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(54) **ELECTROLYTIC SYNTHESIS ANODE AND METHOD FOR PRODUCING FLUORINE GAS**

ANODE FÜR ELEKTROLYTISCHE SYNTHESE UND VERFAHREN ZUR HERSTELLUNG VON FLUORGAS

ANODE DE SYNTHÈSE ÉLECTROLYTIQUE ET PROCÉDÉ DE PRODUCTION DE GAZ FLUORÉ

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Description

Technical Field

- 5 **[0001]** The present invention relates to an anode for electrolytically synthesizing fluorine gas and a method for electrolytically synthesizing fluorine gas.

Background Art

- 10 **[0002]** Fluorine gas and a fluorine containing compound (for example, nitrogen trifluoride) can be synthesized by electrolyzing (electrolytic synthesis) an electrolytic solution containing fluoride ions. In the electrolytic synthesis, a carbon electrode has been generally used as an anode. However, the use of the carbon electrode has posed a problem that a voltage of an electrolytic cell required to obtain a predetermined current becomes a high voltage exceeding 12 V even when electrolyzed with an extremely low current density in some cases. This phenomenon is referred to as an anode effect.

- 15 **[0003]** A cause of the occurrence of the anode effect is as follows. When the electrolytic solution is electrolyzed, fluorine gas generated on the surface of the anode reacts with the carbon forming the anode, and therefore a coating film having a covalently bonded carbon-fluorine bond is formed on the surface of the anode. The coating film have insulation properties and poor wettability with the electrolytic solution, and therefore a current is difficult to flow to the anode, so that the anode effect occurs. Then, when the anode effect progresses, continuous electrolysis becomes impossible in some cases. In order to enable the use of the anode whose surface is coated with the insulating coating film for the electrolytic synthesis, it is necessary to polish the surface to remove the coating film.

[0004] Meanwhile, the use of a metal electrode as the anode has posed a problem that the metal electrode is dissolved or a problem that, due to the formation of an insulating coating film containing oxide or fluoride on the surface of the metal electrode, a current is difficult to flow, so that the power consumption increases in some cases.

- 25 **[0005]** Further, when an electrode obtained by coating a metal substrate with a conductive carbonaceous coating film having a diamond structure (for example, see PTL 1) is used as the anode, electrolytic resistance is suppressed, so that the power consumption can be suppressed in some cases. However, it was impossible to say that the effect is sufficient.

[0006] JP 2008 045205 A, JP 2006 249557 A, JP 2015 178668 A, JP S62 240778 A, US 2005/227078 A1, and RU 2 048 600 C1 disclose anodes that are suitable for electrolytically synthesizing fluorine gas.

Citation List

Patent Literature

- 35 **[0007]** PTL 1: JP 2011-46994 A

Summary of Invention

Technical Problem

- 40 **[0008]** It is an object of the present invention to provide an anode for electrolytic synthesis and an electrolytic synthesis method capable of electrolytically synthesizing fluorine gas with a low power consumption while suppressing electrolytic resistance.

- 45 **Solution to Problem**

[0009] The present invention is defined in the appended claims.

Advantageous Effects of Invention

- 50 **[0010]** The present invention can electrolytically synthesize fluorine gas with a low power consumption while suppressing electrolytic resistance.

Brief Description of Drawings

- 55 **[0011]**

FIG. 1 is a cross-sectional view for explaining the structure of an electrolytic device including an anode for electrolytic

synthesis according to one embodiment of the present invention;

FIG. 2 is a cross-sectional view illustrating the electrolytic device of FIG. 1 virtually cut along a plane different from the plane in FIG. 1;

FIG. 3 is a cross-sectional view illustrating an example of the anode for electrolytic synthesis; and

FIG. 4 is a cross-sectional view illustrating another example of the anode for electrolytic synthesis.

Description of Embodiments

[0012] One embodiment of the present invention will now be described below.

[0013] The structure of an electrolytic device including an anode for electrolytic synthesis according to this embodiment is described referring to FIG. 1 and FIG. 2. FIG. 1 is a cross-sectional view illustrating an electrolytic device virtually cut along a plane orthogonal to and parallel in the vertical direction to the plate surfaces of an anode for electrolytic synthesis 3 and cathodes for electrolytic synthesis 5 of the electrolytic device. FIG. 2 is a cross-sectional view illustrating the electrolytic device virtually cut along a plane parallel to and parallel in the vertical direction to the plate surfaces of the anode for electrolytic synthesis 3 and the cathodes for electrolytic synthesis 5 of the electrolytic device.

[0014] The electrolytic device illustrated in FIGS. 1, 2 includes an electrolytic cell 1 in which an electrolytic solution 10 is stored and the anode for electrolytic synthesis 3 and the cathodes for electrolytic synthesis 5 arranged in the electrolytic cell 1 and immersed in the electrolytic solution 10. The inside of the electrolytic cell 1 is partitioned into an anode chamber 12 and a cathode chamber 14 by a cylindrical partition 7 extending downward in the vertical direction from a lid 1a of the electrolytic cell 1. More specifically, an inner region surrounded by the cylindrical partition 7 is the anode chamber 12 and a region outside the cylindrical partition 7 is the cathode chamber 14.

[0015] The anode for electrolytic synthesis 3 is not limited in shape and may have a columnar shape and, in this example, has a plate shape. The anode for electrolytic synthesis 3 is arranged in the anode chamber 12 such that the plate surfaces thereof are parallel to each other in the vertical direction. The cathodes for electrolytic synthesis 5 have a plate shape and are arranged in the cathode chamber 14 such that the plate surfaces thereof are parallel to the plate surfaces of the anode for electrolytic synthesis 3 and the two cathodes for electrolytic synthesis 5, 5 interpose the anode for electrolytic synthesis 3 therebetween.

[0016] Further, on the plate surfaces opposite to the plate surfaces facing the anode for electrolytic synthesis 3 among both the front and rear plate surfaces of the cathodes for electrolytic synthesis 5, 5, cooling units for cooling the cathodes for electrolytic synthesis 5, 5 and the electrolytic solution 10 are mounted. In the example of the electrolytic device illustrated in FIGS. 1, 2, a cooling pipe 16 in which a cooling fluid flows is mounted as the cooling unit on each of the cathodes for electrolytic synthesis 5, 5.

[0017] As the anode for electrolytic synthesis 3, an electrode having the following configuration is usable. More specifically, the anode for electrolytic synthesis 3 is an electrode including an anode substrate 31 formed of a metallic material and a carbonaceous layer 33 formed of a carbonaceous material and arranged on the surface of the anode substrate 31 as illustrated in FIG. 3. The metallic material forming the anode substrate 31 is an iron-based alloy containing iron and nickel. The iron-based alloy may be an alloy containing iron, nickel, and inevitable impurities or may be an alloy containing iron, nickel, and the other alloy components. The iron-based alloy in the present invention means an alloy containing iron as a main component, i.e., an alloy in which the content of iron among alloy components is the highest.

[0018] The electrical resistance of metal is far lower than the electrical resistance of carbon and is one several tenths to one several hundredths of the electrical resistance of carbon. Therefore, when a metal substrate is adopted as a substrate of the anode for electrolytic synthesis 3 (anode substrate 31), electrolytic resistance in electrolytic synthesis can be made low. When an iron-based alloy having a specific alloy composition is used for the metallic material forming the anode substrate 31, the electrolytic resistance of the carbonaceous layer 33 arranged on the surface of the anode substrate 31 can be suppressed to a low level. Hence, when the anode for electrolytic synthesis 3 of this embodiment is used, fluorine gas can be electrolytically synthesized with a low power consumption while suppressing the electrolytic resistance.

[0019] When electrolytic synthesis is performed using a carbon electrode as the anode in an electrolytic solution containing fluoride ions, the carbon electrode is gradually broken and the bath voltage gradually increases and, due to an increase in the voltage, the breakage of the carbon electrode is further induced. Therefore, when the carbon electrode is broken to some extent, it is necessary to interrupt the electrolytic synthesis once and replace the carbon electrode. Further, the carbon electrode used once cannot be coated with a diamond coating film, and therefore there is no other choice but to discard the used carbon electrode.

[0020] In contrast thereto, the anode for electrolytic synthesis 3 of this embodiment is hard to cause the breakage by electrolysis, and therefore can perform stable electrolytic synthesis. Hence, there is almost no necessity of performing maintenance of the electrolytic cell, such as interrupting electrolytic synthesis and replacing the anode, and thus the maintenance frequency can be sharply reduced. Further, even in a case of the anode used once, a carbonaceous layer can be formed on the surface. Therefore, insofar as the anode substrate does not disappear, the anode can be continuously used by forming the carbonaceous layer on the surface.

[0021] Further, fluorine containing compounds, such as uranium hexafluoride (UF_6), sulfur hexafluoride (SF_6), carbon tetrafluoride (CF_4), and nitrogen trifluoride, can also be chemically synthesized using the electrolytically synthesized fluorine gas as a starting material (not according to the invention). The fluorine gas or the fluorine containing compounds, such as uranium hexafluoride, sulfur hexafluoride, carbon tetrafluoride, and nitrogen trifluoride, are useful in the nuclear industry field, the semiconductor industry field, the pharmaceutical and agrochemical field, the consumer product field, and the like.

[0022] The carbonaceous material forming the carbonaceous layer 33 is not particularly limited insofar as the material contains carbon. Examples of the carbon contained in the carbonaceous layer 33 include crystalline carbon, such as diamond and graphite, amorphous carbon, such as carbon black, carbon nanotube, graphene, diamond-like carbon, and the like.

[0023] Further, the carbonaceous material forming the carbonaceous layer 33 may be a material containing only carbon or may be a material containing a mixture of carbon and other components (for example, mixture of carbon and metal or a mixture of carbon and ceramic). When the carbonaceous material is the mixture of carbon and metal, the metal may be metal (iron, nickel, cobalt, and the like) contained in the metallic material forming the anode substrate 31.

[0024] When the carbonaceous material is the mixture of carbon and other components, the carbon content in the carbonaceous material is preferably higher than the carbon content in the metallic material forming the anode substrate 31 and less than 100 mass%. For example, when the metallic material forming the anode substrate 31 does not contain carbon, the carbon content in the carbonaceous material is preferably more than 0 mass% and less than 100 mass%. When the metallic material forming the anode substrate 31 contains 1.5 mass% of carbon, the carbon content in the carbonaceous material is preferably more than 1.5 mass% and less than 100 mass%.

[0025] The nickel content in the iron-based alloy containing iron and nickel is not particularly limited and is set to 32 mass% or more and 40 mass% or less and preferably set to 34 mass% or more and 38 mass% or less in order to suppress the electrolytic resistance of the carbonaceous layer 33 to a lower level.

[0026] As the metallic material forming the anode substrate 31, an iron-based alloy containing iron, nickel, and cobalt is also usable. The iron-based alloy may be an alloy containing iron, nickel, cobalt, and inevitable impurities or may be an alloy containing iron, nickel, cobalt, and the other alloy components.

[0027] Although the nickel content in the iron-based alloy containing iron, nickel, and cobalt is not particularly limited and is set to 30 mass% or more and 38 mass% or less and preferably set to 31 mass% or more and 35 mass% or less in order to suppress the electrolytic resistance of the carbonaceous layer 33 to a lower level. The cobalt content in the iron-based alloy containing iron, nickel, and cobalt is not particularly limited and is set to 3 mass% or more and 12 mass% or less and preferably set to 4 mass% or more and 7 mass% or less in order to suppress the electrolytic resistance of the carbonaceous layer 33 to a lower level.

[0028] Further, as the metallic material forming the anode substrate 31, an iron-based alloy containing iron, nickel, cobalt, and carbon is also usable. The iron-based alloy may be an alloy containing iron, nickel, cobalt, carbon, and inevitable impurities or may be an alloy containing iron, nickel, cobalt, carbon, and the other alloy components.

[0029] The nickel content in the iron-based alloy containing iron, nickel, cobalt, and carbon is not particularly limited and is set to 20 mass% or more and 36 mass% or less and preferably set to 21 mass% or more and 28 mass% or less in order to suppress the electrolytic resistance of the carbonaceous layer 33 to a lower level.

[0030] The cobalt content in the iron-based alloy containing iron, nickel, cobalt, and carbon is not particularly limited and is set to 3 mass% or more and 20 mass% or less and preferably set to 6 mass% or more and 16 mass% or less in order to suppress the electrolytic resistance of the carbonaceous layer 33 to a lower level.

[0031] The carbon content in the iron-based alloy containing iron, nickel, cobalt, and carbon is not particularly limited and is set to 0.01 mass% or more and 1.5 mass% or less and preferably set to 0.5 mass% or more and 1.0 mass% or less in order to suppress the electrolytic resistance of the carbonaceous layer 33 to a lower level.

[0032] The carbonaceous layer 33 may have a single layer structure illustrated in FIG. 3 or may have a double layer structure illustrated in FIG. 4. More specifically, the carbonaceous layer 33 may contain an inner layer 331 in contact with the anode substrate 31 and an outer layer 332 outside the inner layer 331. Herein, the inner layer 331 is a layer in which at least one of metals (iron, nickel, cobalt, and the like) constituting the iron-based alloy forming the anode substrate 31 and carbon coexist and the outer layer 332 is a layer formed of carbon.

[0033] The inner layer 331 contains metal and carbon constituting the iron-based alloy forming the anode substrate 31 as described above. The carbon content in the inner layer 331 is preferably higher than the carbon content in the metallic material forming the anode substrate 31 and less than 100 mass%. For example, when the metallic material forming the anode substrate 31 does not contain carbon, the carbon content in the inner layer 331 is preferably more than 0 mass% and less than 100 mass%. When the metallic material forming the anode substrate 31 contains 1.5 mass% of carbon, the carbon content in the inner layer 331 is preferably more than 1.5 mass% and less than 100 mass%.

[0034] A method for forming the carbonaceous layer 33 on the surface of the anode substrate 31 is not particularly limited. In a case of the carbonaceous layer 33 having the single layer structure illustrated in FIG. 3, a method including forming the carbonaceous layer 33 on the surface of the anode substrate 31 and a method including modifying a top layer

portion of the anode substrate 31 and forming the carbonaceous layer 33 are mentioned. Examples of the film formation method include, for example, vacuum deposition methods typified by a resistance heating deposition method and an electron beam deposition method and dry film formation methods, such as a sputtering method, an ion plating method, a hot filament chemical vapor deposition (CVD) method, a microwave plasma CVD method, a plasma arc jet CVD method, and a plasma ion implantation method. It is preferable to form the carbonaceous layer 33 under a condition where the temperature of the anode substrate 31 is a temperature lower than 450°C. Examples of the modification method include an ion implantation method using hydrocarbon-based gas or the like, for example.

[0035] Further, in the case of the carbonaceous layer 33 having the double layer structure illustrated in FIG. 4, a method including continuously forming the inner layer 331 and the outer layer 332 of the carbonaceous layer 33 on the surface of the anode substrate 31 and a method including modifying the top layer portion of the anode substrate 31, forming the inner layer 331, and then forming the outer layer 332 on the inner layer 331 are mentioned.

[0036] When the inner layer 331 and the outer layer 332 of the carbonaceous layer 33 are continuously formed on the surface of the anode substrate 31, a method can be adopted, for example, which includes forming the inner layer 331 on the surface of the anode substrate 31 while continuously changing the composition ratio of metal and carbon using the dry film formation methods described above, and then forming the outer layer 332 on the inner layer 331. When the top layer portion of the anode substrate 31 is modified, the inner layer 331 is formed, and then the outer layer 332 is formed on the inner layer 331, a method can be adopted, for example, which includes implanting carbon ions into the top layer portion of the anode substrate 31 by the ion implantation method using hydrocarbon-based gas or the like to modify the top layer portion, forming the inner layer 331 in which the composition ratio of metal and carbon continuously changes, and then forming the outer layer 332 on the inner layer 331 by the dry film formation methods described above.

[0037] As the cathodes for electrolytic synthesis 5, a metal electrode is usable and an electrode containing iron is usable, for example.

[0038] As the electrolytic solution 10, a molten salt is usable and, for example, molten potassium fluoride (KF) containing hydrogen fluoride (HF) is usable.

[0039] When a current with a current density of 0.01 A/cm² or more and 1 A/cm² or less, for example, is supplied between the anode for electrolytic synthesis 3 and the cathodes for electrolytic synthesis 5, anode gas containing fluorine gas (F₂) as a main component is generated in the anode for electrolytic synthesis 3 and cathode gas containing hydrogen gas (H₂) as a main component is generated as a byproduct in the cathodes for electrolytic synthesis 5.

[0040] The anode gas is accumulated in space above the liquid level of the electrolytic solution 10 in the anode chamber 12. The cathode gas is accumulated in space above the liquid level of the electrolytic solution 10 in the cathode chamber 14. Since the space above the liquid level of the electrolytic solution 10 is partitioned by the partition 7 into space in the anode chamber 12 and space in the cathode chamber 14, the anode gas and the cathode gas are not mixed.

[0041] Meanwhile, in the electrolytic solution 10, while an upper portion relative to the lower end of the partition 7 is partitioned by the partition 7, a lower portion relative to the lower end of the partition 7 of the electrolytic solution 10 is not partitioned by the partition 7 and continuous.

[0042] Further, the anode chamber 12 is provided with an exhaust port 21 discharging the anode gas generated in the anode for electrolytic synthesis 3 from the inside of the anode chamber 12 to the outside of the electrolytic cell 1. The cathode chamber 14 is provided with an exhaust port 23 discharging the cathode gas generated in the cathodes for electrolytic synthesis 5, 5 from the inside of the cathode chamber 14 to the outside of the electrolytic cell 1.

[0043] Hereinafter, the anode for electrolytic synthesis according to this embodiment and the method for electrolytically synthesizing fluorine gas or a fluorine containing compound (the latter being not according to the invention) using the same are described in detail.

(1) Electrolytic cell

[0044] Although a material of an electrolytic cell performing electrolytic synthesis is not particularly limited, it is preferable to use copper, soft steel, Monel (Trademark), nickel alloy, fluororesin, and the like from the viewpoint of corrosion resistance.

[0045] In order to prevent the mixing of fluorine gas or a fluorine containing compound electrolytically synthesized by an anode for electrolytic synthesis and hydrogen gas generated in a cathode for electrolytic synthesis, an anode chamber where the anode for electrolytic synthesis is arranged and a cathode chamber where the cathode for electrolytic synthesis is arranged is entirely or partially partitioned by a partition, a diaphragm, or the like as in the electrolytic device illustrated in FIGS. 1, 2.

(2) Electrolytic solution

[0046] An example of an electrolytic solution used when the fluorine gas is electrolytically synthesized is described. When the fluorine gas is electrolytically synthesized, a mixed molten salt of hydrogen fluoride and potassium fluoride is

usable as the electrolytic solution. The molar ratio of the hydrogen fluoride and the potassium fluoride in this electrolytic solution can be set to 1.5 to 2.5:1, for example.

[0047] Alternatively, a mixed molten salt of hydrogen fluoride and cesium fluoride (CsF) and a mixed molten salt of hydrogen fluoride, potassium fluoride, and cesium fluoride are also usable as the electrolytic solution. The composition ratio of the electrolytic solution containing cesium fluoride may be set as follows. More specifically, the molar ratio of the cesium fluoride and the hydrogen fluoride in the electrolytic solution may be set to 1:1.0 to 4.0. The molar ratio of the cesium fluoride, the hydrogen fluoride, and the potassium fluoride in the electrolytic solution may be set to 1:1.5 to 4.0:0.01 to 1.0.

[0048] Next, an example of an electrolytic solution used when the fluorine containing compound is electrolytically synthesized is described. When the fluorine containing compound is electrolytically synthesized, a mixed molten salt of a compound having a chemical structure before fluorination of a fluorine containing compound to be synthesized, hydrogen fluoride, and potassium fluoride is usable as the electrolytic solution. The electrolytic synthesis may be performed by forming the compound having the chemical structure before fluorination into a gaseous state, and then blowing the compound formed into the gaseous state into a mixed molten salt of hydrogen fluoride and potassium fluoride or the electrolytic synthesis may be performed using an electrolytic solution in which the compound having the chemical structure before fluorination is dissolved into a mixed molten salt of hydrogen fluoride and potassium fluoride. The compound having the chemical structure before fluorination reacts with fluorine gas generated in a reaction in the anode for electrolytic synthesis to be a fluorine containing compound.

[0049] For example, when nitrogen trifluoride is electrolytically synthesized, a mixed molten salt of hydrogen fluoride and ammonium fluoride (NH_4F) or a mixed molten salt of hydrogen fluoride, potassium fluoride, and ammonium fluoride is usable as the electrolytic solution.

[0050] In the case of the mixed molten salt of hydrogen fluoride and ammonium fluoride, the molar ratio of the hydrogen fluoride and the ammonium fluoride in the electrolytic solution can be set to 1.5 to 2.5:1, for example.

[0051] The hydrogen fluoride generally contains moisture in a proportion of 0.1 mass% or more and 5 mass% or less. When the moisture contained in the hydrogen fluoride exceeds 3 mass%, the hydrogen fluoride may be used for the electrolytic solution after the moisture contained in the hydrogen fluoride is reduced to 3 mass% or less by a method described in JP 7-2515 A, for example. In general, it is difficult to simply reduce the moisture amount in the hydrogen fluoride. Therefore, when fluorine gas or a fluorine containing compound is electrolytically synthesized in an industrial manner, it is preferable to use hydrogen fluoride having a moisture content of 3 mass% or less from the viewpoint of cost.

(3) Anode for electrolytic synthesis

[0052] The shape of the anode for electrolytic synthesis is not particularly limited and can be freely selected from a plate shape, a mesh shape, a punching plate shape, a rounded plate-like shape, a shape by which generated bubbles are guided to the rear surface of an electrode, a three-dimensional structure considering the circulation of an electrolytic solution, and the like because the anode substrate is formed of a metallic material.

(4) Cathode for electrolytic synthesis

[0053] As described above, a metal electrode is usable as the cathode for electrolytic synthesis. Examples of the types of the metal forming the metal electrode include iron, copper, nickel, and Monel (Trademark), for example. The shape of the cathode for electrolytic synthesis is the same as the shape of the anode for electrolytic synthesis.

EXAMPLES

[0054] Hereinafter, the present invention is more specifically described by giving Examples and Comparative Examples.

[Comparative Example 1]

[0055] Granular graphite "SIGRAFINE (Registered Trademark) ABR" manufactured by SGL Carbon was processed into a plate 2 cm in length, 1 cm in width, and 0.5 cm in thickness, a metal bar for power supply was attached thereto, and then masking was applied such that the electrode surface was formed into a rectangular shape 1 cm in length and 1 cm in width to be used as an electrode.

[0056] An electrolytic device having a similar configuration to that of the electrolytic device illustrated in FIGS. 1, 2 was produced using the electrode as an anode and using a Monel (trademark) plate as a cathode. As a reference electrode, a corrosion potential of nickel was used. As an electrolytic solution, a mixed molten salt ($\text{KF} \cdot 2\text{HF}$) of potassium fluoride and hydrogen fluoride was used.

[0057] Constant voltage electrolysis was performed such that the potential of the anode was constant at 6 V based on the corrosion potential of nickel to electrolytically synthesize fluorine gas. The current at this time was 0.148 A and the apparent

current density was 0.148 A/cm^2 . Hence, the electrolytic resistance of the anode was $40.5 \text{ } \Omega$ ($= 6/0.148$).

[Comparative Example 2]

[0058] Electrolytic synthesis was performed in the same manner as in Comparative Example 1, except forming a conductive diamond coating film by a thermal CVD method on the surface of the anode. The current at this time was 0.260 A and the apparent current density was 0.260 A/cm^2 . Hence, the electrolytic resistance of the anode was $23.1 \text{ } \Omega$ ($= 6/0.260$).

[Comparative Example 3]

[0059] Electrolytic synthesis was performed in the same manner as in Comparative Example 2, except performing constant current electrolysis instead of the constant voltage electrolysis. The current was 0.148 A and the current density was 0.148 A/cm^2 . The voltage of the anode based on the reference electrode at this time was 5.23 V . Hence, the electrolytic resistance of the anode was $35.3 \text{ } \Omega$ ($= 5.23/0.148$).

[Example 1]

[0060] Electrolytic synthesis was performed in the same manner as in Comparative Example 1, except using the following electrode as the anode. The anode used in Example 1 includes an anode substrate formed of a metallic material and a carbonaceous layer formed of a carbonaceous material and arranged on the surface of the anode substrate. The metallic material forming the anode substrate was an iron-based alloy containing iron, nickel, and cobalt. The iron content was $63.5 \text{ mass\%}$, the nickel content was $31.5 \text{ mass\%}$, and the cobalt content was $5.0 \text{ mass\%}$. The dimension of the anode substrate is 2 cm in length, 1 cm in width, and 1 mm in thickness. Masking was applied such that the electrode surface was formed into a rectangular shape 1 cm in length and 1 cm in width.

[0061] The carbonaceous layer arranged on the surface of the anode substrate has a double layer structure containing an inner layer and an outer layer. The analysis using X-ray photoelectron spectroscopy (XPS) shows that the inner layer is a layer containing carbon and metal (iron, nickel, cobalt) and the outer layer is a diamond-like carbon layer substantially containing only carbon.

[0062] The inner layer is formed by implanting carbon ions into a top layer portion of the anode substrate by a plasma ion implantation method to modify the top layer portion. The outer layer is formed by laminating carbon on the inner layer by the plasma ion implantation method.

[0063] The current in the constant voltage electrolysis was 0.454 A and the apparent current density was 0.454 A/cm^2 . Hence, the electrolytic resistance of the anode was $13.2 \text{ } \Omega$ ($= 6/0.454$). A value of the electrolytic resistance of the anode is approximately half of that in Comparative Example 2, which shows that the electrolytic resistance of the anode dramatically decreases.

[Comparative Example 4]

[0064] Electrolytic synthesis was performed in the same manner as in 1, except using an anode substrate formed of nickel. The current at this time was 0.27 A and the apparent current density was 0.27 A/cm^2 . Hence, the electrolytic resistance of the anode was $22.2 \text{ } \Omega$ ($= 6/0.27$). Further, when the constant voltage electrolysis was continued, a current was gradually difficult to flow, so that the current decreased to 0.14 A and the electrolytic resistance of the anode increased to $42.9 \text{ } \Omega$ ($= 6/0.14$).

[Comparative Example 5]

[0065] Electrolytic synthesis was performed in the same manner as in 1, except using the anode substrate formed of iron. The current at this time was 0.24 A and the apparent current density was 0.24 A/cm^2 . Hence, the electrolytic resistance of the anode was $25.0 \text{ } \Omega$ ($= 6/0.24$). Further, when the constant voltage electrolysis was continued, a current was gradually difficult to flow, so that the current decreased to 0.14 A and the electrolytic resistance of the anode increased to $42.9 \text{ } \Omega$ ($= 6/0.14$).

[Example 2]

[0066] Electrolytic synthesis was performed in the same manner as in 1, except performing constant current electrolysis instead of the constant voltage electrolysis. The current is 0.148 A and the current density is 0.148 A/cm^2 . The voltage of the anode based on the reference electrode at this time was 4.60 V . Hence, the electrolytic resistance of the anode was

31.1 Q (= 4.60/0.148). Since the power consumption is proportional to the voltage, the power consumption was reduced by 20% or more ($100 - 4.6/6 \times 100$) as compared with that in Comparative Example 1.

[0067] The constant current electrolysis was performed at the same current for further 500 hours while supplying hydrogen fluoride. As a result, the voltage did not change, the current efficiency of the generation of fluorine gas was 99%, and no deteriorations were observed on the surface of the anode after the completion of the electrolysis.

[Example 3]

[0068] Electrolytic synthesis was performed in the same manner as in Example 1, except that the metallic material forming the anode substrate was an iron-based alloy containing iron, nickel, and cobalt, the iron content was 61.8 mass%, the nickel content was 32.0 mass%, and the cobalt content was 6.2 mass%. The current at this time was 0.472 A and the apparent current density was 0.472 A/cm². Hence, the electrolytic resistance of the anode was 12.7 Ω (= 6/0.472).

[Example 4]

[0069] Electrolytic synthesis was performed in the same manner as in Example 1, except that the metallic material forming the anode substrate was an iron-based alloy containing iron, nickel, and cobalt, the iron content was 52.0 mass%, the nickel content was 38.0 mass%, and the cobalt content was 10.0 mass%. The current at this time was 0.411 A and the apparent current density was 0.411 A/cm². Hence, the electrolytic resistance of the anode was 14.6 Ω (= 6/0.411).

[Example 5]

[0070] Electrolytic synthesis was performed in the same manner as in Example 1, except that the metallic material forming the anode substrate was an iron-based alloy containing iron and nickel, the iron content was 65.0 mass%, and the nickel content was 35.0 mass%. The current at this time was 0.373 A and the apparent current density was 0.373 A/cm². Hence, the electrolytic resistance of the anode was 16.1 Ω (= 6/0.373).

[Example 6]

[0071] Electrolytic synthesis was performed in the same manner as in Example 1, except that the metallic material forming the anode substrate was an iron-based alloy containing iron, nickel, cobalt, and carbon, the iron content was 61.2 mass%, the nickel content was 30.0 mass%, the cobalt content was 8.0 mass%, and the carbon content was 0.8 mass%. The current at this time was 0.448 A and the apparent current density was 0.448 A/cm². Hence, the electrolytic resistance of the anode was 13.4 Q (= 6/0.448).

[Example 7]

[0072] Electrolytic synthesis was performed in the same manner as in 1, except that the carbonaceous layer arranged on the surface of the anode substrate was a diamond-like carbon layer having a single layer structure formed by a plasma CVD method. The current at this time was 0.432 A and the apparent current density was 0.432 A/cm². Hence, the electrolytic resistance of the anode was 13.9 Ω (= 6/0.432).

[Table 1]

	Anode	In 6 V constant voltage electrolysis		In 0.148 A constant current electrolysis	
		Current (A)	Resistance (Ω)	Voltage (V)	Resistance (Ω)
Comp. Ex. 1	SGL carbon	0.148	40.5		
Comp. Ex. 2	SGL carbon + Conductive diamond coating film	0.260	23.1		
Comp. Ex. 3	SGL carbon + Conductive diamond coating film			5.23	35.3
Ex. 1	Fe-63.5/Ni-31.5/Co-5.0	0.454	13.2		

(continued)

5	Anode	In 6 V constant voltage electrolysis		In 0.148 A constant current electrolysis	
		Current (A)	Resistance (Ω)	Voltage (V)	Resistance (Ω)
	Comp. Ex. 4	Ni	0.27→0.14	22.2→42.9	
10	Comp. Ex. 5	Fe	0.24→0.14	25.0→42.9	
	Ex. 2	Fe-63.5/Ni-31.5/Co-5.0		4.60	31.1
	Ex. 3	Fe-61.8/Ni-32.0/Co-6.2	0.472	12.7	
15	Ex. 4	Fe-52.0/Ni-38.0/Co-10.0	0.411	14.6	
	Ex. 5	Fe-65.0/Ni-35.0	0.373	16.1	
	Ex. 6	Fe-61.2/Ni-30.0/Co-8/C-0.8	0.448	13.4	
20	Ex. 7	Fe-63.5/Ni-31.5/Co-5.0 (single-layered carbonaceous layer)	0.432	13.9	

[0073] As is understood from Table 1, Examples 1 to 7 used the anodes in which the anode substrate was formed of the iron-based alloy containing iron and nickel and the carbonaceous layer was provided on the surface of the anode substrate, and therefore were able to stably reduce the resistance in the constant voltage electrolysis as compared with Comparative Examples 1, 2 using the carbon anodes and Comparative Examples 4, 5 using the metal anodes. Further, it was found that, when the anode substrate was formed of the iron-based alloy containing iron, nickel, and cobalt, the resistance in the constant current electrolysis can also be reduced as compared with Comparative Example 3 using the carbon anode.

Reference Signs List

[0074]

- 1 electrolytic cell
- 3 anode for electrolytic synthesis
- 5 cathode for electrolytic synthesis
- 10 electrolytic solution
- 31 anode substrate
- 33 carbonaceous layer
- 331 inner layer
- 332 outer layer

Claims

1. An anode for electrolytic synthesis for electrolytically synthesizing fluorine gas comprising:

an anode substrate formed of a metallic material; and
a carbonaceous layer formed of a carbonaceous material and arranged on a surface of the anode substrate,
wherein
the metallic material is an iron-based alloy containing iron and nickel,
wherein the iron-based alloy contains
32 mass% or more and 40 mass% or less of nickel; or
30 mass% or more and 38 mass% or less of nickel and 3 mass% or more and 12 mass% or less of cobalt; or
20 mass% or more and 36 mass% or less of nickel, 3 mass% or more and 20 mass% or less of cobalt, and 0.01
mass% or more and 1.5 mass% or less of carbon.

2. The anode for electrolytic synthesis according to Claim 1, wherein

the carbonaceous layer contains an inner layer in contact with the anode substrate and an outer layer outside the inner layer,
the inner layer is a layer in which at least one of metals constituting the iron-based alloy and carbon coexist, and the outer layer is a layer formed of carbon.

3. A method for producing fluorine gas comprising:
electrolyzing an electrolytic solution containing hydrogen fluoride to electrolytically synthesize fluorine gas using the anode for electrolytic synthesis according to Claim 1 or 2.

Patentansprüche

1. Anode für die elektrolytische Synthese zur elektrolytischen Synthese von Fluorgas, umfassend:

ein Anodensubstrat aus einem metallischen Material; und
eine aus einem kohlenstoffhaltigen Material gebildete und auf einer Oberfläche des Anodensubstrats angeordnete kohlenstoffhaltige Schicht,
wobei das metallische Material eine Eisen und Nickel enthaltende Eisenbasislegierung ist,
wobei die Eisenbasislegierung
32 Masse-% oder mehr und 40 Masse-% oder weniger Nickel; I oder
30 Masse-% oder mehr und 38 Masse-% oder weniger Nickel und 3 Masse-% oder mehr und 12 Masse-% oder weniger Kobalt; oder
20 Masse-% oder mehr und 36 Masse-% oder weniger Nickel, 3 Masse-% oder mehr und 20 Masse-% oder weniger Kobalt und 0,01 Masse-% oder mehr und 1,5 Masse-% oder weniger Kohlenstoff enthält.

2. Anode für die elektrolytische Synthese nach Anspruch 1, wobei die kohlenstoffhaltige Schicht eine innere Schicht, die in Kontakt mit dem Anodensubstrat steht, und eine äußere Schicht außerhalb der inneren Schicht, enthält,

die innere Schicht eine Schicht ist, in der mindestens eines der die Eisenbasislegierung bildenden Metalle und Kohlenstoff koexistieren und
die äußere Schicht ist eine Schicht aus Kohlenstoff ist.

3. Verfahren zur Herstellung von Fluorgas, umfassend:
Elektrolysieren einer Fluorwasserstoff enthaltenden Elektrolytlösung zur elektrolytischen Synthese von Fluorgas unter Verwendung der Anode für die elektrolytische Synthese nach Anspruch 1 oder 2.

Revendications

1. Anode de synthèse électrolytique pour synthétiser électrolytiquement un gaz fluoré comprenant :

un substrat d'anode formé d'un matériau métallique ; et
une couche carbonée formée d'un matériau carboné et agencée sur une surface du substrat d'anode, dans laquelle
le matériau métallique est un alliage à base de fer contenant du fer et du nickel,
dans laquelle l'alliage à base de fer contient
32 % en masse ou plus et 40 % en masse ou moins de nickel ; ou
30 % en masse ou plus et 38 % en masse ou moins de nickel et 3 % en masse ou plus et 12 % en masse ou moins de cobalt ; ou
20 % en masse ou plus et 36 % en masse ou moins de nickel, 3 % en masse ou plus et 20 % en masse ou moins de cobalt, et 0,01 % en masse ou plus et 1,5 % en masse ou moins de carbone.

2. Anode de synthèse électrolytique selon la revendication 1, dans laquelle

la couche carbonée contient une couche interne en contact avec le substrat d'anode et une couche externe à l'extérieur de la couche interne,
la couche interne est une couche dans laquelle au moins l'un des métaux constituant l'alliage à base de fer et du carbone coexistent, et

la couche externe est une couche formée de carbone.

3. Procédé de production de gaz fluoré comprenant :

l'électrolyse d'une solution électrolytique contenant du fluorure d'hydrogène pour synthétiser électrolytiquement un gaz fluoré en utilisant l'anode de synthèse électrolytique selon la revendication 1 ou 2.

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FIG. 1

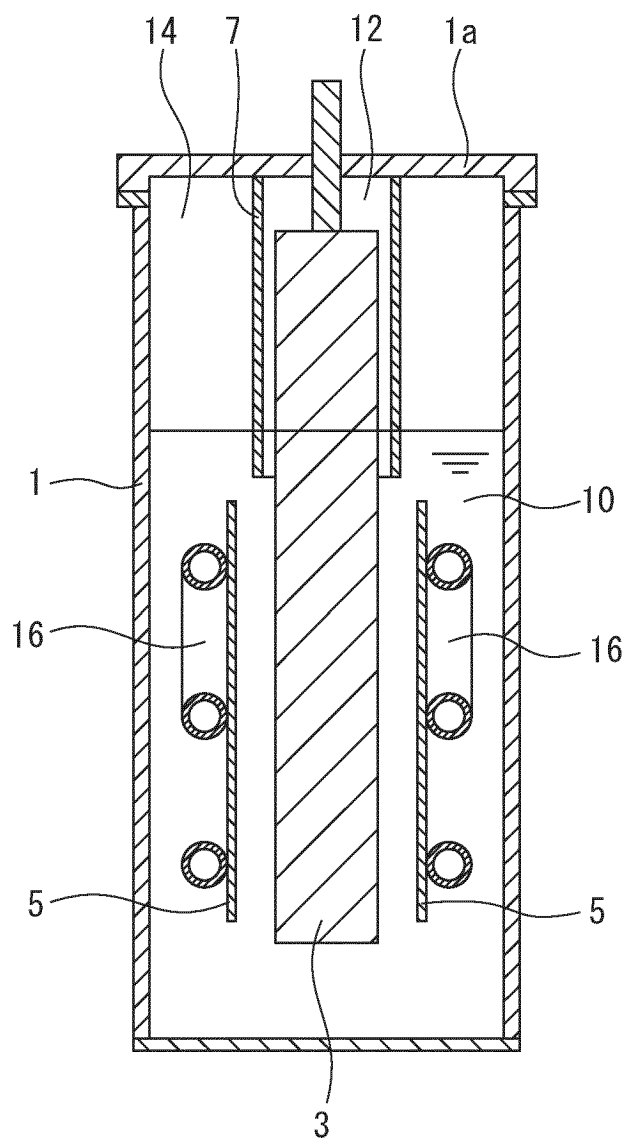


FIG. 2

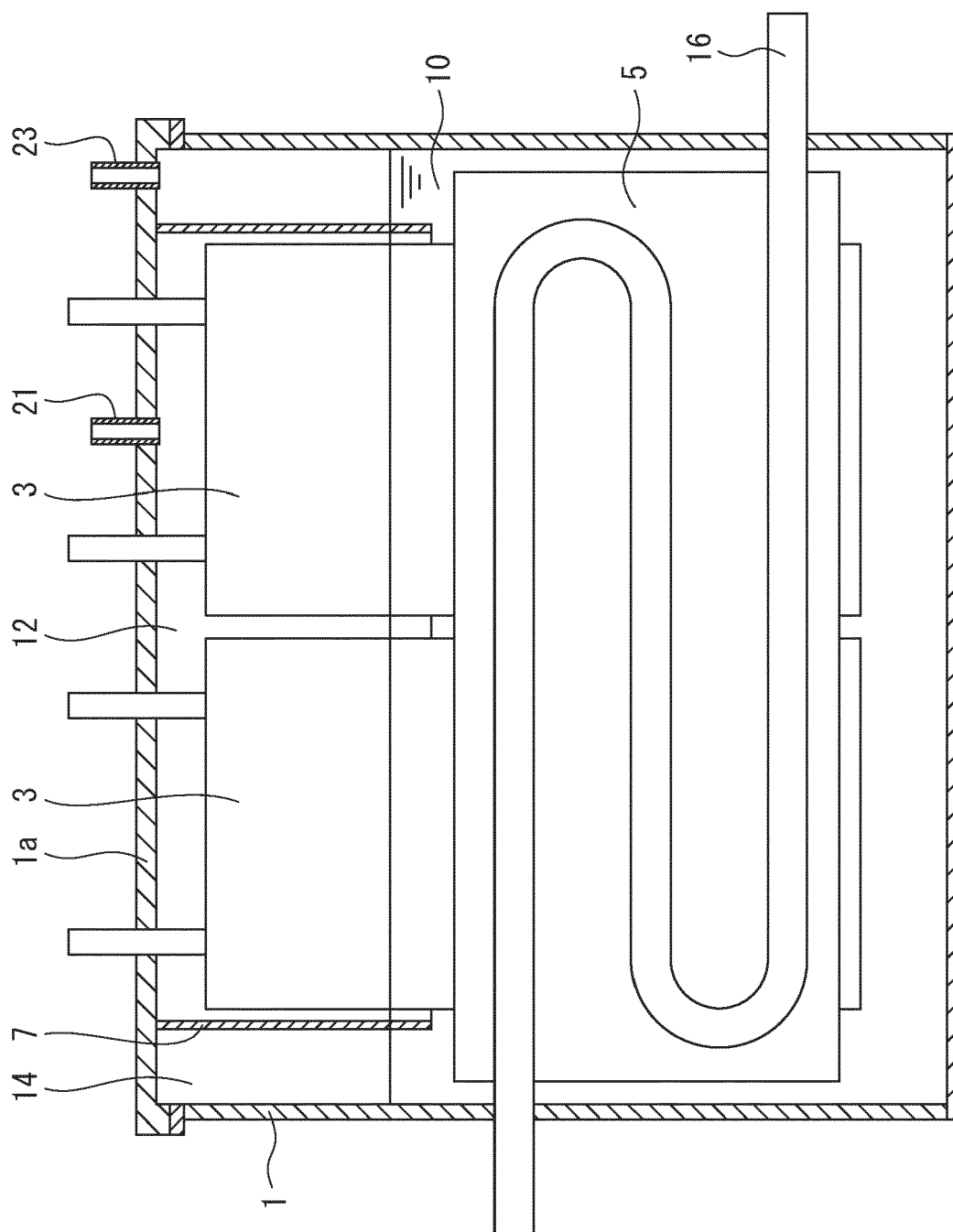


FIG. 3

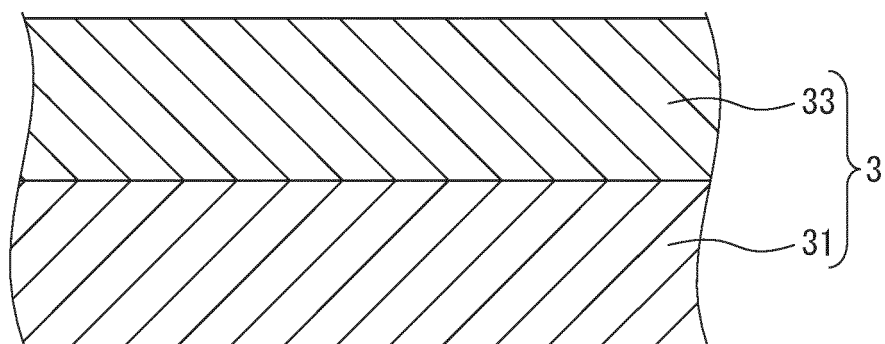
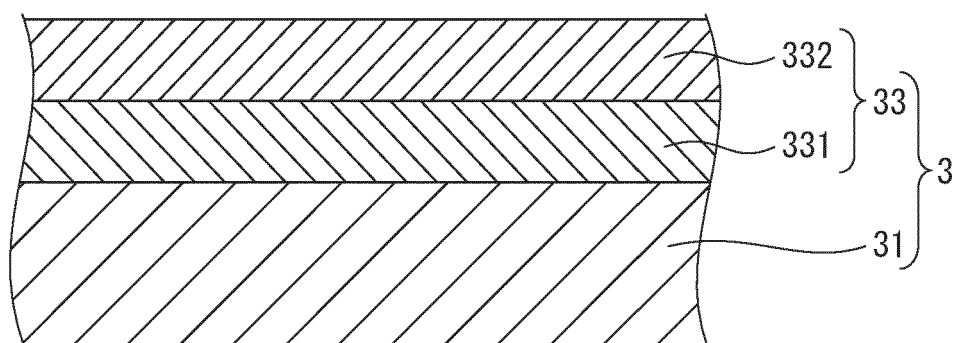


FIG. 4



REFERENCES CITED IN THE DESCRIPTION

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