ELECTROLYTIC PROCESS FOR PRODUCTION
OF FLUORINE

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2 Claims. (Cl. 204—60)

1. This invention relates to an electrolytic apparatus and process for the production of fluorine.

Methods for the electrolytic production of fluorine have long been known; but known methods have possessed disadvantages that prevent large scale low cost production of fluorine. The difficulties are due in large part to the fact that hydrogen fluoride, from which the fluorine is derived by electrolytic decomposition, is substantially non-conductive. To render the hydrogen fluoride sufficiently conductive to permit electrolysis to take place, it is common practice to add a metal fluoride, for example, potassium bifluoride, KHF₂, since this latter material is readily available, and not hygroscopic. By dissolving the potassium bifluoride in liquid anhydrous hydrogen fluoride an electrolyte is formed from which hydrogen and fluoride are evolved upon passage of an electric current therethrough.

The relative proportion of KF to HF in the electrolyte markedly influences the character of the electrolysis. While the electrolyte is most conveniently made up by use of potassium bifluoride (KHF₂ or K₂HF₂) it is more convenient to express composition in terms of KF and HF as if the electrolyte had been actually made from KF and HF. Where the molar ratio is approximately one mole of KF to 8 moles of HF, the electrolyte is fluid at room temperatures. With this electrolyte, it has been necessary to employ an anode of nickel which is rapidly eaten away and forms a fluoride sludge in the bottom of the electrolyte. The cost of nickel anodes and of dismantling and cleaning the electrolyte cell to remove the sludge makes the process expensive.

Efforts to employ an inert material such as carbon or graphite with such a bath has proved unsatisfactory due to the tendency of such anodes to disintegrate. That is after a short period of operation the anodes tend to swell and break and the current ceases to flow.

It is an object of the present invention to provide an improved electrolytic process for production of fluorine wherein a high current density may be obtained at relatively low voltage and without the use of anodes of nickel or other rapidly consumed expensive material. It is a further object to provide an electrolytic system for the production of fluorine gas by the electrolytic decomposition of hydrogen fluoride which is operable at high current efficiency and high current density.

Applicant has discovered that these desirable results may be obtained by electrolysis of baths including hydrogen fluoride and a plurality of fluorides of univalent metals between a copper-filled carbon anode and a suitable cathode. In the preferred embodiment of the invention the system will include an electrolyte comprising potassium fluororide, hydrogen fluoride and lithium fluoride in the proportions of 60% potassium fluoride, 38½% hydrogen fluoride and 1½% lithium fluoride.

The drawings annexed hereto and constituting a part of the disclosure show a suitable electrolytic cell for use in connection with the instant invention. It will be understood, however, that other cell structure suitable for electrolytic production of corrosive gases may be used.

Figure 1 is a perspective view partly broken away of a cell usable in connection with the instant invention. Figure 2 is a vertical sectional view of the electrolytic cell taken on the line 2—2 of Figure 1.

With particular reference to Figure 1 of the drawing, the numeral 1 designates an electrolyte container of generally rectangular form constructed of steel or other suitable material of construction and having temperature control jackets 2 on opposite sides thereof.

The container 1 is provided with a top 3 of similar material having a rectangular steel or Monel metal skirt 4 extending downward within the container 1 and forming a separate chamber for collecting fluorine.

Within the cell there are a pair of cathode plates 5 and 6 which may be steel sheets brazed to copper bars 7 and 8 suspended from electrical connectors 9 and 10. Both of the cathodes 5 and 6 are located outside of the chamber formed by skirt 4 and the connectors 9 and 10 pass up between this skirt and the side walls of the container 1.

Between the two cathodes 5 and 6 a carbon anode 11 is suspended from electrical connectors 12 which extend upward through the chamber formed by skirt 4.

The electrical connectors 9, 10 and 12 are electrically insulated from the top 3 of the cell. The connectors 12 are connected with positive current source (not shown).

Extending downward from the long sides of skirt 4 are a pair of diaphragms 15 and 16 composed of Monel metal screen or preferably perforated Monel metal sheets. If desired, the diaphragm can be continued around the ends of the anodes in the same manner as skirt 4. This provides somewhat greater rigidity for the diaphragm.
A gas outlet conduit 17 for removal of the fluorine product is provided in top 3 and communicates with the anode chamber formed by skirt 4. Outlet conduit 18 for removal of hydrogen is provided in top 3 and communicates with the cathode chamber.

For the addition of hydrogen fluoride to the cell, a pair of pipes 19 and 23 each connected to a serrated distributor 21 are provided.

In accordance with the instant invention, the anodes are copper-filled carbon. That is, anodes containing 35 to 47% of copper in the form of network distributed therethrough. These anodes may be suitably formed by vacuum impregnation of porous carbon with molten copper. The anodes should be made of substantially pure carbon, suitably such as may be derived from petroleum coke. The pure carbon may be mixed with pitch and fired at a temperature just below that at which graphitization occurs. These, when impregnated with copper, have given best results in my work. The electrolyte employed according to a preferred embodiment comprises from 73 to 87% by weight of potassium bifluoride (KHF\(_2\)) 13 to 22% by weight of hydrogen fluoride (liquid anhydrous HF) and from 0.1 to 2.5% by weight of lithium fluoride. A, e.g., between 0.1% and 2.5% of lithium fluoride. In terms of molar relationships, the molar ratios of hydrogen fluoride to potassium fluoride may be between 1.6 to 1 and about 2.1 to 1.

The electrolyte formed as above described melts at a temperature below 100° C. and has been found highly suitable for electrolysis in the instant system between a cathode of copper or iron and an anode of copper filled carbon.

In operation of this cell to produce fluorine, the cell is filled to a point above the bottom of skirt 4 with a suitable electrolyte such as a potassium acid fluoride having the composition above described. Because of the formation of gas bubbles in the electrolyte, the electrolysis causes the liquid level to rise to the operating level L.

The cell is brought to operating temperature, about 100-110° C. and current is applied by the cathodes 5 and 6 and the anodes 11 and the cell is operated with a current flow between these anodes and the cathodes 5 and 6.

During operation of the cell the operating temperature is maintained by passing cooling fluid through the jacket 2, and the hydrogen fluoride content of the electrolyte is maintained by continuously or intermittently introducing makeup hydrogen fluoride through inlets 19 and 23. The gases produced by the cell are withdrawn through outlets 17 and 18.

As an example of the operation of the device in a cell constructed as described above wherein the anodes and the cathodes were spaced a distance of 1½ inches, it was found that fluorine was steadily produced with a current density of 50 amperes per square foot at a temperature of 110° C. The cell operated for a period of 2,550 hours without trouble from polarization from the anode and a current efficiency of 90 to 95%.

While the invention has been described in its operation between an iron cathode and a copper-filled carbon rod, and electrolyte comprising potassium bifluoride, hydrogen fluoride and lithium fluoride in the defined proportions, it will be understood that variations may be made within the spirit of the invention. Accordingly, it is to be understood that the invention is not to be construed as limited to the specific conditions and details described but is intended to include all processes within the scope of the appended claims.

I claim:

1. A process for the electrolytic production of elemental fluorine comprising passing an electric current through an electrolyte between a steel cathode and an anode composed of carbon containing from about 35 to about 47% copper in the form of a network distributed therethrough, the electrolyte consisting essentially of hydrogen fluoride, potassium fluoride and lithium fluoride, the molar ratio of hydrogen fluoride to potassium fluoride being between about 1.6 to 1 and about 2.1 to 1 and the lithium fluoride being present in the amount between about 0.1% and about 2.5% by weight of the total electrolyte, the electrolysis being carried out at a temperature of from about 95 to about 115° C.

2. A process for the electrolytic production of elemental fluorine comprising passing an electric current through an electrolyte between an iron cathode and an anode composed of carbon containing from about 35 to about 47% copper in the form of a network distributed therethrough, the current density being from 40 to 150 amperes per square foot and the electrolyte consisting essentially of hydrogen fluoride, potassium fluoride and lithium fluoride, the molar ratio of hydrogen fluoride to potassium fluoride being between about 1.6 to 1 and about 2.1 to 1 and lithium fluoride being present in amount between 0.1% and 2.5% by weight of the total electrolyte, the electrolysis being carried out at a temperature of from about 95 to about 115° C.

GEORGE C. WHITAKER.

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