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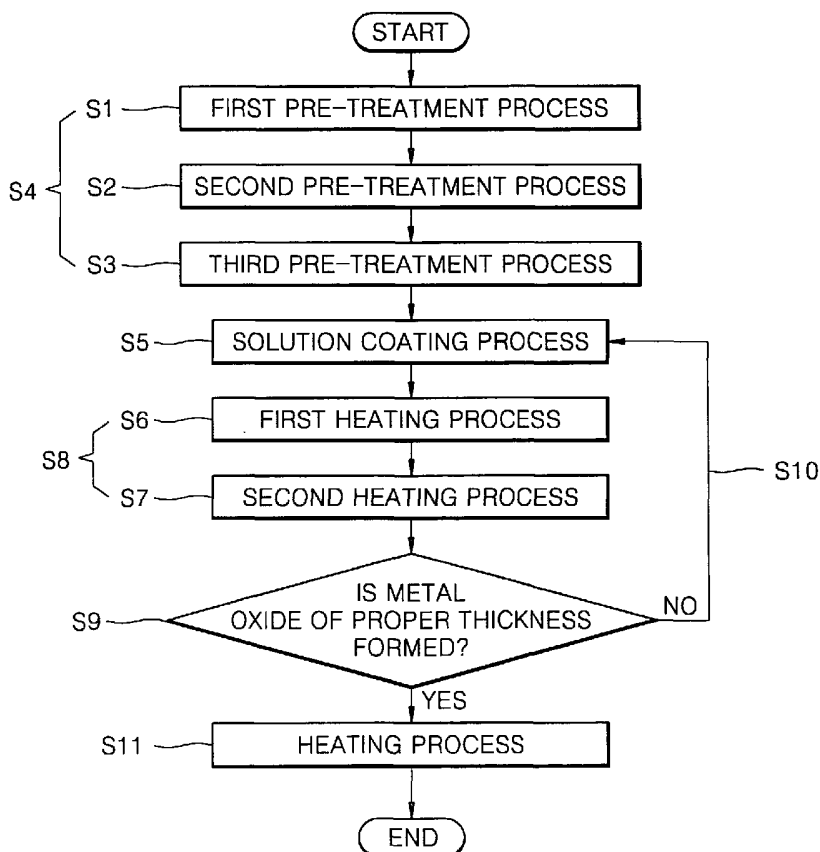
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[Continued on next page]

(54) Title: IONIC WATER ELECTRODE AND METHOD FOR MANUFACTURING THE SAME



(57) Abstract: An ionic water electrode and a method of manufacturing the ionic water electrode are provided. The ionic water electrode is formed by coating a Ti base metal with a metal oxide layer having a composition of $(\text{IrO}_2+\text{SnO}_2)$. Here, the metal oxide layer includes Pt. The method of manufacturing an ionic water electrode includes: (S4) pre-treating the surface of a Ti base metal; (S5) coating the pre-treated surface of the Ti base metal with a source solution having a composition of $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$; (S8) heating the Ti base metal that is coated with the source solution to form a $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ metal oxide on the surface of the Ti base metal; (S10) repeating steps (S5) and (S8) at least two times or more until the $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ metal oxide is formed to a proper thickness; (S11) heating the Ti base metal that underwent step (S10) to increase the stability of the $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ metal oxide formed on the surface of the Ti base metal.



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IONIC WATER ELECTRODE AND METHOD FOR MANUFACTURING THE SAME

Technical Field

5 The present invention relates to an ionic water electrode for generating ionic water and a method for manufacturing the same, and more particularly, to an ionic water electrode and a method for manufacturing the same by which the concentration of available chlorine can be increased.

10

Background Art

 Ionic water refers to acid water and alkaline water, both of which are obtained by passing water between two electrodes and are electrolyzed, and is harmless to men, does not leave a residue, and returns to a natural water state. An electrode (hereinafter referred to as a Pt/Ti or IrO₂/Ti electrode), which is formed by depositing metal, such as Pt, or metal oxide, such as IrO₂, on a Ti base metal, is generally used to generate such ionic water. Here, an electrolyte, such as KCl or NaCl, may be added to the water to generate ionic water, which may result in the generation of chlorine gas.

 Since the ionic water including chlorine gas has a remarkable sterilizing power, it is used for medical use or as a sterilizer in a process of manufacturing food. In addition, the ionic water is used to remove odor of livestock and disinfect and sterilize the livestock. Furthermore, the ionic water is used to prevent disease in the crops or to clean meat, fish, and vegetables.

 However, while chlorine gas is generated from the Pt/Ti or IrO₂/Ti electrode when the Pt/Ti or IrO₂/Ti electrode is positive, Pt or IrO₂ is isolated from the Ti base metal. Due to this isolation, it is not only

difficult to generate chlorine gas and to electrolyze water, but damage to the Pt/Ti or IrO₂/Ti electrode accelerates. As a result, it becomes impossible to create ionic water.

5 Disclosure of the Invention

To solve the above problems, it is an object of the present invention to provide an ionic water electrode and a method for manufacturing the ionic water electrode by which a larger amount of chlorine gas can be generated in a process of creating ionic water.

10 It is another object of the present invention to provide an ionic water electrode and a method for manufacturing the ionic water electrode by which ionic water can be created for a long period of time without isolating the metal oxide from Ti base metal.

Accordingly, to achieve the above objects, there is provided an ionic water electrode where a metal oxide layer having a composition of (IrO₂+SnO₂) is formed on a Ti base metal. Here, the metal oxide layer comprises Pt.

To achieve the above objects, there is provided a method of manufacturing an ionic water electrode. The method includes: (S4) pre-treating the surface of a Ti base metal; (S5) coating the pre-treated surface of the Ti base metal with a source solution having a composition of (IrO₂+SnO₂)Pt; (S8) heating the Ti base metal that is coated with the source solution to form a (IrO₂+SnO₂)Pt metal oxide on the surface of the Ti base metal; (S10) repeating steps (S5) and (S8) at least two times or more until the (IrO₂+SnO₂)Pt metal oxide is formed to a proper thickness; (S11) heating the Ti base metal that underwent step (S10) to increase the stability of the (IrO₂+SnO₂)Pt metal oxide formed on the surface of the Ti base metal.

In the present invention, step (S4) includes: (S1) dipping the Ti base metal into a hydrofluoric acid solution for a predetermined period of

time; (S2) dipping the Ti base metal that underwent step (S1) into a sulfuric acid solution for a predetermined period of time; (S3) dipping the Ti base metal that underwent step (S2) into an oxalic acid solution at a predetermined temperature for a predetermined period of time.

5 In the present invention, the source solution having a composition of $(\text{IrO}_2 + \text{SnO}_2)\text{Pt}$ is manufactured by dissolving $\text{H}_2\text{IrCl}_6\text{XH}_2\text{O}$, SnCl_4 , and $\text{H}_2\text{PtCl}_6\text{H}_2\text{O}$ in a hydrochloric acid solution.

In the present invention, step (S8) includes: (S6) heating the Ti base metal that is coated with the source solution at a temperature of 90
10 °C – 130 °C for 5 – 15 minutes; and (S7) heating the Ti base metal that underwent step (S6) at a temperature of 300 °C – 700°C for 3 – 7 minutes.

In the present invention, in step (S11), the Ti base metal that underwent step (S10) is heated at a temperature of 300 °C – 700°C for
15 40 – 80 minutes.

Brief Description of the Drawings

FIG. 1 is a perspective view of an ionic water electrode according to the present invention;

20 FIG. 2 is a flowchart of a process of manufacturing the ionic water electrode shown in FIG. 1; and

FIG. 3 is a view of a process of manufacturing a source solution which coats a Ti base metal when manufacturing the ionic water electrode shown in FIG. 1.

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Best mode for carrying out the Invention

Hereinafter, a preferred embodiment of an ionic water electrode according to the present invention will be described with reference to the attached drawings.

30 FIG. 1 is a perspective view of an ionic water electrode according

to the present invention. As shown in FIG. 1, the ionic water electrode is formed by coating a Ti base metal 1 with a metal oxide layer having a composition of $(\text{IrO}_2+\text{SnO}_2)$. Here, the metal oxide layer further includes Pt to be made into a metal oxide layer 2 having a composition of $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$.

Next, a method of manufacturing the above-described ionic water electrode will be described.

FIG. 2 is a flowchart of a process of manufacturing the ionic water electrode shown in FIG. 1. FIG. 3 is a view of a process of manufacturing a source solution which coats the Ti base metal 1 when manufacturing the ionic water electrode shown in FIG. 1. As shown in FIGS. 2 and 3, in step S4, the Ti base metal is pre-treated. In step S4, the pre-treated Ti base metal is coated with a source solution having the composition of $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$. In step S8, the Ti base metal is heated to form a $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ metal oxide on the surface of the Ti base metal. In step S9, steps S5 and S8 are repeated at least two times or more until the $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ metal oxide has a proper thickness. In step S10, the Ti base metal is heated to increase the stability of the $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ metal oxide formed thereon. The method of manufacturing the ionic water electrode is achieved by sequentially performing the above-described steps.

The Ti base metal reacts with oxygen in the air in a natural state to form TiO_2 on the surface thereof. Since TiO_2 is an obstacle to the efficient formation of the metal oxide having conductivity, step S4 is required to remove TiO_2 from the surface of the Ti base metal.

Step S4 is composed of first through third pre-treatment processes step S1 through step S3. In step S1, the Ti base metal 1 is dipped into a hydrofluoric acid (HF) solution for a predetermined period of time. In step S2, the Ti base metal 1 is dipped into a sulfuric acid (H_2SO_4) solution for a predetermined period of time. In step S3, the Ti

base metal is dipped into an oxalic acid $((\text{COOH})_2\text{H}_2\text{O})$ solution at a predetermined temperature for a predetermined period of time.

The HF solution used in step S1 has the concentration of 1% – 5%, and the time required for performing step S1 is 1 to 5 minutes. In this embodiment, a HF solution having the concentration of 3% was used and the time required for performing step S1 was 3 minutes.

The H_2SO_4 solution used in step S2 has the concentration of 40% – 80% and the time required for performing step S2 is 10 to 30 minutes. In this embodiment, the concentration of the H_2SO_4 solution was 60% and the time required for performing step S2 was 20 minutes.

The $((\text{COOH})_2\text{H}_2\text{O})$ solution used in step S3 has the concentration of 5 – 15%, the time required for performing step S3 is 3 to 10 minutes, and the temperature of $((\text{COOH})_2\text{H}_2\text{O})$ solution is within a range of 50 – 100 °C. In this embodiment, the concentration of the $((\text{COOH})_2\text{H}_2\text{O})$ solution was 10%, the time required for performing step S3 was 5 minutes, and the temperature of the $((\text{COOH})_2\text{H}_2\text{O})$ solution was 80 °C.

In step S5, the Ti base metal, which underwent step S4, is coated with a source solution to form a metal oxide on the surface of the Ti base metal. The source solution used in step S5 has a composition of $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ and coats the Ti base metal by a known brushing method.

However, this is only an embodiment, and the Ti base metal may be dipped into a $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ solution or may be sprayed with the $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ solution. The $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ solution is made by dissolving $\text{H}_2\text{IrCl}_6\text{H}_2\text{O}$, SnCl_4 , and $\text{H}_2\text{PtCl}_6\text{H}_2\text{O}$ in a hydrochloric acid (HCl) solution. In this embodiment, the concentration of the HCl solution is 15%, $\text{H}_2\text{IrCl}_6\text{H}_2\text{O}$ is 63.6 mM, SnCl_4 is 87.8 mM, and $\text{H}_2\text{PtCl}_6\text{H}_2\text{O}$ is 63 mM.

In step S8, the $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ solution, which coats the Ti base metal, is initially adhered to the surface of the Ti base metal, and step

S8 includes steps S6 and S7. In step S6, the Ti base metal is heated at a temperature of 90 °C – 130 °C for 5 – 15 minutes, and in step S7, the Ti base metal, which underwent step S6, is heated at a temperature of 300 °C – 700 °C for 3 – 7 minutes. In step S6, the (IrO₂+SnO₂)Pt solution, which coats the Ti base metal, is dried, and in step S7, the (IrO₂+SnO₂)Pt solution is formed to a metal oxide layer in a gel-film form on the surface of the Ti base metal. In this embodiment, the temperature in step S6 is 110 °C and the time required for performing step S6 is about 10 minutes. The temperature in step S7 is 500 °C and the time required for performing step S7 is about 5 minutes.

In step S10, steps S5 is repeated after initially performing step S8, and then steps S5 and S8 are alternatively repeated at least two times or more. In step S10, it is determined whether the thickness of the metal oxide formed in step S8 is proper, and then if it is determined that the thickness of the metal oxide is improper, steps S5 and S8 are performed again. If it is that the thickness of the metal oxide is proper, step 11 is performed. Step S10 is required to form a (IrO₂+SnO₂)Pt metal oxide layer to a sufficient thickness on the Ti base metal by performing steps S5 and S8 one time. In this embodiment, steps S5 and S8 are repeated ten times so as to form a (IrO₂+SnO₂)Pt metal oxide layer having a sufficient durability on the Ti base metal. If steps S5 and S8 are repeated less than ten times, a (IrO₂+SnO₂)Pt metal oxide layer having a sufficient uniformity and durability cannot be obtained. If steps S5 and S8 are repeated more than ten times, a (IrO₂+SnO₂)Pt metal oxide layer having a thickness greater than required is formed, thereby decreasing the productivity.

In step S11, the (IrO₂+SnO₂)Pt metal oxide layer, which is formed on the Ti base metal in step S10, is completely heated at a temperature of 300 °C – 700 °C for 40 – 80 minutes to be stabilized. In this embodiment, the temperature in step S11 was 500 °C, and the time

required for performing step S11 was 60 minutes.

According to the ionic water electrode having the above-described structure, it can be seen in table below that the concentration of available chlorine being created is much higher than conventional electrodes Pt/Ti and IrO₂/Ti.

Electrode	Concentration of available chlorine (ppm)
Pt/Ti	21.0
IrO ₂ /Ti	43.0
(IrO ₂ +SnO ₂)/Ti	62.0
(IrO ₂ +SnO ₂)Pt/Ti	63.4

While this invention has been particularly shown and described with reference to a preferred embodiment thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention as defined by the appended claims.

Industrial Applicability

As described above, in an ionic water electrode and a method for manufacturing the ionic water electrode according to the present invention, a larger amount of chlorine gas can be created in a process of creating ionic water. Also, the ionic water can be created for a long period of time without isolating a metal oxide from a Ti base metal.

What is claimed is:

1. An ionic water electrode where a metal oxide layer having a composition of $(\text{IrO}_2+\text{SnO}_2)$ is formed on a Ti base metal.
- 5 2. The ionic water electrode of claim 1, wherein the metal oxide layer comprises Pt.
3. A method of manufacturing an ionic water electrode, the method comprising:
 - 10 (S4) pre-treating the surface of a Ti base metal;
 - (S5) coating the pre-treated surface of the Ti base metal with a source solution having a composition of $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$;
 - (S8) heating the Ti base metal that is coated with the source solution to form a $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ metal oxide on the surface of the Ti
 - 15 base metal;
 - (S10) repeating steps (S5) and (S8) at least two times or more until the $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ metal oxide is formed to a proper thickness;
 - (S11) heating the Ti base metal that underwent step (S10) to increase the stability of the $(\text{IrO}_2+\text{SnO}_2)\text{Pt}$ metal oxide formed on the
 - 20 surface of the Ti base metal.
4. The method of claim 3, wherein step (S4) comprises:
 - (S1) dipping the Ti base metal into a hydrofluoric acid solution for a predetermined period of time;
 - 25 (S2) dipping the Ti base metal that underwent step (S1) into a sulfuric acid solution for a predetermined period of time;
 - (S3) dipping the Ti base metal that underwent step (S2) into an oxalic acid solution at a predetermined temperature for a predetermined period of time.

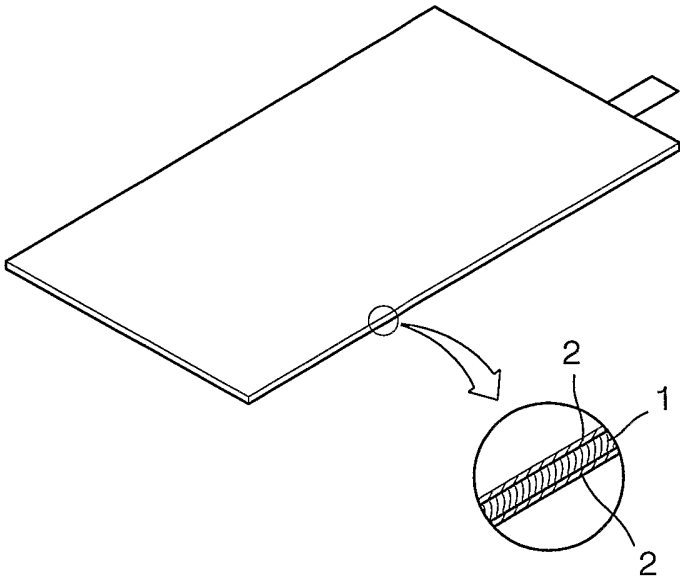
5. The method of claim 3, wherein the source solution having a composition of $(\text{IrO}_2 + \text{SnO}_2)\text{Pt}$ is manufactured by dissolving $\text{H}_2\text{IrCl}_6\text{XH}_2\text{O}$, SnCl_4 , and $\text{H}_2\text{PtCl}_6\text{H}_2\text{O}$ in a hydrochloric acid solution.

5 6. The method of claim 3, wherein step (S8) comprises:
 (S6) heating the Ti base metal that is coated with the source solution at a temperature of $90\text{ }^\circ\text{C} - 130\text{ }^\circ\text{C}$ for 5 – 15 minutes; and
 (S7) heating the Ti base metal that underwent step (S6) at a temperature of $300\text{ }^\circ\text{C} - 700\text{ }^\circ\text{C}$ for 3 – 7 minutes.

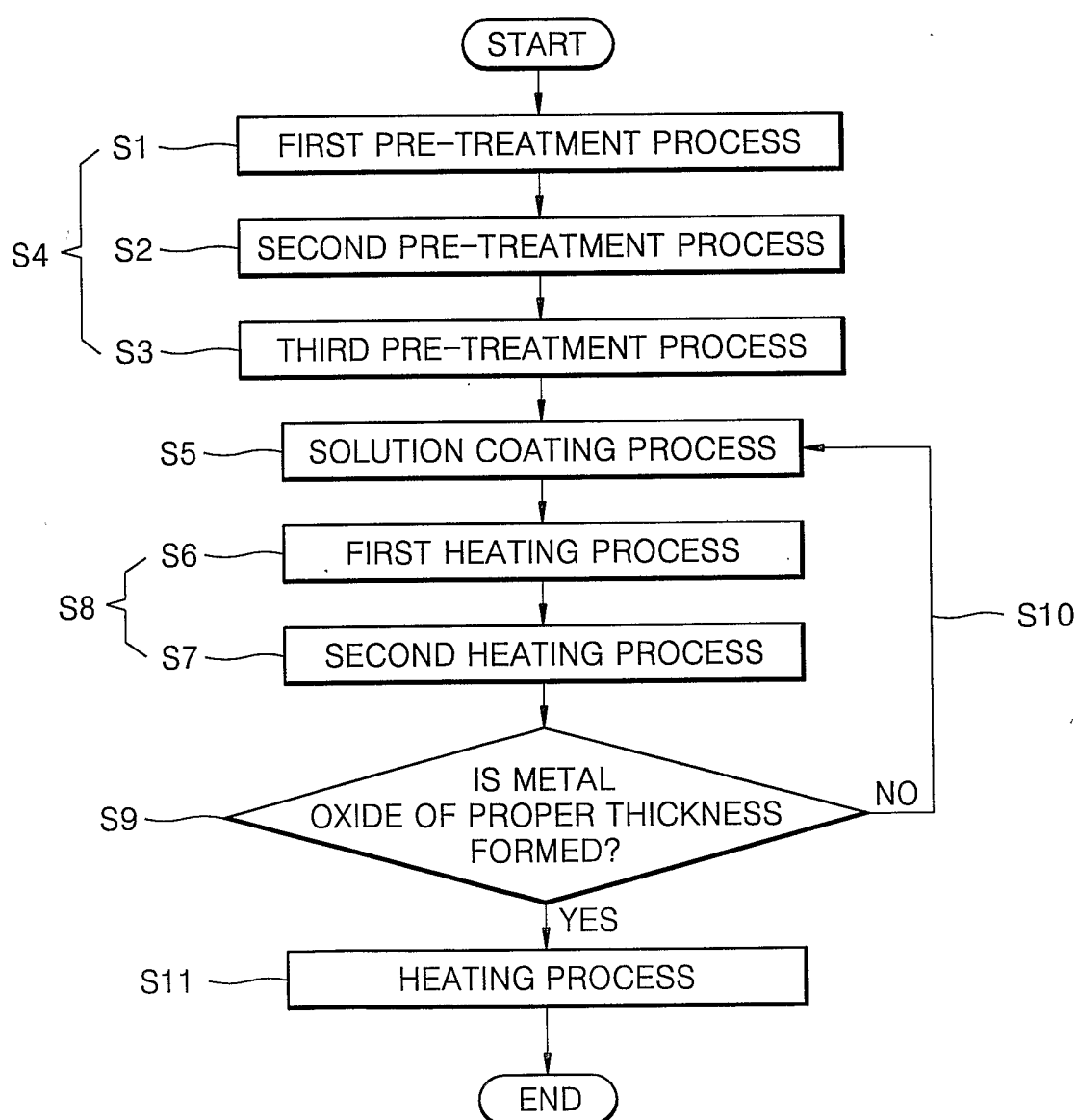
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7. The method of claim 3, wherein in step (S11), the Ti base metal that underwent step (S10) is heated at a temperature of $300\text{ }^\circ\text{C} - 700\text{ }^\circ\text{C}$ for 40 – 80 minutes.

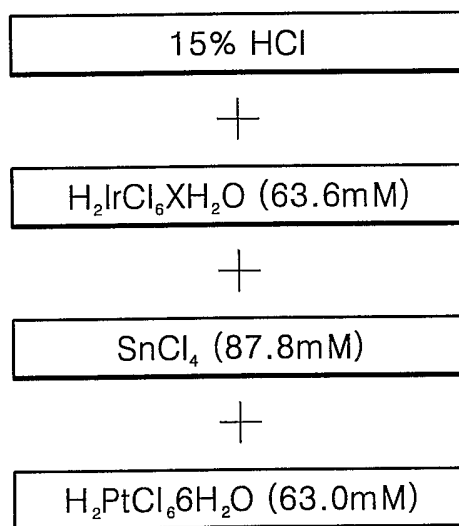
1/3
FIG. 1



2/3
FIG. 2



3/3
FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR02/01108

A. CLASSIFICATION OF SUBJECT MATTER**IPC7 C25B 11/10, C25B 11/08**

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)

IPC7 C25B

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

Korean Patents and applications for inventions since 1975, Korean Utility models and applications for Utility models since 1975,
Japanese Utility models and applications for Utility models since 1975

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

NPS, PAJ "electrode, titanium "

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 5-255881 A (TDK CORPORATION) 5 DECEMBER 1993 See the whole document	1-2
Y	KR 2001-83919 A (ATOFINA) 3 SEPTEMBER 2001 See detailed description and claims	1-2
A	JP 62-284095 A (PERMELEC ELECTRODE LTD) 9 DECEMBER 1987 See the whole document	1-2
A	JP 60-184691 A (PERMELEC ELECTRODE LTD) 20 SEPTEMBER 1986 See detailed description and claims	1-2
A	US 4471006 A (PERMELEC ELECTRODE LTD) 11 SEPTEMBER 1984 See detailed description and claims	1-2

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

* Special categories of cited documents:

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Date of the actual completion of the international search

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Name and mailing address of the ISA/KR

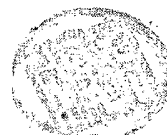
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR02/01108

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