

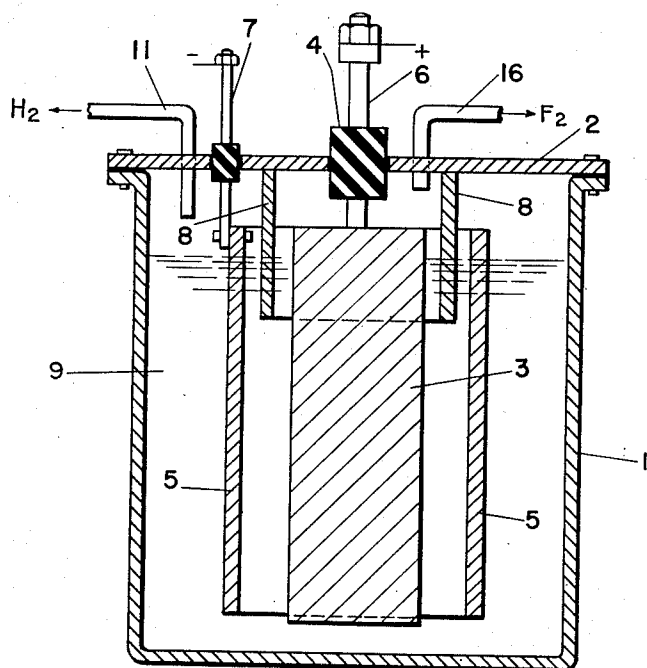
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ELECTROLYTIC METHOD FOR PRODUCTION OF FLUORINE

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ELECTROLYTIC METHOD FOR PRODUCTION
OF FLUORINE

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2 Claims. (Cl. 204—50)

This invention relates to improvements in electrolytic processes and cells for the production of fluorine.

It is well known to effect the electrolysis of fluorides or mixtures containing fluorides in the fused state using carbon electrodes, a particularly suitable electrolyte being the double compound $\text{KF} \cdot 2\text{HF}$ which can conveniently be used at temperatures somewhat below 100°C . When such an electrolysis is carried out it is generally found that after a short time there is a drop in the current density at which the cell can be operated at any given voltage. Where such causes as shortage of hydrofluoric acid in the electrolyte, defective electrical contacts and the like are absent, this drop in the current density is associated with processes of a not fully understood character occurring at the anode of the cell. To this last effect, occurring at the anode, we apply in what follows the term polarisation.

It was observed by the applicants that, in the electrolysis of substantially dry fused fluoride electrolytes, more particularly of the complex $\text{KF} \cdot 2\text{HF}$, the use of anodes of carbon having high permeability has beneficial effects in reducing or practically eliminating polarisation. By continued investigation of anodes of permeable carbon to determine the extent of their effect on polarisation in fluorine cells it has been established that their effect in this respect is related to the permeability. For this purpose and throughout the specification permeability is expressed in terms of the number of cubic feet of air which can be passed per square foot of surface through one inch thickness of the carbon per minute under an imposed pressure of two inches of water.

It has been further established as a result of the investigations that, in the electrolysis of substantially dry fused fluorides, the use of an anode of carbon of permeability not less than 5, very greatly reduces or entirely eliminates polarisation in fluorine cells over long periods of time when the anode current densities employed are those normally used in fluorine cells.

Therefore, according to the invention a process for the production of fluorine comprises the electrolysis of substantially dry fused fluorides e. g. of the approximate composition $\text{KF} \cdot 2\text{HF}$, using as the anode a carbon of permeability not less than 5.

The extent to which the permeability of the carbon anode has an effect on inhibiting polarisation appears in our experience to be related to the current density employed. Thus when operating at a current density of 0.5 amp./square inch anodes constructed of carbon of permeability not less than 5 give good results. When using higher current densities e. g. of 1.0 to 2.0 amp./square inch we find that it is advantageous to use carbon of permeability not less than 20 for the anode. However, we do not wish it to be understood that carbon anodes of high permeability should not be used at the lower current densities. Indeed we have found that extraordinarily good results are achieved by the use of carbon anodes of permeability between 30 and 40 when operating at current densities in the neighbourhood of 0.5 amp./square inch. As an example of such operation a cell using an anode made from carbon of permeability 37.5 has worked at an average current density of 0.45 amp./square inch for 3,000 hours without any sign of trouble due to polarisation.

A cell suitable for carrying out the invention is shown in the attached drawing which represents a vertical section through the said cell. Referring to the drawing, 1 is a container of mild steel or other suitably resistant material this container being closed by a lid 2 of similar material. The anode 3 is of carbon of the required per-

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meability and is supported by an electrically-conducting rod 6 which passes through the lid 2 and is insulated therefrom by an insulator 4. The said anode is only partially immersed in the electrolyte 9 as illustrated by the drawing. At a distance from the anode, and wholly or partially surrounding it, is the cathode 5, which may be of mild steel, copper or other material substantially resistant to the electrolyte and products of electrolysis. The cathode is supported by an electrically-conducting rod 7, which rod is insulated from the cell lid through which it passes. Between the anode and cathode is a diaphragm or skirt 8 which depends from the cell lid and dips into the electrolyte 9, thus serving to keep separate the gases evolved at the electrodes. Exits 10 and 11 through the cell lid are provided for the fluorine and hydrogen evolved at the anode and cathode respectively. Heating means not shown are also provided.

Example

A cell of the kind described was fitted with an anode $13\frac{1}{2}'' \times 13\frac{1}{2}'' \times 3''$ constructed of carbon of permeability 37.5. The electrolyte was of the approximate composition $\text{KF} \cdot 2\text{HF}$ and contained initially less than 0.5% of water. For the electrolysis the cell was warmed to about 75°C . and throughout operation was maintained between this temperature and 90°C . The electrolysis was continued for 3,000 hours during which time the HF content of the electrolyte was maintained between 40% and 42% by periodic additions of anhydrous hydrogen fluoride. At the end of 3,000 hours the cell was still giving fluorine of excellent quality and there was no indication of polarisation.

Since many changes may be made in the details and illustration set forth above without departing from the spirit and scope of the invention, it is to be understood that the invention is not limited to such details, except as indicated in the appended claims.

We claim:

1. A process for the production of fluorine comprising electrolyzing substantially dry mixtures of fused fluorides of the approximate composition $\text{KF} \cdot 2\text{HF}$, the said electrolysis being effected in a container of suitably resistant material between a cathode of material resistant to the action of the electrolyte, and an anode of porous carbon only partially immersed in said electrolyte, said carbon having a permeability of not less than 5, the unit of permeability being expressed in terms of the number of cubic feet of air which can be passed per square foot of surface through one inch thickness of the carbon per minute under an imposed pressure of two inches of water and removing the generated fluorine from the space above the anode.

2. A process for the production of fluorine comprising electrolyzing in a suitable container substantially dry fused mixtures of fluorides of the approximate composition $\text{KF} \cdot 2\text{HF}$, the cathode being of material resistant to the action of the electrolyte and the anode being only partially immersed in the said electrolyte and being of carbon of permeability greater than 20, the unit of permeability being expressed in terms of the number of cubic feet of air which can be passed per square foot of surface through a one inch thickness of the carbon per minute under an imposed pressure of two inches of water and removing the generated fluorine from the space above the anode.

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