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ELECTROLYTIC PRODUCTION OF FLUORINE

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The present invention relates to the electrolytic production of fluorine.

It is known that fluorine can be produced electrolytically from fused alkali metal bifluorides or from solutions of alkali metal fluorides in hydrogen fluoride. In the beginning of the process oxygen is first obtained, since the electrolyte always contains some water. At the same time the water present therein causes the electrolysis to proceed in a very irregular manner and also the voltage varies considerably. Attempts have been made to remove the traces of water present by the electrolysis itself, but this requires electrolysis for many hours, whereby the variations of the voltage are reduced but not completely removed.

I have now found that fluorine can be produced directly in a uniform manner and without the undersirable generation of oxygen by subjecting the alkali metal bifluorides prior to their serving as the electrolyte in the electrolysis vessel itself to a severe drying operation, preferably by passing a current of dry air or other dry inert gas through the sufficiently comminuted salt at an elevated temperature, but below the melting point of the salt, until the hydrogen fluoride given off by the alkali metal bifluoride when occasionally heated to decomposition, has a specific conductivity, after condensation, at 0° C. of less than 0.2 reciprocal ohm. Preferably the electrolysis vessel is tight to the air so that no water vapour can enter the electrolytic chamber. For this purpose every opening of the vessel must be avoided and an insulating tightening between the anode and the metallic diaphragm and another one between the vessel serving as the cathode and the diaphragm or the anode must be provided. In case the diaphragm consists of copper it is not absolutely necessary that the tightening between the anode and the diaphragm is an insulating one.

The same result is obtained when the electrolyte salt is dried outside the electrolysis vessel and in that case prevented from taking up even traces of water vapour while it is filled into the electrolysis vessel. This result is best obtained by connecting the drying chamber with the electrolysis vessel, so that the dried salt can be brought from the drying chamber to the electrolysis vessel without coming into contact with the atmosphere. Accordingly the drying chamber is to be regarded as part of the electrolysis system.

Since in the course of the electrolysis the electrolyte becomes poorer in hydrogen fluoride whereby the solidification point of the electrolyte, the internal electric resistance and accordingly the decomposing voltage are increased, it is necessary for a continuous operation to replace the hydrogen fluoride in the electrolyte solution or melt. If hydrogen fluoride prepared in the usual manner and containing more or less water is used for this purpose, the disengagement of fluorine is decreased and unfavourably influenced in the aforesaid manner and the anodic voltage is increased. In order to continue the electrolysis without trouble, the hydrogen fluoride in the electrolyte is replaced by such hydrogen fluoride as contains only an extremely small amount of water, namely such that the condensed hydrogen fluoride has a specific conductivity at 0° C. of less than 0.02 reciprocal ohm.

The following example will further illustrate the nature of this invention which, however, is out limited thereto.

Example

Potassium bifluoride dried in the usual manner is subjected to electrolysis in an electrolyzing vessel, between a copper cathode and a graphite anode. Electrolysis takes place very irregularly. The voltage varies between 10 and more than 30 volts whereby the current intensity decreases with increasing voltage. With an increasing current density, the variations of the voltage occur more readily and with a type of apparatus used for these experiments it was not possible to increase the current density to substantially more than 0.1 ampere per square centimeter. The said variations of the voltage occur very often at the beginning of the electrolysis but less often after a longer time, but even after 15 hours of operation they are

not entirely avoided and the disengagement of fluorine is very irregular.

In accordance with the present invention the same salt is dried within the electrolysis vessel by means of a current of dry air passed through at a temperature below the melting point of the salt. When the salt thus treated is electrolyzed, the electrolysis proceeds in a very uniform manner and without variations of the voltage. When operating with a tension below 10 volts the current density can be increased, in the case of the apparatus above referred to, to more than 0.3 ampere per square centimeter without the voltage being substantially increased or the electrolysis becoming irregular.

After a long time of operation the melt becomes lower in hydrogen fluoride and in order to continue the electrolysis without interruption, hydrogen fluoride is added. When this is carried out by producing hydrogen fluoride from potassium bifluoride and absorbing it in the melt, very great variations of voltage and current density take place in electrolysis, and it was found that the water content of the added hydrogen fluoride is the cause. The said variations of current density and tension are not observed, if care is taken that the added hydrogen fluoride is practically free from water, that is that it has the specific conductivity indicated above. When adding to a used up melt hydrogen fluoride of this kind the electrolysis can be continued without variations.

What I claim is:

1. The process of producing fluorine which comprises passing a current of a dry inert gas through an alkali metal bifluoride in the electrolysis system at an elevated temperature, but below the melting point of the salt, until the hydrogen fluoride given off by the salt when occasionally heated to decomposition has a specific conductivity at 0° C. of less than 0.02 reciprocal ohm, and carrying out electrolysis with the salt in a liquid condition while avoiding access of moisture.

2. The process of producing fluorine which comprises passing a current of a dry inert gas through an alkali metal bifluoride in the electrolysis vessel at an elevated temperature, but below the melting point of the salt until the hydrogen fluoride given off by the salt when occasionally heated to decomposition has a specific conductivity at 0° C. of less than 0.02 reciprocal ohm, carrying out electrolysis with the salt in a liquefied condition while avoiding access of moisture, adding hydrogen fluoride free from water and having a specific conductivity at 0° C., of not more than 0.02 reciprocal ohm to the electrolyte, in order to maintain its liquid condition and continuing electrolysis.

3. The process of producing fluorine which comprises passing a current of a dry inert gas through potassium bifluoride in the electrolysis system at an elevated temperature, but below the melting point of the salt, until the hydrogen fluoride given off by the salt when occasionally heated to decomposition has a specific conductivity at 0° C. of less than 0.02 reciprocal ohm, and carrying out electrolysis with the salt in a liquid condition while avoiding access of moisture.

4. The process of producing fluorine which comprises passing a current of a dry inert gas through potassium bifluoride in the electrolysis vessel at an elevated temperature, but below the melting point of the salt until the hydrogen fluoride given off by the salt when occasionally heated to decomposition has a specific conductivity at 0° C. of less than 0.02 reciprocal ohm, carrying out electrolysis with the salt in a liquefied condition while avoiding access of moisture, adding hydrogen fluoride free from water and having a specific conductivity at 0° C. of not more than 0.02 reciprocal ohm to the electrolyte, in order to maintain its liquid condition and continuing electrolysis.

In testimony whereof I have hereunto set my hand.

KARL FREDENHAGEN.