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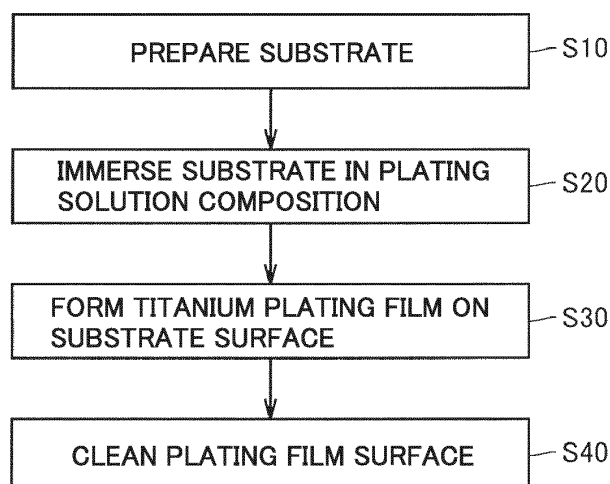
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(54) **MOLTEN SALT TITANIUM PLATING SOLUTION COMPOSITION AND METHOD FOR MANUFACTURING TITANIUM-PLATED MEMBER**

(57) A molten-salt titanium plating solution composition contains: ions of at least one Group I metal selected from the group of lithium and sodium, fluoride ions, and titanium ions. The molten-salt titanium plating solution

composition contains less than or equal to 5 mol% of potassium ions with respect to 100 mol% of all ion components contained in the molten-salt titanium plating solution composition.

FIG.2



Description

TECHNICAL FIELD

[0001] The present disclosure relates to a molten-salt titanium plating solution composition and a method for manufacturing a titanium-plated member. The present disclosure claims priority to Japanese Patent Application No. 2017-100757 filed on May 22, 2017, the disclosure of which is hereby incorporated by reference in its entirety.

BACKGROUND ART

[0002] As a titanium plating method, a method of plating in molten salt has been studied. For example, Japanese Patent Laying-Open No. 2015-193899 (PTL 1) discloses that a plating bath containing KF-KCl to which K_2TiF_6 and TiO_2 are added is used to form an alloy film of Fe and Ti on the surface of an Fe wire. NPL 1 discloses that a plating bath containing LiF-NaF-KF to which K_2TiF_6 is added is used to form a titanium film on the surface of a substrate of Ni and Fe.

CITATION LIST

PATENT LITERATURE

[0003] PTL 1: Japanese Patent Laying-Open No. 2015-193899

NON PATENT LITERATURE

[0004] NPL 1: A. ROBIN et.al., "ELECTROLYTIC COATING OF TITANIUM ONTO IRON AND NICKEL ELECTRODES IN THE MOLTEN LiF+NaF+KF EUTECTIC", Journal of Electroanal. Chem., 230 (1987), pp. 125-141

SUMMARY OF INVENTION

[0005] According to an aspect of the present disclosure, a molten-salt titanium plating solution composition contains: ions of at least one Group I metal selected from the group of lithium and sodium, fluoride ions, and titanium ions. The molten-salt titanium plating solution composition contains less than or equal to 5 mol% of potassium ions with respect to 100 mol% of all ion components contained in the molten-salt titanium plating solution composition.

[0006] According to an aspect of the present disclosure, a method for manufacturing a titanium-plated member includes: preparing a substrate having an electrically conductive surface; immersing the substrate in the molten-salt titanium plating solution composition; and forming a titanium plating film on the surface of the substrate by applying electric current to cause the substrate immersed in the molten-salt titanium plating solution composition to serve as a cathode and cause the surface of the substrate to be coated with titanium.

BRIEF DESCRIPTION OF DRAWINGS

[0007]

Fig. 1 is a schematic cross-sectional view showing an example of a part of a titanium-plated member.

Fig. 2 is a flowchart showing a procedure for manufacturing a titanium-plated member.

Fig. 3 is a schematic cross-sectional view showing an example of a state in which a substrate is immersed in a molten-salt titanium plating solution composition.

Fig. 4 is a graph showing the corrosion current density of each electrode in a physiological saline solution.

Fig. 5 is a graph showing a correlation between the potential and the current density of each electrode in a simulated seawater.

Fig. 6 is a graph showing a correlation between the potential and the current density of each electrode in a simulated electrolyte for a polymer electrolyte fuel cell (PEFC).

Fig. 7 is another graph showing a correlation between the potential and the current density of each electrode in a simulated electrolyte for a polymer electrolyte fuel cell (PEFC).

DETAILED DESCRIPTION

[Problem to be Solved by the Present Disclosure]

[0008] In order to obtain a film having a smooth surface in titanium plating, it is important that fluoride ions (F^-) be present in a molten-salt titanium plating solution composition. As a fluoride ion source, potassium fluoride (KF) is widely used. KF is a good fluoride ion source, and a molten-salt titanium plating solution composition containing potassium ions (K^+) generated from KF exhibits good plating performance in titanium plating.

[0009] According to studies by the inventors, it has been found that titanium plating performed in a plating bath containing a high content of K^+ results in metal fog of potassium and generation of potassium metal in the plating bath. Further, it has also been found that the current efficiency is deteriorated due to current flowing through the potassium metal between a cathode and an anode during plating.

[0010] It is one of objects to provide a molten-salt titanium plating solution composition that enables generation of metal fog during plating to be suppressed.

[Advantageous Effect of the Present Disclosure]

[0011] The molten-salt titanium plating solution composition enables generation of metal fog during plating to be suppressed.

[Description of Embodiments of the Present Disclosure]

[0012] Initially, embodiments of the present disclosure are described one by one.

[1] According to an aspect of the present disclosure, a molten-salt titanium plating solution composition (hereinafter also referred to as "plating solution composition") contains: ions of at least one Group I metal selected from the group of lithium and sodium, fluoride ions, and titanium ions. The molten-salt titanium plating solution composition contains less than or equal to 5 mol% of potassium ions with respect to 100 mol% of all ion components contained in the plating solution composition.

Because of a strong bonding strength of titanium with oxygen, titanium is likely to react with water to form oxide and hydroxide, and is therefore not suitable for plating from an aqueous solution. In order to form a titanium plating film on a substrate, a plating bath of a molten-salt titanium plating solution composition made up of a molten salt containing titanium ions is therefore used.

It is known that, in order to obtain a titanium plating film having a smooth surface from a molten-salt titanium plating solution composition, the presence of fluoride ions in the molten-salt titanium plating solution composition is important. Therefore, as a molten-salt titanium plating solution composition, a composition containing a predetermined amount of a metal fluoride serving as a source of fluoride ions is selected. Potassium fluoride is used as a metal fluoride serving as a source of fluoride ions.

According to studies by the inventors, however, when a titanium plating film is formed from a plating solution containing a high content of potassium fluoride, metal fog of potassium is generated during formation of the plating film. Because there is a sufficient separation between the redox potential of potassium and the redox potential of titanium, usually potassium is not electrodeposited in a condition where titanium is electrodeposited. Metal fog of potassium, however, has a redox potential closer to the redox potential of titanium. Therefore, in a condition where titanium is electrodeposited, metal fog of potassium is likely to be generated simultaneously.

If metal fog is generated, potassium metal suspends in the plating bath. During plating, current flows through the potassium metal between a cathode and an anode, resulting in deterioration of current efficiency. It is therefore necessary to suppress generation of metal fog from the plating bath.

The molten-salt titanium plating solution composition of the present disclosure can form a titanium plating film having high surface smoothness while suppressing generation of metal fog. Specifically, the molten-salt titanium plating solution composition of the present disclosure contains fluoride ions and can therefore form a titanium plating film having high surface smoothness. In addition, the molten-salt titanium plating solution composition of the present disclosure contains, as cations, ions of at least one Group I metal selected from the group of lithium and sodium having a lower reduction potential (harder to reduce) than potassium, and the content of potassium ions in the plating solution composition is less than or equal to 5 mol%. In the condition where titanium plating is performed, metal fog is less likely to be generated from lithium ions and sodium ions. The content of potassium in the molten-salt titanium plating solution composition is sufficiently low. Therefore, generation of metal fog during plating can be suppressed.

[2] A ratio of the fluoride ions to all anions contained in the molten-salt titanium plating solution composition may be more than or equal to 30 mol% and less than or equal to 100 mol%. The molten-salt titanium plating solution

composition containing fluoride ions at this ratio enables a titanium-plated member having a titanium plating film excellent in surface smoothness to be manufactured.

[3] The molten-salt titanium plating solution composition may further contain chloride ions. The molten-salt titanium plating solution composition containing fluoride ions as well as chloride ions can be reduced in melting point by depression of melting point. As a result, a titanium plating film can be formed at a lower temperature.

[4] The molten-salt titanium plating solution composition may contain more than or equal to 30 mol% and less than or equal to 50 mol% of the fluoride ions, with respect to 100 mol% of a total of the chloride ions and the fluoride ions. The content falling in this range enables further reduction of the melting point of the molten-salt titanium plating solution composition. As a result, a titanium plating film can be formed at a still lower temperature.

[5] The molten-salt titanium plating solution composition preferably contains more than or equal to 0.1 mol% and less than or equal to 12 mol% of the titanium ions with respect to 100 mol% of all cations contained in the molten-salt titanium plating solution composition. Accordingly, a titanium plating film having high surface smoothness can be formed with a high yield.

[6] The molten-salt titanium plating solution composition is used for manufacturing an insoluble electrode. Thus, an insoluble electrode having a titanium plating film excellent in surface smoothness can be manufactured.

[7] The molten-salt titanium plating solution composition is used for manufacturing a current collector. Thus, a current collector having a titanium plating film excellent in surface smoothness can be manufactured.

[8] The molten-salt titanium plating solution composition is used for manufacturing a biomaterial. Thus, a biomaterial having a titanium plating film excellent in surface smoothness can be manufactured. Such a biomaterial can also be excellent in corrosion resistance.

[9] According to an aspect of the present disclosure, a method for manufacturing a titanium-plated member includes: preparing a substrate having an electrically conductive surface; immersing the substrate in the above-described molten-salt titanium plating solution composition; and forming a titanium plating film on the surface of the substrate by applying electric current to cause the substrate immersed in the molten-salt titanium plating solution composition to serve as a cathode and cause the surface of the substrate to be coated with titanium. Thus, a titanium-plated member having a titanium plating film with high surface smoothness can be manufactured while generation of metal fog is suppressed.

[Details of Embodiments of the Invention]

[0013] Next, an embodiment of a molten-salt titanium plating solution composition and a method for manufacturing a titanium-plated member in the present disclosure is described in detail in the following. The expression "A to B" herein specifies an upper limit and a lower limit of a range (i.e., more than or equal to A and less than or equal to B). In the case where A is not accompanied by a unit but only B is accompanied by a unit, the unit for B is identical to the unit for A.

[Molten-Salt Titanium Plating Solution Composition]

[0014] A molten-salt titanium plating solution composition in the present embodiment contains ions of at least one Group I metal selected from the group of lithium (Li^+) and sodium (Na^+), fluoride ions (F^-), and titanium ions (Ti^{n+} (n is an integer of 2 or more and 4 or less, the same applies as well to the following)). The plating solution composition contains less than or equal to 5 mol% of potassium ions (K^+) with respect to 100 mol% of all ion components contained in the plating solution composition.

[0015] Preferably, the plating solution composition further contains chloride ions (Cl^-).

[0016] The plating solution composition can be prepared as a molten salt by dissolving a titanium compound serving as a source of Ti^{n+} in a mixture of at least one of lithium fluoride (LiF) and sodium fluoride (NaF) and at least one of lithium chloride (LiCl) and sodium chloride (NaCl), for example. In this case, the plating solution composition may contain, as Ti^{n+} in a titanium compound, multiple types of titanium that are different in valence.

[0017] Examples of the titanium compound serving as a source of Ti^{n+} may include hexafluorotitanic acid (H_2TiF_6), potassium hexafluorotitanate (K_2TiF_6), ammonium hexafluorotitanate ($(\text{NH}_4)_2\text{TiF}_6$), sodium hexafluorotitanate (Na_2TiF_6), potassium titanium oxalate dihydrate ($\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$), titanium chloride (III) (TiCl_3), titanium chloride (IV) (TiCl_4), and the like. Potassium hexafluorotitanate (K_2TiF_6) and potassium titanium oxalate dihydrate ($\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$) contain potassium ions, and therefore, these titanium compounds are used at respective contents so that the K^+ content with respect to 100 mol% of all ion components contained in the plating solution composition is less than or equal to 5 mol%, or these titanium compounds are used together with another titanium compound (such as titanium chloride (IV) or the like, for example) that generates no K^+ .

[0018] In the plating solution composition that is a molten salt, LiF , NaF , LiCl , and NaCl are ionized to be present in the form of Li^+ , Na^+ , F^- , and Cl^- . The titanium compound is also ionized to be present in the form of Ti^{n+} . It is preferable to prepare, as a molten salt, a plating solution composition containing: ions of at least one Group I metal selected from

the group of Li^+ and Na^+ ; F^- ; Cl^- ; and Ti^{n+} in this way.

[0019] The fact that Li^+ , Na^+ , F^- , Cl^- , and Ti^{n+} are present in the plating solution composition of the present embodiment can be confirmed, for example, by dissolving the plating solution composition in a solution of a mixture of nitric acid and hydrofluoric acid, and analyzing the solution by ICP (Inductively Coupled Plasma Spectrometry) or IC analysis (Ion Chromatography). As an ICP apparatus, iCAP6200 or the like manufactured by Thermo Fisher Scientific Inc. may be used, for example.

[0020] The ratio of the fluoride ions to all anions contained in the molten-salt titanium plating solution composition may be more than or equal to 30 mol% and less than or equal to 100 mol%. The molten-salt titanium plating solution composition containing fluoride ions at such a ratio enables manufacture of a titanium-plated member having a titanium plating film excellent in surface smoothness. The ratio of fluoride ions to all anions is preferably more than or equal to 40 mol% and less than or equal to 90 mol%, and more preferably more than or equal to 45 mol% and less than or equal to 75 mol%.

[0021] Preferably, the content of F^- with respect to 100 mol% of a total of Cl^- and F^- is more than or equal to 30 mol% and less than or equal to 50 mol%. When the ratio of Cl^- relative to F^- is increased, the melting point of the plating solution composition is once reduced by depression of melting point, and thereafter increased again. The melting point depression effect is large when the ratio of the F^- content relative to 100 mol% of the total content of Cl^- and F^- falls in a predetermined range. Specifically, reduction of the melting point is large when the content of F^- with respect to 100 mol% of the total of Cl^- and F^- is more than or equal to 30 mol% and less than or equal to 50 mol%, which facilitates plating at a lower temperature. More preferably, the content of F^- with respect to 100 mol% of the total of Cl^- and F^- is more than or equal to 30 mol% and less than or equal to 45 mol%, because reduction of the melting point is larger.

[0022] The content of Ti^{n+} in the plating solution composition is not particularly limited, but set appropriately depending on plating conditions. However, an excessively high content of Ti^{n+} may cause unnecessary precipitates to be formed, which increases reduction of current efficiency. In contrast, an excessively low content of Ti^{n+} does not allow a titanium plating film to be formed sufficiently. The content of Ti^{n+} is therefore preferably less than or equal to 20 mol% and more preferably less than or equal to 12 mol%, with respect to 100 mol% of all cations in the plating solution composition. The content of Ti^{n+} is preferably more than or equal to 0.1 mol%, and more preferably more than or equal to 0.5 mol%, with respect to 100 mol% of all cations in the plating solution composition. In other words, the content of titanium ions with respect to 100 mol% of all cations contained in the molten-salt titanium plating solution composition is preferably more than or equal to 0.1 mol% and less than or equal to 12 mol%.

[Method for Manufacturing Titanium-Plated Member]

[0023] Next, referring to Figs. 1 to 3, a method for manufacturing a titanium-plated member in the present embodiment is described. Fig. 1 is a schematic cross-sectional view showing an example of a part of a titanium-plated member. Fig. 2 is a flowchart showing a procedure for manufacturing a titanium-plated member. Fig. 3 is a schematic cross-sectional view showing an example of a state in which a substrate is immersed in a molten-salt titanium plating solution composition.

[0024] Referring to Fig. 1, a titanium-plated member 1 is made up of a substrate 10 and a titanium plating film 20 (hereinafter also referred to simply as "plating film 20") formed on a surface of substrate 10. Plating film 20 is a film made of titanium. Referring to Figs. 2 and 3, titanium-plated member 1 is manufactured through steps S10 to S40 shown in Fig. 2. A method for manufacturing titanium-plated member 1 according to the present embodiment includes: the step of preparing substrate 10 having an electrically conductive surface (S10); the step of immersing substrate 10 in plating solution composition 50 (S20); and the step of forming titanium plating film 20 on the surface of substrate 10 by applying electric current to cause substrate 10 immersed in plating solution composition 50 to serve as a cathode and cause the surface of substrate 10 to be coated with titanium (S30). Further, the method for manufacturing titanium-plated member 1 preferably includes the step of cleaning a surface of plating film 20 (S40). The method for manufacturing titanium-plated member 1 of the present embodiment may include any step besides the steps S10, S20, S30, and S40. In the following, each of these steps is described.

[0025] First, substrate 10 having an electrically conductive surface is prepared (S10). The material forming substrate 10 is not particularly limited as long as the material has an electrically conductive surface. Examples of substrate 10 include, for example, a substrate made of iron or nickel, a substrate made of an alloy of them, or a multilayer substrate having a surface made of a layer of iron or nickel or an alloy thereof.

[0026] The shape of substrate 10 is not particularly limited. For example, substrate 10 in the shape of any of various shapes such as plate, column, pipe, mesh, or the like may be employed as substrate 10.

[0027] Next, substrate 10 is immersed in plating solution composition 50 (S20). As plating solution composition 50, a plating solution composition prepared in the above-described way is used.

[0028] Referring to Fig. 3, in the present embodiment, plating solution composition 50 contains ions of at least one Group I metal selected from the group of lithium (Li^+) and sodium (Na^+), fluoride ions (F^-), titanium ions (Ti^{n+}), and chloride ions (Cl^-). Further, plating solution composition 50 is prepared so that the content of potassium ions (K^+) with respect to 100 mol% of all ion components contained in plating solution composition 50 is less than or equal to 5 mol%.

[0029] In the present embodiment, preferably plating solution composition 50 is prepared so that the ratio of the fluoride ions to all anions contained in the molten-salt titanium plating solution composition is more than or equal to 30 mol% and less than or equal to 100 mol%. Further, preferably plating solution composition 50 is prepared so that plating solution composition 50 contains more than or equal to 30 mol% and less than or equal to 50 mol% of F^- , with respect to 100 mol% of the total of Cl^- and F^- . Preferably plating solution composition 50 is prepared so that plating solution composition 50 contains more than or equal to 0.1 mol% and less than or equal to 12 mol% of Ti^{n+} with respect to 100 mol% of all cations contained in plating solution composition 50.

[0030] Next, electric current is applied to cause substrate 10 immersed in plating solution composition 50 to serve as a cathode, and cause the surface of substrate 10 to be coated with titanium, to thereby form titanium plating film 20 on this surface (S30). The step of forming plating film 20 is performed in the following way. With substrate 10 immersed in plating solution composition 50, electric current is applied by applying a voltage between an anode 30 and substrate 10 serving as a cathode that are immersed in plating solution composition 50 to cause electrolysis of plating solution composition 50. Accordingly, on the surface of substrate 10 serving as a cathode, titanium ions are reduced to titanium and the surface of substrate 10 is coated with titanium. Thus, plating film 20 is formed on the surface of substrate 10.

[0031] Electrolysis of plating solution composition 50 is preferably performed so that the absolute value of the current density, on substrate 10, of current flowing between anode 30 and substrate 10 is more than or equal to 1 mA/cm² and less than or equal to 500 mA/cm², and more preferably performed so that the absolute value of the current density is more than or equal to 1 mA/cm² and less than or equal to 300 mA/cm². When electrolysis of plating solution composition 50 is performed so that the absolute value of the current density of current flowing between anode 30 and substrate 10 is more than or equal to 1 mA/cm², plating film 20 can be formed on the surface of substrate 10 in a shorter time. When electrolysis of plating solution composition 50 is performed so that the absolute value of the current density of current flowing between anode 30 and substrate 10 is less than or equal to 500 mA/cm², particularly less than or equal to 300 mA/cm², plating film 20 having higher surface smoothness can be formed.

[0032] Finally, the surface of plating film 20 is cleaned (S40). On the surface of plating film 20 thus formed, components contained in plating solution composition 50 remain. Therefore, a cleaning agent can be used to clean the surface of plating film 20 to thereby remove the components remaining on the surface of plating film 20. As the cleaning agent, water may be used. In other words, substrate 10 on which plating film 20 is formed may be cleaned with water. Further, in order to remove a substance such as poorly water-soluble substance that is difficult to remove with only water, a cleaning agent other than water may be used such as a cleaning agent containing water-soluble salt having a high compatibility with components contained in plating solution composition 50, instead of or in combination with water. In this way, titanium-plated member 1 having a surface of substrate 10 coated with plating film 20 is manufactured.

[Titanium-Plated Member]

[0033] Titanium-plated member 1 manufactured in this way can be used in a variety of fields, as a member having a protective film with a high hardness and a high surface smoothness as well as excellent corrosion resistance and excellent wear resistance.

[0034] The ratio of average surface roughness R_a to average thickness R of plating film 20 ($(R_a/R) \times 100$ (%)) of titanium-plated member 1 manufactured by the above-described method is preferably less than or equal to 10%, and more preferably less than or equal to 5%. With the ratio falling in this range, titanium-plated member 1 having plating film 20 with a sufficiently high surface smoothness can be provided.

[0035] Average surface roughness R_a of plating film 20 can be measured through observation of a cross section with an SEM (Scanning Electron Microscope) or by means of a surface roughness meter. Average thickness R of plating film 20 can be determined through observation of a cross section with an SEM. Average surface roughness R_a of plating film 20 refers to an arithmetic mean roughness R_a specified under JIS B 0601 (2001). Average thickness R of plating film 20 may be an arithmetic mean thickness of plating film 20 determined from thicknesses at any 10 points on an SEM image, for example.

[0036] Preferably, the molten-salt titanium plating solution composition is used for manufacturing an insoluble electrode. With such a molten-salt titanium plating solution composition for manufacturing an insoluble electrode, an insoluble electrode having a titanium plating film excellent in surface smoothness can be manufactured.

[0037] Preferably, the insoluble electrode is used for manufacturing hydrogen. When the insoluble electrode is used for manufacturing hydrogen, the electrode can be provided as a hydrogen-manufacturing insoluble electrode with a low resistance. Accordingly, hydrogen with a high purity can be manufactured.

[0038] Preferably, the molten-salt titanium plating solution composition is used for manufacturing a current collector. With such a current-collector-manufacturing molten-salt titanium plating solution composition, a current collector having a titanium plating film with excellent surface smoothness can be manufactured.

[0039] Preferably, the current collector is used for a fuel cell. A current collector for a fuel cell can be provided as a fuel-cell current collector having a good electrical conductivity. Particularly when the current collector is used for a fuel

cell, the current collector is more preferably used for a polymer electrolyte fuel cell.

[0040] Preferably, the molten-salt titanium plating solution composition is used for manufacturing a biomaterial. With such a biomaterial-manufacturing molten-salt titanium plating solution composition, a biomaterial having a titanium plating film with an excellent surface smoothness can be manufactured. This biomaterial is also excellent in corrosion resistance.

[0041] The use of the biomaterial is preferably selected from the group consisting of spinal fixation device, fracture fixation device, artificial joint, artificial heart valve, intravascular stent, denture base, artificial dental root, and orthodontic wire.

[Summary]

[0042] As seen from the above, molten-salt titanium plating solution composition 50 according to the present embodiment enables generation of metal fog during plating to be suppressed. Further, in accordance with the method for manufacturing titanium-plated member 1, titanium-plated member 1 having plating film 20 with high surface smoothness can be manufactured.

[0043] In the above description of the embodiment, molten-salt titanium plating solution composition 50 containing chloride ions (Cl^-) is described. Molten-salt titanium plating solution composition 50, however, may be prepared without containing Cl^- . As a molten-salt titanium plating solution composition 50 containing no Cl^- , molten-salt titanium plating solution composition 50 can be prepared to contain other anions instead of Cl^- . In this case, the aforementioned other anions are preferably selected that are stable at the plating temperature and will not form a residue such as salt that is difficult to remove after plating.

[0044] Preferably, as the molten-salt titanium plating solution composition, plating solution composition 50 is prepared to contain more than or equal to 30 mol% and less than or equal to 50 mol% of F^- with respect to 100 mol% of the total of Cl^- and F^- , and contain more than or equal to 0.1 mol% and less than or equal to 12 mol% of Ti^{n+} with respect to 100 mol% of all cations contained in plating solution composition 50. The limitations on respective contents are not requisite ones. The contents can be set appropriately in consideration of the required plating temperature and plating performance.

EXAMPLES

[0045] The above-described embodiments are hereinafter described more specifically with reference to Examples. The present disclosure is not limited to these Examples. In Table 1, Experiment No. 1 is an example where a plating solution composition of an Example within the range of the molten-salt titanium plating solution composition of the present disclosure was used. Experiment Nos. 2 to 4 are each an example where a plating solution composition of a comparative example out of the range of the molten-salt titanium plating solution composition of the present disclosure was used.

<<Example 1>>

[Preparation of molten-salt titanium plating solution composition and manufacture of titanium-plated member]

[0046] Molten-salt titanium plating solution compositions of Experiment Nos. 1 to 4 were each prepared by dissolving, in the main agent for the plating solution composition shown in Table 1, one or both of K_2TiF_6 powder and TiCl_4 gas as a titanium source at a ratio of 2 mol of the total of one or both of K_2TiF_6 powder and TiCl_4 gas with respect to 100 mol of the main agent. Further, through the steps S10 to S40 of the method for manufacturing a titanium-plated member as described above (see Fig. 2), each of the molten-salt titanium plating solution compositions of Experiment Nos. 1 to 4 was used to plate a surface of a respective substrate (made of nickel, 0.1 mm in thickness, 5 mm $\times$ 25 mm in size). In this way, titanium-plated members of Experiment Nos. 1 to 4 were produced. Subsequently, for each of the titanium-plated members of Experiment Nos. 1 to 4, the plating performance was evaluated. Further, whether or not metal fog was generated in the process of performing titanium plating for each of Experiment Nos. 1 to 4 was confirmed by visual inspection. The results are shown in Table 1. As to the evaluation of the plating performance, specifically the ratio of an abnormal plating portion resulting from discoloration of the plated surface and/or lack of plating on the surface to be plated, for example, was evaluated based on the area ratio (%) of the abnormal plating portion. In Table 1, the level of the plating performance is classified into those termed "good," "average," "somewhat poor" and "poor" respectively. "Good" means that the abnormal portion is less than 5%, "average" means that the abnormal portion is more than or equal to 5% and less than 20 %, "somewhat poor" means that the abnormal portion is more than or equal to 20% and less than 50%, and "poor" means that the abnormal portion is more than or equal to 50%. In Table 1, as to whether or not metal fog was generated, "small amount was generated" means that white smoke was confirmed during cleaning with water, and "generated" means that white smoke and sparks were confirmed.

[Table 1]

Experiment No.		1	2	3	4
main agent		LiF-LiCl	LiF-KCl	LiF-NaF-KF	KF-KCl
makeup of plating solution composition (molar ratio)	LiF	45	45	46.5	0
	LiCl	55	0	0	0
	NaF	0	0	11.5	0
	KF	0	0	42	45
	KCl	0	55	0	55
	K ₂ TiF ₆	2	1	1	2
	TiCl ₄	0	1	1	0
ratio of K ⁺ (mol%) to 100 mol% of all ion components		1.8	27	21	48
F ⁻ /(Cl ⁻ +F ⁻) (mol%)		51	46	96	51
ratio of Ti ⁿ⁺ (mol%) to 100 mol% of all cations		1.9	1.9	1.9	1.9
plating temperature (°C)		650	350 to 500	600 to 700	650
plating performance		good	poor	good	good
generation of metal fog		no metal fog was generated	small amount was generated	generated	generated

[0047] As shown in Table 1, as to Experiment No. 1, the plating performance was good and generation of metal fog was not confirmed. Thus, generation of metal fog of potassium could be suppressed by performing titanium plating using a molten-salt titanium plating solution composition in which the content of K⁺ with respect to 100 mol% of all ion components contained in the molten-salt titanium plating solution composition was less than or equal to 5 mol%. The plating performance was also good in the case of a molten-salt titanium plating solution composition containing K⁺ at a smaller content and containing Li⁺ as main cations instead.

[0048] In contrast, as to Experiment No. 2, poor plating performance and generation of a small amount of metal fog were confirmed. As to Experiment Nos. 3 and 4, while the plating performance was good, generation of metal fog was confirmed. Thus, metal fog of potassium was generated in the case of a molten-salt titanium plating solution composition in which the content of K⁺ with respect to 100 mol% of all ion components contained in the molten-salt titanium plating solution composition was more than 5 mol%.

<<Example 2>>

[Preparation of molten-salt titanium plating solution composition and manufacture of titanium-plated member]

[0049] Molten-salt titanium plating solution compositions of Experiment Nos. 5 to 16 were each prepared by dissolving, in the main agent for the plating solution composition shown in Tables 2 to 4, one or both of K₂TiF₆ powder and TiCl₄ gas as a titanium source at the ratio shown in Tables 2 to 4 with respect to 100 mol of the main agent.

[0050] The molten-salt titanium plating solution composition of Experiment No. 5 contains more than 5 mol% of K⁺ with respect to 100 mol% of all ion components contained in the molten-salt titanium plating solution composition, and is therefore a Comparative Example. Respective molten-salt titanium plating solution compositions of Experiment Nos. 6 to 16 each contain less than or equal to 5 mol% of K⁺ with respect to 100 mol% of all ion components contained in the molten-salt titanium plating solution composition, and are therefore Examples.

[0051] Respective molten-salt titanium plating solution compositions of Experiment Nos. 7 and 15 are Examples containing no chloride ions. Respective molten-salt titanium plating solution compositions of Experiment No. 8, Nos. 10 to 12, and No. 16 are Examples in which the content of fluoride ions with respect to 100 mol% of the total of chloride ions and fluoride ions is more than or equal to 30 mol% and less than or equal to 50 mol%. It should be noted that the

molten-salt titanium plating solution composition of Experiment No. 12 contains more than 12 mol% of titanium ions with respect to 100 mol% of all cations contained in the molten-salt titanium plating solution composition. The molten-salt titanium plating solution composition of Experiment No. 16 contains less than 0.1 mol% of titanium ions with respect to 100 mol% of all cations contained in the molten-salt titanium plating solution composition.

[0052] Next, each of the molten-salt titanium plating solution compositions of Experiment Nos. 5 to 16 was used to plate a surface of a respective substrate (made of nickel, 0.1 mm in thickness, 5 mm × 25 mm in size) with titanium through the steps S10 to S40 of the method for manufacturing a titanium-plated member as described above (see Fig. 2). Thus, titanium-plated members of Experiment Nos. 5 to 16 were manufactured. Further, as to the titanium-plated members of Experiment Nos. 5 to 16, the plating performance was evaluated by the same evaluation method as Example 1. As to the titanium-plated members of Experiment Nos. 5 to 16, whether or not metal fog was generated in the process of titanium plating was also confirmed by the same evaluation method as Example 1. The results are shown in Tables 2 to 4.

[0053] The correlations between respective molten-salt titanium plating solution compositions of Experiment Nos. 5 to 16 and respective titanium-plated members of Experiment Nos. 5 to 16 are as follows. Specifically, a titanium-plated member produced using the molten-salt titanium plating solution composition of Experiment No. 5 corresponds to the titanium-plated member of Experiment No. 5. The same applies as well to the subsequent Experiments, i.e., a titanium-plated member produced using a molten-salt titanium plating solution composition of Experiment No. "X" corresponds to a titanium-plated member of Experiment No. "X" (X is an arbitrary numeral).

[Table 2]

Experiment No.		5	6	7	8
main agent		LiF-KCl-KF	LiF-KCl-KF	LiF	LiF-LiCl
makeup of plating solution composition (molar ratio)	LiF	45	45	100	30
	LiCl	55	55	0	70
	NaF	0	0	0	0
	KF	8	6	0	0
	KCl	0	0	0	0
	K ₂ TiF ₆	2	2	2	2
	TiCl ₄	0	0	0	0
ratio of K ⁺ (mol%) to 100 mol% of all ion components		5.1	4.3	1.8	1.8
F ⁻ /(Cl ⁻ +F ⁻) (mol%)		54	53	100	38
ratio of Ti ⁿ⁺ (mol%) to 100 mol% of all cations		1.8	1.8	1.9	1.9
plating temperature (°C)		650	650	900	650
plating performance		good	good	good	good
generation of metal fog		small amount was generated	not generated	not generated	not generated

[Table 3]

Experiment No.		9	10	11	12
main agent		LiF-LiCl	LiF-LiCl	LiF-LiCl	LiF-NaCl
makeup of plating solution composition (molar ratio)	LiF	50	50	50	40
	LiCl	50	50	50	0
	NaF	0	0	0	0
	KF	8	0	0	0
	KCl	0	0	0	0
	K ₂ TiF ₆	2	0	0	2
	TiCl ₄	0	13	14	0
	NaCl	0	0	0	60
ratio of K ⁺ (mol%) to 100 mol% of all ion components		1.8	0	0	1.8
F ⁻ /(Cl ⁻ +F ⁻) (mol%)		55	33	32	46
ratio of Ti ⁿ⁺ (mol%) to 100 mol% of all cations		1.9	11.5	12.3	1.9
plating temperature (°C)		650	650	650	750
plating performance		good	good	poor	good
generation of metal fog		not generated	not generated	not generated	not generated

[Table 4]

Experiment No.		13	14	15	16
main agent		LiF-LiCl	LiF-LiCl	LiF-NaF	LiF-LiCl
makeup of plating solution composition (molar ratio)	LiF	20	60	30	45
	LiCl	80	40	0	55
	NaF	0	0	70	0
	KF	0	0	0	0
	KCl	0	0	0	0
	K ₂ TiF ₆	2	2	2	0.03
	TiCl ₄	0	0	0	0
ratio of K ⁺ (mol%) to 100 mol% of all ion components		1.8	1.8	1.8	0.03
F ⁻ /(Cl ⁻ +F ⁻) (mol%)		29	64	100	45
ratio of Ti ⁿ⁺ (mol%) to 100 mol% of all cations		1.9	1.9	1.9	0.03
plating temperature (°C)		700	750	700	650
plating performance		somewhat	good	good	poor
generation of metal fog		not generated	not generated	not generated	not generated

[0054] As shown in Tables 2 to 4, in the case of the molten-salt titanium plating solution composition of Experiment No. 5 containing more than 5 mol% of K⁺ with respect to 100 mol% of all ion components contained in the molten-salt titanium plating solution composition, metal fog of potassium was generated. In contrast, in the case of the molten-salt titanium plating solution compositions of Experiment Nos. 6 to 16 containing less than or equal to 5 mol% of K⁺ with respect to 100 mol% of all ion components, it was confirmed that no metal fog of potassium was generated.

[0055] As seen from the above, molten-salt titanium plating solution composition 50 and the method for manufacturing titanium-plated member 1 according to the present embodiment enable generation of metal fog during plating to be suppressed.

<<Example 3>>

[Corrosion resistance to physiological saline solution]

[0056] The corrosion resistance of the following Ti-plated product to physiological saline solution was evaluated through the following procedure.

Production of Specimens

[0057] The molten-salt titanium plating solution composition of Experiment No. 8 was used and, through the steps S10 to S40 of the method for manufacturing a titanium-plated member described above (see Fig. 2), the surface of a nickel porous substrate (3 cm × 5 cm × 1 mm, porosity: 96%, average pore size: 300 μm, hereinafter referred to as "nickel porous material") was plated with titanium. Thus, a Ti-plated product to serve as a specimen of an Example was prepared.

[0058] In contrast, as specimens of a comparative example, a Ni porous material (product name: "Celmet®" manufactured by Sumitomo Electric Industries, Ltd.) and a Ti metal sheet (manufactured by Nilaco Corporation) were prepared.

Corrosion Resistance Test

[0059] Cyclic voltammetry was conducted under the following conditions. The results are shown in Fig. 4. In Fig. 4, the specimen of the Example and the specimens of the Comparative Example (Ni porous material and Ti metal sheet) are expressed as "Ti-plated product," "Ni" and "Ti" respectively.

<Conditions for Cyclic Voltammetry>

[0060]

electrolyte: 0.9 mass% sodium chloride aqueous solution (physiological saline solution)
working electrode: specimen of Example or specimen of Comparative Example (Ti-plated product, Ni, or Ti)
reference electrode: Ag/AgCl electrode
counter electrode: Ni metal sheet
scan rate: 10 mV/sec
solution temperature: 25°C

[0061] It has been proved from the results in Fig. 4 that the Ti-plated product of the Example is lower in corrosion current density than the Ni porous material of the Comparative Example, and is thus stable in an environment of physiological saline solution. It is seen from this result that the Ti-plated product of the Example is suitable as a biomaterial. Further, the Ti-plated product of the Example is lower in corrosion current density than the Ti metal sheet of the Comparative Example. It is seen from this result that the structure of a metal porous material instead of a metal sheet is used to further improve the stability in an environment of physiological saline solution.

<<Example 4>>

[Corrosion resistance to saline solution simulating seawater]

[0062] The corrosion resistance of the following Ti-plated product to saline solution simulating seawater was evaluated through the following procedure.

Production of Specimens

[0063] As a specimen of the Example, a Ti-plated product manufactured by the same method as the Ti-plated product used for Example 3 was prepared. As a specimen of the Comparative Example, a Ti metal sheet (manufactured by Nilaco Corporation) was prepared.

Corrosion Resistance Test

[0064] Cyclic voltammetry was conducted under the same conditions as those indicated above in the section [Corrosion resistance to physiological saline solution], except that 3.3 mass% saline solution simulating seawater was used as electrolyte. The results are shown in Fig. 5. In Fig. 5, the specimen of the Example and the specimen of the Comparative Example are expressed as "Ti-plated product" and "Ti commercial product" respectively.

[0065] It has been proved from the results in Fig. 5 that the Ti-plated product of the Example is lower in current density than the Ti commercial product of the Comparative Example, and thus exhibits high corrosion resistance to seawater. It is seen from the above that the Ti-plated product of the Example is promising as an insoluble electrode (anode) for electrolysis of salt.

<<Example 5>>

[Evaluation of suitability for polymer electrolyte fuel cell]

[0066] The suitability of the following Ti-plated product for polymer electrolyte fuel cell was evaluated through the following procedure.

Production of Specimen

[0067] As a specimen of the Example, a Ti-plated product manufactured by the same method as the Ti-plated product used in Example 3 was prepared. As specimens of the Comparative Example, an Ni porous material (product name: "Celmet®" manufactured by Sumitomo Electric Industries, Ltd.) and a Ti metal sheet (manufactured by Nilaco Corporation) were prepared.

Evaluation of Suitability

[0068] Cyclic voltammetry was conducted under the same conditions as those indicated above in the section [Corrosion resistance to physiological saline solution], except that 10 mass% sodium nitrate aqueous solution (adjusted to pH = 3 by adding nitric acid) (simulated PEFC electrolyte) was used as electrolyte. The results are shown in Figs. 6 and 7. In Figs. 6 and 7, the specimen of the Example and the specimens (Ni porous material and Ti metal sheet) of the Comparative Example are expressed as "Ti-plated product," "comparative Ni" and "comparative Ti" respectively. In Fig. 6, respective plots for "Ti-plated product" and "comparative Ti" depicting a correlation between the potential and the current density of the electrode overlap each other, and therefore, Fig. 7 shows these plots by expanding the scale of the vertical axis (current density) so that the plot depicting the correlation for "Ti-plated product" can be distinguished from the plot depicting the correlation for "comparative Ti."

[0069] It has been proved from the results in Figs. 6 and 7 that the Ti-plated product for the Example is lower in current density than the comparative Ni of the Comparative Example, and therefore promising as a current collector material to be used for a polymer electrolyte fuel cell.

[0070] It should be construed that the embodiments and examples disclosed herein are given by way of illustration in all respects, not by way of limitation in any aspect. It is intended that the scope of the present invention is defined by claims, not by the description above, and encompasses all modifications and variations equivalent in meaning and scope to the claims.

REFERENCE SIGNS LIST

[0071] 1 titanium-plated member; 10 substrate; 20 plating film; 30 anode; 40 container; 50 plating solution composition

Claims

1. A molten-salt titanium plating solution composition comprising:

ions of at least one Group I metal selected from the group of lithium and sodium;
fluoride ions; and
titanium ions,
the molten-salt titanium plating solution composition containing less than or equal to 5 mol% of potassium ions with respect to 100 mol% of all ion components contained in the molten-salt titanium plating solution composition.

2. The molten-salt titanium plating solution composition according to claim 1, wherein a ratio of the fluoride ions to all anions contained in the molten-salt titanium plating solution composition is more than or equal to 30 mol% and less than or equal to 100 mol%.

3. The molten-salt titanium plating solution composition according to claim 1 or 2, further comprising chloride ions.

4. The molten-salt titanium plating solution composition according to claim 3, wherein the molten-salt titanium plating solution composition contains more than or equal to 30 mol% and less than or equal to 50 mol% of the fluoride ions, with respect to 100 mol% of a total of the chloride ions and the fluoride ions.

5. The molten-salt titanium plating solution composition according to any one of claims 1 to 4, wherein the molten-salt titanium plating solution composition contains more than or equal to 0.1 mol% and less than or equal to 12 mol% of the titanium ions with respect to 100 mol% of all cations contained in the molten-salt titanium plating solution composition.

6. The molten-salt titanium plating solution composition according to any one of claims 1 to 5, wherein the molten-salt titanium plating solution composition is used for manufacturing an insoluble electrode.

7. The molten-salt titanium plating solution composition according to any one of claims 1 to 5, wherein the molten-salt titanium plating solution composition is used for manufacturing a current collector.

8. The molten-salt titanium plating solution composition according to any one of claims 1 to 5, wherein the molten-salt titanium plating solution composition is used for manufacturing a biomaterial.

9. A method for manufacturing a titanium-plated member, the method comprising:

preparing a substrate having an electrically conductive surface;
immersing the substrate in a molten-salt titanium plating solution composition according to any one of claims 1 to 5; and
forming a titanium plating film on the surface of the substrate by applying electric current to cause the substrate immersed in the molten-salt titanium plating solution composition to serve as a cathode and cause the surface of the substrate to be coated with titanium.

FIG.1

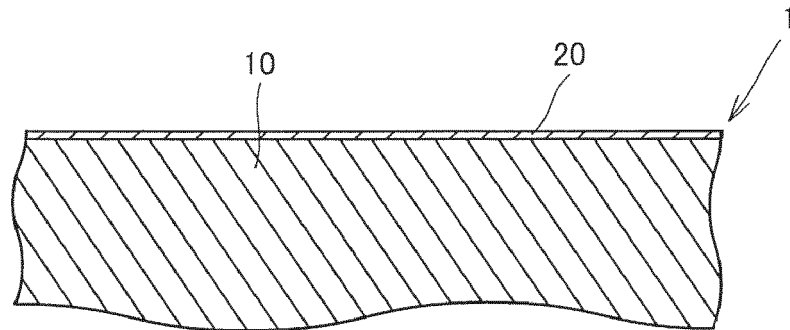


FIG.2

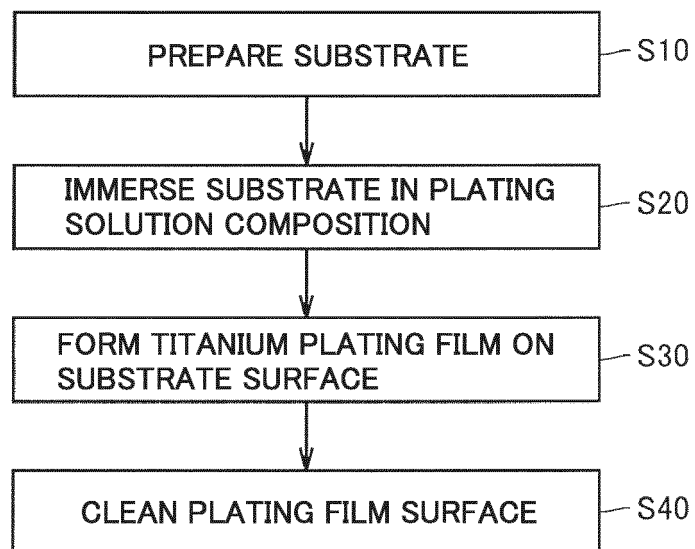


FIG.3

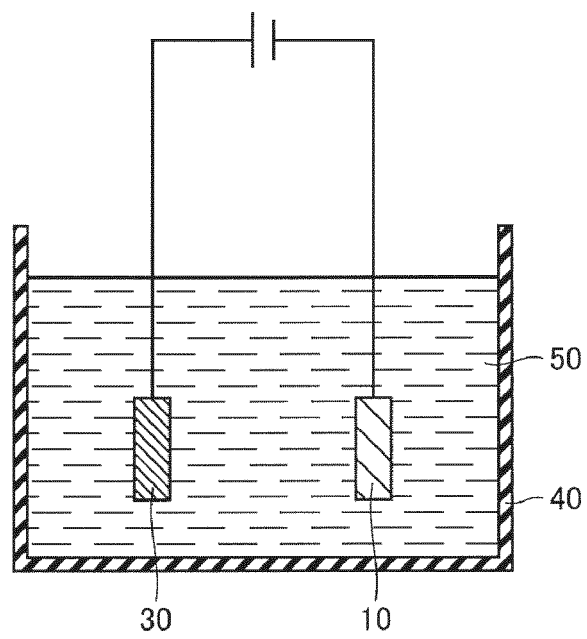


FIG.4

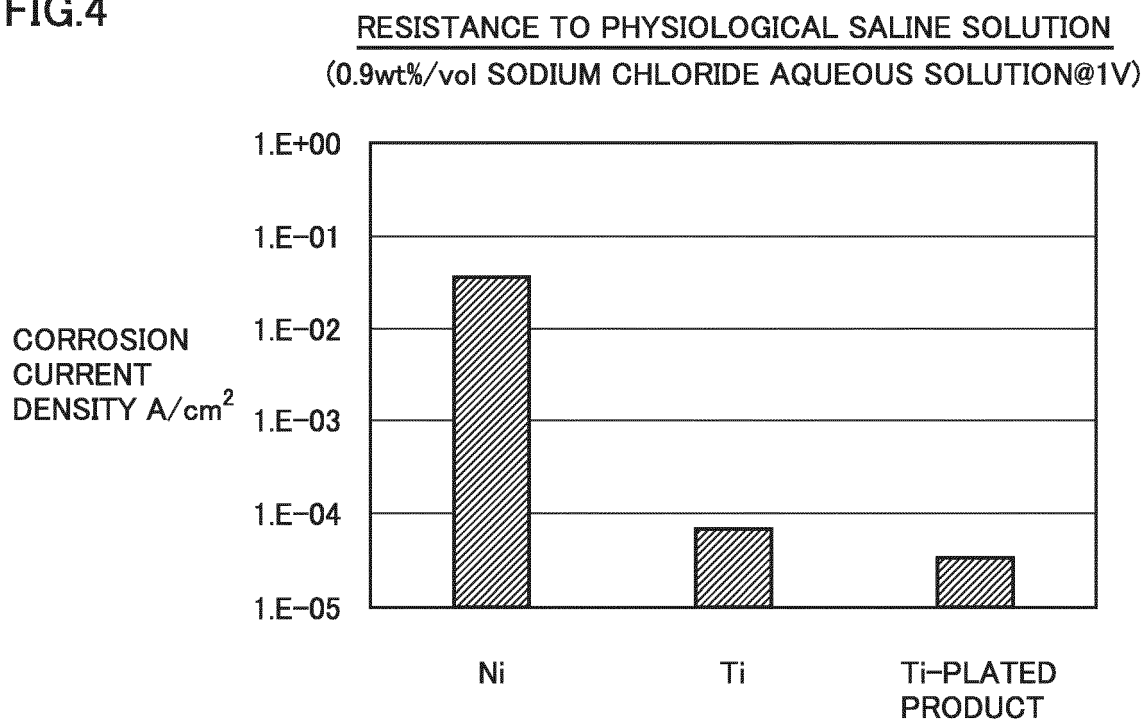


FIG.5

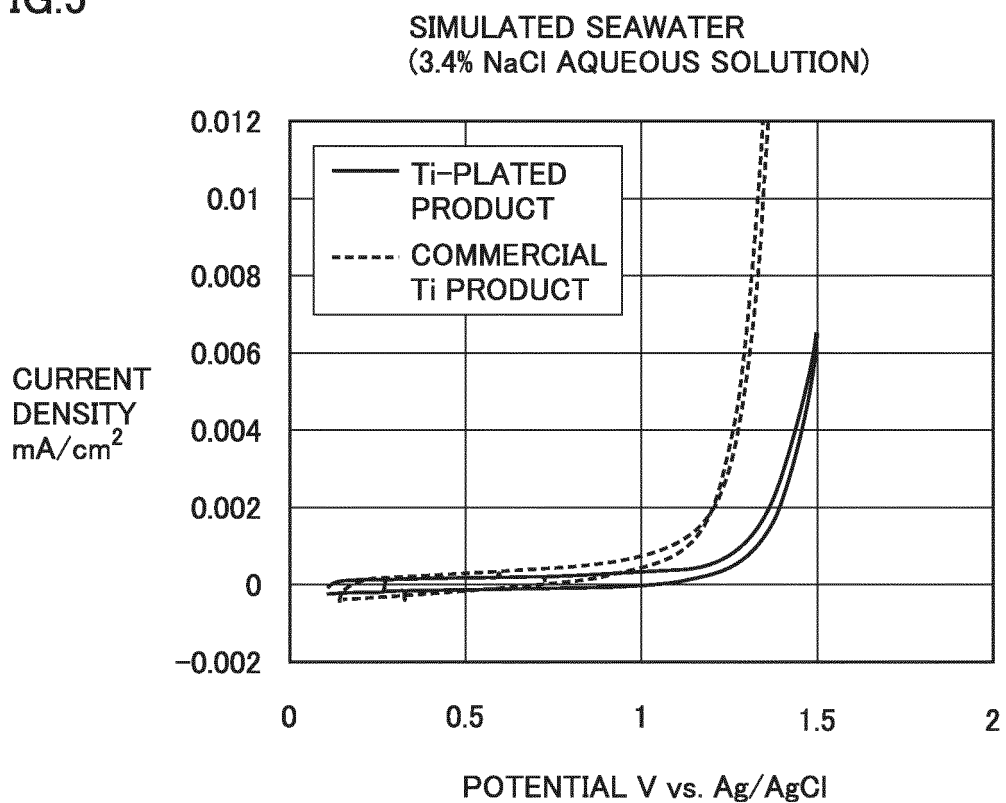


FIG.6

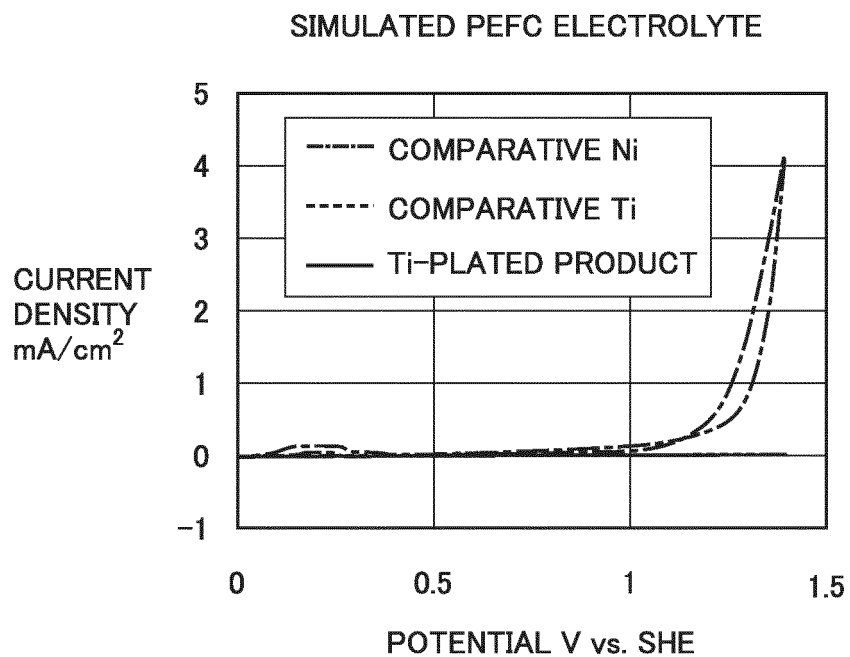
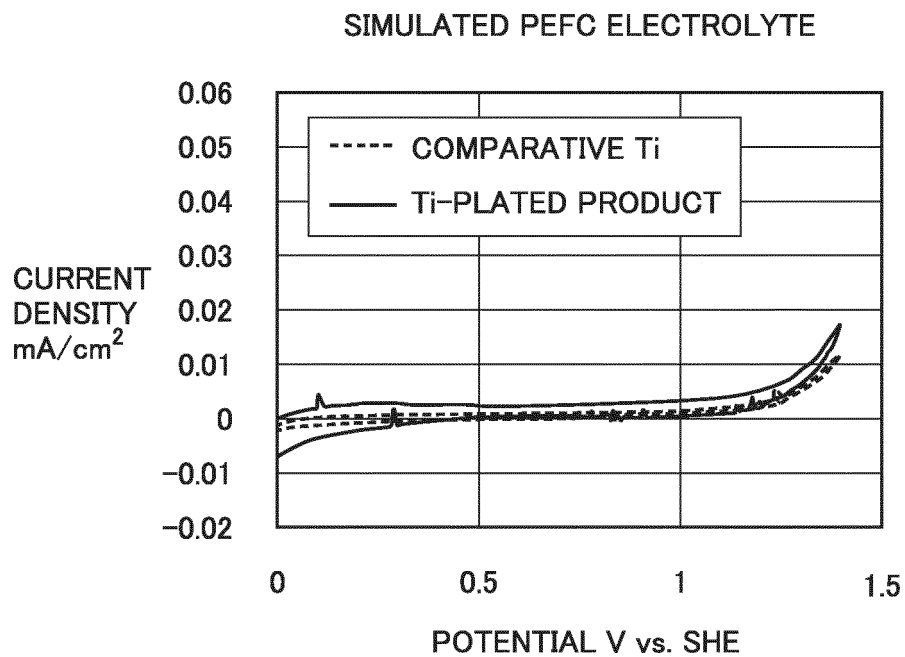


FIG.7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2018/009739

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C25D3/66(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)

Int.Cl. C25D3/66

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2018

Registered utility model specifications of Japan 1996-2018

Published registered utility model applications of Japan 1994-2018

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.
A	JP 51-138511 A (SONY CORP.) 30 November 1976, claims, examples 2-3 & US 4082628 A, claims, examples 1-2 & GB 1542074 A & DE 2623740 A & FR 2312575 A & SE 7606022 A & CA 1107229 A & AU 1424576 A	1-9
A	CLAYTON, F. R. et al., "Electrochemical Studies of Titanium in Molten Fluorides", J. Electrochem. Soc. ELECTROCHEMICAL SCIENCE AND TECHNOLOGY, 1973, vol. 120, no. 9, pp. 1193-1199	1-9
A	JP 6-173065 A (JAPAN ENERGY CORP.) 21 June 1994, claims, example 1 (Family: none)	1-9
A	SONG, Jianxun et al., "The Influence of Fluoride Anion on the Equilibrium between Titanium Ions and Electrodeposition of Titanium in Molten Fluoride-Chloride Salt", Materials Transactions, 2014, vol. 55, no. 8, pp. 1299-1303	1-9
A	JP 50-136238 A (TOYOTA CENTRAL RESEARCH AND DEVELOPMENT LABORATORIES, INC.) 29 October 1975, example 1 (Family: none)	1-9

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

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Date of the actual completion of the international search
07 May 2018 (07.05.2018)Date of mailing of the international search report
22 May 2018 (22.05.2018)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

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Patent documents cited in the description

- JP 2017100757 A [0001]
- JP 2015193899 A [0002] [0003]

Non-patent literature cited in the description

- **A. ROBIN.** ELECTROLYTIC COATING OF TITANIUM ONTO IRON AND NICKEL ELECTRODES IN THE MOLTEN LiF+NaF+KF EUTECTIC. *Journal of Electroanal. Chem.*, 1987, vol. 230, 125-141 [0004]