**EUROPEAN PATENT APPLICATION**

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| Document number(s) of the earlier application(s) in accordance with Art. 76 EPC: | 10152341.3 / 2 213 770 |

| Applicant: | PERMELEC ELECTRODE LTD. Fujisawa-shi, Kanagawa 252-0816 (JP) |

| Inventors: | • Tasaka, Akimasa Kyoto-shi Kyoto, 610-1125 (JP) |

| Representative: | Grünecker, Kinkeldey, Stockmair & Schwanhäusser Anwaltssozietät Leopoldstrasse 4 80802 München (DE) |

Remarks:

This application was filed on 13-12-2012 as a divisional application to the application mentioned under INID code 62.

**Anode for electrolysis and method of electrolytically synthesizing fluorine-containing substance using the anode for electrolysis**

The present invention provides an electrode for electrolysis, wherein the electrode comprises: a substrate comprising an electrically conductive material, wherein the surface of the substrate is made of glassy carbon; and an electrically conductive diamond film with which at least part of the substrate is coated.
Description

TECHNICAL FIELD

[0001] The present invention relates to an anode material which, when used in applications such as electrolysis in an electrolytic bath containing hydrofluoric acid, does not produce the anode effect even upon application of a high-current-density voltage thereto and which is free from the serious sludge generation caused by electrode dissolution, can inhibit CF₄ generation, and enables the electrolysis to continue stably without suffering electrode disintegration. The invention further relates to a method of electrolysis.

BACKGROUND ART

[0002] An electrolytic process in which a solution prepared by dissolving an inorganic or organic compound in anhydrous hydrofluoric acid (anhydrous HF) is used as an electrolytic bath to electrolytically synthesize an inorganic fluorine compound, organic fluorine compound, or fluorine gas is in practical use.

[0003] Since anhydrous HF has insufficient electrical conductivity, an alkali metal fluoride such as, e.g., potassium fluoride (KF) or alkaline-earth-metal fluoride (hereinafter referred to as a conduction aid) is often added to the electrolytic bath when the system is intended to be operated at a high current density.

[0004] Fluorine gas (F₂), which is in wide use as a fluorinating agent in the synthesis of resins, synthesis of chemicals, synthesis of medicines, etc., is synthesized by electrolyzing a KF/HF electrolytic bath prepared by adding potassium fluoride (KF) as a conduction aid to HF. Nitrogen trifluoride gas (NF₃), which is in wide use as a dry etchant or cleaning gas in the field of, e.g., semiconductors, is synthesized by electrolyzing an NH₄F/HF electrolytic bath prepared by dissolving ammonia, as a substance to be fluorinated, in HF.

[0005] Furthermore, there is a process in which a solution prepared by dissolving an inorganic or organic compound, as a substance to be fluorinated, in anhydrous HF is used as an electrolytic bath and this electrolytic bath is electrolyzed at a voltage lower than voltages which result in fluorine gas generation, whereby a perfluoro compound is synthesized. This process is known as Simon's process.

[0006] In all these electrolytic processes, materials usable as electrolyzers and electrode materials are limited because of the marked corrosiveness of HF. In particular, the materials usable as anode materials are limited to nickel and carbon.

[0007] When nickel is used as an anode, wear of this anode is considerably accelerated. Carbon is hence frequently employed as anodes.

[0008] Advantages of carbon anodes include reduced susceptibility to the electrode wear occurring in nickel electrodes. However, carbon anodes often pose a problem that the phenomenon in which the electrode is passivated, i.e., the so-called anode effect, occurs to make it difficult to continue the electrolysis.

[0009] Anode reactions occurring when a carbon anode is used include a reaction generating fluorinated graphite, besides the discharge reaction of fluoride ions which is the desired reaction. On the other hand, the generated fluorinated graphite is partly decomposed either through pyrolysis due to the Joule's heat resulting from the electrode reaction or by a disproportionation reaction. The fluorinated graphite, which is a covalent compound, shows low wettability to the electrolytic bath. Because of this, when the rate of generating fluorinated graphite is higher than the rate of decomposing the fluorinated graphite, the electrode surface is coated with the fluorinated graphite to produce the anode effect. The rate of generating fluorinated graphite depends on current density and, hence, the anode effect becomes more apt to occur as current density increases.

[0010] In the case where water is present in an electrolytic bath, the decomposition reaction of water, which proceeds at a less potential than the discharge reaction of fluoride ions, occurs preferentially and at this time the reaction of the water with the carbon anode generates oxidized graphite. This oxidized graphite is chemically unstable and, hence, a substitution reaction with fluorine readily proceeds to generate fluorinated graphite. Consequently, the higher the water concentration in the electrolytic bath, the more the formation of fluorinated graphite is accelerated and the more the anode effect is apt to occur.

[0011] Accordingly, in order to inhibit the anode effect from occurring at a carbon anode, it is therefore necessary to minimize the water concentration in the electrolytic bath and to conduct electrolysis at a current density lower than the current density at which the anode effect begins to occur (critical current density). In actual industrial electrolysis, a complicated operation such as, e.g., dehydrating electrolysis, is performed for the former purpose, and a limited operating current density is used for the latter purpose. Because of these measures, the rate of generating a target substance is limited and this inhibits the profitability of electrolytic synthesis from improvement.

[0012] On the other hand, HF intercalates into the carbon electrode to expand the electrode and this expansion often causes the electrode to crack or disintegrate. For the purpose of preventing the infiltration of HF into the carbon electrode, techniques have been put to practical use such as, e.g., a technique in which the surface of an electrode is coated with nickel by thermal spraying or plating. However, no essential solution has been found because nickel itself is problematic as will be described later. A technique in which the concentration of a conduction aid, e.g., KF, in an electrolytic bath is increased to thereby lower the vapor pressure of HF is also applied. However, the increased concentration of a conduction aid elevates the melting point of the electrolytic bath and
hence necessitates a higher operating temperature. This technique therefore has limitations.

[0013] Nickel is widely used as the anode in electrolysis in an electrolytic bath prepared by adding a substance to be fluorinated, such as, e.g., ammonia, an alcohol, or an amine, to anhydrous HF. Although nickel anodes have the advantage of being free from the anode effect occurring in carbon anodes, wear of the nickel anodes proceeds during electrolysis.

[0014] Nickel anodes are worn in an amount corresponding to 3-5% of the quantity of electricity applied, and the cost of replacing the worn nickel anodes is almost comparable to the power cost for the electrolysis. In addition, nickel dissolves in the electrolytic bath to increase the viscosity of the electrolytic bath, making it difficult to control the temperature of the electrolytic bath. Therefore, periodic electrolytic-bath replacement also becomes necessary. As described above, anode replacement, electrolytic-bath replacement, and operation stops accompanying the replacement are indispensable to nickel anodes and are factors which inhibit the profitability of electrolytic synthesis from improvement.

[0015] Patent document 1 discloses: an electrode comprising a silicon substrate having a surface coated with a boron-doped diamond film; and a method of electrolytic fluorination in which the electrode is used. Patent document 2 discloses: an electrode comprising an electrically conductive carbon-material substrate having a surface coated with electrically conductive diamond; and a method of electrolytically synthesizing a fluorine-containing substance using the electrode.


SUMMARY OF THE INVENTION

TECHNICAL PROBLEMS

[0017] The present inventors diligently made investigations. As a result, they found that the invention described in patent document 1 has a problem that the silicon substrate is corroded by the HF present in the electrolytic bath and, hence, it is difficult to maintain the electrode structure. Moreover, they found that the invention described in patent document 2 has a problem that when the electrolytic bath has a high HF concentration, in particular, when the molar concentration of HF in the electrolytic bath is not lower than 3 times the molar concentration of a substance to be fluorinated or of a conduction aid, then HF infiltration into the carbon substrate occurs to disintegrate the carbon substrate.

[0018] As described above, an electrode which is free from the anode effect and disintegration occurring in carbon electrodes is free from the wear occurring in nickel electrodes is desired as an electrode for electrolysis in electrolytic baths containing HF.

SOLUTION TO THE PROBLEMS

[0019] The present invention provides an electrode for electrolysis which includes: a substrate comprising an electrically conductive material, wherein the surface of the substrate is made of glassy carbon; and an electrically conductive diamond film with which at least part of the substrate is coated. The invention further provides a method of electrolytically synthesizing fluorine or a fluorine-containing compound in an HF-containing electrolytic bath using the electrode.

[0020] That is, the present invention includes the following aspects in its broadest configurations:

(1) An electrode for electrolysis, which comprises:

- a substrate comprising an electrically conductive material, wherein the surface of the substrate is made of glassy carbon; and
- an electrically conductive diamond film with which at least part of the substrate is coated.

[0021] (2) A method of electrolytically synthesizing fluorine or a fluorine-containing compound, wherein the method comprises conducting electrolysis using the electrode for electrolysis according to the above (1) in an electrolytic bath comprising hydrofluoric acid and, added thereto, a substance to be fluorinated.

[0022] (3) The method of electrolytically synthesizing fluorine or a fluorine-containing compound according to the above (2), wherein the electrolytic bath further comprises a fluoride of an alkali metal or a fluoride of an alkaline earth metal (hereinafter referred to as a conduction aid).

[0023] (4) The method of electrolytically synthesizing fluorine or a fluorine-containing compound according to the above (2) or the above (3), wherein the electrolytic bath has a molar concentration of hydrofluoric acid which is at least 3 times the molar concentration of the substrate to be fluorinated or of the conduction aid in the electrolytic bath.

[0024] The invention will be explained below in detail. As a result of diligent investigations made by the present inventors, it has been found that an electrically conductive substrate the surface of which is made of glassy carbon and an electrode for electrolysis obtained by coating at least part of the conductive substrate with an electrically conductive diamond film undergo neither the anode effect nor electrode wear nor electrode disintegration in
and are electrodes capable of long-term continuous electrolysis.

[0025] Glassy carbon is a carbon material having a glassy appearance and produced from cellulose, a cellulosic resin, or a thermosetting resin, e.g., a furan resin, as a precursor, and by molding the precursor and then subjecting the molded precursor to solid-phase carbonization. Features thereof include high hardness, chemical stability, wear resistance, and impermeability to gases and liquids. Glassy carbon has a homogeneous amorphous structure with no crystal form. Although there are many voids in the structure, most of the voids are closed cells and, hence, there are almost no open cells. In the conductive-diamond electrode employing glassy carbon, which has such features, as a conductive substrate, HF is less apt to intercalate into inner parts of the substrate even in an electrolytic bath having a high HF concentration. This electrode hence does not suffer electrode expansion and succeeding electrode disintegration.

[0026] The glassy carbon is also called vitreous carbon. The glassy carbon used in the present invention is not particularly limited, but, for examples, GC series products manufactured by TOKAI CARBON CO., LTD., and SPI-Glas series products manufactured by SPI Supplies, can be exemplified. Especially, from the standpoint of low gas permeability, GC-10 (trade name, manufactured by TOKAI CARBON CO., LTD.) and SPI-Glas 10 (trade name, manufactured by SPI Supplies) are preferable. US patent 6,241,956 discloses a method for producing a glassy carbon, which is herein incorporated by reference.

[0027] Furthermore, the coating of the part of the surface of the substrate with electrically conductive diamond prevents the anode effect, which is attributable to the formation of fluorinated graphite, and electrode wear.

[0028] For example, perfluorotrimethylamine can be efficiently synthesized using an electrolytic bath having the composition (CH₃)₃NF·5HF. In the case of using a nickel electrode, it is necessary to add CsF·2HF for preventing the passivation trouble. However, even when CsF·2HF is added, electrode wear proceeds. In the case where carbon is used as an anode, the anode effect occurs and the infiltration of HF into the substrate occurs to cause electrode disintegration. In the case where a known electrode obtained by coating the surface of an electrically conductive carbon material substrate with electrically conductive diamond is used, HF infiltration into the substrate occurs to cause electrode disintegration.

[0029] In contrast, in the case where an electrode obtained by using a substrate comprising an electrically conductive material wherein the surface of the substrate is made of glassy carbon and coating at least part of the surface of the substrate with an electrically conductive diamond film is used, the anode effect, electrode wear, and electrode disintegration are prevented from occurring and long-term continuous electrolysis becomes possible.

ADVANTAGEOUS EFFECTS OF THE INVENTION

[0030] The invention provides an electrode which comprises a substrate comprising an electrically conductive material, wherein the surface of the substrate is made of glassy carbon, and an electrically conductive diamond film with which at least part of the surface is coated, and which is for use in, e.g., the synthesis of an inorganic fluorine compound, organic fluorine compound, and fluorine gas through the electrolysis of an electrolytic bath containing HF. The invention further provides a method of electrolytically synthesizing fluorine or a fluorine-containing compound using the electrode. The electrode and the synthesis method prevent the anode effect, electrode wear, and electrode disintegration from occurring even in an electrolytic bath having a high HF concentration, and render long-term continuous electrolysis possible. The productivity of inorganic fluorine compounds, organic fluorine compounds, and fluorine gas is improved.

DESCRIPTION OF EMBODIMENTS

[0031] The electrode for electrolysis of the invention is explained in detail. The conductive substrate of the electrode of the invention is not particularly limited in its shape so long as the substrate has a surface made of glassy carbon. Platy, rod, pipe, or spherical shape or the like can be used. The glassy carbon constituting the surface has a gas permeability of preferably 10⁻⁷ cm²/sec or lower, more preferably 10⁻¹⁰ cm²/sec or lower.

Examples of glassy carbon that satisfies the preferred gas permeability include GC-10 (trade name, manufactured by TOKAI CARBON CO., LTD.) and SPI-Glas 10 (trade name, manufactured by SPI Supplies) and SPI-Glas 20 (trade name, manufactured by SPI Supplies). Moreover, examples of glassy carbon that satisfies the more preferred gas permeability include GC-10 and SPI-Glas 10.

[0032] Methods for coating at least part of the surface of the conductive substrate with a conductive diamond film are not particularly limited, and any desired method can be used. Typical production processes include hot-filament CVD (chemical vapor deposition) process, microwave CVD process, the plasma-arc jet process, and physical vapor deposition (PVD) process. A suitable method can be selected from these.

[0033] Whichever method is employed for coating with a conductive diamond film, a mixed gas composed of hydrogen gas and a carbon source as a raw material for diamond is used. An element having a different valence (hereinafter referred to as dopant) is added to the mixed gas in a slight amount in order to impart electrical conductivity to the diamond. The dopant preferably is boron,
phosphorus, or nitrogen. The content of the dopant is preferably 1-100,000 ppm, more preferably 10-10,000 ppm as ratio of dopant atom to carbon atom. Whichever method for diamond film coating is used, the conductive diamond film deposited is polycrystalline, and amorphous carbon and a graphite ingredient remain in the diamond film.

From the standpoint of the stability of the diamond film, it is preferred that the content of the amorphous carbon and graphite ingredient should be lower. It is preferred that in Raman spectroscopy, the ratio I(D)/I(G), wherein I(D) is the intensity for a peak appearing around 1,332 cm\(^{-1}\) (in the range of 1,312-1,352 cm\(^{-1}\)), which is assigned to diamond, and I(G) is the intensity for a peak appearing around 1,560 cm\(^{-1}\) (in the range of 1,540-1,580 cm\(^{-1}\)), which is assigned to the G band of graphite, should be 1 or larger. Namely, it is preferred that the content of diamond should be higher than the content of graphite.

An explanation is given on hot-filament CVD, which is a typical process for coating with a conductive diamond film.

An organic compound serving as a carbon source, such as, e.g., methane, an alcohol, or acetone, and a dopant are fed to the filament together with hydrogen gas, etc. The filament is heated to a temperature at which hydrogen radicals or the like generates, i.e., 1,800-2,800°C, and an electrically conductive substrate is disposed in the atmosphere so as to have a temperature in a region where diamond deposition occurs (750-950°C). The rate of feeding the mixed gas depends on the size of the reaction vessel. However, it is preferred to use a pressure of 15-760 Torr.

It is preferred to grind the surface of the conductive substrate because the grinding improves adhesion between the substrate and the diamond layer. Preferably, the surface is ground so as to result in an arithmetic mean roughness Ra of 0.1-15 μm and a maximum height Rz of 1-100 μm. Applying a diamond powder as nuclei to the substrate surface is effective in growing an even diamond film. Usually, a layer of fine diamond particles having a diameter of 0.001-2 μm deposits on the substrate. Although the thickness of the diamond film can be regulated by changing deposition time, the thickness thereof preferably is 1-10 μm from the standpoint of profitability.

In the present invention, fluorine or a fluorine-containing compound is synthesized by an electrolytic synthesis method. The method is not particularly limited, but the method comprising conducting electrolysis using the electrode for electrolysis according to the present invention in an electrolytic bath comprising hydrofluoric acid and, added thereto, a substance to be fluorinated, is preferable. The electrolytic bath may further comprise a fluoride of an alkali metal or a fluoride of an alkaline earth metal. These fluorides (i.e., conduction aids) may be used alone or in combination of two or more thereof.

In the method of electrothetically synthesizing fluorine or a fluorine-containing compound according to the present invention, it becomes possible to adjust a molar concentration of hydrofluoric acid such that it is at least 3 times the molar concentration of the substance to be fluorinated or of the conduction aid in the electrolytic bath.

As the material of the electrolyzer, a soft steel, nickel alloy, fluororesin, or the like can be used from the standpoint of resistance to corrosion by HF. It is preferred to wholly or partly separate the anode side from the cathode side with a partition, diaphragm, or the like in order to prevent the F\(_2\) or fluorine compound synthesized at the anode from mingling with the hydrogen gas generated at the cathode.

A slight amount of HF accompanies the inorganic or organic fluorine compound or fluorine gas generated at the anode, and this HF can be removed by passing this product through a column packed with granular sodium fluoride. By-products such as nitrogen, oxygen, and dinitrogen monoxide also generate in slight amounts. Of these by-products, the dinitrogen monoxide can be removed by passing the product through water and sodium thiosulfate. The oxygen can be removed by activated carbon. Thus, an inorganic or organic fluorine compound or fluorine gas, having a low by-product content can be obtained.

**EXAMPLES**

The invention will be explained below in detail based on Examples. However, the invention should not be construed as being limited to the following Examples.

**EXAMPLE 1**

A glassy-carbon plate (GC-10, manufactured by TOKAI CARBON CO., LTD.) was used as a conductive substrate to produce a conductive-diamond electrode under the following conditions using a hot-filament CVD apparatus.

First, an abrasive material composed of diamond particles having a diameter of 1 μm was used to grind the surface of the substrate. The ground substrate surface had a Ra of 0.2 μm and a ten-point surface roughness Rz of 6 μm. Subsequently, diamond particles having an average particle diameter of 4 nm were applied as nuclei to the substrate surface. Thereafter, the substrate was attached to the hot-filament CVD apparatus. A mixed gas prepared by adding 1 vol% methane gas and 0.5 ppm trimethylboron gas to hydrogen gas was continuously passed through the apparatus at a rate of 5 L/min. While thus passing the mixed gas, the internal pressure of the apparatus was kept at 75 Torr and a voltage was applied to the filament to elevate the temperature thereof to 2,400°C. At this point of time, the substrate had a temperature of 860°C.

The CVD operation was continued for 8 hours. After completion of the CVD operation, the substrate was...
analyzed. It was ascertained through Raman spectroscopy and X-ray diffractometry that diamond had deposited. The ratio of a peak intensity at 1,332 cm\(^{-1}\) to a peak intensity at 1,560 cm\(^{-1}\) in Raman spectroscopy was 1/0.4. Moreover, part of this substrate was destroyed and examined with SEM. As a result, it was found to have a thickness of about 4 \(\mu m\).

[0045] The conductive-diamond electrode produced was attached as an anode in an anhydrous HF bath kept at 0°C. A nickel plate and platinum were used as a cathode and a reference electrode, respectively, and the anode was examined for current-potential curve by constant-current chronopotentiometry.

[0046] Immediately after initiation of the examination, the anode potential at a current density of 5 mA/cm\(^2\) was 0.6 V. Thereafter, the anode potential was measured while stepwise increasing the current density by 5 mA/cm\(^2\) at a time. As a result, the anode potential at a current density of 200 mA/cm\(^2\) was 3.2 V.

[0047] The electrolysis was stopped, and the anode was taken out and examined for appearance. As a result, neither electrode disintegration nor the shedding of the conductive diamond film was observed.

(COMPARATIVE EXAMPLE 1)

[0048] Electrolysis was conducted under the same conditions as in Example 1, except that a graphite plate was used as an anode. This anode was thus examined for current-potential curve in the anhydrous HF bath kept at 0°C.

[0049] Immediately after initiation of the examination, the anode potential at a current density of 5 mA/cm\(^2\) was 0.7 V. Thereafter, the anode potential was measured while stepwise increasing the current density by 5 mA/cm\(^2\) at a time. As a result, at a current density of 70 mA/cm\(^2\), the anode potential increased abruptly and almost no current came to flow, making it difficult to continue the electrolysis.

[0050] The electrolysis was stopped and the anode was taken out. As a result, the anode was found to have broken into powder in the electrolyzer.

(COMPARATIVE EXAMPLE 2)

[0051] Electrolysis was conducted under the same conditions as in Example 1, except that a nickel plate was used as an anode. This anode was thus examined for current-potential curve in the anhydrous HF bath kept at 0°C.

[0052] Immediately after initiation of the examination, the anode potential at a current density of 5 mA/cm\(^2\) was 0.6 V. Thereafter, the anode potential was measured while stepwise increasing the current density by 5 mA/cm\(^2\) at a time. As a result, at the time when the current density reached 50 mA/cm\(^2\), the anode potential began to increase with the lapse of time. Finally, almost no current came to flow, making it difficult to continue the electrolysis.

[0053] The electrolysis was stopped and the anode was taken out. As a result, electrode disintegration was not observed. A surface of this electrode was analyzed. As a result, Ni-F bonds were observed. It was thus presumed that an insulating NiF\(_2\) coating film had formed on the electrode surface.

(COMPARATIVE EXAMPLE 3)

[0054] A conductive-diamond electrode was produced in the same manner as in Example 1, except that a silicon plate was used as a conductive substrate.

[0055] The electrode was examined for current-potential curve in an anhydrous HF bath kept at 0°C under the same electrolysis conditions as in Example 1, except that the electrode produced was used as an anode.

[0056] Immediately after initiation of the examination, the anode potential at a current density of 5 mA/cm\(^2\) was 0.6 V. Thereafter, the anode potential was measured while stepwise increasing the current density by 5 mA/cm\(^2\) at a time. As a result, at a current density of 200 mA/cm\(^2\), the anode potential was 3.8 V.

[0057] The electrolysis was stopped, and the anode was taken out and examined for appearance. As a result, that part of the anode which was immersed in the electrolytic bath was found to be partly deprived of the diamond film, and it was observed that the exposed part of the silicon substrate surface where the diamond film was lost suffered corrosion.

(COMPARATIVE EXAMPLE 4)

[0058] A conductive-diamond electrode was produced in the same manner as in Example 1, except that a graphite plate was used as a conductive substrate.

[0059] The electrode was examined for current-potential curve in an anhydrous HF bath kept at 0°C by the same method as in Example 1, except that the electrode produced was used as an anode.

[0060] Immediately after initiation of the examination, the anode potential at a current density of 5 mA/cm\(^2\) was 0.6 V. Thereafter, the anode potential was measured while stepwise increasing the current density by 5 mA/cm\(^2\) at a time. As a result, at a current density of 70 mA/cm\(^2\), the anode potential increased abruptly and almost no current came to flow, making it difficult to continue the electrolysis.

[0061] The electrolysis was stopped and the anode was taken out. As a result, the anode was found to have broken into powder in the electrolyzer.

(EXAMPLE 2)

[0062] A glassy-carbon plate was used as a conductive substrate to produce a conductive-diamond electrode in the same manner as in Example 1 using the hot-filament CVD apparatus.
This electrode was attached to a (CH₃)₄NF·5HF electrolytic bath immediately after preparation of the bath. A nickel plate and Cu/CuF₂ were used as a cathode and a reference electrode, respectively, and constant-current electrolysis was conducted at a current density of 100 mA/cm². Immediately after initiation of the electrolysis, the anode potential was measured and was found to be 4.6 V. At the time when the electrolysis had continued for 200 hours, the anode potential was 4.8 V.

The electrolysis was stopped, and the anode was taken out and examined for appearance. As a result, neither electrode disintegration nor the shedding of the conductive diamond film was observed. No anode effect was observed throughout the 200-hour electrolysis.

Electrolysis was conducted in a (CH₃)₄NF·5HF electrolytic bath immediately after preparation of the bath, in the same manner as in Example 2 except that a graphite plate was used as an anode. Immediately after initiation of the electrolysis, the anode potential increased abruptly and almost no current came to flow, making it difficult to continue the electrolysis.

The electrolysis was stopped, and the anode was taken out and examined for contact angle between a surface of the electrode and water. As a result, the contact angle was found to be 150 degrees. It was hence ascertained that the so-called anode effect had occurred.

Electrolysis was conducted in a (CH₃)₄NF·5HF electrolytic bath immediately after preparation of the bath, in the same manner as in Example 2 except that a nickel plate was used as an anode. Immediately after initiation of the electrolysis, the anode potential began to increase gradually. Finally, after 70 hours had passed since the initiation of the electrolysis, the anode potential was 4.6 V. However, after 70 hours had passed since the initiation of the electrolysis, the anode potential was 4.6 V. However, after 70 hours had passed since the initiation of the electrolysis, the anode potential began to increase gradually. Finally, almost no current came to flow, making it difficult to continue the electrolysis.

The electrolysis was stopped, and the anode was taken out. As a result, the anode was found to have broken into powder in the electrolyzer.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof. The present application is based on Japanese Patent Application No. 2009-021157 filed on February 2, 2009, and the contents are incorporated herein by reference.

**Claims**

1. A method of electrolytically synthesizing fluorine of a fluorine-containing compound, wherein the method comprises conducting electrolysis using an electrode for electrolysis in an electrolytic bath comprising anhydrous hydrogen fluoride or anhydrous hydrogen fluoride to which a substance to be fluorinated is added, wherein the electrode for electrolysis comprises:

   a. a substrate comprising an electrically conductive material, wherein the surface of the substrate is made of glassy carbon; and

   an electrically conductive diamond film with which at least part of the substrate is coated.

2. The method according to claim 1, wherein the substrate consists of glassy carbon.
## DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>X, D</td>
<td>US 2006/219570 A1 (FURUTA TSUNETO [JP] ET AL) 5 October 2006 (2006-10-05) * abstract * * paragraphs [0037] - [0049], [0051] - [0054] * * examples 1-3 * * claims *</td>
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The present search report has been drawn up for all claims

Place of search: The Hague

Date of completion of the search: 13 February 2013

Examiner: Riba Vilanova, Marta
**EUROPEAN SEARCH REPORT**

**DOCUMENTS CONSIDERED TO BE RELEVANT**

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| A        | EP 1 031 645 A (CSEM)  
30 August 2000 (2000-08-30)  
* paragraphs [0009], [0010], [0015], [0019] - [0026]  
* claims 1-3  
* figure 1  
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5 June 2001 (2001-06-05)  
* abstract  
* column 1, line 9 - column 2, line 7  
* column 4, line 46 - column 5, line 7  
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**TECHNICAL FIELDS SEARCHED (IPC)**

The present search report has been drawn up for all claims.

**Place of search**
The Hague

**Date of completion of the search**
13 February 2013

**Examiner**
Riba Vilanova, Marta

**CATEGORY OF CITED DOCUMENTS**

- **X**: particularly relevant if taken alone
- **Y**: particularly relevant if combined with another document of the same category
- **A**: technological background
- **D**: non-written disclosure
- **P**: intermediate document

- **T**: theory or principle underlying the invention
- **E**: earlier patent document, but published on, or after the filing date
- **D**: document cited in the application
- **L**: document cited for other reasons
- **A**: member of the same patent family, corresponding document
This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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<td>US 2007215460 A1</td>
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