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MANUFACTURE OF FLUORINE BY ELECTROLYSIS

Filed Oct. 31, 1944

3 Sheets-Sheet 1

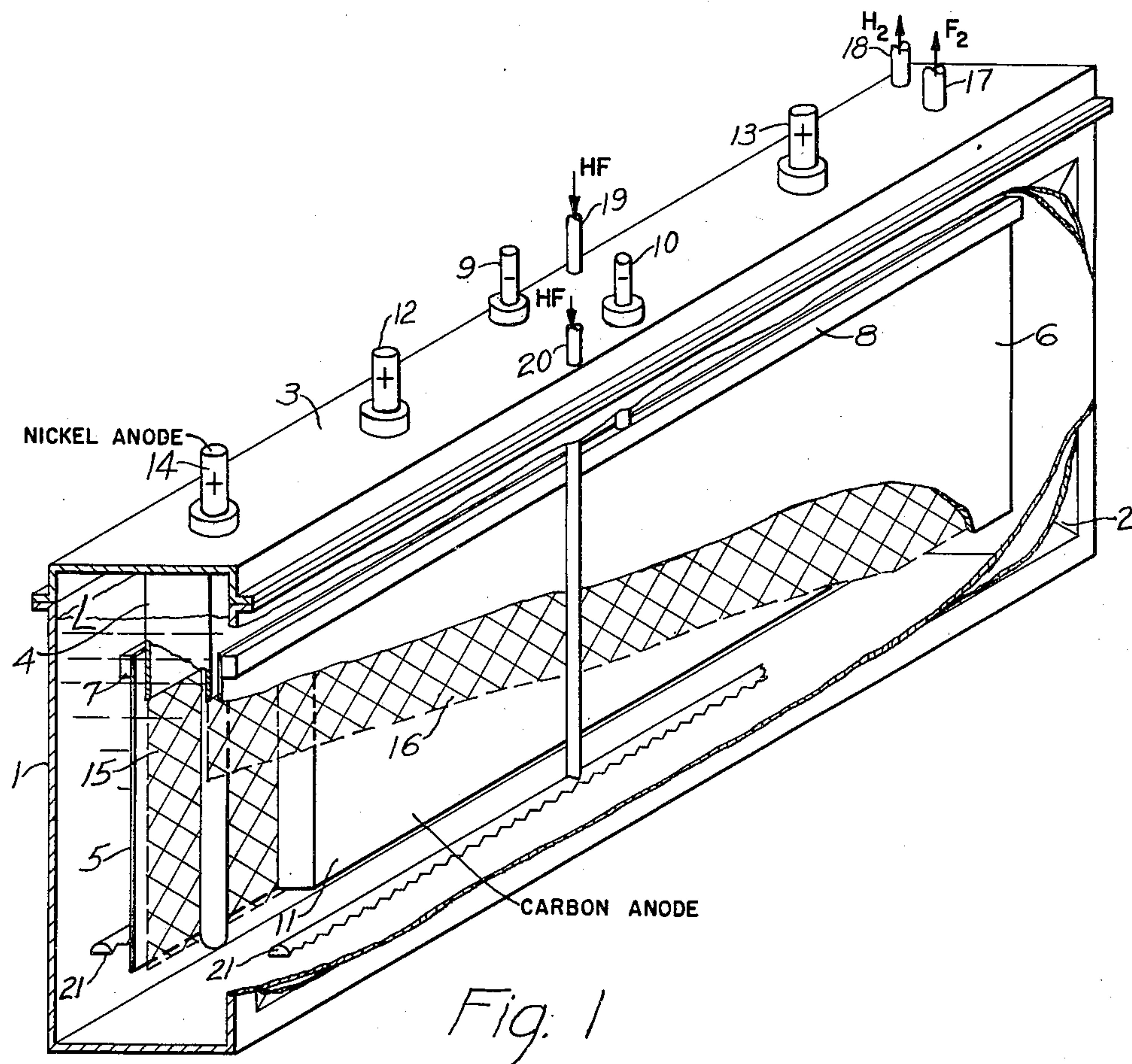


Fig. 1

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3 Sheets-Sheet 2

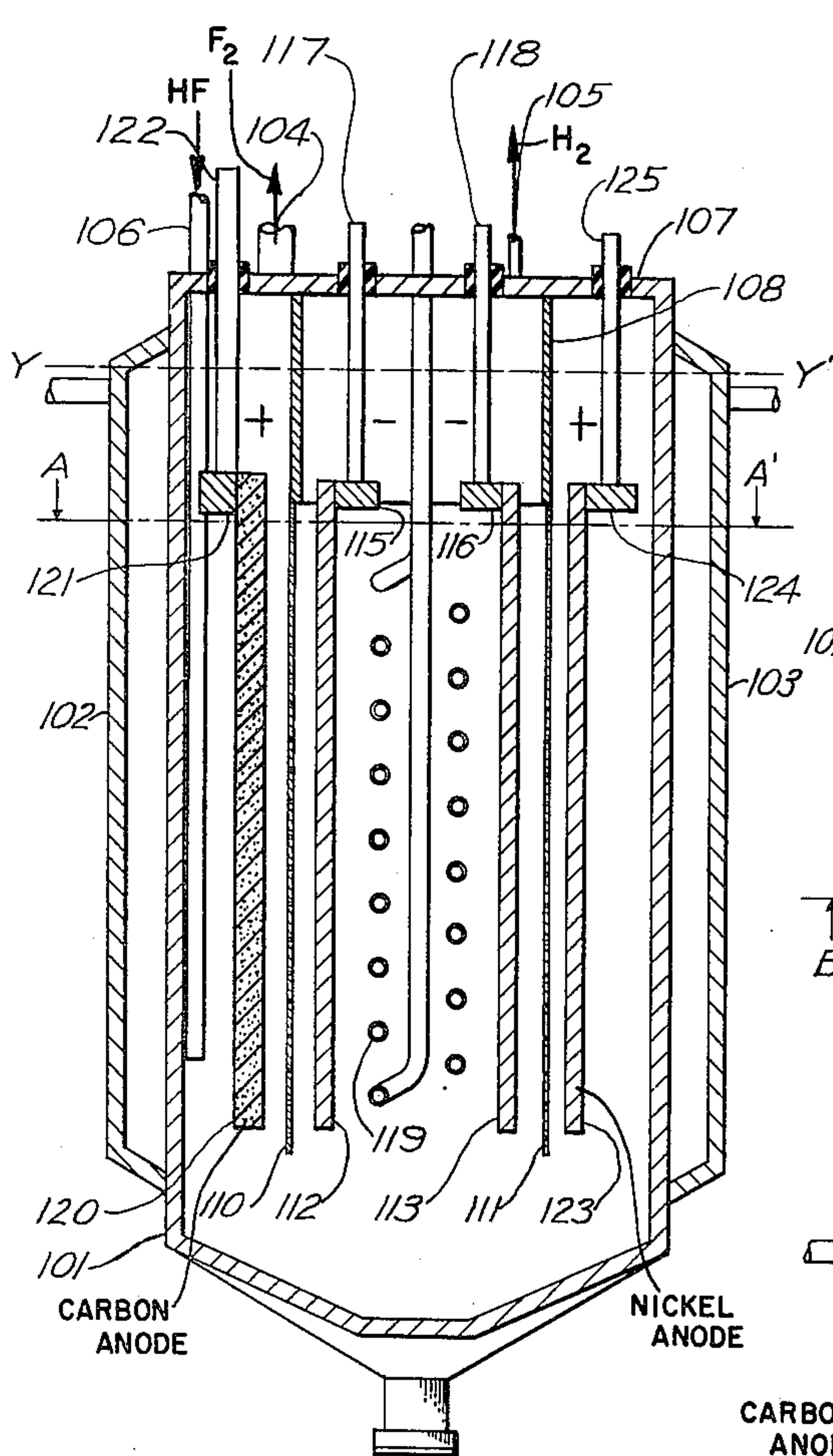


Fig. 2

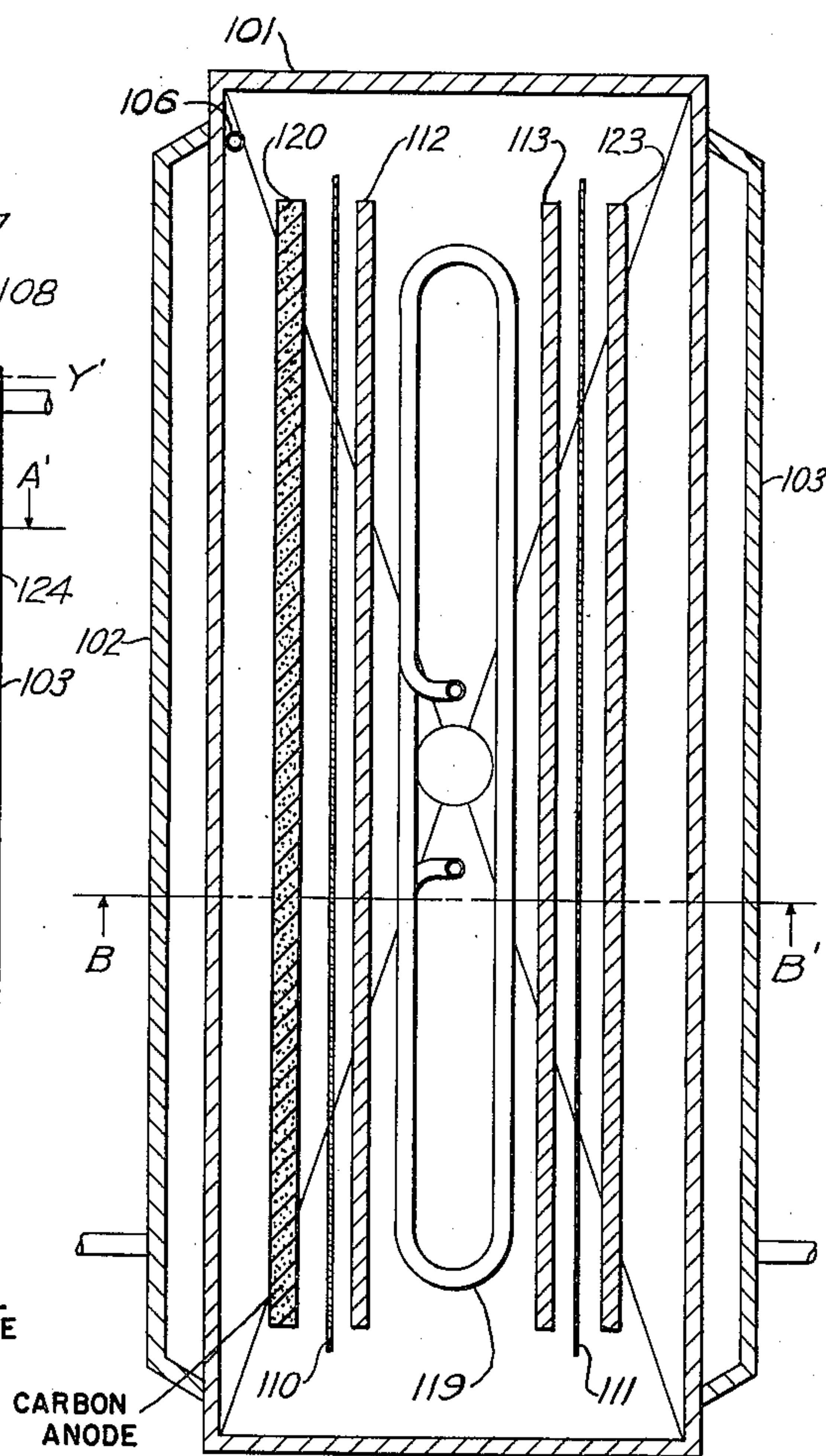


Fig. 3

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3 Sheets-Sheet 3

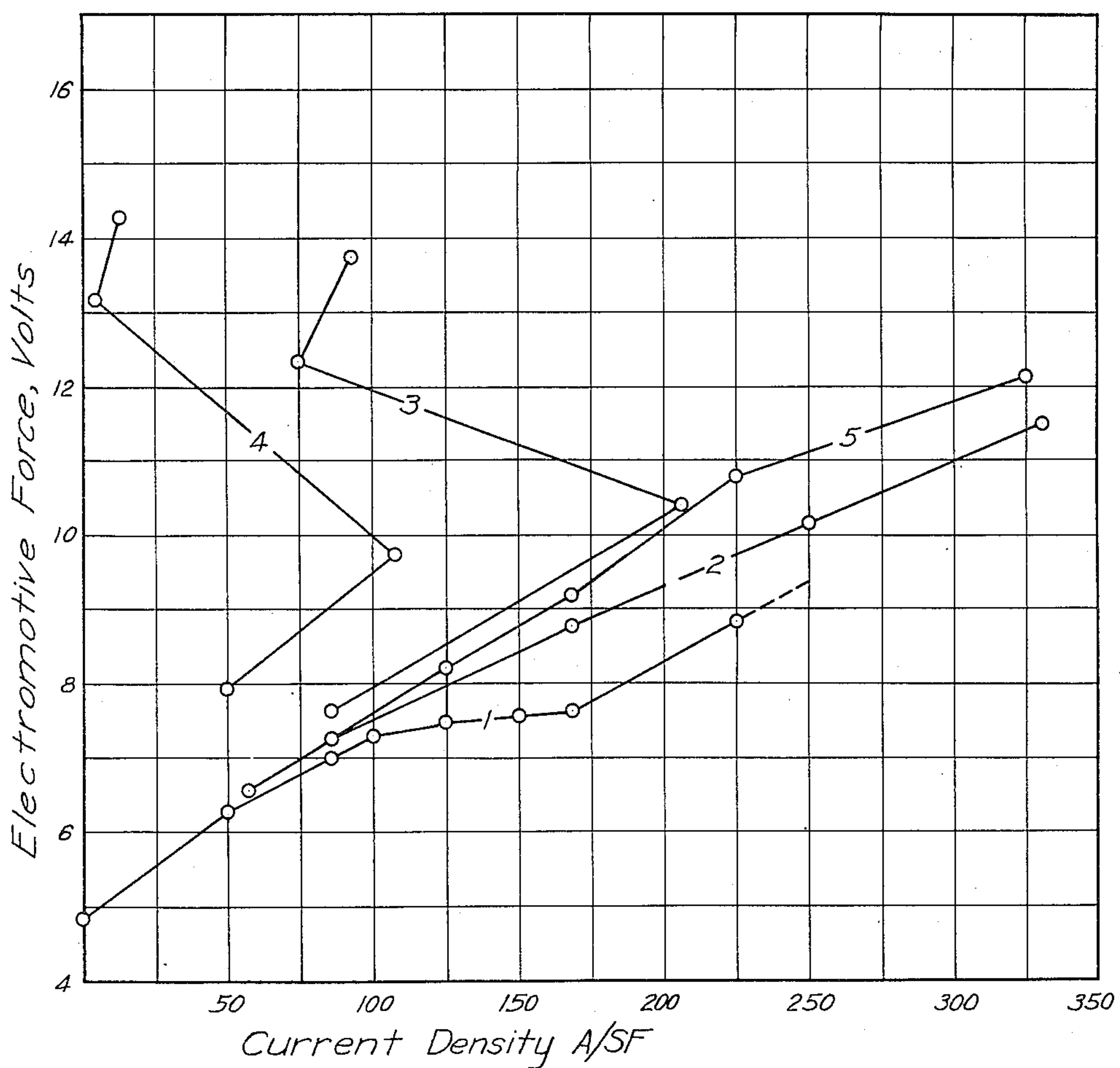


Fig. 4

- 1.-New Carbon Anode.
- 2.-After 31 hr. at 200 A/SF.
- 3- " 54 hr. " " " "
- 4- " 74 hr. " 160 " "
- 5- " " " " " "+46AH w. Ni.

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MANUFACTURE OF FLUORINE BY
ELECTROLYSIS

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9 Claims. (Cl. 204—60)

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This invention relates to the manufacture of fluorine and is particularly concerned with the electrolysis of alkali-metal acid fluorides.

In the past it has been proposed to produce fluorine by electrolysis of anhydrous alkali-metal acid fluoride electrolytes, using carbon or nickel anodes. Nickel anodes are destroyed rather rapidly by the combined effect of the electrolyte and generated fluorine. The overall efficiency of the cell is reduced to the extent the generated fluorine combines with nickel, and the cost of the product is increased not only by this amount but by an additional amount representing the cost of nickel anodes destroyed and the labor involved in their frequent replacement.

Because of the inertness of carbon the use of carbon anodes has been proposed. However, their behavior has been found to be peculiarly erratic. A condition resembling polarization frequently arises preventing further operation of the cell. As the electrolysis with a carbon anode continues, the optimum current density gradually diminishes until fluorine production falls to an insignificant quantity. If an attempt is made to maintain fluorine production by increasing the potential difference across the cell, a point is reached at which further increase results in a fall rather than a rise in current density and fluorine production. This voltage maximum falls more rapidly as the current density of operation is increased. Consequently, the useful period of operation is shorter at high current densities than at low current densities.

Attempts to overcome this "polarization" by reversing the direction of current in the cell are of only limited value. It is possible in this way to restore momentarily the electrolytic activity of the cell but fluorine production falls rapidly to that under the previous condition of "polarization."

In addition to these difficulties, traces of moisture in the electrolyte seem to cause a violent disturbance to the smooth generation of fluorine.

While there is some question as to whether such difficulties are as troublesome at high temperatures as at low temperatures, high temperature operation has other objections which render its use undesirable. Thus, although steel can be used as a material of construction for operation at temperatures below about 200° C., operation at higher temperatures produces too rapid destruction of the metal to permit its practical use. Carbon has been proposed for this purpose but is relatively costly and relatively fragile, and its use entails an increased charge for equipment.

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Most metals are sufficiently attacked under conditions of electrolysis to make their use economically unfeasible. Ceramic equipment aside from its objectionable reactions to temperature changes is subject to destruction by the hydrogen fluoride present in the electrolyte.

It is an object of the present invention to provide a method of using carbon anodes whereby the difficulties of using such anodes are substantially reduced, and the problems which arise in low temperature operations involving their use are solved. Further objects of the invention are to improve the current efficiency and power efficiency of the electrolytic process for making fluorine, and to accomplish these and other purposes at relatively low cost.

In accordance with the present invention an alkali-metal acid fluoride electrolyte is first subjected to a conditioning treatment by electrolysis employing a nickel anode, and the conditioned electrolyte is electrolyzed to produce fluorine using a carbon anode. The conditioning treatment may be conducted while the cell is operating with a carbon anode or between operations with a carbon anode and it may be conducted continuously or intermittently. Since nickel is consumed much more rapidly when it is connected anodically and only infrequent conditioning maintains a high level of efficiency, I prefer to effect the conditioning intermittently. Thus when the efficiency of the electrolysis drops substantially, electrolysis is conducted for a short period with a nickel anode. I have found that by this treatment the electrolytic activity of the cell is restored. After restoration of the cell activity, the electrolysis may be conducted for a relatively long period of time before again becoming unproductive. The nickel anode can then be used to restore the activity of the cell in the same manner as previously, and this series of operations can be continued practically indefinitely, the electrolysis being conducted for long periods using a carbon anode and for short periods using a nickel anode.

The beneficial results of the electrolysis with a nickel anode are obtained whether the same carbon anode or a different carbon anode is employed in subsequent periods of electrolysis. Moreover, carbon anodes which are incapable of producing any substantial quantity of fluorine initially can be used with a high efficiency after a preliminary conditioning of the electrolyte by means of a nickel anode.

The initial conditioning treatment is not merely a dehydration of the electrolyte to remove final

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traces of moisture, for in some cases carbon anodes do not perform satisfactorily even in anhydrous electrolytes until after the nickel conditioning treatment. Once an electrolyte has been conditioned, the reconditioning periods required for maintaining satisfactory operation are relatively short, constituting only a small fraction of the total operating time of the cell.

The process of the present invention is particularly applicable to electrolyses at temperatures between 90° and 200° C., using a potassium acid fluoride electrolyte containing potassium fluoride and hydrogen fluoride in ratios between about 1½ and 3 molecules of HF for each molecule of KF. While the invention is not considered to be limited to these conditions, the current densities which may be obtained at temperatures below about 90° C. are relatively low, and as previously explained temperatures higher than 200° C. are particularly destructive to equipment. At temperatures between 90° and 200° C. the necessity for maintaining a fluid electrolyte and the desirability of avoiding an excessive quantity of hydrogen fluoride in the gaseous fluoride product dictate the use of electrolytes within the specified limits of composition. The lower HF ratios are applicable more particularly to the higher operating temperatures and vice versa. For instance, HF ratios of 1.8 to 2.0 are especially suitable for operating at temperatures of 100–110° C. The addition of another alkali-metal fluoride, e. g. lithium fluoride, to reduce the melting point of the electrolyte does not interfere with the satisfactory performance of the process and in general the preferred temperatures and ratios of HF to total alkali-metal fluoride fall within those specified for electrolytes containing potassium as the sole alkali-metal.

Apparatuses suitable for carrying out the process of the invention are illustrated diagrammatically in Figures 1, 2 and 3 wherein

Figure 1 shows a perspective view of one form of electrolytic cell with one end removed and parts cut away to expose features of internal construction and

Figures 2 and 3 show, respectively, a vertical section (on line BB' of Figure 3) and a horizontal section (on line AA' of Figure 2) of another form of electrolytic cell for use in accordance with the invention.

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 and 13 which extend upward through the chamber formed by skirt 4.

At one end of the cell, a nickel rod 14 is provided, also located between the cathodes and

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extending up through the chamber formed by skirt 4. This nickel rod forms its own electrical connector. All of the electrical connectors 9, 10, 12, 13 and 14 are electrically insulated from the top 3 of the cell. At least one of the electrical connectors 12 and 13 and the rod 14 connect with means (not shown) for connecting a positive current source to connector 12 or 13 and independently to rod 14 so that the latter can be used periodically as anode while anode 11 is used continuously.

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 20 each connected to a serrated distributor 21 are provided.

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 approximate composition $KF \cdot 1.8HF$. 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 120° C., and current is applied by the small nickel anode 14 and the cathodes 5 and 6 to condition the electrolyte for electrolysis by the large carbon anode 11. After the electrolyte is satisfactorily conditioned, the current is switched from anode 14 to anode 11 and the cell is operated with a current flow between this anode and the cathodes 5 and 6 until it is desired to recondition the electrolyte.

During operation of the cell the operating temperature is maintained by passing cooling fluid through the jackets 2, and the hydrogen fluoride content of the electrolyte is maintained by continuously or intermittently introducing makeup hydrogen fluoride through inlets 19 and 20. The gases produced by the cell are withdrawn through outlets 17 and 18.

With reference to the apparatus illustrated in Figures 2 and 3, the cell comprises a generally rectangular vessel 101 having cooling jackets 102 and 103 extending the length of the vessel 101, and outlet 104 for fluorine, outlet 105 for hydrogen, and inlet 106 for hydrogen fluoride extending through the top 107.

Projecting from the top 107 into the cell is a rectangular skirt 108 having diaphragms 110 and 111 extending downward from its two long sides and defining a central cathode chamber and two anode chambers.

Two steel cathodes 112 and 113 are supported by copper bus bars 115 and 116 connected to a suitable current source (not shown) by way of copper rods 117 and 118 extending up through the top 107 and insulated therefrom.

Between the two cathodes, a cooling coil 119 is provided to cool the electrolyte in this region.

On the left-hand side of the cell as viewed in the drawing, an anode 120 composed of carbon

is supported by a copper bus bar 121, suspended from copper rod 122, connected to a suitable current source (not shown).

On the right-hand side of the cell, a nickel anode 123 is supported by a copper bus bar 124 on a copper rod 125 also arranged for connection to the same current source as rod 122.

In Figure 2 the line YY' represents the normal level of electrolyte in the cell.

Example 1

To illustrate the beneficial effect of the process of the invention, the results of a group of demonstrative tests are plotted graphically in Figure 4 of the attached drawings. Current densities from 0 to 350 amperes per square foot are plotted along the horizontal axis and voltages from 4 to 16 are plotted vertically.

The tests illustrated were conducted using a small diaphragm cell of steel charged with about 3.3 kilograms of a potassium acid fluoride of the approximate composition $KF \cdot 1.8HF$ which varied somewhat during the test. The temperature was maintained at about $110^\circ C$. The carbon (ungraphitized) anodes used had an effective area of $17\frac{1}{2}$ square inches and the nickel anode was a strip of pure cathodic nickel with an effective area of $13\frac{3}{4}$ square inches.

Graph 1 shows the effect of voltage variation upon current densities with a new carbon anode employed in an electrolyte which had been subjected to a preconditioning treatment by electrolysis with a nickel anode. As indicated by this graph, an increase in current density from 100 to 225 amperes per square foot was effected by an increase of voltage from about 7.3 to 8.8

The cell was then operated for 31 hours at a current density maintained at about 200 amperes per square foot. Graph 2 shows that after this period of operation the operating characteristics of the carbon anode were still quite stable. While a higher voltage was necessary for the same current density, an increase in current density from 100 to 225 amperes per square foot was effected by a voltage rise from 7.5 to 9.8.

After the cell was operated for another 23 hours at an approximately constant current density of 200 amperes per square foot, further tests were made and the values shown by graph 3 were obtained. This graph shows that after 54 hours of operation, the anode was still capable of giving fair performance up to a current density of about 210 amperes per square foot. However when an attempt was made to secure a higher current density by increasing the voltage, the result was an abrupt decrease in the current density to about 75 amperes per square foot at a voltage of about 12.4. Still further increase in the voltage failed to cause any substantial increase in current density.

A second carbon anode similar to the one employed in the tests illustrated by graphs 1, 2 and 3 was operated over an extended period at a substantially constant current density of 160 amperes per square foot. After 74 hours of operation under these conditions a test of the cell at various voltages gave the results shown by graph 4. This graph indicates that the maximum, then obtainable current density was slightly more than 100 amperes per square foot, and that further increase in the voltage, instead of increasing the current density, caused a reduction of current density to a value approaching zero.

The carbon anode was then replaced by the nickel anode, using the same cell and the same

electrolyte, and the cell was operated for about $\frac{3}{4}$ of an hour at a current density of about 70 amperes per square foot of effective nickel anode surface.

The nickel anode was then removed and replaced by the carbon anode and operation resumed. The results obtained with the carbon anode when tested to determine the effect of voltage on current density immediately after restoration of activity by the nickel anode are shown by graph 5. As readily apparent from this graph, the activity of the cell after this nickel anode treatment was radically different from that shown by graph 4 and closely approximated its activity after the 31 hour period of operation shown by graph 2, with no recession of current density even though the impressed voltage was sufficient to produce current densities substantially above 300 amperes per square foot and was several volts higher than the critical point prior to the nickel anode treatment.

Example 2

In a cell of the type illustrated in Figures 2 and 3 and having an effective anode area (one side only) of $3\frac{1}{2}$ square feet of carbon (ungraphitized) and a like area of nickel and charged with 1500 pounds of $KF \cdot 2HF$ electrolyte containing 2% of LiF , fluorine was generated at an anodic current density between 14 and 72 amperes per square foot and a temperature between $100^\circ C$ and $105^\circ C$ using the carbon anode 120 and the corresponding cathode 112 for 47,500 ampere hours. During this period hydrogen fluoride was added periodically by way of inlet 106 to replace that consumed and evaporated.

Attempts to increase the current density above 72 amperes per square foot during this period were unsuccessful, the impression of higher voltages causing a definite drop in current density.

The cathode 112 and anode 120 were then disconnected from the current source and the cathode 113 and anode 123 were connected, and operated for $3\frac{1}{2}$ hours at a current density of 114 amperes per square foot. Electrodes 113 and 123 were then disconnected and electrodes 112 and 120 were reconnected. The carbon anode was operated at current densities above 140 amperes per square foot without polarization for many hours. Over a considerable period these high densities were maintained by alternating electrolyses with the nickel anode and its mating cathode after periods of 30,000 to 90,000 ampere hours of operation with the carbon anode and its mating cathode. Out of more than 373,000 ampere hours of operation, only about 7,000 ampere hours on nickel (less than 2% of the total) were required to maintain satisfactory operation with the carbon anode at a current density of 140 amperes per square foot.

The invention is capable of application in other types of equipment as well as those described above. Thus instead of maintaining the electrolyte in a single cell and alternating electrodes, the electrolyte may be withdrawn from the carbon anode cell periodically, and passed to a nickel anode cell for restoration of its activity, and then returned to the same carbon anode cell or a different one, or the electrolyte may be passed, either continuously or intermittently through a bank of cells, including a nickel anode cell so that each increment of electrolyte is periodically electrolyzed in the nickel anode

It will be understood that I intend to include variations and modifications of the invention and that the preceding examples are illustrations only and in no wise to be construed as limitations upon the invention, the scope of which is defined in the appended claims, wherein I claim:

1. In the manufacture of fluorine by electrolysis of a potassium hydrogen fluoride containing between $1\frac{1}{2}$ and 3 mols of HF per mol of KF, the electrolytic method which comprises maintaining the electrolyte in an electrolytic cell at a temperature between 90° and 200° C. and passing an electrolyzing current through the cell by means of a cathode and a carbon anode and briefly interrupting said electrolyzing step when polarization of the carbon anode occurs and passing a current through the cell by means of a cathode and a nickel anode during said interruption to reduce said polarization.
2. In the manufacture of fluorine by electrolysis of a potassium hydrogen fluoride electrolyte containing between 1.8 and 2.0 mols of HF per mol of KF, the electrolytic method which comprises maintaining the electrolyte in an electrolytic cell at a temperature between 100° and 110° C. and passing an electrolyzing current through the cell by means of a cathode and a carbon anode and briefly interrupting said electrolyzing step when polarization of the carbon anode occurs and passing a current through the cell by means of a cathode and a nickel anode during said interruption to reduce said polarization.
3. A method of decreasing the polarization effect which arises in the electrolysis of a potassium hydrogen fluoride electrolyte containing between $1\frac{1}{2}$ and 3 mols of HF per mol of KF in an electrolytic cell utilizing a carbon anode which comprises passing a current through the cell by means of a cathode and a nickel anode while continuing the electrolysis with said carbon anode.
4. The method of claim 3 wherein the current is passed through the cell with the nickel anode continuously during the electrolysis with the carbon anode.
5. The method of claim 3 wherein the current is passed through the cell with the nickel anode intermittently during the electrolysis with the carbon anode.

6. In the manufacture of fluorine by electrolysis with a cathode and a carbon anode of an alkali-metal acid fluoride electrolyte, the method which comprises first conditioning said electrolyte by passing an electric current through said electrolyte by means of a cathode and a nickel anode, ceasing said conditioning, and electrolyzing said electrolyte utilizing a cathode and a carbon anode, briefly interrupting said electrolyzing step when polarization of the carbon anode occurs and passing a current through the electrolyte by means of a cathode and a nickel anode during said interruption to reduce the polarization.
7. The method of claim 6 wherein the electrolyte is a potassium hydrogen fluoride.
8. In the manufacture of fluorine by electrolysis of an alkali-metal acid fluoride electrolyte, the method which comprises electrolyzing said electrolyte by means of a cathode and carbon anode, and briefly interrupting said electrolysis when polarization of the carbon anode occurs and passing an electric current through the electrolyte by means of a cathode and nickel anode during said interruption to reduce said polarization.
9. The method of claim 8 wherein the electrolyte is a potassium hydrogen fluoride.

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