April 8, 1952 W. N. HOWELL ET AL 2,592,144

PROCESS FOR THE ELECTROLYTIC PRODUCTION OF FLUORINE

Filed May 11, 1949 2 SHEETS—SHEET 1

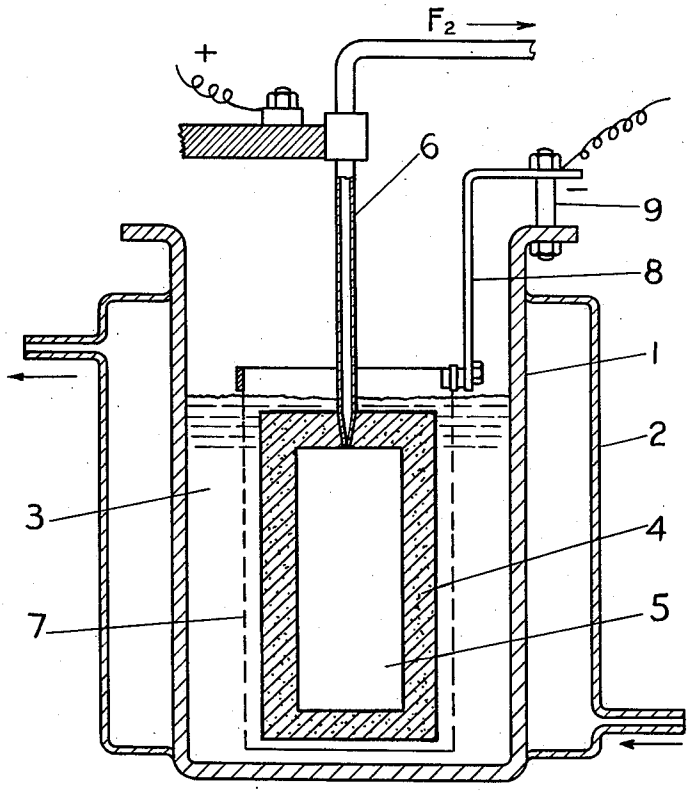


FIG. 1

Inventors:
William Norman Howell,
Harold Hill,
By Cushman, Darby & Cushman
Attorneys.

PROCESS FOR THE ELECTROLYTIC PRODUCTION OF FLUORINE

Filed May 11, 1949 2 SHEETS—SHEET 2

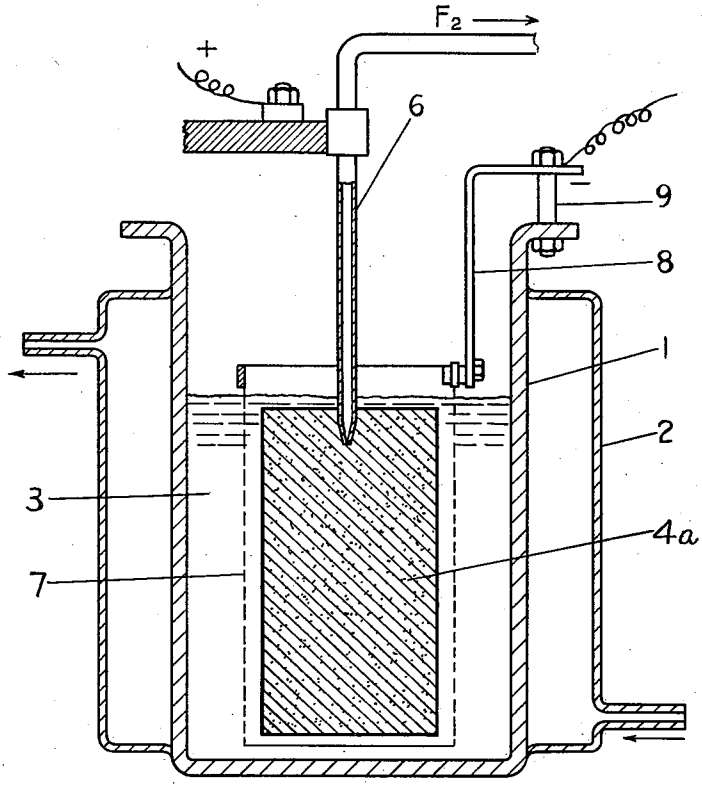


FIG. 2

Inventors:
William Norman Howell,
Harold Hill,
By Cushman, Darby & Cushman
Attorneys.

Patented Apr. 8, 1952 2,592,144

UNITED STATES PATENT OFFICE

2,592,144

PROCESS FOR THE ELECTROLYTIC PRODUCTION OF FLUORINE

William Norman Howell, Hale, Liverpool, and Harold Hill, Runcorn, England, assignors to Imperial Chemical Industries Limited, a corporation of Great Britain

Application May 11, 1949, Serial No. 92,606
In Great Britain May 14, 1948

6 Claims. (Cl. 204—60)

1

This invention relates to improvements in electrolytic apparatus and processes, and in particular, to apparatus and processes for the electrolytic production of fluorine.

Processes for the production of gaseous fluorine have been described in which a liquid comprising hydrogen fluoride and an alkali metal fluoride is subjected to electrolysis between a metallic or carbon cathode and an anode which is more or less resistant to fluorine and to the electrolyte at the temperature of electrolysis. Materials which have been used as anodes in such processes include platinum, carbon and nickel. Hydrogen is evolved at the cathode and fluorine, with varying amounts of oxygen and other impurities, dependent on impurities in the raw materials of the electrolyte, at the anode. Both anode and cathode gases contain greater or less amounts of hydrogen fluoride, depending on the temperature at which electrolysis is carried out and on the composition of the electrolyte.

Mixtures of hydrogen and fluorine give rise to violent explosions. It has therefore been regarded as essential in fluorine cell construction to provide means for keeping separate the gases evolved at the cathode and the anode respectively. Various methods of construction have been suggested for this purpose, as for example, the use of U-shaped or V-shaped cells having the electrodes in the side limbs and widely separated from each other. In another method of construction the upper portion of the cell is divided into cathode and anode compartments by means of a solid partition which may have a downward extension provided with slots or other apertures. Still another method of preventing the mixing of the electrolytic gases employs impervious partitions attached to the cover of the cell and dipping a short distance into the electrolyte. Due to the corrosive nature of the electrolyte and of the products of electrolysis, partitions require to be of robust construction in order to ensure reasonable durability; their use generally involves an anode-cathode separation of at least several centimeters. Further, when partitions are employed, it may be necessary, in order to avoid troubles arising from bipolarity of the partition, to restrict the overall voltage of the cell.

A principal object of this invention is the provision of new improvements in the process for the electrolytic production of fluorine and an apparatus for carrying out such processes. A further object is the provision of a new method of withdrawing fluorine generated during electrolysis from the electrolytic cell and the provision of new types of fluorine-producing cells which make possible this new type of operation. Another object is the provision of new types of such cells which have a relatively long period of life, i. e., in which the components of the cell are relatively slowly destroyed due to the corrosive action of the electrolyte and the electrolysis products under the conditions of electrolysis. Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

2

These objects are accomplished according to the present invention by a process which comprises electrolysing a liquid mixture of the fluoride of a metal belonging to group 1A of the periodic table and having an atomic weight greater than 38 and less than 133, and hydrogen fluoride, and removing fluorine from the electrolysis zone through the material of a gas-permeable, porous anode which is wholly immersed in the electrolyte and resistant to attack by the electrolyte and by fluorine under the conditions of electrolysis.

A more complete understanding of the new procedures and apparatus involved with this invention can be had by reference to the accompanying drawings in which:

Figure 1 is a diagrammatic side view of a preferred form of cell for use in this invention in which the anode is constructed with a hollow interior which is connected to the exterior of the cell by a suitable conduit and in which fluorine developed by the electrolysis is gathered in the hollow interior, which is held entirely free of electrolyte, and withdrawn through the conduit.

Figure 2 is an alternative form of cell for use in the invention having an anode which is not provided with any interior chamber and in which fluorine is collected by passing through the pores of the gas-permeable anode and conveyed out of the cell through a conduit suitably infixed and located in the anode. It is here to be noted that the total immersion of the anode in the electrolyte is an essential feature of the invention. If the anode is not so located, but obtrudes above the level of the electrolyte surface, fluorine

escapes from the non-submerged part of the anode, and only a portion of the gas passes through the provided conduit.

Referring in detail to the drawings, in Figure 1 the cell comprises a mild steel container 1 for the electrolyte 3. A jacket 2 adapted for water or steam heating surrounds the container 1. The anode 4 is formed from a block of porous carbon wholly immersed in the electrolyte and has a central chamber 5 into the upper end of which is inserted with a forced fit a tapered copper tube 6 so as to make a substantially gas-tight joint when sealed by the molten electrolyte. The copper tube in addition to providing an exit for the fluorine from the chamber 5, serves the function of a support for the anode and of a means of conducting the electric current thereto. Surrounding the anode and located a short distance therefrom is a cathode 7 of mild steel gauze, supported by a copper rod 8 which also serves as a conductor for the electric current. In the drawing, the copper rod 8 is secured to an insulating pillar 9 bolted to the wall of the cell container, this rod and the tube 6 may, however, be supported in any convenient manner by means external to the cell.

Referring to Figure 2, in which parts similar to those shown in Figure 1 are similarly numbered, the cell again comprises a mild steel container 1 for the electrolyte 3, and a jacket 2, adapted for water or steam heating surrounds the container. The anode 4*a* is composed of a solid block of porous carbon wholly immersed in the electrolyte and has a copper tube 6 infixed in its upper end. As long as the anode mass is wholly submerged in the electrolyte the fluorine, passing through the pores of the carbon mass 4*a*, leaves the said mass substantially entirely through the copper tube 6, which tube also serves the function of a support for the anode and of a means of conducting the electric current thereto. The other features shown in Figure 2 are identical with those shown in Figure 1.

Procedures of this present invention are further illustrated by the following examples of actual operations in accordance with the invention.

Example 1

The container of the cell was a steam-jacketed mild steel vessel having the internal dimensions 10½" x 5½" and 7½". The anode block was cut from porous carbon having a permeability of 17. The dimensions of the block were 3" deep x 1¾" wide x 2" thick, and a vertical cylindrical well ½" in diameter was drilled to a depth of 2½" in the upper 1¾" x 2" face. A copper tube, which fitted tightly into the upper part of the well, served as fluorine outlet and as the electrical connection to the anode, and was clamped so as to hold the upper face of the anode about 2½" below the surface of the electrolyte. The cathode, a piece of 10 mesh mild steel gauze 12" x 1½" was bent to form an open-ended rectangular box having 3" sides 1½" deep. This was slipped over the anode and held so that the gauze was about ½" from the four vertical faces of the anode.

Sufficient molten electrolyte of the approximate composition KF+1.8 HF was placed in the cell container to fill it to a depth of 6½" when the electrodes were in position. Impurities in the electrolyte comprised small amounts of sulphur and silicon compounds and moisture.

When the anode and cathode supports were connected to the positive and negative terminals respectively of a source of direct current it was found that at an applied potential of about 5 volts and upwards fluorine could be collected from the copper tube at a pressure corresponding to 3" to 4" head of water.

The following measurements were made when the cell voltage was 7 volts and the temperature of the electrolyte 97° C.:

Current, 11.5 amps.
Anode current density (based on surface area of vertical faces), 0.5 amps./sq. in.
HF content of anode gas, 12%.
Fluorine content of anode gas, after removing HF, 89.5–91.5% (the balance was mainly oxygen, arising from moisture present in the electrolyte).
Current efficiency on fluorine, 75% of theory.

Example 2

Using the cell and electrode assembly of Example 1 with a fresh batch of electrolyte analysing approximately KF+1.8 HF, at a temperature of 96° C., the following current-voltage relationships were observed while fluorine of good quality was issuing from the anode compartment:

Current (amps.)	Voltage
14	7.2
34	9.9
48	11.7
70	14.75

The anode current density at an applied voltage of 14.75 volts was 3.1 amps./sq. in., calculated on the surface area of the vertical faces. The cathode current density, calculated as for a continuous sheet having the same overall dimensions as the gauze cathode, was 3.9 amps./sq. in.

Particularly good results are obtained, employing the above-described process, when the liquid electrolyte is such that it makes a contact angle greater than 90° with the anode surface. This condition may be realized by the use of graphite or amorphous carbon of high permeability as anode material in conjunction with a substantially anhydrous electrolyte composed of hydrogen fluoride and potassium fluoride in a molar ratio less than approximately 2.5:1. Preferably the molar ratio of hydrogen fluoride to the alkali metal fluoride should be between 1.8:1 and 2:1.

The gas conduit through which the anode gases leave the cell may be a tube of copper or other material which is resistant to corrosion by the electrolyte and the cell gases, and which becomes anodically passive under the conditions of electrolysis. The tube may serve as the electrical connection to the anode. It may, however, be of non-conducting material, in which case the current is conducted to the anode by separate and conventional means.

An electrolytic cell can be formed from a wide variety of materials and in any desirable shape. Obviously, the cell should be made of a material which is not readily attacked by the electrolyte or products of reaction and a suitable material is mild steel. Cylindrical or rectangular shapes are suitable for the container which is preferably provided with a jacket for heating the container with hot water or steam or with some other means for heating such as electrical immersion heaters or the like.

The anode may take a variety of shapes and is of necessity made from some material which is

porous and gas-permeable but relatively impermeable to the electrolyte under the electrolysis conditions. As indicated in connection with the drawings, the anode can be formed without any interior chamber in which case the generated fluorine is removed through a suitably positioned conduit connected or fastened to the anode. Both the anode and connecting conduits should be made from a material which is not readily attacked by the electrolyte or product gases during electrolysis. Suitable materials for the anode include porous graphite or amorphous carbon and suitable materials for the gas exit pipe include copper. In one of the preferred forms of the cell, the anode is formed of a block of porous carbon having a centrally drilled chamber into which is press-fitted a tapered copper pipe so as to make a substantially gas-tight connection when sealed with molten electrolyte. The gas exit tube, in addition to forming an exit for the fluorine, can also serve to support the anode and to make electrical connection thereto.

The method which has been found suitable for forming the porous anode is to cut it to the required shape in such a way that none of the original outer surfaces of the block remain on the shaped anode. A suitable porous carbon or graphite is one having a permeability not less than 10, permeability as employed herein being the number of cubic feet of air per square foot of surface capable of passing through a one inch thickness of the anode material per minute against two inches water pressure.

The cell cathode can be formed in any desirable shape and from any suitably inert material. Preferably the cathode is shaped so as completely to surround the anode at a spaced short distance therefrom. Suitable materials for making the cathode include mild steel gauze which can be supported by a copper rod to serve as a conductor for the electrolysis current.

The electrolyte for use in the new process consists of a mixture of hydrogen fluoride and the fluoride of an alkali metal of atomic weight between 38 and 133 which includes potassium, rubidium and caesium fluorides. Mixtures of these alkali metal fluorides may also be employed.

Particular voltage and current densities employed using the procedures and apparatus of this invention are not critical and the voltage may vary, for example, between 5 and 15 volts and the current between 5 and 100 amperes. Furthermore, the cell may be operated at subnormal or super-atmospheric pressures although it is preferable to operate the cell with a slight pressure, e. g., a pressure equal to 1 to 5 inches of water, in order to insure that the interior chamber in the anode remains free of an electrolyte.

The temperature of electrolysis may be varied but should be sufficiently high to keep the electrolyte in liquid condition and, preferably, should be between 80° C. and 110° C. In operating the cell, the anode must be positioned so as to be wholly immersed in the electrolyte.

The novel principles of this invention are broader than the specific embodiments recited above and rather than unduly extend this disclosure by atempting to list all the numerous modifications which have been conceived and reduced to practice during the course of this development, these novel features are defined in the following claims:

1. A process for the production of fluorine which comprises flowing an electric current through a liquid electrolyte mixture consisting essentially of hydrogen fluoride and a fluoride salt selected from the group consisting of potassium, rubidium and caesium fluorides and mixtures thereof, between a porous anode made of a material from the group consisting of graphite and amorphous carbon having a permeability not less than 10 and an insoluble cathode, said anode being wholly immersed in said electrolyte, and removing substantially all the fluorine generated by the electrolysis through the pores of the anode from the interior of the anode.

2. A process as claimed in claim 1, wherein said electrolyte is a mixture of hydrogen fluoride and potassium fluoride with the molar ratio of HF to KF being between about 1.8 to 1 and 2.5 to 1.

3. A process as claimed in claim 1, wherein said cathode is made of metal gauze.

4. In a process for the production of fluorine, the steps which comprise wholly immersing a porous chambered anode of carbon having a permeability not less than 10 in an electrolyte consisting essentially of hydrogen fluoride and potassium fluoride in molar ratio of between 1.8 to 1 and 2.5 to 1, passing an electric current through said electrolyte between said anode and an insoluble cathode and removing the fluorine from the electrolytic zone through the porous walls of said anode.

5. A process for the production of fluorine which comprises flowing an electric current through a liquid electrolyte mixture consisting essentially of hydrogen fluoride and a fluorine salt from the group consisting of potassium, rubidium and caesium fluorides, and mixtures thereof, the molar ratio of HF to fluorine salt being between about 1.8 to 1 and 2 to 1, between a hollow anode of porous carbon having a permeability of not less than 10 wholly immersed in said electrolyte and an insoluble cathode while maintaining the temperature of the electrolyte between 80° and 110° C., maintaining a pressure equal to 1 to 5 inches of water within the hollow interior of said anode, and removing the fluorine from the electrolytic zone through the porous walls of said anode.

6. A process as claimed in claim 5, wherein the electric voltage is between about 5 and 15 volts and the current between about 5 and 100 amperes.

WILLIAM NORMAN HOWELL.
HAROLD HILL.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,000,815	Berl	May 7, 1935
2,207,734	Heise et al.	July 16, 1940
2,468,766	Low	May 3, 1949

OTHER REFERENCES

Office of Technical Services publication P. B. 32.205, "The Generation of Fluorine," June 15, 1943.