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K. E. STUART ET AL

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ELECTROLYTIC CELL

Filed March 15, 1944

3 Sheets-Sheet 1

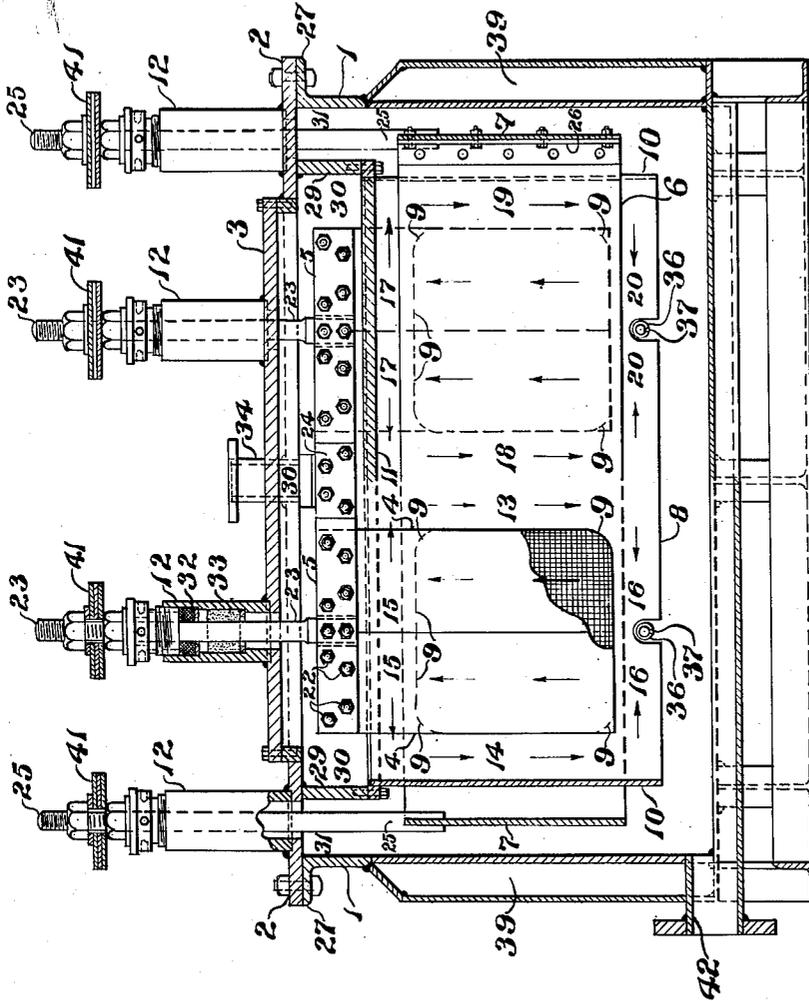


Fig. 1

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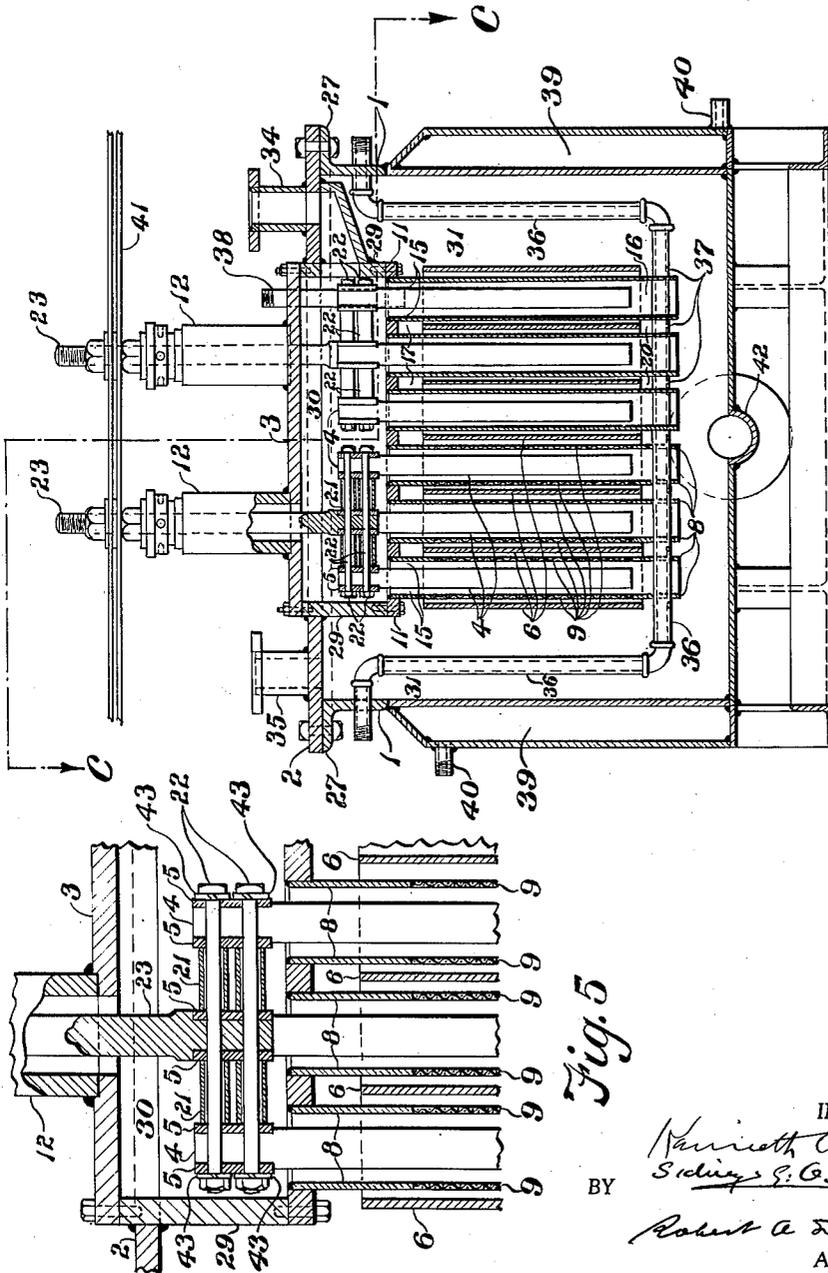


Fig. 2

Fig. 5

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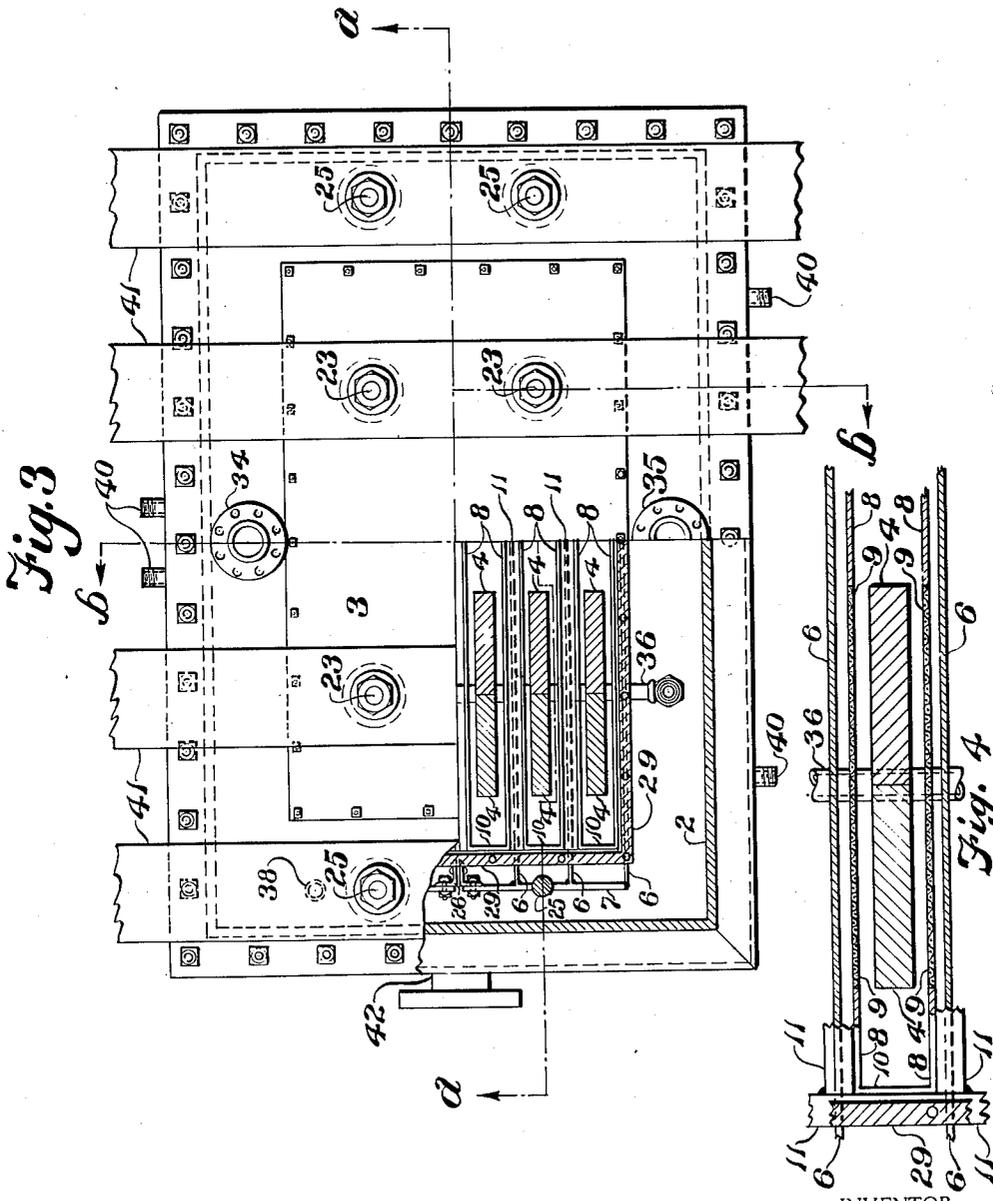


Fig. 3

Fig. 4

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# UNITED STATES PATENT OFFICE

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## ELECTROLYTIC CELL

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3 Claims. (Cl. 204—247)

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Our invention relates to electrolytic cells for production of elemental fluorine from hydrogen fluoride.

It is known that anhydrous hydrogen fluoride forms with anhydrous alkali metal fluorides of the group consisting of sodium, potassium and lithium fluorides, complexes having the general formula  $RF \cdot nHF$ , in which  $n$  may have any value up to 4, or even more. The melting points of these complexes range from those of the salts themselves to below ordinary atmospheric temperature, the complexes being therefore normally solid or liquid.

When these liquid or molten complexes are electrolyzed, fluorine collects at the anode and hydrogen at the cathode, leaving the salt unaffected. The  $HF$  can be replaced during the electrolysis, either continuously or intermittently. Thus the salt acts as a convenient absorbent and vehicle for electrolysis of the hydrogen fluoride in liquid phase.

For this purpose the complexes formed with the potassium salt, having the formula  $KF \cdot nHF$ , are generally preferred. The melting points and vapor pressures of these complexes have been studied by others and graphs of melting points have been published showing several sharp downward cusps, corresponding to eutectics. One of these has a composition of  $KHF_2$  or  $KHF \cdot HF$  and a melting point of about  $235^\circ C$ . Another has a composition of  $KF \cdot 1.9HF$  and a melting point of about  $65^\circ C$ . These are naturally favorable for electrolytic decomposition of the hydrogen fluoride. The vapor pressure of  $HF$  from decomposition of these complexes at or above their melting points is in general such that the electrolytic decomposition products tend to be considerably diluted with hydrogen fluoride. However, in the case of the eutectics, and in particular  $KF \cdot 1.9HF$ , the dilution is comparatively slight.

Fluorine is the most reactive of all the elements. Elemental fluorine attacks all organic substances, under favorable conditions converting the carbon completely to carbon fluorides. It also converts water to oxygen, ozone and  $F_2O$ . Elemental fluorine attacks all metals, including the noble metals, and hydrogen fluoride attacks nearly all metals except the noble metals. However, the fluorides of many metals, including several of the commonest, such as iron and copper, are substantially insoluble in the above described electrolytes and form films over the metals which are very persistent under electrically neutral conditions and even quite persistent under anodic conditions. Under cathodic conditions the hy-

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drogen of course protects the metal. These films are of high electrical resistance or non-conducting and render such metals unfit for use as anodes, but do not necessarily prevent their use for the purpose of electrical connections to the anodes. While not perfectly resistant in such connections, under certain conditions such metals as iron and copper are sufficiently resistant to be practicable for the purpose.

A notable exception to the metals, with respect to their general behavior toward fluorine, is nickel. The fluoride of nickel does not form a protective film over the metal. This renders possible the use of nickel anodes in electrolytic hydrogen-fluorine cells. However, the attack on the nickel is extremely vigorous and the electrolyte becomes quickly contaminated with nickel fluoride. Frequent cleaning of the electrolyte is therefore necessary and the cost of the nickel is a large item of expense.

Carbon does not afford as simple a solution of the problem of providing a practicable anode material for fluorine cells as it does in the case of chlorine cells. Carbon of different grades, graphitized and ungraphitized, behaves differently with respect to a given electrolyte, and carbon of a given grade behaves differently with respect to different electrolytes; also, a carbon of given grade when dipped into an electrolyte behaves differently beneath and above the surface of the electrolyte. Thus, graphitized carbon dipping into electrolyte of relatively high  $HF$  content, e. g.,  $KF \cdot 1.8HF$  at  $100^\circ C$ ., swells in the gas space above the electrolyte so much that the effect can be noted visually. This, of course, tends to cause breakage at the electrolyte level and wherever the carbon is confined by the electrical contacts. The graphite probably also swells beneath the surface of the electrolyte. In any case, if it does not break above the electrolyte, it quickly disintegrates beneath the surface. However, notwithstanding the fact that cells using the  $KHF_2$  electrolyte normally operate at higher temperature, e. g.,  $235^\circ C$ ., the same graphitized carbon appears to last indefinitely where completely immersed in this electrolyte and also in the gas space above it, provided it does not become mechanically broken at the electrical contacts. Ungraphitized carbon, on the other hand, unless it should become mechanically broken at the electrical contacts, appears to last indefinitely in electrolyte of  $KF \cdot 1.8$  to  $2HF$ . It is believed that there is some swelling of the ungraphitized carbon, though not so much as that of graphitized carbon under the same conditions. Also,

it is found that ungraphitized carbon is notably hardened during its use in a fluorine cell.

Breakage at the electrical contacts may be caused by the swelling of the anode just described or from other causes, such as the following: where metal, such as iron or copper, makes contact with the anode, if fluorine or electrolyte is allowed to penetrate between the surfaces of contact the metal becomes quickly coated with the non-conducting film referred to above. This results in high electrical resistance and local heating. If electrolyte be present, the HF is driven out of it by the heat until only KF is left. Eventually this insulates the joint completely; but in the meantime it exerts terrific pressure between the surfaces and is liable to cause breakage of the anode either from mechanical pressure or from high temperature or both.

When carbon or graphite anodes are used, more or less difficulty may be experienced from the phenomena known as "polarization" and "anode effect." It is known that the former is due in large measure to moisture in the electrolyte and the latter to gas films forming upon the surface of the anode. However, with anhydrous electrolyte, effective circulation and good electrical contact, polarization and anode effect do not constitute difficulties, even though the anodes are of carbon, graphitized or ungraphitized, particularly at current densities below 100 amperes per square foot, and such anodes are therefore often preferred, on account of their relative cheapness.

It has been stated above that iron and copper become coated with protective films and are therefore practicable materials from which to construct certain parts of hydrogen-fluorine cells. Neither of these metals, when anodic, will last long in the high melting electrolyte, such as  $\text{KHF}_2$ , although copper is superior to iron under these conditions. However, with the low melting electrolyte, such as  $\text{KF} \cdot 1.8\text{HF}$ , iron is quite practicable, especially for the cathode and electrically neutral main cell body and wire screen "diaphragms," which are used to keep the hydrogen and fluorine from recombining, which they will do instantly and explosively if allowed to come together.

Another problem in the design of electrolytic hydrogen fluorine cells is the sealing of the openings through which the electrical conductors enter the cell and insulation of these conductors from the cell body. For this purpose Portland cement or calcium fluoride with a binder of cement may be used.

It will therefore be seen that the design of a commercially practicable electrolytic hydrogen-fluorine cell involves problems of materials of construction for the cell body, electrodes and insulators, as well as of securing good circulation and replenishment of the HF, besides the usual practical problems of compactness, accessibility, etc. The object of this invention is therefore to produce a compact, durable and efficient electrolytic cell for production of fluorine from hydrogen fluoride and one that can be produced at commercially feasible cost.

Referring to the drawings:

Figure 1 is a side elevation of the cell, partly in section along line *a-a* of Figure 3.

Figure 2 is an end elevation of the cell, partly in section along line *b-b* of Figure 3.

Figure 3 is a plan view of the cell, partly in section along the line *c-c* of Figure 2.

Figure 4 is a horizontal section through a pair

of anodes and the cathodes co-operating therewith at each side and diaphragm between, to an enlarged scale.

Figure 5 is a sectional elevation through an assembly of three anodes, to an enlarged scale.

Referring to the figures:

It will be seen that the cell consists essentially of a tank 1, a cover structure 2, 3, an anode assembly 4, 5, a cathode structure 6, 7, a diaphragm structure 8, 9, 10, 11, and insulators 12.

Tank 1, cover 2, 3, cathode structure 6, 7 and diaphragm structure 8, 9, 10, 11 may be of copper or iron by which latter term it is intended to include commercial steels, or any other suitable metal, depending upon the range of HF content in the electrolyte, and the corresponding temperature range within which it is intended to operate the cell, the iron being in general preferred in the low temperature range, i. e., 90° to 110° C. and copper in the high temperature range, i. e., 235° to 250° C.

While the anodes 4 may be of nickel or carbon, which may be graphitized or ungraphitized, depending upon the electrolyte to be used, carbon anodes are preferred on account of their cheapness and longer life.

Referring to Figure 2, it will be seen that anodes 4 and cathodes 6 alternate, with diaphragms 8, 9 lying between. The diaphragms consist of plates 8, in which are installed wire screen windows 9, as indicated by the dotted lines so designated in Figure 1. The function of screen windows 9 is to permit passage of ions between the electrodes, while preventing mingling of the fluorine formed on one side with the hydrogen formed on the other. Heretofore, it has been supposed that in order to prevent mingling of the gases the screen should have a very fine mesh, e. g., 40 wires per inch. However, the screen is subject to corrosion and screens of such fineness have a very unsatisfactory life. We have now found that the gases are so buoyant in the electrolyte, and their bubbles stream upward with such velocity that they are readily deflected off the wires of the screen. There is therefore no need to use screens of such fineness as heretofore thought necessary. In practice we have been able to use screens as coarse as 5 to 7 mesh and we find that the screen best suited to our purpose is that of 6 mesh, .092-inch wire. Such a screen is about 1/8 inch in thickness. Plates 8 may be of the same thickness as the wire screen, so that the edges of plates and screen will be flush. The screen and plate may be welded along the seam. Anodes 4 are of such proportions, e. g., approximately 6 1/4 x 1 1/4 inches by 18 inches long, that when two are mounted edge to edge and the upper one-third is reserved for circulation and electrical connections, there will be presented by the lower two-thirds a surface of substantially square shape and having an area, with the dimensions assumed, of approximately one square foot upon each face. Two pairs of anode blades are mounted in alignment, with a clearance 13 between as seen in Figure 1. In Figure 1 the section at the left of the center line is in the plane of the face of a set of anodes, one corner of an anode being broken away to show a part of the wire screen diaphragm window 9 beyond it, the rest of the diaphragm window being indicated by dotted lines. To the right of the center line the section is in the plane of the face of a cathode, the diaphragm window and anodes beyond being likewise indicated by dotted lines. It will be seen that plates 8 extend well above and below dia-

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phragm windows 9, and are joined together at their outer edges by plates 10. Each pair of plates 8, with adjoining plates 10, therefore completely encloses the lower or electrolytically active part of a set of four anode blades. Clearances 13 which separate pairs of anode blades and clearances 14 between the outer edges of outer anode blades and plates 10 form passages for downward circulation of electrolyte. With anodes of the dimensions assumed, clearances 13 are preferably not less than six and clearances 14 not less than 3 inches wide. The electrolyte level is maintained at approximately 3 inches above diaphragm level. These dimensions are not critical in themselves, but only as illustrative of proportions, which are important.

Circulation of the electrolyte is set up by rising gas bubbles. The circulation on the anode side of diaphragms 8, 9 is upward over the active faces of the electrodes, outward in each direction in the passages 15 between the anodes and plates 8 above the diaphragm windows, downward through passages 13 and 14 and inward in each direction in the passages 16 beneath the diaphragm windows, as indicated by the arrows in Figure 1. In Figures 3 and 4 passages 13 and 14 are seen in cross section.

The spaces between successive pairs of diaphragms 8, 9 in which cathodes 6 are housed, are open at their sides, and the cathodes extend beyond into the main body of electrolyte filling tank 1. The object of this is to permit the electrical connections to the cathode structure to be made outside the diaphragm structure, where space is restricted.

The paths of circulation of the electrolyte on the cathode sides of the diaphragms 8, 9 are similar in elevation to those on the anode sides, i. e., upward along the faces of the cathodes, outward in each direction in the passages 17 above the cathode, downward in passages 18 between the diaphragm windows and 19 outside the diaphragm windows and inward in each direction in the passages 20 beneath the cathodes.

Referring to Figures 1, 2 and 5:

Anodes 4 are arranged in groups of six in three pairs. The three pairs are spaced apart by sleeves 21 and the blades of each pair clamped between plates 5, the entire assembly being secured together by bolts 22. In order to take up any expansion of bolts 22 spring washers 43 are preferably introduced between outer plates 5 and the nuts and heads of bolts 22. These are clearly shown in Figure 5. Each group of anodes is served by its own electrical conductor 23. In the drawing there are twenty-four anodes, hence four anode conductors. Each anode conductor is connected to its group of anodes by squaring its lower end and clamping the squared end between the middle pair of plates 5, the anodes of the middle pair being notched to provide room for the squared end of the anode conductor. Thus each group of six anodes hangs freely from its anode conductor and does not have to be exactly spaced with reference to the other groups. In order to preserve accurate alignment of the anodes making up the sets of four of Figure 1, however, a fish plate 24 may be carried across between adjacent groups.

We have found that good contact between plates 5 and the carbon of the anodes is of the utmost importance, otherwise electrolyte will penetrate and, losing its HF content, gradually be converted to a high melting non-conducting layer. To prevent this, we have found it very

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effective to introduce into the contact joints a carbonaceous material, such as finely divided carbon in a volatile vehicle, which may be aqueous and is afterward vaporized out, as by baking. It should be noted that the function of such material differs from the normal function of such compositions when used in ordinary electrical contacts, since it includes prevention of penetration of the electrolyte into the contact and protection of the metal contact surface against corrosion.

Cathodes 6 are likewise assembled in groups of three by end plates 7, and each group of three cathodes is served by two cathode conductors 25. Since there are six rows of anodes active on both sides, there must be seven cathodes. The odd cathode is mounted between the two groups of angles 25. There is thus provided a certain amount of adjustment of the spacing between the two groups of cathodes.

The main body of the cell or tank 1 is flanged at 27 to conform with cover 2. Between flange 27 and cover 2 a copper gasket (not shown) may be bolted to render the joint gas and liquid tight.

Depending from cover 2 and paralleling the side walls thereof are inner partition walls 29. Partitions 29 divide the space above the electrolyte level into two gas chambers, the one 30 central and anodic and the other 31 circumferential and cathodic.

Against the lower edges of partitions 29 is bolted a gridlike member 11, made up of bars of rectangular cross section having a width equal to the distance between diaphragm plates 8, on their cathode sides. The bars of grid member 11 are spaced apart by a distance equal to the center to center distance of the cathodes, and welded at their ends to cross bars of like section. Plates 8 and 10 are then welded to the bars of grid member 11, and thus firmly held in proper space relationship to each other and to the electrodes. The normal electrolyte level is that of the upper face of grid member 11.

Above gas chamber 30 cover 2 may be cut away as shown, providing a rectangular opening in cover 2 to facilitate removal of the anode assembly without disturbing the cathode or diaphragm structures, this opening being closed by plate 3. Furthermore it is apparent from the drawings that the entire anode and cathode assembly may be removed by lifting cover 2.

Anode and cathode connectors 23 and 25 are led out through plate 3 and cover 2, respectively, by means of stuffing boxes 12, which also serve as insulators. Insulators 12 are rendered gas tight by means of non-conducting pressure-plastic material, referred to above, as indicated at 32, such as certain polymerization products, which do not concern this invention. In the case of the anode insulators, which are subjected to fluorine, this material is protected by non-conducting composition indicated at 33. This may be largely of calcium fluoride, with a suitable binder, such as Portland cement or sodium silicate.

The exit for fluorine from chamber 30 is by way of pipe 34 and that for hydrogen from chamber 31 by way of pipe 35.

HF must of course be supplied to the electrolyte continuously or at frequent intervals. For this purpose sparger pipes 36 are provided. These are two in number and extend crosswise of the electrode assemblies, preferably beneath the contiguous edges of each pair of anodes. Pipes 36 are provided with holes 37 of their lower sides, one for each set of electrodes.

Pipe 34 communicates with gas chamber 30 through one of the side walls of partition 29, as shown in Figure 2. Pipe 35 communicates with gas chamber 31 through cover 2. HF feed pipes 36 pass through the side walls of tank 1. Plate 3, with the anode assembly suspended from it, may therefore be lifted without disturbing any of the gas pipe connections.

The supply of HF to the cell is regulated so as to keep the electrolyte level constant. It is found that this affords a very simple and convenient method of regulation. For this purpose open-mouthed well pipe 38 is provided. This dips beneath the surface of the electrolyte, preferably in a position to collect hydrogen evolved at the cathode. The upper end of pipe 38 is connected to a pressure-responsive device outside the cell. The hydrogen displaces the electrolyte, building up a pressure in pipe 38 corresponding to the head of electrolyte to above its open end. This pressure acts upon the pressure-responsive device, which is thereby caused to indicate variations in electrolyte level.

It should be noted that plates 8 and 10 form anode compartments, each substantially completely enclosing one set of anodes but providing ample room for circulation of electrolyte and open at their tops for discharge of fluorine. There is therefore no possible way by which the fluorine can escape from these anode compartments to the cathode compartments intervening between them which does not involve a check in the upward movement of the gas bubbles and sharp lateral detour through the wire screen of the diaphragm windows. The same is true with regard to escape of hydrogen to the anode compartments. Since the paths provided for circulation of the electrolyte are clear and definite, there is little or no tendency for electrolyte to pass from one compartment to the other through the screens, hence little or no mingling of the gases. Hydrogen and fluorine combine instantly without ignition. Any mingling of the gases in these cells would therefore be indicated by explosions which generally take place between minute quantities of gases causing only pops, but could easily become serious. In normal operation of the cell of the present invention no explosions, even of infinitesimal intensity, are noted.

In the figures the anode compartments are shown as open at their bottoms. This is however optional. If preferred these compartments may be closed at their bottoms by plates (not shown) similar to plates 10. In that case, the cathode insulators may be dispensed with and the cathodes connected directly to the walls of tank 1, which then becomes cathodic. However, in that case it becomes necessary to insulate grid member 11 from partition walls 29, which turns out to be more of a complication than insulating the cathodes from the main body of the cell.

Since there is no liquid effluent from hydrogen-fluorine cells and much heat is generated within them, it is in general necessary to cool these cells. This may be done as by means of jacket 39 extending around the sides of the cell. The cell is then cooled by passing cooling liquid or vapor through the jacket as through pipe connections 40 at a temperature somewhat below that at which it is desired to maintain the cell. If the cell is to operate at 110° C. the cooling medium may be steam at atmospheric pressure; or water may be allowed to boil and reflux in the jacket.

If desired the bottom of the cell can likewise be jacketed, but in the drawings the cell is shown

with an unjacketed bottom, permitting the electrolyte to be melted by application of heat as from gas burners (not shown). Electric current is supplied to conductors 23 and 25 by bus bars 41.

Pipe 42 is provided for drawing off used electrolyte as for cleansing.

The cell illustrated and described above, equipped with carbon anodes, may be operated continuously for considerable periods without interruption for repairs or other reason, at a voltage below nine and current efficiency of 90 per cent or higher.

While we have illustrated and described a cell equipped with carbon anodes, we do not wish to be limited thereto, as any metal whose fluoride is non-adherent is more or less suitable for use as an anode in this cell, although in general metallic anodes do not last as long as carbon anodes and yield a somewhat lower current efficiency.

Although we have illustrated and described the curtain walls or diaphragms enclosing the anodes as constructed of imperforate plate with screen windows opposite the anodes only, we do not wish to be limited to this construction, as the diaphragms may be constructed entirely of screen. Also, if preferred, plates 10, which join plates 8 to complete the enclosure about the anodes, may be omitted. Likewise although we prefer woven wire screen, we do not wish to be limited thereto, as perforated plates having openings of like size are more or less equivalent thereto.

It is to be understood that the above particular description is by way of illustration, and that changes, omissions, additions, substitutions and/or modifications might be made within the scope of the claims without departing from the spirit of the invention.

We claim as our invention:

1. An electrolytic cell for production of hydrogen and fluorine from a molten, substantially anhydrous electrolyte consisting of hydrogen fluoride absorbed in alkali metal fluoride, comprising a normally level metal tank, a gas and liquid retaining cover therefor, an opening in said cover, a cover plate for said opening, an anodic electrode withdrawable through said opening, a cathodic electrode spaced from said anodic electrode, an electrical conductor extending through said cover plate connected to and supporting said anodic electrode, means for insulating said conductor from said cover plate and forming a gas tight closure between said conductor and said cover plate, means for supporting said cathodic electrode, and means for collecting the gases evolved upon said anodic and cathodic electrodes respectively in separate chambers, said tank having outlets therein for separately delivering said gases from said chambers.

2. An electrolytic cell for production of hydrogen and fluorine from a molten, substantially anhydrous electrolyte consisting of hydrogen fluoride absorbed in alkali metal fluoride, comprising a normally level metal tank, a gas and liquid retaining cover therefor, an anodic electrode, a cathodic electrode spaced from said anodic electrode, partition walls depending from said cover paralleling the walls of said tank and dividing the gas space beneath said cover into anodic and cathodic gas chambers, said anodic gas chamber being closed at the top by a cover plate, said anodic electrode being withdrawable through said anodic gas chamber, an electrical conductor extending through said cover plate, connected to and supporting said

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anodic electrode, an electrical conductor extending through said cover connected to and supporting said cathodic electrode, means for insulating said conductors from said cover and cover plate and forming gas tight closures between said conductors and said cover plate, a conduit through said cover outside and clear of said cover plate communicating with said anodic gas chamber through one of said partition walls and a second conduit through said cover outside and clear of said cover plate communicating with said cathodic gas chamber.

3. An electrolytic cell for production of hydrogen and fluorine from a molten, substantially anhydrous electrolyte consisting of hydrogen fluoride absorbed in alkali metal fluoride, comprising a rectangular normally level metal tank, a gas and liquid retaining first cover therefor, means defining a centrally located opening in said first cover, a gas and liquid retaining second cover for said opening, a plurality of flat parallel spaced, aligned, anodic electrodes, a plurality of parallel, flat cathodic electrodes spaced from and alternating with said anodic elements, electrical conductors extending through said first cover and conductively connected to and supporting said cathodic electrodes, electrical conductors extending through said second cover and conductively connected to and supporting said anodic electrodes, means for insulating said conductors from said covers and forming gas tight closures between said conductors and respective cover, partition walls depending from said first cover paralleling the walls of said tank and dividing the gas space in said cell into anodic and cathodic gas chambers, metal curtain walls depending from said first cover between the electrodes and forming inverted gas conveying chan-

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nels above said cathodic electrodes, said metal curtain walls adapted to be submerged in the electrolyte and to receive gas evolved upon said cathodic electrodes and deliver said gas to the cathodic gas chamber, metal screens depending between the anodic and cathodic electrodes from said curtain walls, a first conduit communicating with said anodic gas chamber through said first cover and said partition wall for withdrawing from the cell the gases evolved at the anodic elements, and a second conduit in said first cover communicating with said cathodic gas chamber for withdrawing from the cell the gases evolved at the cathodic elements.

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