United States Patent [19]

Tricoli et al.

[11] **3,773,644**

[45] **Nov. 20, 1973**

[54] **ELECTROLYTIC CELL FOR THE PRODUCTION OF FLUORINE**

[75] Inventors: **Antonio Tricoli,** Milan; **Alberto Battarra,** Alessandria; **Giovanni Rebua,** Milan; **Luigi Bestetti,** Monza, all of Italy

[73] Assignee: **Montecatini Edison S.p.A.,** Milan, Italy

[22] Filed: **June 1, 1971**

[21] Appl. No.: **148,831**

[30] **Foreign Application Priority Data**

June 1, 1970 Italy 25390 A/70

[52] **U.S. Cl.** ..... **204/252,** 204/243 R, 204/247, 204/266, 204/286, 204/294

[51] **Int. Cl.** **B01k 3/10**

[58] **Field of Search** ..... 204/60, 243 R, 247, 204/266, 290 R, 294, 252, 286

[56] **References Cited**

UNITED STATES PATENTS

2,562,150	7/1951	Osborne	204/286
2,624,703	1/1953	Park	204/286
3,146,179	8/1964	Davies	204/247
3,060,115	10/1962	Hawpin et al	204/294
3,303,119	2/1967	Dell	204/294

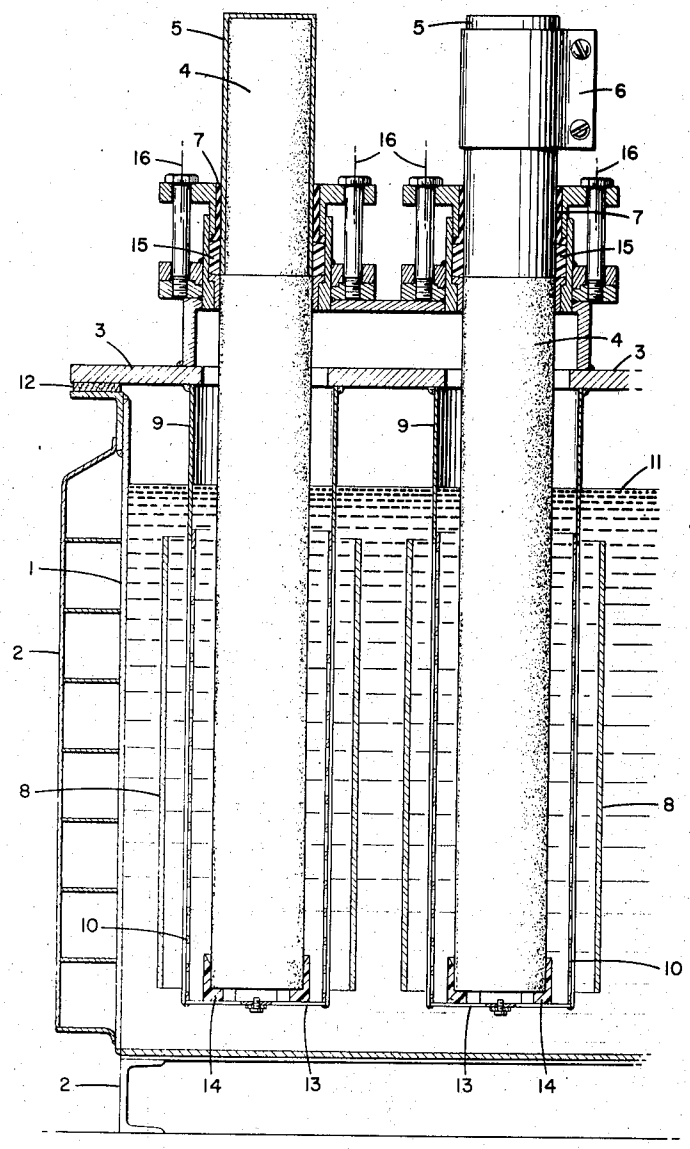
Primary Examiner—John H. Mack
Assistant Examiner—W. I. Solomon
Attorney—Stevens, Davis, Miller and Mosher

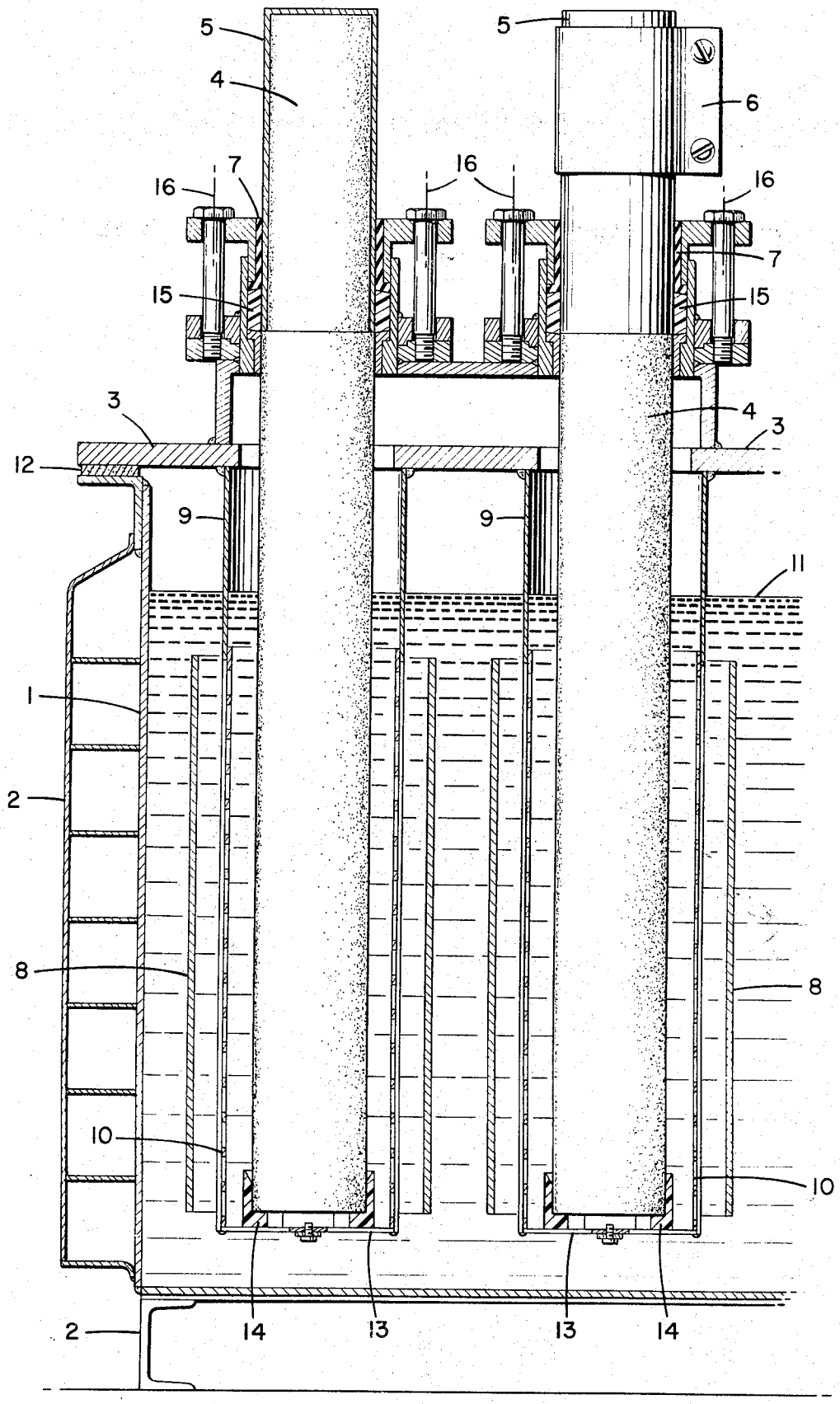
[57] **ABSTRACT**

An improved electrolytic cell for the production of fluorine is disclosed which is characterized by being provided with carbon anodes protruding from the cell, each anode having its section protruding from the cell covered by a gasproof coat made of a good conducting material through which the electrical connection for the current to the anode is assured. The coat may consist of a cap coupled by forcing on to the anode and thus snugly fitting over and upon the end of the anode. The anodes are supported by the cell cover through a stuffing box arrangement and are substantially round in cross-section. A cathode associated with each anode coaxially with respect thereto consists of a substantially cylindrical pipe, with provision for a diaphragm consisting of a substantially cylindrical pipe, coaxial with the anode, and disposed between the anode and the cathode.

3 Claims, 1 Drawing Figure

United States Patent [19] [11] **3,773,644**
Tricoli et al. [45] **Nov. 20, 1973**




5
4
5
6
16
7
16
16
7
15
15
3
4
3
12
9
9
11
1
2
8
8
10
10
2
14
13
13
14

ELECTROLYTIC CELL FOR THE PRODUCTION OF FLUORINE

The present invention relates to an improved electrolytic cell for the production of fluorine.

Tee process of the electrolytic production of fluorine by using a fused mixture of potassium fluoride and hydrofluoric acid as electrolyte is already well known. To carry out the process, use is made of electrolytic cells comprising a certain number of cathodes and anodes immersed in the electrolyte and a diaphragm separating the cathodic zone from the anodic zone for preventing the developed gaseous hydrogen and fluorine from mixing with each other.

The process carried out at high electrolysis temperatures of the order of 250°C, and which found broad use mainly in Germany, was afterwards given up and preference was given to a process developed in the United States, and now generally employed, which uses cells operating at medium temperatures. These last-mentioned cells make use of an electrolyte having a composition corresponding approximately to KF.1.8 HF and operate at a temperature between 85° and 110°C with anodes made of nickel or amorphous carbon. Several constructional designs for such cells have been developed while the use of amorphous carbon anodes has by now become general, solving in large part the most serious problems posed by anodic corrosion and polarization. The structure and the operational characteristics of such cells are described in the following articles: "Fluorine generation, handling and disposal" in *Industrial and Enginnering Chemistry*, Vol. 39, No. 3 of March 1947; "Moderni aspetti e sviluppi della chimica del fluoro" by D. Sianesi in La chimica e l'industria, Vol. 46, No. 8 of August 1964.

The amorphous carbon anodes of these known cells are partially immersed in the electrolyte and are supported by a metal beam placed inside the cell. The anodes are tightly fastened to said beam by means of bolts in order to bring about good metal-to-carbon electrical contact for the current to the cell.

The drawbacks of these prior cells are due to the worsening of the metal-to-carbon electrical contact with the passage of time. In fact, during the operation of the cell a deposit of high electrical resistance products forms in the connection interstice between the metal and the carbon, both in consequence of the corrosion due to the vapors developed in the anodic zone and the seepage of electrolyte between the carbon and the metal. This deposit not only decreases the electric efficiency but also gives rise to overheating which, when a predetermined temperature is reached, allows the anodes to be attacked by the fluorine with consequent development of CF_4 -- which brings the phenomenon to evidence — even before variations in voltage or current become apparent. The carbon-fluorine reaction, whem initiated, goes on until a complete break in the anodes takes place, whereupon it becomes necessary to stop the operation of the cell, to remove the cover, and to repair or replace the anodic unit. These operations for repair or replacement are time-consuming and involve substantial maintenance expenses.

It follows that the life of a conventional cell is determined above all by the life of the anodic unit.

An object of the present invention is to provide an improved cell which will eliminate or reduce to a minimum these and other drawbacks.

More particularly, an object of this invention is the elimination of the anodes-carrying beam and the accompanying electrical connection inside the cell.

A further object of this invention is to provide a low resistance electrical connection of constant efficiency through the entire cell operation time or cycles, an electrical efficiency which, in comparison with the efficiency herebefore obtainable from a conventional anodic unit, is far superior and which suffers no deterioration in the long run.

A still further object is a construction and arrangement making it possible to detect, on an assembled and operating cell, the particular anode or anodes which may have broken and therefore require replacement, as well as making it possible to replace an accidentally broken anode without being forced to remove the cell cover, thus requiring a stoppage of the cell which is far shorter than the stoppage heretofore required by a conventional type cell.

Finally, a still further object of this invention is a construction and arrangement that will bring about a decrease — compared with conventional cells — in the amount of the corrosion products (forming during the cell operation and ending by mixing with the electrolyte thus requiring a periodical replacement of the said electrolyte) and the elimination of the CF_4 from the fluorine and consequently also from the products obtained via fluorination with fluorine.

These and other objects of the invention will become apparent to those skilled in the art from the following detailed description, and are readily attained by an improved electrolytic cell for the production of fluorine which, according to this invention, is provided with carbon anodes protruding from the cell, each anode having its section protruding from the cell covered by a gasproof coat made of a good electrically-conducting material, through which and by which the electrical connection for the current to the cell is assured.

This invention will now be described in greater detail by reference to the accompanying drawing which shows schematically the cross-section of a cell in accordance with the invention.

Referring to the drawing, the electrolytic cell for the production of fluorine according to this invention comprises: tank **1**, made of "Monel"-alloy sheet metal for containing the electrolyte and surrounded by jacket **2** or other means suitable for heating or cooling the contents of the tank;

cover **3** made of steel;

a certain number of anodes **4** made of amorphous carbon, cylindrically shaped and vertically positioned, partially dipping in electrolyte **11**, each of the anodes protruding from the cover of the cell, their section protruding from the cover being provided with coat **5**, made of suitable metal (copper, for example), and the current input connection being placed outside the cell and completed through suitably shaped copper clamps **6**, said anodes being mechanically supported by the cell cover but being electrically insulated therefrom by means of stuffing box **7** made of an insulating material (e.g., polytetrafluoroethylene) which provides a gas-tight connection preventing the escape of the gases (fluorine and hydrogen fluoride) that develop inside the cell;

an electrolyte-immersed cathode consisting of as many steel pipes **8** as there are anodes, each arranged concentrically with respect to an anode and welded together in such a way as to constitute a whole unit whereby the electric current is led through two or more round steel bars (not shown in the drawing for simplicity and which also support the cathode inside the cell) passing through the cell cover **3** from which they are electrically insulated by means of a gastight stuffing box which prevents escape of the gases (hydrogen and hydrogen fluoride) developing within the cell;

diaphragms equal in number to the number of the anodes, their upper part consisting of pipes **9** made of Monel-alloy metal and welded at their top end to the cell cover **3** and extending downwardly into the electrolyte **11** so to provide a gasproof barrier, their lower part consisting of a Monel-alloy metal plate **10** (which may or may not be perforated) completely immersed in the electrolyte, the diaphragm having a cylindrical pipe shape and a diameter corresponding to that of the Monel-alloy pipe section.

The diaphragms **9** and **10** are located concentrically with respect to the amorphous carbon anodes, and are equally spaced with respect to the same anodes and the steel pipes **8** constituting the cathode.

Pipes (not shown in the drawing) are provided for the separate introduction of hydrofluoric acid into the cell.

A seal **12** is provided between tank **1** and cover **3** of the cell.

The tubular diaphragms **10** have their lower end terminating in a grid-protected opening **13** to which bushing **14**, preferably made of polytetrafluoroethylene, is attached for the main purpose of self-centering the anode **4** during the assembly stage, while having also the additional function of supporting it in proper position within the cell.

The stuffing box unit **7**, which, as indicated above, has the double task of supporting anode **4** while electrically insulating it from the cell cover **3** and of preventing the escape of fluorine and hydrogen fluoride from the cell, consists of sleeve **7** assembled in such a way as to slide along the anode axis and acting on elastic gasket **15** due to the force developed by bolts shown only by their axes **16** in the drawing. The sleeve **7** and the gasket **15** are preferably made of polytetrafluoroethylene. The assembly and disassembly of the individual anodes is made easy and quick by this stuffing box arrangement which assures perfect tightness against the escape of gases forming inside the cell.

The section of each anode protruding from the cell is provided with a coat **5** made of an electrically conducting material (copper, for example) through which the electrical connection is achieved and the anode section protruding from the cell is made gasproof. This avoids losses of fluorine and hydrogen fluoride through the porosity of the amorphous carbon anode. The coat **5** can have various constructions and for example may consist of a copper cap coupled to the anode end by a force fit.

The electrical connection to the anodes realized in this way, owing to the fact of complete freedom from corrosion or electrolyte seepage between the amorphous carbon and the metal parts, offers a low electrical resistance which suffers no alteration with the passage of time, thus assuring constantly a high current efficiency throughout the entire operation time. Such an electrical connection for the anodes gives in addition no excessive overheating — which overheating together with corrosion phenomena cause premature breaking of the anodes and development of CF_4 in prior art electrolytic cells — and on the contrary insure a long life for the anode of the electrolytic cell of the present invention.

The above description makes it clear how with an operating cell there is the possiblity of insuring the desired correspondence of the current flow to a predetermined value, by measuring the current anode by anode with the help of a direct current ammeter. In the event an anode gets broken, it is possible to immediately detect and replace the broken anode without having to remove either the cell cover or the other anodes, only a short interruption of the cell operation being required for the purpose.

It has been experimentally proved that the life of each anode which is a part of this cell is much longer than the life of the anodes in the conventional cells and which carry an anodic current skin density of about 0.1 A/cm^2, in the latter case being below or at the most equal to four months. On the other hand, anodes provided with the new electrical connection of the present invention, when likewise operating at a current density of about 0.1 A/cm^2, work perfectly after 15 months from starting without showing any sign of decay and in fact give good indication of a useful life much longer than 15 months.

It has been experimentally found also that, upon comparing the anodes of the conventional type cells and the anodes of the cells according to the present invention kept operating at about 0.15 A/cm^2 anodic current skin density, an anode life of 1 to 2 months is obtained in the first case while in the second case a life well above 12 months is obtained. It has been in fact observed that the latter anodes appeared fully as efficient after 12 months from the startup as in the beginning of the run.

Some detailed working examples are hereinafter given simply for illustrative purpose.

EXAMPLE 1

Use was made of a cell according to the present invention and comprising a tank made of Monel-alloy, having a rectangular horizontal section and provided with a jacket for cooling the electrolyte as well as with a steel cover attached to the tank by means of bolts.

The anodes were 22 in number, made of amorphous carbon cylindrically shaped, 80 mm in diameter and arranged in two rows. The anode section dipped into the electrolyte to an extent of 450 mm. The anodes were independent of each other as regards the electrical connection placed outside the cell. The anode section outside the cell was fully copper coated and was provided with a copper clamp through which the current input was assured.

The tightness against gas and the electrical insulation were provided by a stuffing box for each anode.

Twenty two gasproof Monel-alloy diaphragms in the form of a 120 mm diameter pipe, placed concentrically with respect to the anodes, were partially dipped in the electrolyte to a depth of 60 mm. Each of these diaphragms had its upper end welded to the cell cover and carried, fastened to its lower end, a pipe consisting of a Monel-alloy screen or net, having a diameter of 120 mm and a height of 390 mm, fully immersed in the electrolyte.

Twenty two steel pipes, having a diameter of 160 mm and a length of 390 mm, positioned concentrically with respect to the anodes and their diaphragms, were welded together and fully immersed in the electrolyte to constitute the cathode.

The electrolyte was a mixture of hydrofluoric acid and potassium fluoride having a composition of about KF.1.8 HF. The operating temperature was approximately 100°C.

The cell was run with an anodic current skin density of about 0.1 A/cm². The recorded life of the anodes was more than 15 months, corresponding for the particular cell to a total of 24.10^6 A/h.

When, after 15 months from the cell run start, the cell was stopped for inspection purposes and the anodes were drawn out, it was observed that they were all in the best of condition and had a resistance — at the copper-to-carbon connection — equal to the resistance they had when new, namely lower than 1000 microhms. The value of this resistance was measured between the anode ends, one of which was coated and the other bare.

EXAMPLE 2

Cover, cathode and diaphragm of the types commonly used in the conventional cells for fluorine production (for further information about the structure of this cell style, see the above-cited articles) were assembled to form a cell consisting of a Monel-alloy tank shaped and dimensioned the same as in the previous example.

In particular, the anodic unit consisted of 8 anode pairs of amorphous carbon having a rectangular section, and supported by an anode-carrying metal beam to which the anodes were tightly bolted. The anode-carrying beam placed inside the cell was in its turn supported by three copper current-carrying bars which protruded from the cover through stuffing box devices.

The distances between the anodes, diaphragms and cathodes were the same as in the previous example.

The cell was operated at about 0.1 A/cm² anodic current skin density.

Several runs were carried out but no run lasted longer than four months, corresponding to a total of $6.4.10^6$ A/h. In a period shorter than or at the most equal to four months since the cell run began, the breaking of one or more anodes was recorded. This required the disassembly of the cell for replacement of the anode unit. At the end of each run it was observed that the resistance between the carbon anodes and the metal beam had a value well above the value shown at the beginning of the run. The resistance of the new anode unit was lower than 1,000 microhms per anode (the metering of this resistance having been carried out between the anode end and the metal beam), but at the end of each run it reached values ranging from 40,000 to 100,000 microhms through the broken anodes while values up to 10,000 microhms were recorded through the undamaged anodes.

EXAMPLE 3

Use was made of an experimental cell according to this invention. The cell consisting of a Monel-alloy tank having a rectangular horizontal section, provided with a cooling jacket and a steel cover.

The anodes were two in a number made of amorphous carbon. Their shape and dimensions as well as the electrical connection type were the same as in Example 1.

The Monel-alloy diaphragms were two in number and the cathode consisted of two steel pipes. They too had shape, dimensions and constructional details the same as specified in Example 1.

The electrolyte had a composition of approximately KF.1.8 HF. The operating temperature was about 100°C.

The cell was operated at an anodic current skin density of about 0.15 A/cm².

On this case, although the anodic current skin density was significantly higher, the life of the anodes still appeared to be longer than 12 months.

EXAMPLE 4

Cover, cathode, anode and diaphragm as commonly used for fluorine producing cells of conventional style were assembled to form an experimental cell consisting of a tank the same as described in Example 3.

In particular, the anodes were two in number made of amorphous carbon and rectangularly shaped. They were tightly bolted to an anode-carrying metal beam placed inside the cell.

The distances between the anodes, diaphragms and cathodes as well as the electrolyte employed and the operating temperature were the same as specified in the preceding examples.

The cell was run with an anodic current skin density of about 0.15 A/cm².

At this significantly higher anodic current skin density, the life of the anodes appeared to be less than or at the most equal to two months.

The above examples clearly show that the improved cell according to this invention increases the life of the anodes and consequently decreases the number of the plant stoppages.

Moreover, the occasional breaking of an anode can be immediately detected from outside the cell and the replacement of the individual broken anode requires a time much shorter than the same operation requires for a conventional cell. Maintenance costs are consequently substantially reduced both because the work for replacing any individual broken anode is remarkably simplified and because in an event the breaking of the individual anodes occurs more rarely in the improved cell construction of the present invention.

Moreover, because the new electrical connection between the carbon anodes and the metal parts is located outside the cell, and consequently not adversely influenced by corrosion phenomena, the result is that said connection suffers no loss of efficiency in the long run and the electric efficiency thereof always remains at a desirably high value.

What is claimed is:

1. An improved electrolytic cell for the production of flourine comprising

a metal tank adapted for containing an electrolyte,

a metal cover on said tank,

at least one anode made of amorphous carbon partially dipping in the metal tank and partially protruding, in an insulating gastight connection, through and above said cover, wherein the part protruding from said cover is covered by a gas-proof copper coat assuring electrical connection to said anode outside said tank,

a cathode inside said tank made of a metal pipe coaxially arranged with respect to said anode, the electrical connection to said cathode being effected inside the tank, and

a diaphragm, inside said tank, made of a metal pipe welded to said cover, said diaphragm being coaxially arranged with respect to said anode and placed between said anode and said cathode in order to prevent mixing of the hydrogen and fluorine developed at said cathode and anode respectively.

2. The electrolytic cell of claim 1, wherein said anode is supported by said cell cover through a stuffing box device.

3. The electrolytic cell of claim 1, wherein said anode has a substantially round cross section.

* * * * *