in which electrolyte is passed once through the electrolysis cell without being circulated. In the case of "one-pass", the anolyte volume means the volume of electrolyte on the side of anode present within the electrolytic cell.

[0047] Fig.2-1 shows an example of the sulfuric acid electrolysis method and the sulfuric acid electrolysis apparatus by the present invention, in which sulfuric acid is electrolyzed while anolyte and catholyte are being circulated. Electrolyte containing sulfate ion is supplied to the anode compartment 3 of the electrolysis cell 21 from the anolyte feed line 18 by means of the anolyte feed pump 19 and the flow meter 20, electrolyzed in the anode compartment 3 and circulated through the circulation line 25 to the anode compartment 3 by means of the flow meter 22 and the anolyte circulation/

discharge pump 23. The generated gas is separated by the gas-liquid separator on the anode side 26 and discharged from the generated gas outlet 27. When the electrolysis completes, the produced solution of oxidizing agent is discharged through the oxidizing agent solution discharge line 24 by means of the flow meter 22 and the anolyte circulation/discharge pump 23. On the other hand, on the side of cathode, the electrolyte containing sulfate ion is supplied to the cathode compartment 4 of the electrolysis cell 21 through the catholyte feed line 28 by means of the catholyte feed pump 29 and the flow meter 30, electrolyzed in the cathode compartment 4 and circulated to the cathode compartment 4 through the catholyte circulation line 34 by means of the flow meter 31 and the catholyte circulation/discharge pump 32. The generated gas is separated by the gas-liquid separator on the cathode side 35 and discharged from the generated gas outlet 36. When the electrolysis completes, the catholyte is discharged through the catholyte outlet line 33 by means of the flow meter 31 and the catholyte circulation/discharge pump 32. The electrolysis cell 21 is cooled by the cooling jacket 15 and the cooling water circulation line 37. The temperature of electrolyte is measured at the anolyte outlet 1 illustrated in Fig.1.

[0048] Fig. 2-2 shows another example of the sulfuric acid electrolysis method and the sulfuric acid electrolysis apparatus by the present invention, in which only catholyte is circulated, with no circulation of anolyte to produce the solution of oxidizing agent in the one-pass process. The explanation of the process of Fig. 2-2 is omitted because the process of Fig. 2-2 is exactly the same as Fig. 2-1, applying the same numerals, except that in Fig.2-2, the anolyte is not circulated and the solution of oxidizing agent is produced in one-pass process.

[Examples]

[0049] The following is explanation of the present invention, in detail, in reference to examples and comparative examples. Provided, however, the present invention shall not be limited to these examples.
Measurement of the Raman spectrometry characteristics of the electrode prepared by the present invention, measurement of the thickness of the electrically conductive diamond electrode layer, measurement of the boron concentration, the durability test of the electrode, measurement of the potential window, preparation of electrolyte containing sulfate ion used for the electrolysis, and measurement of the concentration of oxidizing agent of the produced solution of oxidizing agent are conducted by the methods described below.

<Measurement of the Raman Spectrometry Characteristics>

[0050] The Raman spectrometry of the electrode surface was conducted to confirm that the electrically conductive diamond had been prepared and to measure the A/B intensity ratio.

- Measuring instrument : Raman spectrometry photometer manufactured by Thermo Fisher Scientific Inc.
- Model : AIMEGA XR
- Laser beam : 532 nm
- Exposure time : 2.00 sec.
- Exposure times : 20
- Background exposure times : 20
- Grating : 672 lines/mm
- Width of measurement : 700-2000 cm^{-1}
- Spectroscope aperture : 25μm slit
- Low resolution measured in the macroscopic test room
- Measuring spots : The longest length of the electrode, which is the full span from the both edges of the electrode is divided into 3 portions equally and measurement was made at the center of each portion and the mean value was examined.
- Spectra correction : From the intensity of the full scope, the intensity at 2000cm^{-1} was deducted.
- Diamond component : Peak intensity in the range of wave number 1300$\pm$50cm^{-1} or Intensity at wave number 1300cm^{-1} when peak Is not confirmed
- Non-diamond component : Peak intensity in the range of wave number 1500$\pm$50cm^{-1} or Intensity at wave number 1500cm^{-1} when peak Is not confirmed.

It was judged that the electrically conductive diamond electrode had been prepared when Raman active was shown in the range of wave number 1300$\pm$50cm^{-1}, that is, the peak or the broad wave-shape was shown in the range of wave number 1300$\pm$50cm^{-1}.

<Measurement of Electrically conductive Diamond Layer Thickness>

[0051] The longest length of the electrode, which is the full span from the both edges of the electrically conductive diamond electrode was divided and cut equally into 5 portions of the substrate. At least one single section of all cut samples obtained was observed and photographed at an accelerating voltage of 10 kV and 8000 magnifications using the scanning electron microscope (Brand Name : JSM6490 manufactured by JEOL Ltd.), and the layer thickness was obtained from the mean.

<Measurement of Boron Concentration>

[0052] The surface of the prepared electrode was measured using the secondary ion mass spectrometer (Brand name: PHI ADEPT1010 manufactured by Ulvac-Phi Inc.) with O_2^+ as primary ion, primary ion energy of 3keV, detection domain 100 μm φ, and secondary ion polarity positive. The concentration conversion was made in such a manner that the reference density standard of B in SiC composition was also measured and obtained relative sensitivity coefficient was substitutively applied to the sample.

<Durability Test for Electrically conductive Diamond Electrodes>

[0053] Using the electrodes of anode and cathode prepared, oxidizing agent solution was formed on the conditions given below by the sulfuric acid electrolysis apparatus as shown in Fig. 2-1, in which the electrolysis cell 21 with a diaphragm as shown in Fig. 1 was installed.

Current density : 100 A/dm^2
Electrolysis time : 12 h
Anolyte volume : 200 ml
Electrolyte temperature : 35 degrees Celsius
Cooling water temperature : 15 degrees Celsius
Anolyte flow rate : 1 l/min
Catholyte flow rate : 1 l/min
Anode electrolyte : 4.2 mol/l sulfuric acid (prepared by diluting sulfuric acid for industrial use manufactured by Kanto Chemical Co., Inc. with pure water for electronics industries)
Cathode electrolyte : 4.2 mol/l sulfuric acid (prepared by diluting sulfuric acid for industrial use manufactured by Kanto Chemical Co., Inc. with pure water for electronics industries)
Diaphragm : POREFLON™ manufactured by Sumitomo Electric Fine Polymer, Inc.

After the completion of electrolysis, the electrodes were visually observed for exfoliation of electrically conductive diamond layer and the degree of durability evaluated was classified
as:

Durability ○	No exfoliation observed
Durability Δ	Exfoliation slightly observed
Durability x	Exfoliation more than a half of the area observed

<Measurement of Potential Window>

[0054] For the measurement of potential window, the oxidation- reduction potential was measured by means of cyclic voltammogram. More in detail, electric potential was measured applying 4.2 mol/l of sulfuric acid as electrolyte, an electrode with electrically conductive diamond layer formed on the substrate as working electrode, a platinum wire as counter electrode, mercurous sulphate reference electrode, at the time when electric current of ±50 mA/dm^2 flew at 50 mV/s of potential sweeping and the potential window was determined from the value of oxidation-reduction potential.

<Sulfuric Acid Mass required for Preparing Electrolyte>

[0055] The mass of 98% sulfuric acid required for preparing 1 liter of electrolyte was calculated from Equation (6) and the obtained volume of 98% sulfuric acid (manufactured by Kanto Chemical Co., Inc.) was collected in 1 liter measuring flask, to which ultrapure water was added to prepare 1 liter of electrolyte, in total.

$$C(g) = \text{Concentration (mol/l) of electrolyte containing sulfate ion to be prepared} \times \text{molar mass of sulfuric acid (98 g/mol)} \times 100 / 98 \quad \cdot\cdot\cdot (6)$$

C(g) : Mass of 98% sulfuric acid required to prepare 1 liter of electrolyte

<Acid concentration>

[0056] Acid concentration was calculated from the Equation (7) below based on the concentration (mol/l) of electrolyte containing sulfate ion applied in Equation (6)

$$\text{Acid concentration} = \text{Concentration of electrolyte containing sulfate ion to be prepared} \times 2 \quad \cdot\cdot\cdot (7)$$

<Measurement of Oxidizing Agent >

[0057] In a 100 ml Erlenmeyer flask, 0.4 ml of produced oxidizing agent solution was collected, to which hyperpure water was added to prepare 3 ml of the sample solution. A 200 g/l solution was prepared with potassium iodide (manufactured by Wako Pure Chemical Industries, Ltd.) and hyperpure water. The solution was added by 5 ml to the sample solution to color with free iodine and the Erlenmeyer flask of sample solution was filled with nitrogen, hermetically sealed up with a silicone rubber, and left for 30 minutes. Then, 0.02 mol/l sodium thiosulfate solution (manufactured by Wako Pure Chemical Industries, Ltd. Co., Ltd.) was dropped until the sample solution became colorless. Measurement was conducted three times for each sample and using the mean, the concentration of the oxidizing agent was calculated by Equation (8)

$$\text{Total conc. of Oxidizing agent (mol/l)} = [\text{Titer (ml)} \times Na_2S_2O_3 \text{ conc. (0.02 mol/l)}] / [\text{Sample volume (ml)} \times \text{Stoichiometric coefficient of } Na_2S_2O_3 \text{ (2)}] \quad \cdot\cdot\cdot (8)$$

<Current Efficiency of Oxidizing Agent >

[0058] Current efficiency was calculated from Equation (9) using the value obtained from the measurement of the concentration of oxidizing agent of the produced oxidizing agent solution.

$$\text{Current Efficiency (\%)} = [\text{Increased amount of oxidizing agent (mol/l)} \times \text{anolyte volume (l)} \times 100] / [\text{Electric current value (A)} \times \text{Electrolysis time (s)} / \text{Reaction electron number of peroxodisulfuric acid (2)} / 96485] \quad \cdot\cdot\cdot (9)$$

<Formation of Diamond Layer by Hot Filament CVD Method>

[0059] The electrically conductive diamond electrode by the present invention was manufactured in the following manner.

[0060] A electrically conductive substrate, which was single-crystal Si was installed in the device, after the surface of the substrate was polished, washed and treated for diamond particles seeding. While hydrogen, methane and Ar+ trimethyl borate were being supplied as introduction gas at 5 l/min. and the pressure inside the device was maintained at 60 Torr, electric power was applied to the filament and the temperature was raised to 2300 degrees Celsius. At this time, the temperature of the substrate was 800 degrees Celsius.

[0061] Trimethyl borate was introduced into the device by bubbling Ar into the container filled with liquid trimethyl borate. The quality of layer was changed by changing the flow rates of methane and trimethyl borate. The thickness of the layer was changed by changing the time for forming the layer.

<Example 1>

[0062] The solution of oxidizing agent was produced by electrolyzing sulfuric acid on the conditions to be described, using the sulfuric acid electrolysis apparatus with diaphragm installed as shown in Fig. 2-1 incorporating the electrolysis cell 21 applying the electrically conductive diamond electrode with an electrolysis area of 1.000 dm^2 for both anode and cathode as shown in Fig.1 while anolyte and catholyte were being circulated. Characteristics of the prepared electrode are shown in Table 1.

[0063] Production of oxidizing agent was performed on the conditions of Table 1 and those of the following, using the electrolytic cell with diaphragm applying prepared electrodes both for the anode and the cathode. A 98 % sulfuric acid (manufactured by Kanto Chemical Co., Inc.) was taken by 403 g in a 1 liter measuring flask, to which hyperpure water was added to dilute to 1 liter in total to prepare electrolyte containing 4.2 mol/l of sulfate ion. From it, 300 ml was used as anolyte and 300 ml was used as catholyte. Based on Equation (7), the acid concentration was calculated to be 18.4 mol/l.

Cell current : 100 A
Current density : 100 A/dm^2
Electrolysis time : 20 min.
Anolyte volume : 300 ml
Electrolyte temperature : 28 degrees Celsius
Cooling water temperature : 15 degrees Celsius
Anolyte flow rate : 1 l/min
Catholyte flow rate : 1 l//min
Anode electrolyte : 4.2 mol/l sulfuric acid
Cathode electrolyte : 4.2 mol/l sulfuric acid
Diaphragm : POREFLON™ (manufactured by Sumitomo Electric Fine Polymer, Inc.)

[0064] The results of the obtained oxidizing agent solution are given in Table 6 and as below.
Using the produced oxidizing agent solution, titration was performed according to the measuring method of the concentration for the oxidizing agent. The solution became colorless when 0.02 mol/l sodium thiosulfate solution was dropped by 44.00 ml. Further, the measurement repeated twice in the same manner and the results were, respectively 44.00 ml and 44.00 ml. Applying the mean value of 44.00 ml, the concentration of oxidizing agent was calculated from Equation (8), and 1.10 mol/l was obtained. Current efficiency was calculated by Equation (9), applying the concentration of oxidizing agent and 53% was obtained.

<Examples 2~10>

[0065] In Examples 2~10, the oxidizing agent solution was obtained by the same method as described in Example 1, except that the electrode applied as anode was changed as in Tables 1 and 2 regarding the thickness of electrically conductive diamond layer, the potential window, the A/B, and the boron concentration by changing the methane flow rate, the trimethyl borate flow rate and the layer forming time was applied. The results of the obtained oxidizing agent solution are given in Tables 6 and 7.

<Examples 11~14>

[0066] The oxidizing agent solution was obtained by the same method as described in Example 1, except that the sulfate ion concentration and the acid concentration in the electrolyte were changed as described in Tables 2~3. The results of the obtained oxidizing agent solution are given in Tables 7 and 8.

<Examples 15~16>

[0067] The oxidizing agent solution was obtained by the same method as described in Example 1, except that the anolyte volume, the current value/anolyte volume, and the electrolysis time were changed as in Table 3, and that the anolyte circulation was not performed, that is, one pass of anolyte applied, using the sulfuric acid electrolysis apparatus as shown in Fig. 2-2, which incorporated the electrolysis cell 21 with diaphragm applying the electrically conductive diamond electrode with 1.000 dm^2 of the electrolysis area as anode and cathode as shown in Fig.1. The results of the obtained oxidizing agent solution are given in Table 8.

<Examples 17~24>

[0068] The oxidizing agent solution was obtained by the same method as described in Example 1, except that the anolyte volume, the current value/anolyte volume, the electrolysis time and the electric quantity per unit volume were changed as described in Tables 3 and 4. The results of the obtained oxidizing agent solution are given in Tables 8 and 9.

<Example 25>

[0069] The oxidizing agent solution was obtained by the same method as described in Example 1, except that niobium was applied as the substrate material. The results of the obtained oxidizing agent solution are given in Table 9.

[0070]

1) As the results of Examples 1~4, it is known that the narrower the potential window is and the smaller the A/B ratio is, the current efficiency becomes high and the cell voltage becomes low, where A = Intensity at wave number 1300cm^{-1} in the Raman spectroscopic analysis, and B = Intensity at wave number 1500cm^{-1} in the Raman spectroscopic analysis. On the other hand, in Example 2, exfoliation of the electrically conductive diamond layer was confirmed very slightly in the visual observation of the electrode after durability test.
2) As the results of Examples 5 and 6, it is known, compared with the result of Example 1, that the thinner the electrically conductive diamond layer is, the higher the current efficiency of oxidizing agent and the lower the cell voltage become. As the reason, it is considered that the thinner the electrically conductive diamond layer is, the narrower the potential window and the smaller the A/B ratio become, where A = Intensity at wave number 1300cm^{-1} in the Raman spectroscopic analysis, and B = Intensity at wave number 1500cm^{-1} in the Raman spectroscopic analysis. Whereas, Example 6 gave a lower current efficiency of oxidizing agent and a higher cell voltage, compared with the result of Example 1.
3) As the results of Examples 7~10, it is known, compared with the result of Example 1, that the higher the boron concentration is, the higher the current efficiency of oxidizing agent becomes, and concomitantly, the concentration of oxidizing agent become high and the cell voltage becomes low. As the reason, it is considered that the higher the boron concentration is, the narrower the potential window and the smaller the A/B ratio become, where A = Intensity at wave number 1300cm^{-1} in the Raman spectroscopic analysis, and B = Intensity at wave number 1500cm^{-1} in the Raman spectroscopic analysis. On the other hand, in Example10, exfoliation of the electrically conductive diamond layer was confirmed very slightly in the visual observation of the electrode after durability test.
4) As the results of Examples 11 and 12, it is known, compared with the result of Example 1, that the lower the sulfate ion concentration is, the lower the current efficiency of oxidizing agent becomes. As the reason, it is considered that the lower the sulfate ion concentration is, the less the reactant becomes. Besides, it is known, compared with the result of Example 1, that the lower the acid concentration is, the higher the cell voltage becomes. As the reason, the low conductivity is considered due to the low acid concentration. As the results of Examples 13 and 14, it is known, compared with the result of Example 1, that the higher the acid concentration is, the lower the current efficiency becomes. As the reason, it is considered that the higher the acid concentration is, the easier the oxidizing agent decomposes. Besides, compared with the result of Example 1, the higher the sulfate ion concentration was, the higher the cell voltage became. As the reason, it is considered that the increased viscosity due to the high sulfate ion concentration contributes to poor gas liberation, increased bubble fraction, decreased conductivity of electrolyte, and increased cell voltage.
5) As the results of Examples 15~18, it is known, compared with the result of Example 1, that the larger the X = current value/anolyte volume (A/l) is, the higher the current efficiency of oxidizing agent becomes, and that concomitantly, the solution with high concentration of oxidizing agent is obtained. On the other hand, the larger the X=current /value/anolyte volume (A/l) was, the higher the cell voltage became. It is considered that the gas filled in the cell caused the increase of cell voltage. In Examples 17 and 18, the cell voltage was good but the current efficiency was low.
6) As the results of Examples 19 and 20, it is known, compared with the result of Example 1, that the lower the current density (A/dm2) is, the lower the current efficiency of oxidizing agent becomes and concomitantly the lower the concentration of oxidizing agent becomes. On the other hand, as the results of Examples 21 and 22, it is known, compared with the result of Example 1, that the higher the current density (A/dm^2) is, the higher the current efficiency of oxidizing agent becomes, but adversely the higher the cell voltage becomes. This is considered due to generated

gas filled in the cell.

7) As the results of Example 23, it is known, compared with the result of Example 1, that the lower the electric quantity per unit volume is, the higher the current efficiency of oxidizing agent becomes, and concomitantly, the concentration of oxidizing agent becomes low. On the other hand, as the results of Example 24, it is known that the higher the electric quantity per unit volume is, the lower the current efficiency of oxidizing agent becomes, and the higher the concentration of oxidizing agent becomes.

8) As the results of Example 25, it is known, compared with the result of Example 1, that when niobium is applied as the substrate material, the current efficiency of oxidizing agent and concomitantly the concentration of oxidizing agent are good but a slight exfoliation of the layer on the electrode surface was confirmed in the visual observation after the durability test of the electrode.

<Comparative Examples 1~4>

[0071] The oxidizing agent solution was obtained by the same method as described in Example 1, except that the electrode applied as anode was changed as in Table 5 regarding the thickness of electrically conductive diamond layer, the potential window, and the A/B by changing the methane flow rate, the trimethyl borate flow rate and the layer forming time. The results of the obtained oxidizing agent solution are given in Table 10.

[0072] In Comparative Example 1, desirable results were obtained in terms of cell voltage and current efficiency of the oxidizing agent, but it was visually observed after the durability test of the electrode that most of the layer of the electrode surface had been exfoliated.

In Comparative Example 2, degradation of the layer was not confirmed from visual observation of the electrode surface after the durability test of the electrode, but the cell voltage during electrolysis was high and the current efficiency from the obtained solution containing oxidizing agent was revealed to be low.

In Comparative Example 3, desirable results were obtained in terms of cell voltage and current efficiency, but it was visually observed after the durability test of the electrode that most of the layer of the electrode surface had been exfoliated.

In Comparative Example 4, degradation of the layer of the electrode was not confirmed from visual observation after the durability test of the electrode, but the cell voltage during electrolysis was high and the current efficiency from the obtained solution containing oxidizing agent was revealed to be low.

In Comparative Example 5, degradation of the electrode was observed during electrolysis, and carbon powder was visually confirmed in the electrolyte and electrolysis was suspended.

[0073]

Table 1 Electrolysis Conditions

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Anode and Cathode	Coating Material	Electrically conductive Diamond					
	Substrate Material	Electrically conductive Silicon					
	Diamond Layer Thickness (μm)	10	10	10	10	1.5	23
	Potential Window (V)	2.63	2.12	3.40	2.80	2.12	3.30
	A/B	4.50	1.80	6.20	6.30	1.58	6.00
	Conc. of Boron (ppm)	3000	3000	3000	3000	3000	3000
Conc. of Sulfate Ion in Electrolyte (mol/l)		4.2	4.2	4.2	4.2	4.2	4.2
Conc. of Acid in Electrolyte (mol/l)		8.4	8.4	8.4	8.4	8.4	8.4
Anolyte Volume (ml)		300	300	300	300	300	300
Electrolysis Area (dm^2)		1.000	1.000	1.000	1.000	1.000	1.000

(continued)

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Current Value (A)		100	100	100	100	100	100
Current Density (A/dm^2)		100	100	100	100	100	100
Current Value/Anolyte Volume (A/l)		333	333	333	333	333	333
Electrolysis Time (min)		20	20	20	20	20	20
Electric Quantity per unit volume (x10^{4}As/l)		40	40	40	40	40	40
Diaphragm		Used					

[0074]

Table 2 Electrolysis Conditions

		Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Anode and Cathode	Coating Material	Electrically conductive Diamond					
	Substrate Material	Electrically conductive Silicon					
	Diamond Layer Thickness (μm)	10	10	10	10	10	10
	Potential Window (V)	3.50	3.20	2.60	2.15	2.63	2.63
	A/B	6.00	5.50	3.20	1.62	4.50	4.50
	Conc. of Boron (ppm)	700	1200	5000	7000	3000	3000
Conc. of Sulfate Ion in Electrolyte (mol/l)		4.2	4.2	4.2	4.2	1.9	2.5
Conc. of Acid in Electrolyte (mol/l)		8.4	8.4	8.4	8.4	3.8	5.0
Anolyte Volume (ml)		300	300	300	300	300	300
Electrolysis Area (dm^2)		1.000	1.000	1.000	1.000	1.000	1.000
Current Value (A)		100	100	100	100	100	100
Current Density (A/dm^2)		100	100	100	100	100	100
Current Value/Anolyte Volume (A/l)		333	333	333	333	333	333
Electrolysis Time (min)		20	20	20	20	20	20
Electric Quantity per unit volume (x10^{4}As/l)		40	40	40	40	40	40
Diaphragm		Used					

[0075]

Table 3 Electrolysis Conditions

		Example 13	Example 14	Example 15	Example 16	Example 17	Example 18
Anode and Cathode	Coating Material	Electrically conductive Diamond					
	Substrate Material	Electrically conductive Silicon					
	Diamond Layer Thickness (μm)	10	10	10	10	10	10
	Potential Window (V)	2.63	2.63	2.63	2.63	2.63	2.63
	A/B	4.50	4.50	4.50	4.50	4.50	4.50
	Conc. of Boron (ppm)	3000	3000	3000	3000	3000	3000
Conc. of Sulfate Ion in Electrolyte (mol/l)		8.5	16.0	4.2	4.2	4.2	4.2
Conc. of Acid in Electrolyte (mol/l)		17.0	32.0	8.4	8.4	8.4	8.4
Anolyte Volume (ml)		300	300	11	20	1000	1200
Electrolysis Area (dm^2)		1.000	1.000	1.000	1.000	1.000	1.000
Current Value (A)		100	100	100	100	100	100
Current Density (A/dm^2)		100	100	100	100	100	100
Current Value/Anolyte Volume (A/l)		333	333	9091	5000	100	83
Electrolysis Time (min)		20	20	0.7	1.3	66.7	80.0
Electric Quantity per unit volume ($x10^4 As/l$)		40	40	40	40	40	40
Diaphragm		Used					

[0076]

Table 4 Electrolysis Conditions

		Example 19	Example 20	Example 21	Example 22	Example 23	Example 24	Example 25
Anode and Cathode	Coating Material	Electrically conductive Diamond						
	Substrate Material	Electrically conductive Silicon						Niobium
	Diamond Layer Thickness (μm)	10	10	10	10	10	10	10
	Potential Window (V)	2.63	2.63	2.63	2.63	2.63	2.63	2.63
	A/B	4.50	4.50	4.50	4.50	4.50	4.50	4.50
	Conc. of Boron (ppm)	3000	3000	3000	3000	3000	3000	3000
Conc. of Sulfate Ion in Electrolyte (mol/l)		4.2	4.2	4.2	4.2	4.2	4.2	4.2
Conc. of Acid in Electrolyte (mol/l)		8.4	8.4	8.4	8.4	8.4	8.4	8.4
Anolyte Volume (ml)		300	300	300	300	300	300	300
Electrolysis Area (dm^2)		1.000	1.000	1.000	1.000	1.000	1.000	1.000
Current Value (A)		20	50	200	280	100	100	100
Current Density (A/dm^2)		20	50	200	280	100	100	100
Current Value/Anolyte Volume (A/l)		67	167	667	933	333	333	333
Electrolysis Time (min)		100	40	10	7.1	1.0	50	20
Electric Quantity per unit volume (x10^{4}As/l)		40	40	40	40	2	100	40
Diaphragm		Used						

[0077]

Table 5 Electrolysis Conditions

		Compar. Example 1	Compar. Example 2	Compar. Example 3	Compar. Example 4	Compar. Example 5
Anode and Cathode	Coating Material	Electrically conductive Diamond				Carbon
	Substrate Material	Electrically conductive Silicon				-
	Diamond Layer Thickness (μm)	10	10	0.8	26	-
	Potential Window (V)	1.97	3.90	1.99	3.60	1.90
	A/B	2.00	7.20	1.49	6.30	-
	Conc. of Boron (ppm)	3000	3000	3000	3000	-
Conc. of Sulfate Ion in Electrolyte (mol/l)		4.2	4.2	4.2	4.2	4.2
Conc. of Acid in Electrolyte (mol/l)		8.4	8.4	8.4	8.4	8.4
Anolyte Volume (ml)		300	300	300	300	300
Electrolysis Area (dm^2)		1.000	1.000	1.000	1.000	1.000
Current Value (A)		100	100	100	100	100
Current Density (A/dm^2)		100	100	100	100	100
Current Value/Anolyte Volume (A/l)		333	333	333	333	333
Electrolysis Time (min)		20	20	20	20	20
Electric Quantity per unit volume ($x10^4$As/l)		40	40	40	40	40
Diaphragm		Used				

[0078]

Table 6 Test Results

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Current Efficiency (%)	53	55	49	50	56	40
Conc. of Oxidizing Agent (mol/l)	1.10	1.14	1.02	1.04	1.04	1.16
Cell Voltage (V)	10.200	9.800	10.800	10.790	9.620	11.200
Durability	○	Δ	○	○	Δ	○

[0079]

Table 7 Test Results

	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Current Efficiency (%)	38	41	54	55	30	42

(continued)

	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Conc. of Oxidizing Agent (mol/l)	0.79	0.85	1.12	1.14	0.62	0.87
Cell Voltage (V)	11.000	10.900	9.800	9.500	10.400	10.300
Durability	○	○	○	Δ	○	○

[0080]

Table 8 Test Results

	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18
Current Efficiency (%)	51	35	55	54	50	49
Conc. of Oxidizing Agent (mol/l)	1.06	0.73	1.14	1.12	1.04	1.02
Cell Voltage (V)	11.300	12.900	12.100	11.800	10.200	10.200
Durability	○	○	○	○	○	○

[0081]

Table 9 Test Results

	Example 19	Example 20	Example 21	Example 22	Example 23	Example 24	Example 25
Current Efficiency (%)	46	49	54	55	97	34	53
Conc. of Oxidizing Agent (mol/l)	0.95	1.02	1.12	1.14	0.05	1.76	1.10
Cell Voltage (V)	6.400	7.902	13.200	15.000	10.200	10.200	10.300
Durability	○	○	○	○	○	○	Δ

[0082]

Table 10 Test Results

	Compar. Example 1	Compar. Example 2	Compar. Example 3	Compar. Example 4	Compar. Example 5
Current Efficiency (%)	54	33	54	32	Electrolysis suspended due to severe degradation
Conc. of Oxidizing Agent (mol/l)	1.12	0.68	1.12	0.66	
Cell Voltage (V)	10.000	12.800	9.800	12.500	
Durability	×	○	×	○	

[Industrial Applicability]

[0083] The diamond electrode by the present invention is effective to form oxidizing agent stably, in particular, when it is used as anode for the sulfuric acid electrolysis and the effect is further enhanced when it is used, at the same time, as cathode for the sulfuric acid electrolysis. Furthermore, the electrically conductive diamond electrode by the present invention can be used as anode and cathode for other electrolyses.

[Reference Signs List]

[0084]

1 : Anolyte outlet
2 : Catholyte outlet
3 : Anode compartment
4 : Cathode compartment
5 : Anode power supply terminal
6 : Cathode power supply terminal
7 : Anolyte inlet
8 : Catholyte inlet
9 : Porous PTFE diaphragm
10 : Electrically conductive diamond anode
11 : Electrically conductive substrate
12 : Electrically conductive diamond cathode
13 : Electrically conductive substrate
14 : Sealing material
15 : Cooling jacket
16 : Cooling water outlet
17 : Cooling water inlet
18 : Anolyte feed line
19 : Anolyte feed pump
20 : Flow meter
21 : Electrolysis cell
22 : Flow meter
23 : Anolyte circulation/discharge pump
24 : Oxidizing agent solution discharge line
25 : Anolyte circulation line
26 : Gas-liquid separator on the anode side
27 : Generated gas outlet
28 : Catholyte feed line
29 : Catholyte feed pump
30 : Flow meter
31 : Flow meter
32 : Catholyte circulation/discharge pump
33 : Catholyte outlet line
34 : Catholyte circulation line
35 : Gas-liquid separator on the cathode side
36 : Generated gas outlet
37 : Cooling water circulation line

Claims

1. Electrically conductive diamond electrode comprising an electrically conductive substrate and an electrically conductive diamond layer coated on the surface of the electrically conductive substrate **characterized in that**:

1) the thickness of the electrically conductive diamond layer is in the range of 1~25μm,
2) the potential window fulfills Equation (1) and
3) the ratio (A/B) of the diamond component A and the non-diamond component B by the Raman spectroscopic

analysis fulfills Equation (2) :

$$2.1\text{V} \leqq \text{potential window} \leqq 3.5\text{V} \quad \cdot\cdot\cdot (1)$$

$$1.5 < A/B \leqq 6.5 \quad \cdot\cdot\cdot (2)$$

, wherein:

A: Intensity at the wave number 1300cm^{-1} by the Raman spectroscopic analysis
B: Intensity at the wave number 1500cm^{-1} by the Raman spectroscopic

2. The electrically conductive diamond electrode as defined in Claim 1, **characterized in that** the electrically conductive diamond layer contains boron in the range of 1000~6000 ppm.

3. The electrically conductive diamond electrode as defined in Claim 1 or Claim 2, **characterized in that** the electrically conductive substrate is silicon substrate.

4. A sulfuric acid electrolysis method, wherein an anode compartment is separated from a cathode compartment by a diaphragm, an electrically conductive diamond anode is installed in the anode compartment, a cathode is installed in the cathode compartment, electrolyte containing sulfate ion is supplied to the anode compartment and the cathode compartment, respectively, from the outside, oxidizing agent is formed in the anode electrolyte in the anode compartment by electrolysis, **characterized in that** the electrically conductive diamond electrode as defined in any one of Claim 1~3 is applied and the concentration of sulfate ion in the electrolyte is in the range of 2~14 mol/l.

5. The sulfuric acid electrolysis method as defined in Claim 4, **characterized in that** the acid concentration of the electrolyte containing sulfate ion is in the range of 4~28 mol/l.

6. A sulfuric acid electrolysis apparatus, wherein an anode compartment is separated from a cathode compartment by a diaphragm, an electrically conductive diamond anode is installed in the anode compartment, a cathode is installed in the cathode compartment, electrolyte containing sulfate ion is supplied to the anode compartment and the cathode compartment, respectively, from the outside, oxidizing agent is formed in the anode electrolyte in the anode compartment by electrolysis, **characterized in that** the electrically conductive diamond electrode as defined in any one of Claim 1~3 is applied and a fluororesin type cation exchange membrane or a hydrophilically treated porous fluororesin membrane is applied as diaphragm.

7. The sulfuric acid electrolysis method, wherein an anode compartment is separated from a cathode compartment by a diaphragm, an electrically conductive diamond anode is installed in the anode compartment, a cathode is installed in the cathode compartment, electrolyte containing sulfate ion is supplied to the anode compartment and the cathode compartment, respectively, from the outside, oxidizing agent is formed in the anode electrolyte in the anode compartment by electrolysis, **characterized in that** the electrically conductive diamond electrode as defined in any one of Claim 1~3 is applied and the electrolyte containing sulfate ion is electrolyzed on a condition to satisfy Equation (3) and Equation (4) :

$$100 \leqq X \leqq 10000 \quad \cdot\cdot\cdot (3)$$

$$25 < Y < 250 \quad \cdot\cdot\cdot (4)$$

, wherein:

X=current /anolyte volume (A/l)
Y=current density (A/dm^2)

8. The sulfuric acid electrolysis method as defined in Claim 7 **characterized in that** a solution containing sulfate ion

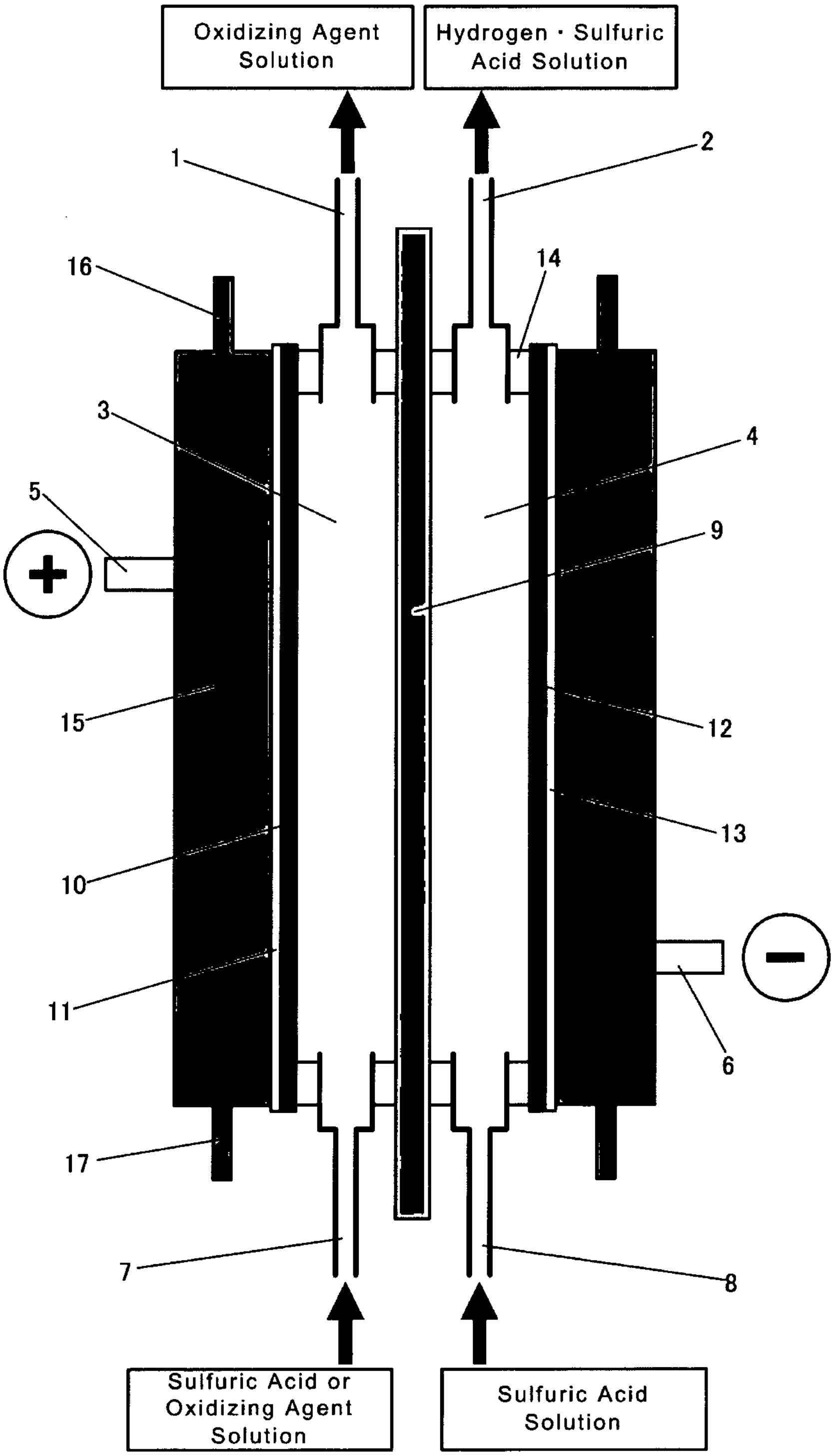
is electrolyzed on a condition to satisfy Equation (5) :

$$18000 \leqq Z \leqq 1080000 \cdots (5)$$

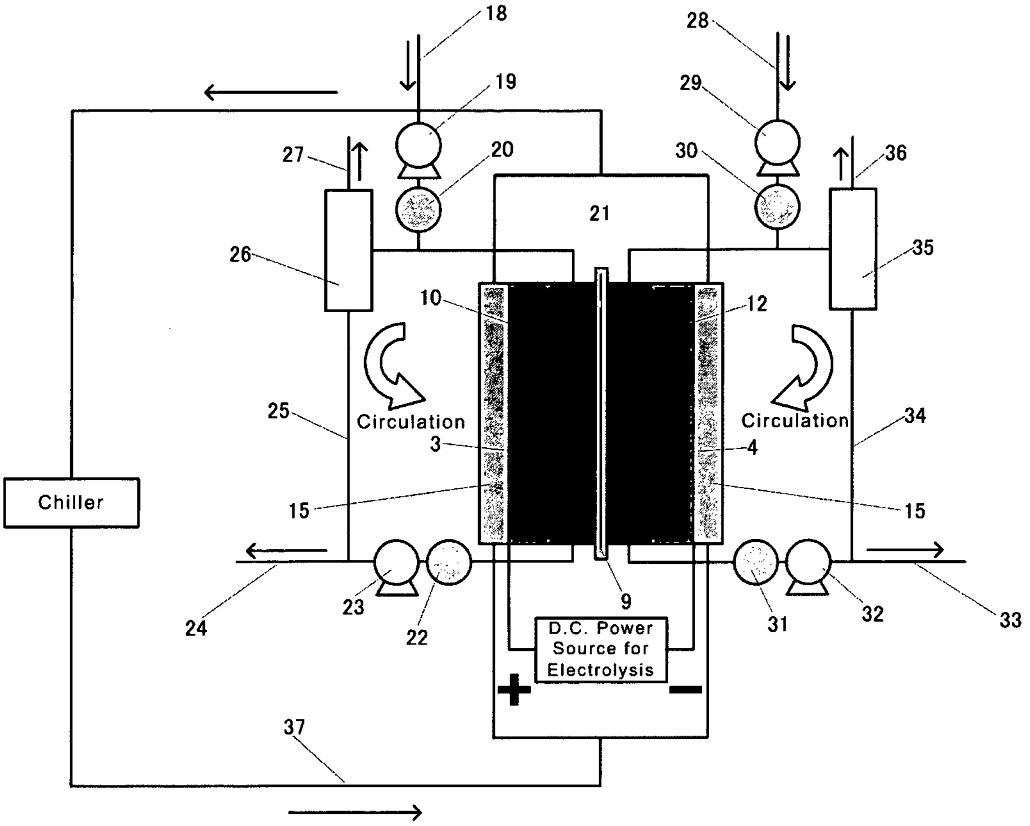
, wherein:

Z= electric charge per unit volume (C/l) = current value × electrolysis time / anolyte volume (A・s/l)

【Fig.1】


Oxidizing Agent Solution
Hydrogen · Sulfuric Acid Solution
1
2
16
14
3
4
5
9
+
15
12
13
10
−
11
6
17
7
8
Sulfuric Acid or Oxidizing Agent Solution
Sulfuric Acid Solution

【Fig. 2－1】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12
Circulation
Circulation
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34
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Chiller
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D.C. Power Source for Electrolysis
+
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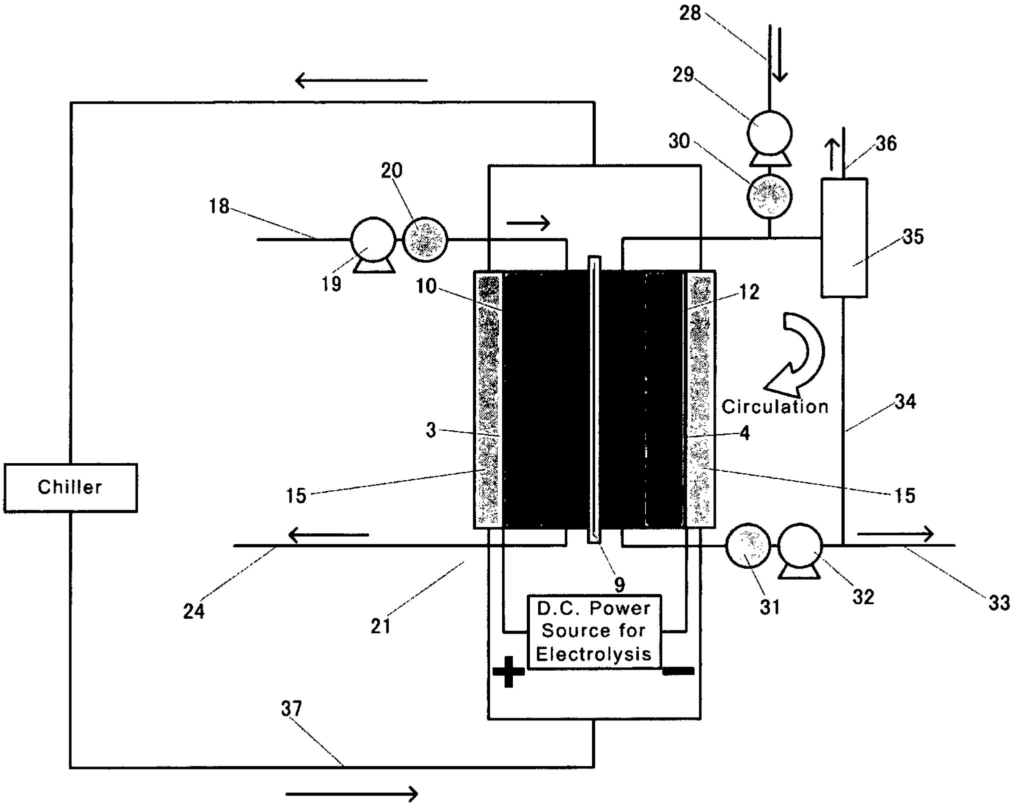
37

【Fig. 2－2】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D.C. Power Source for Electrolysis
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INTERNATIONAL SEARCH REPORT	International application No. PCT/JP2011/076781

A. CLASSIFICATION OF SUBJECT MATTER
C25B11/06(2006.01)i, *C01B31/06*(2006.01)i, *C25B1/28*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25B11/06, C01B31/06, C25B1/28

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2002-4073 A (Degussa AG.), 09 January 2002 (09.01.2002), claims; paragraphs [0001], [0010] to [0032]; fig. 1 & US 2002/0014418 A1 & EP 1148155 A2 & DE 10019683 A & DE 50106427 D & AU 3710001 A & BR 101530 A & PL 347119 A & CZ 20011317 A & SK 5202001 A & CA 2344499 A & IL 142638 D & TW 524893 B & AT 297477 T & ES 2240269 T & AR 27804 A & ZA 200103205 A	1-8

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search 22 December, 2011 (22.12.11)	Date of mailing of the international search report 10 January, 2012 (10.01.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/076781

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 2010-34521 A (Chlorine Engineers Corp. Ltd.), 12 February 2010 (12.02.2010), paragraph [0040] & US 2009/0325390 A1 & KR 10-2010-0003230 A	7,8
Y	JP 2010-31362 A (Chlorine Engineers Corp. Ltd., Toshiba Corp., Shibaura Mechatronics Co., Ltd.), 12 February 2010 (12.02.2010), paragraphs [0013] to [0019] & US 2009/0321272 A1 & KR 10-2010-0003229 A	7,8

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