ELECTROLYTIC FLUORINE CELL

Filed April 28, 1950

FIG. 1.

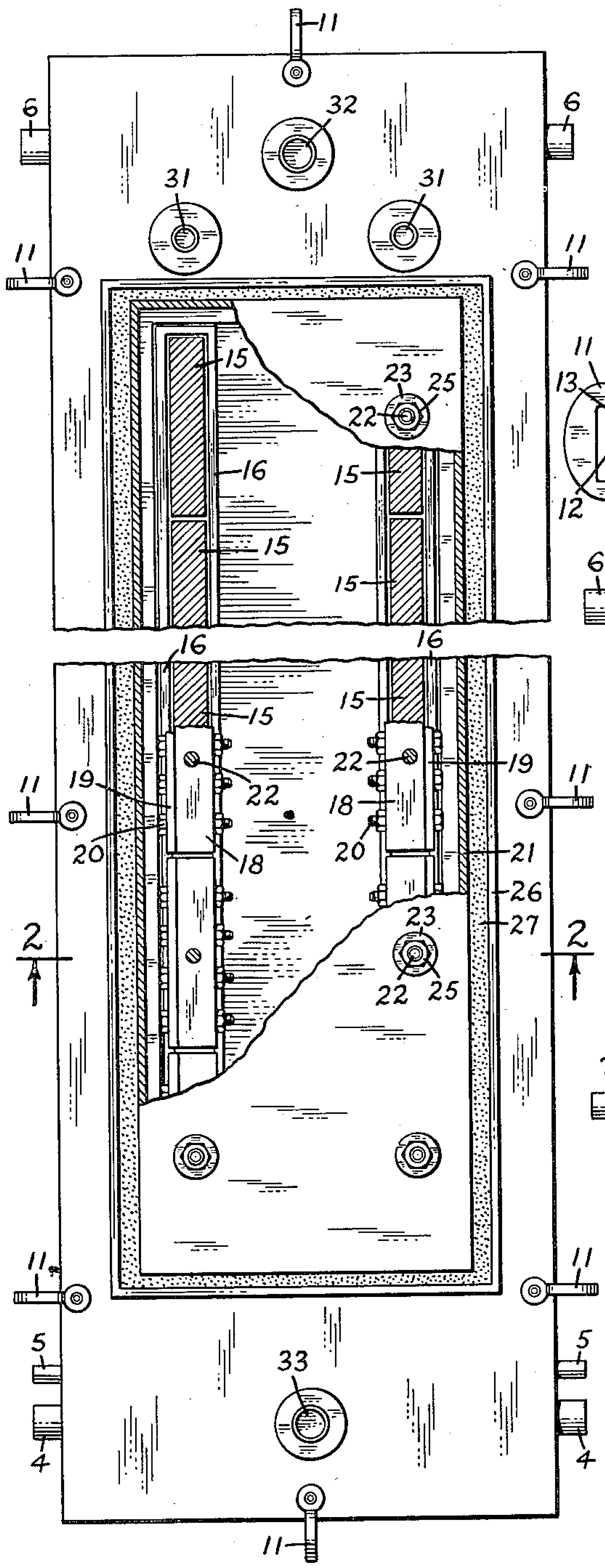
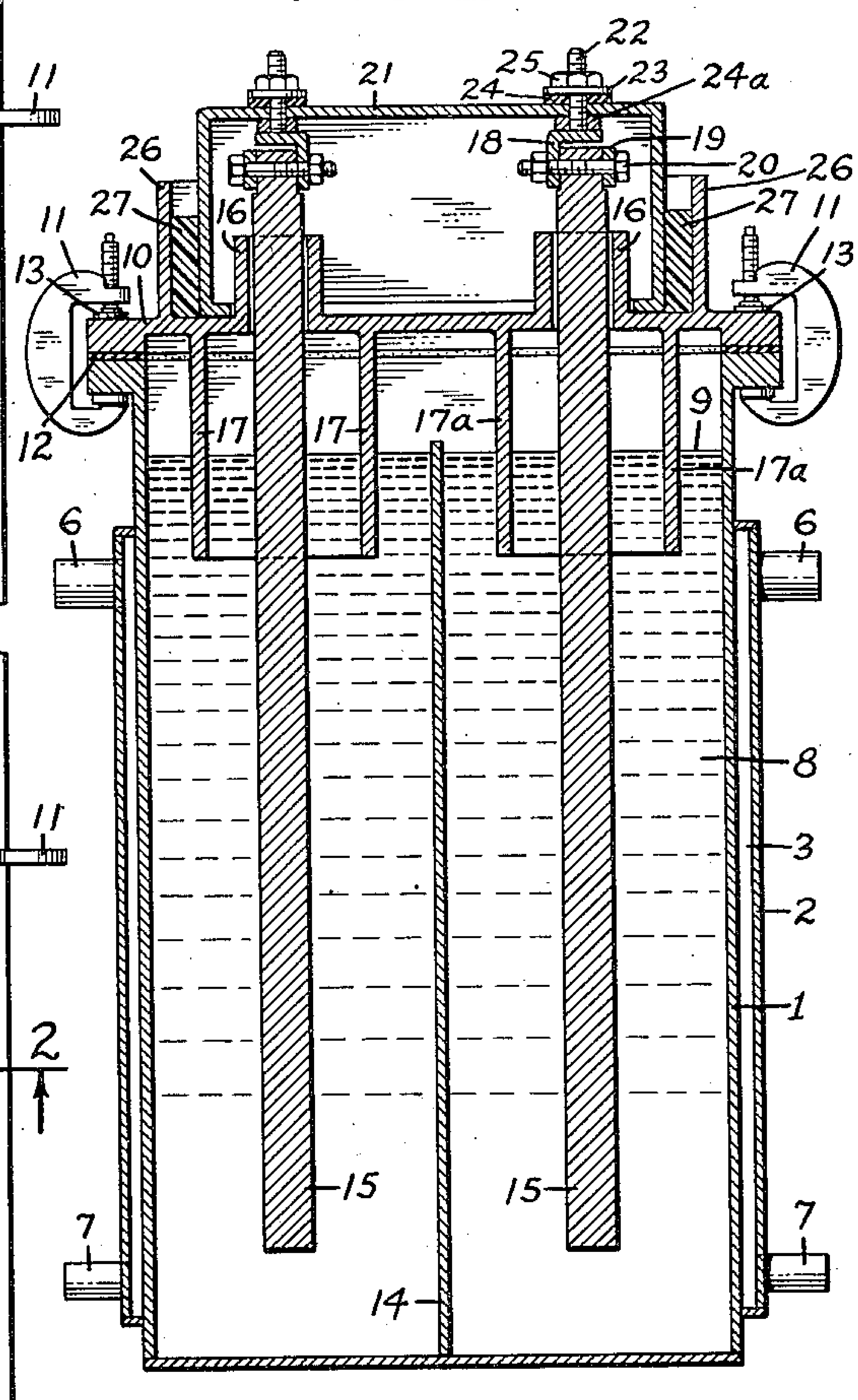


FIG. 2.



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Patented Jan. 6, 1953 2,624,703

UNITED STATES PATENT OFFICE

2,624,703

ELECTROLYTIC FLUORINE CELL

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Application April 28, 1950, Serial No. 158,634

10 Claims. (Cl. 204—247)

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This invention relates to improvements in electrolytic cells and is particularly concerned with improvements in electrode-metal contacts, such as the carbon anode-metal contacts employed in electrolytic fluorine cells.

Commercial electrolytic fluorine cells with carbon as the anode material have been successfully developed. However, they have been subjected to the important disadvantage of deterioration of their carbon anode-metal contacts. The basic cause of failure has been penetration of electrolyte between the carbon and metal forming an insulating layer. Such an insulating layer increases the resistance of the contact, develops excessive temperatures and causes distortion of the metal and premature cracking of the carbon anode. Various methods to improve the carbon anode-metal contact have been proposed, for example, by using an electrode paste at the carbon-metal interface. However, in general, these methods have proved inadequate to prevent impairment of the contact.

An object of the present invention is to provide an improved electrolytic fluorine cell simple in structure and efficient in operation.

Another object is to provide electrode-metal contacts, particularly carbon anode-metal contacts, having an improved life.

A further object is to provide carbon anode-metal contacts operating in an atmosphere of evolved gas but protected from electrolyte spray.

Further objects will appear from the following description of the invention.

In the electrolytic cell of my invention, the upper end of an inert electrode extends through an opening in the cell top, and the top has a vertical extension which projects upwardly around the periphery of the opening and forms a wall spaced closely to the adjacent face of the electrode. The width of this space in relation to its length is so small that electrolyte splash and spray do not pass through. Even though solidified electrolyte may partially fill the space, no deleterious effect upon the electrode is produced thereby. Each opening in the cell top may embrace one or several electrodes. An electrically conductive electrode connector fixed to the top of the electrode projects upwardly through a cap which surrounds the wall and rests on the cell top. A second extension projects upwardly from the top and forms a wall around the cap. The space between this wall and the cap is filled with an inert plastic mass to provide a seal between the cap and the top.

In order to provide a more complete under-

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standing of my invention, there follows a description of a practical specific embodiment thereof. This description should be considered in connection with the accompanying drawings wherein

Fig. 1 is a section in plan partly cut away to show the interior construction above the cell top.

Fig. 2 is a section in end elevation on line 2—2 in Fig. 1.

Referring to the drawings: The cell illustrated comprises a rectangular tank 1 surrounded by a jacket 2. The tank 1 and the jacket 2 consist preferably of steel. The jacket space 3, provided with water inlets 4, steam inlets 5, water outlets 6, and condensate outlets 7, is employed for circulation of a heating or cooling medium to maintain the desired temperature within the cell. The interior 8 of the tank is filled with electrolyte up to the level indicated by 9. The tank 1 has a top 10 which is attached to the tank by C-clamps 11. Sealing gaskets 12 and 13 act to insulate the top from the tank and the C-clamps, respectively. Extending longitudinally in the center of the cell and connected to the bottom of the tank is a cathode 14, constructed preferably of steel. Two parallel groups of anodes made up of a number of carbon elements 15 extend through openings in the top. Each group of anodes comprises, for instance, 12 to 15 carbon elements. Vertical extensions 16 project upwardly from the top, around the periphery of the openings, forming walls at least about 1″ high and spaced not more than about ⅛″ from the faces of the anodes, preferably about 4″ high and spaced about $\frac{1}{16}$″ from the faces of the anodes. By thus constructing the cell, electrolyte splash and spray are prevented from passing through the openings. Gas barrier members 17 and 17*a*, extending continuously around each group of anodes and spaced from them and from the cell wall and central cathode, depend from the top and are of suitable length to extend into the electrolyte to a substantially lesser depth than the anodes and central cathode. The members 17 and 17*a* serve to separate the vapor space above the level of the electrolyte into anode and cathode compartments. The top 10 and gas barrier members 17 and 17*a* are constructed advantageously of magnesium. An electrically conductive angle bar 18 overlies the end of each anode and a portion of one face thereof. Alternatively, a single angle strip may serve for all the anodes of each group and simultaneously serve as a bus bar for current supply. An electrically conductive plate 19 overlies a corresponding portion of the opposite face of the anode. Bolts 20 compress the anode between the angle bar and the plate. A cap 21, turned in at its base for stiffness and made preferably of steel, surrounds vertical extensions 16 and rests on the top. An electrically conductive rod 22 is fixed to the overlying end of the angle bar and projects upwardly through the cap. Angle bar 18, plate 19 and rod 22 are constructed preferably of copper, and bolts 20 are constructed preferably of steel. Sealing gaskets 24 and 24*a* are placed on the rod on both sides of the cap. A nut 25, or other suitable means, draws the angle bar firmly upward against gasket 24*a* and compreses gasket 24 between the cap and a washer 23. Projecting upwardly from the top and forming a wall around the cap, is an extension 26. An inert plastic mass 27, for example, a mixture of 36% potassium fluoride, 25% hydrogen fluoride and 39% fluorspar, is placed between extension 26 and the cap thereby sealing the joint between the cap and the top. Other suitable sealing materials are semi-plastic polymers such as polytetrafluoroethylene and polymonochlorotrifluoroethylene.

In operation, the cell illustrated in the drawings is charged with electrolyte to approximately the level indicated in Fig. 2. The electrolyte consists effectively of a mixture comprising 41% to 45% hydrogen fluoride, 1% lithium fluoride and the remainder potassium fluoride. This electrolyte is maintained at a temperature of about 100° to 110° C. An electrolyzing current is supplied at a current density of about 100 amperes per sq. ft. with a potential difference of about 10 volts across the terminals of the cell. Fluorine is liberated at the anodes and is withdrawn from the anode compartments through outlets 31. Hydrogen is liberated at the cathode and is withdrawn from the cathode compartment through outlet 32. As the electrolysis proceeds the electrolyte is generated by introducing hydrogen fluoride below the surface of the electrolyte through inlet 33.

By employing magnesium in the construction of the top and gas barriers of my electrolytic cell, I have found it unnecessary to insulate them from the carbon anodes. This simplification in cell structure is made possible by the discovery that the anodic magnesium develops a non-conducting barrier film in a fluorine cell melt and, consequently, does not cause liberation of fluorine in the hydrogen compartment of the cell with its resultant danger of explosion from recombining hydrogen and fluorine.

By means of the present invention, deterioration and early failure of the carbon anode-metal contacts in electrolytic fluorine cells are prevented, and the cost of operation is substantially reduced. It is to be understood, however, that the improvements in cell construction described are considered to be broadly new not only for electrolytic fluorine cells but for other electrolytic cells where similar problems exist.

I claim:

1. In an electrolytic cell, an improved cell top and electrode assembly comprising a cell top, a carbon electrode extending through an opening in the cell top, a vertical extension projecting upwardly from the top, around the periphery of the opening and forming a wall spaced closely to the face of the electrode, a metallic electrode connector fixed to the top of said electrode and projecting upwardly through a gas-tight cap surrounding said extension and resting on the cell top, an extension projecting upwardly from the top, forming a wall around the cap, and an inert plastic mass between the latter wall and the cap sealing the joint between the cap and the top.

2. In an electrolytic fluorine cell, an improved cell top and anode assembly comprising a cell top, a carbon anode extending through an opening in the cell top, a vertical extension projecting upwardly from the top, around the periphery of the opening and forming a wall at least about 1'' high and spaced not more than about ⅛'' from the face of the anode, a metallic anode connector fixed to the top of said anode and projecting upwardly through a gas-tight cap surrounding said extension and resting on the cell top, an extension projecting upwardly from the top, forming a wall around the cap, and an inert plastic mass between the latter wall and the cap sealing the joint between the cap and the top.

3. In an electrolytic fluorine cell, an improved cell top and anode assembly comprising a cell top constructed of magnesium and insulated from the cell body, a carbon anode extending through an opening in the cell top, a vertical extension projecting upwardly from the top, around the periphery of the opening and forming a wall at least about 1'' high and spaced not more than about ⅛'' from the face of the anode, a metallic anode connector fixed to the top of said anode and projecting upwardly through a gas-tight cap surrounding said extension and resting on the cell top, an extension projecting upwardly from the top, forming a wall around the cap, and an inert plastic mass between the latter wall and the cap sealing the joint between the cap and the top.

4. In an electrolytic fluorine cell, an improved cell top and anode assembly comprising a cell top constructed of magnesium and insulated from the cell body, a carbon anode extending through an opening in the cell top, a vertical extension projecting upwardly from the top, around the periphery of the opening and forming a wall at least about 1'' high and spaced not more than about ⅛'' from the face of the anode, an electrically conductive angle bar overlying the upper end of the anode and a portion of one face thereof, an electrically conductive plate overlying a corresponding portion of the opposite face of said anode, means for compressing said anode between said angle bar and plate, a gas-tight cap surrounding said extension and resting on the cell top, an electrically conductive rod fixed to the overlying end of the angle bar and projecting upwardly through said cap, an extension projecting upwardly from the top, forming a wall around the cap, and an inert plastic mass between the latter wall and the cap sealing the joint between the cap and the top.

5. In an electrolytic fluorine cell, an improved cell top and anode assembly comprising a cell top constructed of magnesium and insulated from the cell body, a carbon anode extending through an opening in the cell top, a vertical extension projecting upwardly from the top, around the periphery of the opening and forming a wall about 4'' high and spaced about 1/16'' from the face of the anode, an electrically conductive angle bar overlying the upper end of the anode and a portion of one face thereof, an electrically conductive plate overlying a corresponding portion of the opposite face of said anode, means for compressing said anode between said angle bar and plate, a gas-tight cap surrounding said

extension and resting on the cell top, an electrically conductive rod fixed to the overlying end of the angle bar and projecting upwardly through said cap, an extension projecting upwardly from the top, forming a wall around the cap, and an inert plastic mass between the latter wall and the cap sealing the joint between the cap and the top.

6. In an electrolytic fluorine cell, an improved cell top and anode assembly comprising a cell top constructed of magnesium and insulated from the cell body, a carbon anode extending through an opening in the cell top, a vertical extension projecting upwardly from the top, around the periphery of the opening and forming a wall about 4'' high and spaced about $\frac{1}{16}$'' from the face of the anode, an electrically conductive angle bar overlying the upper end of the anode and a portion of one face thereof, an electrically conductive plate overlying a corresponding portion of the opposite face of said anode, means for compressing said anode between said angle bar and plate, a gas-tight cap surrounding said extension and resting on the cell top, an electrically conductive rod fixed to the overlying end of the angle bar and projecting upwardly through said cap, an extension projecting upwardly from the top, forming a wall around the cap, and a plastic mass of potassium fluoride, hydrogen fluoride and fluorspar between the latter wall and a cap sealing the joint between the cap and the top.

7. An improved electrolytic fluorine cell comprising a jacketed, rectangular metal tank for holding the electrolyte, a vertical metal cathode extending longitudinally in the center of the cell and electrically connected to the cell body, a cell top constructed of magnesium and insulated from the cell body, a carbon anode extending through an opening in the cell top, the top having a vertical extension projecting upwardly around the periphery of the opening and forming a wall about 4'' high and spaced about $\frac{1}{16}$'' from the face of the anode, a magnesium gas barrier integral with the top and projecting downwardly into the electrolyte to a substantially lesser depth than the anode and central cathode and spaced intermediately between the anode, on the one hand, and the cell wall and central cathode, on the other hand, a copper angle bar overlying the upper end of the anode and a portion of one face thereof, a copper plate overlying a corresponding portion of the opposite face of said anode, means for compressing said anode between said angle bar and plate, a metal gas-tight cap turned in at its base surrounding said upwardly projecting extension and resting on the cell top, a copper rod fixed to the overlying end of the angle bar and projecting upwardly through said metal cap, a sealing gasket on the rod, means on said rod for drawing the angle bar firmly upward against said cap and for compressing said gasket against said cap, an extension projecting upwardly from the top, forming a wall around the cap, and a plastic mass of potassium fluoride, hydrogen fluoride and fluorspar between the latter wall and the cap sealing the joint between the cap and the top.

8. In an electrolytic fluorine cell, an improved cell top and anode assembly comprising a cell top, two groups of anodes, each group containing a plurality of carbon anodes extending through an opening in the cell top, vertical extensions projecting upwardly from the top, around the peripheries of the openings and forming walls at least about 1'' high and spaced not more than about ⅛'' from the faces of the anodes, a metallic anode connector fixed to the top of each anode and projecting upwardly through a gas-tight cap surrounding said extensions and resting on the cell top, an extension projecting upwardly from the top, forming a wall around the cap, and an inert plastic mass between the latter wall and the cap sealing the joint between the cap and the top.

9. An improved electrolytic fluorine cell comprising a jacketed, rectangular metal tank for holding the electrolyte, a vertical metal cathode extending longitudinally in the center of the cell and electrically connected to the cell body, a cell top constructed of magnesium and insulated from the cell body, two groups of anodes, each group containing a plurality of carbon anodes extending through an opening in the cell top, the top having vertical extensions projecting upwardly around the peripheries of the openings and forming walls about 4'' high and spaced about $\frac{1}{16}$'' from the faces of the anodes, magnesium gas barriers integral with the top and projecting downwardly into the electrolyte to a substantially lesser depth than the anodes and central cathode and extending continuously around each group of anodes, a copper angle bar overlying the upper end of each anode and a portion of one face thereof, a copper plate overlying a corresponding portion of the opposite face of said anode, means for compressing said anode between said angle bar and plate, a metal gas-tight cap turned in at its base surrounding said upwardly projecting extensions and resting on the cell top, copper rods fixed to the overlying ends of the angle bars and projecting upwardly through said metal cap, sealing gaskets on the rods, means on said rods for drawing the angle bars firmly upward against said cap and for compressing said gaskets against said cap, an extension projecting upwardly from the top, forming a wall around the cap, and a plastic mass of potassium fluoride, hydrogen fluoride and fluorspar between the latter wall and the cap sealing the joint between the cap and the top.

10. In an improved electrolytic fluorine cell, a cell container having a substantially vertical wall, said container constituting a cathode and adapted to contain electrolyte, a carbon anode within said cell, a magnesium cell top insulated from the cell container but electrically connected to the carbon anode, a cooling jacket adjacent said wall of the cell container, and a magnesium gas barrier projecting downwardly from the cell top within said container and extending below the top of the cooling jacket.

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