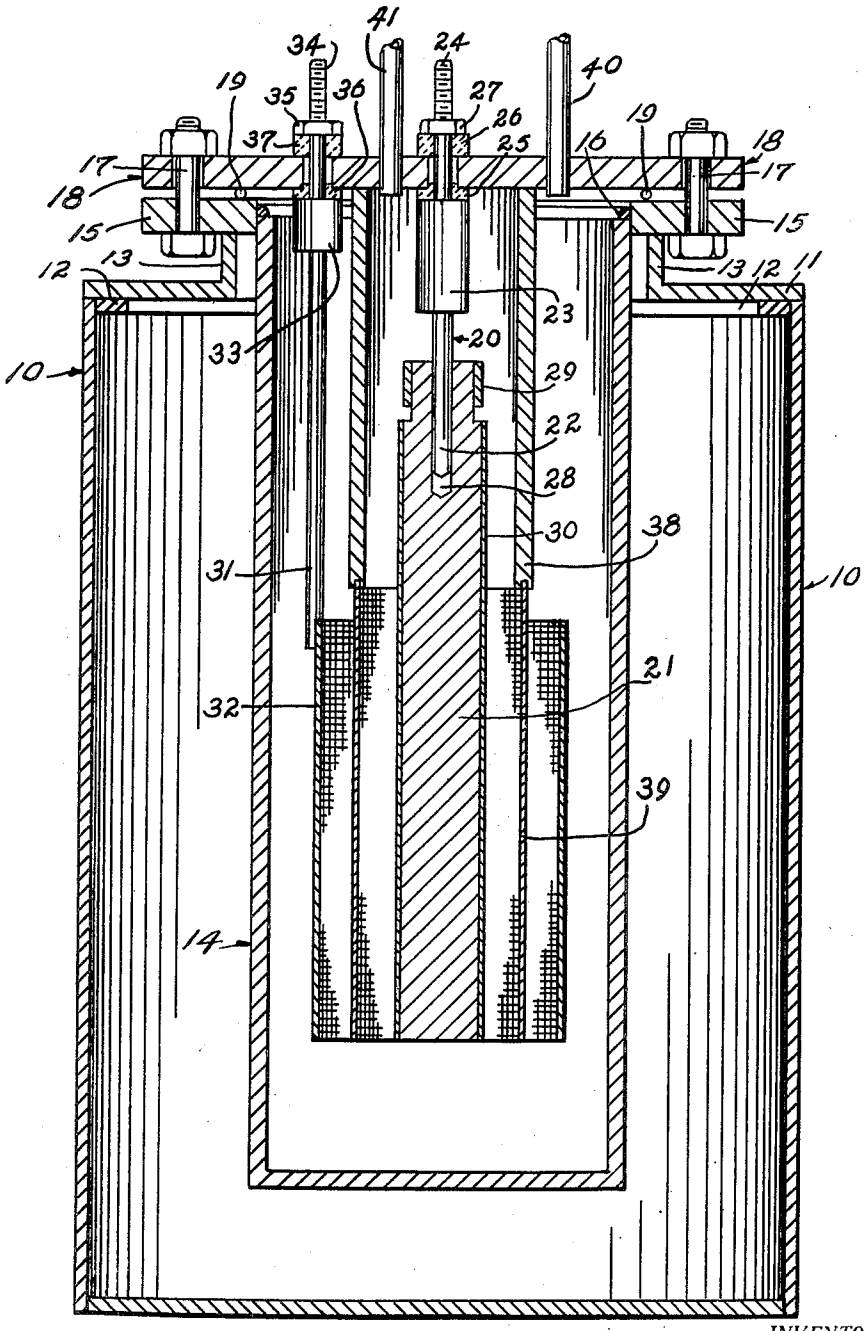
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ELECTROLYTIC PRODUCTION OF FLUORINE

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## ELECTROLYTIC PRODUCTION OF FLUORINE

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5 Claims. (Cl. 204—60)

1

This invention relates to the manufacture of fluorine and more especially to a process for generating elemental fluorine by the electrolysis of hydrogen fluoride in an electrolyte comprising hydrogen fluoride and potassium fluoride.

This application is a division of my copending application Serial No. 792,248, filed December 17, 1947, as is also my copending application Serial No. 75,138, filed Feb. 8, 1949.

In the past, great difficulty has been experienced in the generation of fluorine by electrolysis of hydrogen fluoride due to the extremely corrosive nature of fluorine and hydrogen fluoride and to polarization effects; and, especially, difficulty has been encountered in securing satisfactory results both initially and over extended periods of time. Accordingly, the principal object of the invention is to reduce objectionable corrosion and polarization whereby to enable smooth starting and long continued production of fluorine with a minimum of polarization difficulties.

More specifically, an object of the invention is to provide improved cell operation by the use of a special anode in combination with the electrolyte above indicated, such anode being provided with a thin coating of nickel on a carbon anode body which may or may not be copper-filled according to choice whereby such anode effectively is intiailly a nickel anode and after a period of operation sufficient to eliminate water from the electrolyte becomes a carbon anode during subsequent operation.

Other and more limiting objects will be in part apparent and in part pointed out hereinafter in connection with the accompanying drawings wherein the figure is a central vertical section taken through the vertical axis of a cylindrical cell in connection with which the invention is realized.

Referring now to the drawing, the numeral 10 indicates a receptacle adapted to contain a heat transfer medium such as water for maintaining a suitable operating temperature. Supported on the upper rim of the cylinder wall of the receptacle 10 is a cover 11 provided with an annular rib 12 serving as a positioning element. Extending upwardly from the cover element 11 and surrounding a central opening therein is a flange 13 adapted to support and position the cell proper. The cell proper may consist of a cylindrical receptacle 14 having an annular flange 15 welded thereto at its upper end and adapted to rest upon the flange 13 for support. The flange 15 may be secured to the receptacle 14 by welding as indicated at 16. Secured to the flange 15 by

2

suitable bolts 17 is a cover plate 18. In order to form a gas-tight cell between the flange 15 and the cover plate 18, there is provided a gasket which may take the form of a soft copper wire ring 19.

Sealed through the cover plate 18 is a supporting device 20 for the special anode 21. This device may consist of a rod 22 having a collar 23 and a threaded upper end 24. Received on the rod 22 and abutting against the collar 23 is a lower gasket 25 engaging the lower surface of the cover plate 18. Also received on the rod 22 is an upper gasket 26 engaging the upper surface of the cover plate 18. The nut 27 serves to clamp the gaskets in sealing relation as indicated. The anode 21 is provided at its upper end with a drill hole 28 within which is tightly received the lower end of the rod 22. In order to secure good contact between the anode 21 and the rod 22 a reenforcing band 29, which may be of copper, is placed on the upper end of the copper filled carbon anode.

The preferred anode is made up by first shaping a porous carbon body, placing the same in a vacuum vessel containing molten copper and, after the gases have been exhausted from the porous carbon body, immersing the latter in the molten copper. In this way the pores of the carbon rod are filled with copper so that there is provided a carbon matrix filled with copper with both carbon and copper being continuous throughout. The drill hole 28 is then formed in the copper filled carbon cylinder and the rod 22 is pressed into place, and the reenforcing band 29 is applied. The resulting carbon anode is then placed in a nickel plating solution and a thin coating of nickel 30 is applied. While the thickness of the coating 30 is not sharply critical, it should be a thin coating and preferably is of the order of from 0.00002 to 0.0001 of an inch.

Also sealed through the cover plate 18 are three rods 31 (only one thereof being shown for clarity of illustration) serving as supports for the cathode 32 which may be perforated sheet metal or wire screen. The rods 31 are provided with collars 33 and threaded upper ends 34 whereby the nut 35 serves to clamp gaskets 36 and 37 against the lower and upper surfaces of the cover plate 18. Interposed between the anode 21 and the cathode 32 is a cylindrical partition made up of a wall 38 which is imperforate and a screen portion 39 which is perforated or reticulated. This partition serves to separate the cell into an anolyte compartment and a catholyte compartment. The screen permits interchange of electrolyte

and the migration of ions but serves to deflect the gases generated by electrolysis from passage between the anolyte and catholyte compartments. An exit pipe 40 leads out of the catholyte compartment while a similar exit pipe 41 leads out of the anolyte compartment. A filling opening (not shown) may be provided for the introduction of electrolyte or components thereof to the cell. This, in its simplest form, may be simply a threaded opening in the cover plate 18 provided with a threaded plug for sealing it when the cell is in use. It then becomes possible to introduce such materials beneath the surface of the electrolyte if desired by introducing a conduit through such openings to a point below the surface.

The operation of the cell above described in the manner now to be set forth, embodies the process which constitutes the present invention. This process comprises passing current through an electrolyte comprising KF and HF preferably in proportion from 1.75 to 2.1 mols of HF per mol of KF and preferably containing from 0.8 to 0.1% of LiF by weight based upon the combined weight of KF and HF, and between a carbon anode (porous or copper-filled) and a cathode, the anode being initially coated with a thin coating of metallic nickel, and continuing to pass current between said anode and cathode after said coating of metallic nickel has disintegrated. This process assumes that the electrolyte, as made up, will contain a proportion of water unavoidably introduced as impurity in the materials making up the electrolyte, especially the anhydrous HF which usually contains from .005% to .01% water. The initial moisture content may be substantially more than usual impurity without interfering with successful operation of the present process since the excess will be electrolyzed away before nickel begins to corrode. After the moisture content has been reduced to a point where corrosion of the nickel begins, or, as is usually the case, the moisture content is already at that point, there is ordinarily still too much moisture for successful carbon anode operation. Just what the maximum allowable moisture concentration for carbon anode operation is I have not been able to ascertain on a quantitative basis, but I have found that after the electrolyte has been "broken in" the addition of a small per cent of the volume of the electrolyte (less than 5% by weight, preferably 1% to 2% by weight) of HF containing as much as .01% water can be made without raising the moisture content of the entire body of electrolyte too much for operation with the novel anode. The same is true with a similar anode not having the nickel plate if somehow the "breaking in" has been successfully accomplished, although the nickel plated anode, even after the nickel coating has disintegrated is in my experience less likely to exhibit unwetted areas when removed from the electrolyte. It appears that when an anode has been once polarized, it never conducts current as well as the anode according to the present invention which does not polarize in the initial cell operation. Anodes according to the invention are rated at 50 amperes (at 10 volts) conservatively and frequently carry 70 or even more at that voltage as compared with 20 or possibly less for an anode of the same size and construction but not nickel plated. The amount of current seems to be proportioned to the wetted area of the anode. The mere fact that an anode has never polarized would not appear to be a sufficient explanation for continued high current carrying power and I believe that after the disintegration of the nickel metal coating there may remain some part of the nickel in the form of nickel fluoride or some complex with other compounds present. In any event, there definitely is improved freedom from polarization and continued improved current carrying power.

While I have shown and described a suitable fluorine cell in connection with which my invention may be realized, it is to be understood that cells of other design could be used. The electrolyte described gives a very successful result, but the invention can be realized more or less well in connection with the use of electrolytes of different composition, for example HF and KF in the proportions indicated but with omission of LiF. While the nickel coated, copper-filled carbon anode is the most satisfactory, it is possible to realize the invention in connection with a nickel coated carbon anode which is not copper-filled. While the nickel coated carbon anode is essential, the present invention does not reside in the anode as an article of manufacture but in the process whereby such an anode is utilized in a hydrogen fluoride-alkali metal fluoride electrolyte and the operation of the cell for a period of time more than sufficient to consume or disintegrate the metallic nickel coating on the anode. An anode of the construction described above might be used in other connections, and that construction forms the subject matter of another divisional application of the same parent application, both being identified above.

Having thus described my invention, what I claim is:

1. A process of generating fluorine comprising passing current through an electrolyte comprising KF and HF and containing from .005% to .01%, based upon the HF content, of water as an impurity between a carbon anode and a cathode, said anode being initially coated with a thin coating of metallic nickel, and continuing to pass current between said anode and cathode after said coating of metallic nickel has disintegrated.

2. A process of generating fluorine comprising passing current through an electrolyte comprising KF and HF and from .005% to .01%, based upon the HF content, of water between a carbon anode and a cathode, said anode being initially coated with a thin coating of metallic nickel, and continuing to pass current between said anode and cathode after said coating of metallic nickel has disintegrated, KF and HF being present in said electrolyte in proportion from 1.75 to 2.1 mols of HF per mol of KF.

3. A process of generating fluorine comprising passing current through an electrolyte comprising KF and HF in proportion of from 1.75 to 2.1 mols of HF per mol of KF and from 0.8 to 0.1% of LiF by weight based upon the combined weight of KF and HF and from .005 to .01%, based upon the HF content, of water between a carbon anode and a cathode, said anode being initially coated with a thin coating of metallic nickel, and continuing to pass current between said anode and cathode after said coating of metallic nickel has disintegrated.

4. A process of generating fluorine comprising passing current through an electrolyte comprising KF and HF in proportion of from 1.75 to 2.1 mols of HF per mol of KF and 0.8 to 0.1% by LiF by weight based upon the combined weight of KF and HF and from .005% to .01%, based upon the weight of HF, of water between a carbon anode and a cathode, said anode being composed of

porous carbon impregnated with metallic copper and initially coated with a coating of metallic nickel of a thickness from .00002 to .0001 of an inch, continuing to pass current between said anode and cathode after said coating of metallic nickel has disintegrated and thereafter adding HF containing water in proportion from .005% to 0.01% by weight said HF being added in small increments, each being less than 5% of the volume of the entire body of electrolyte.

5. A process of generating fluorine comprising passing current through an electrolyte comprising KF and HF in proportion of from 1.75 to 2.1 mols of HF per mol of KF and 0.8 to 0.1% of LiF by weight based upon the combined weight of KF and HF and from .005% to .01%, based upon the weight of HF, of water between a carbon anode and a cathode in a fluorine cell containing a single anode, said anode being composed of porous carbon impregnated with metallic copper and initially coated with a coating of metallic nickel of a thickness from .00002 to .0001 of an inch, continuing to pass current between said anode and cathode after said coating of metallic nickel has disintegrated and thereafter adding HF containing water in proportion from .005% to 0.01% by weight said HF being added in small increments, each being less than 5% of the volume of the entire body of electrolyte.

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