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UNITED STATES ATOMIC ENERGY COMMISSION

CARBON ANODES FOR FLUORINE CELLS

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CARBON ANODES FOR FLUORINE CELLS

The selection of the best carbon anodes for fluorine cells is dependent upon a number of inter-related factors involved in cell construction and operation. Particular consideration is given to the effect of impurities upon corrosion and the limiting current density for polarization of the electrodes. A brief resume' of earlier studies on the production of fluorine is given in order to show first, the inter-relationship between these factors, and second, to serve as a basis for a series of tests to select better anodes for improved cell designs.

Polarization and corrosion must be controlled if the present carbon anodes are to achieve their greatest efficiency. It has been shown by numerous authors that impurities, such as oxygen, water, and active sulphur compounds, are effective catalysts and promoters of corrosion and anode polarization; recent experiments in the fluorine plant and laboratory have indicated that although the limiting current density for carbon anodes is below 25 amperes per square foot in the presence of impurities, purification of the electrolyte enabled current densities of greater than 1000 amperes per square foot to be reached with porous carbon anodes. The experiments also indicated that the purification of the electrolyte decreases the cell corrosion by a large degree.

The Modified Hooker Cell

The cell design and operation is an essential part of anode selection. A description of the cells and their operation is given as a basis for the discussion of the carbon anodes which are being used here in Hooker cells, modified Hooker cells and laboratory cells.

The Hooker cells are similar to duPont and General Chemical Cells in that flat carbon blades are used as anodes. The anode assembly of the Hooker Cell consists of fourteen, 18 x 6.25 x 1.25 inch carbon blades arranged in two parallel rows of seven each. The blades are bolted to a heavy inverted copper channel running between the two rows, using four bolts and a separate copper cover plate for each blade. The joints between the carbon and the copper are made with a commercial carbon-water paste from which the water is driven by heating after the bolts are drawn up tight. Two of the anode assemblies are placed in a single cell which is run at approximately 1500 amps., corresponding to a current density of about 50 amps/sq. ft.

Maintenance costs are high because of corrosion at the anode contact and throughout the cell, particularly at the steel-mesh diaphragm. In order to cope with this expense, the Hooker cell is designed for rapid and cheap replacement of electrodes and diaphragms as unit assemblies.

Modifications of the cell were made to improve the anode connection and the diaphragm life. The carbon anode was copper plated over the contact area and was found to be in good condition after operation for the usual life period of the carbon-powder contact. In accordance with the experience of Harshaw and others, a perforated monel plate was found to have much better corrosion resistance than the steel-mesh diaphragm. The monel diaphragm and the copper plated contact were incorporated in a new modified Hooker cell. Other changes included a solid copper anode hanger and an increase in the width of the anode blades from 6 to 8

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inches. The number of blades was decreased from 28 to 24 per cell.

Corrosion and Anode Polarization in the Modified Cells

A number of the new cells were assembled, but all except one of the new cells were found to polarize after operation for a few hours or days. A cell designed for operation at 2000 amperes would carry only a few hundred amperes even at the full voltage of the rectifier. Examination of the cells indicated that the monel diaphragms were poorly positioned and were crooked. The diaphragm could interfere with circulation of the electrolyte and could also cause points of high current density by bi-polar action. The positioning of the monel plate was corrected by insulating spacers as a temporary measure. Copper sulphate from the plating bath was noted on the anode just above the copper plate. This was removed mechanically because it was suspected that sulfate could be a cause of polarization. However, after these changes were made the cell's continued to polarize.

Further experiments showed that the starting polarization could be avoided with many cells by initial operation for several days at a low current density. With other cells the polarization could be broken by operation at higher voltages for a time.

Two corrosion problems caused a cell to shut down after operation for a month. First, the steel hanger supporting the monel diaphragm corroded to form a layer of corrosion products about 1/2 inch thick.

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The corrosion layer forced the diaphragm out of position and snapped off the 5/8 inch supporting bolts. Second, the carbon anodes were found to be severely corroded above the electrolyte level in the areas not covered by the copper plating.

In the succeeding cell the steel hanger was eliminated by bolting the monel diaphragm directly to the steel skirt of the gas divider. Insulated bolts and an insulating gasket were used in order to decrease bi-polar currents in the diaphragm and the cell walls and to permit partial measurements of these currents by using the diaphragm as an auxiliary electrode. Measures were undertaken to prevent corrosion of the carbon anode and its contact. As an hypothesis, it was supposed that the corrosion of the anode was caused by some oxygen compound. Several sources were considered such as oxygen in the nitrogen, sulfate residue from the plating salts, various impurities in the KF-HF electrolyte and in the added HF. Known impurities were H_2O , SO_2 and various oxygen compounds of sulfur and silica. As an orientation test on the possibility of protecting the carbon from the corrosion by impurities, experimental electrodes were installed. In one type the joint through the gas space, that is, the section of the anode between the copper bus and the electrolyte, was made with an impregnated carbon (Karbate). The active electrode section was made by threading five rods (one-inch diameter, YAA carbon) into the impregnated carbon section. These sample electrodes together with copper plated electrodes were put back into the old electrolyte used in the previous

run. It was hoped also that the first run would function as a "conditioning run" serving to purify the electrolyte by deposition of impurities on the electrodes or by reaction with hydrogen or fluorine at the electrodes.

The cell was run for nearly another month, and was then found to be in much better condition than after the "conditioning" run. Only one anode was damaged as compared with twenty in the earlier run.

Among the test anodes, the contacts made from carbon to carbon and from carbon to copper plate were corroding but a copper plated joint filled with Karbate cement was in nearly its original condition.

However, another factor having a bearing on the anode contact was noted, that is, the general corrosion in the cell was much less. The iron divider skirt was corroded only slightly where before the corrosion layer had been a half-inch thick. The corrosion of the copper cover plates was on the order of a tenth of that during the previous run.

Wetting of the Anodes

A marked contrast was noted between the appearance of the electrodes which had been in the cell through both runs and the electrodes used in the second run alone which were black, not wet by the electrolyte, and not corroded. The carbons left in from the first run were white and completely wet by the electrolyte except for several small spots from which the surface had been ground off at the end of the "conditioning" run.

The good appearance of these small unwet spots raised the question about the desirability of wetting the carbon anode surface. A possible connection between the addition of LiF, anode polarization and wetting of the carbon was discussed by Schumb, Young, and Radimer (1) in 1947 as follows:

"With the idea of reducing the proportion of hydrofluoric acid in the electrolyte and so diminishing the losses by vaporization from the bath, a number of experiments were carried out with the addition of a second metal fluoride to the mixture of KH F_2 and HF. Of the alkali fluorides other than that of potassium, most success was obtained with lithium fluoride, which is slightly soluble in the conventional electrolyte at 100°C . The exact solubility has not yet been ascertained with certainty, but it is probable that not much over 1% of lithium fluoride is truly dissolved, and possibly even less than this quantity. The effect of this small percentage of lithium fluoride is noticed, however, in a lowering of the freezing point, so that the electrolyte may be employed at temperatures well below 100°C . without solidification. Alternatively, the addition of lithium fluoride permits reducing the percentage of hydrogen fluoride in the bath at 100°C with resulting advantages in the operation of the cell, especially in greater freedom from anodic polarization problems.

A troublesome feature attending the employment of lithium fluoride (or aluminum fluoride) in the electrolyte is the fact that the concentration of the added fluoride appears to diminish progressively with time, until finally it reaches such a small value that its beneficial effects disappear. Apparently, the lithium fluoride is carried down into the sludge at the bottom of the cell, for it was observed that, if the sludge is stirred up after disappearance of the lithium fluoride from the electrolyte, there is temporary improvement in the operation of the cell as regards polarization difficulties. Similarly, when aluminum metal was caused to dissolve in the electrolyte to form aluminum fluoride, the clear, supernatant liquid was practically free of dissolved aluminum after standing for some time; this indicated that the true solubility of aluminum fluoride in this medium must be quite small and that the colloidal dispersion first formed is later deposited as a sludge on the bottom of the container.

The exact role played by lithium fluoride in preventing the incidence of polarization is not clear; whether the phenomenon is essentially dependent on the colloidal characteristics of the solid when dispersed to allow its contact with the electrodes, or whether the added salt improves the wetting

characteristics of the electrolyte and so obviates polarization of the carbon anodes by an insulating gas film, are matters of conjecture."

Fredenhagen and Krefft (2) in 1929 commented on the wetting of carbon anodes as follows:

"Schmelzen bis zu einem Gehalt von etwa 1,8 Mol HF benetzen Graphit- und Kohle - elektroden praktisch nicht und können daher in diesen Schmelzen bei der Fluorelektrolyse als Anodenmaterial verwendet werden. Bei grösserem HF - Gehalt tritt Benetzbarkeit bei gleichzeitiger Zerstörung der Elektroden während der Elektrolyse ein."

A similar comment on the effect of wetting the anode was made in 1950 by Cady (3) as follows:

"When the content of hydrogen fluoride is too great, a flow of current through the cell causes the carbon or graphite anode to swell rapidly and to fall to pieces. An electrode can be completely disintegrated within a very short time, and no fluorine is set free. This change appears to take place only when the electrolyte wets the anode. When a carbon anode performs properly either in a medium-temperature or in a high-temperature cell, it is not wetted by the electrolyte."

Analyses showed that the LiF added to prevent polarization had almost disappeared from the electrolyte at the end of the first (conditioning) run. The LiF seems to collect in the sludge. Accordingly, the LiF does not make a significant difference in the freezing point of the electrolyte or the vapor pressure of the HF. Furthermore, the LiF did not prevent polarization. The purpose of adding LiF, therefore, remains indefinite. However, the addition of LiF has the definite disadvantage of sludging up the cells. It is also noteworthy that the LiF added to prevent polarization of the anodes costs about as much as the anodes. The uncertainty about the desirability and the mechanism of wetting the anodes raised other questions about the use of LiF; Did the LiF present in the initial run have anything to do with the polarization and decomposition of the anode?

Schumb et al. (1) note that "A troublesome feature attending the employment of lithium fluoride (or aluminum fluoride) in the electrolyte is -----that the colloidal dispersion first formed is later deposited as sludge". Schumb prepared aluminum fluoride by dissolving aluminum metal in the electrolyte. It is not explained how this was done. We have found that it is difficult to dissolve aluminum unless the electrolyte contains impurities or the aluminum is exposed to oxygen in some form to give the oxide which the electrolyte removes rapidly.

The observation on the effect of oxygen and impurities on the dissolving rate of aluminum ties in the question of impurities with corrosion in the cell, with polarization of the anodes, with decomposition of the anodes, with failure of the anode contact, and the limiting current density of carbon anodes. The action of lithium and aluminum fluorides in preventing polarization would follow directly if they were effective in removing harmful impurities from the electrolyte by carrier precipitation.

Other observations on the role of LiF in preventing polarization were made by J. T. Pinkston, (4) who describes the effect of LiF as follows:

"At an early stage in the investigation, the effect of LiF on the electrolyte was studied. -----The cell operated fairly well, -----A similar cell ----- the carbon electrodes were not being wetted by the electrolyte-----they were clean and black. Accordingly, lithium fluoride was added to the second cell. It was reassembled, run for a short time on nickel anodes for water removal and then operated-----.

Further study revealed that aluminum fluoride and sodium fluoride were also effective. Since lithium fluoride was less readily precipitated from the electrolyte by reaction with contaminants than were the other two, it became our standard additive."

The experiment as described above by Pinkston is wholly inconclusive to

answer the question of the action of LiF. It is not at all apparent that LiF, NaF, and AlF_3 are effective agents in causing the wetting of anodes in the electrolyte which is loaded with KF. Moreover, the action demonstrating the advantage of LiF was tied in with a preliminary run using nickel anodes. It is well known that conditioning with nickel anodes will remove impurities which may cause the polarization of carbon anodes. Accordingly, this experiment does not describe any unique advantage which can be attributed to the LiF.

The Effect of Impurities on Anode Polarization

The importance of removing impurities from the electrolyte to be used with carbon anodes has been described and emphasized by many writers all the way back to F. C. Mathers (5) who first used carbon anodes successfully:

"A fresh bath, prepared from potassium fluoride and commercial hydrofluoric acid, always contained some water which had to be electrolyzed out at a low current density before fluorine was obtained. If the current density was too high, polarization resulted and the voltage rose to 50 to 100 volts. There was sparking through the oxygen gas film, suffusing the bath with a blue luminescence. A current density of 2 to 3 amperes per square decimeter was passed until a test of the anode gas showed the presence of fluorine, after which a much higher current was used without polarization resulting.

If anhydrous acid is used instead of the commercial product the period of drying and preliminary electrolysis to remove water will be materially shortened."

Similar observations on the polarization caused by water were made by Fredenhagen (2), who noted that the polarization could also be caused by the addition of water to a working cell and that polarization could be avoided if the electrolyte were dried:

---"die Elektrolyse bis zu einem Wassergehalt von angenähert 1% bei etwa 4 V-- einer Stromdichte von 0.1 Amp./ cm^2 , wobei jedoch nur Wasser zersetzt wird. Bei geringerem Wassergehalt -- die Spannung steigt merklich an, -----.

Arbeitet man aber in ganz trocknen Schmelzen, so erhält man eine völlig störungsfreie Entwicklung von reinem Fluor bei einer Betriebsspannung, die bis zu---einer Stromdicht von 0.3 Amp/cm^2 . Man Könnte nun daran denken, die Schmelzen dadurch von dem Wasser ---herauselektrolysiert. --- Ausserdem gelingt es aber infolge der Polarisierung der Zelle nur sehr schwer, durch Elektrolyse das Wasser völlig zu entfernen, da die Strom stärke trotz hoher Betriebsspannungen von mehr als 35 V auf sehr geringe Beträge herabsinken.

Bei noch höheren Spannungen treten an der Anode Funkenbildungen und Zerstörung der Elektrode ein. Der Weg, die Schmelze durch Elektrolyse von Wasserspuren zu befreien, ist zudem sehr unökonomisch und zeitraubend, da man wegen der dauernd eintretenden hohen Spannungsschwankungen und dem damit verbundenen Herabsinken der Stromstärken auf sehr geringe beträge herab tagelang elektrolysieren muss, bis die letzten Wasserspuren zersetzt sind. Aus diesem Grunde ist es unbedingt Zweckmassig, von vornherein, völlig trockenes Kaliumbifluorid zu verwenden und zwar von einem Grade der Wasserfreiheit, wie er vor unserem Versuchen noch nicht verwandt sein durfte. Man erhält dann sofort eine gleichmassige und störungsfreie Fluorentwicklung-----.

Man kann auch an Beziehungen denken zu dem grossen Einfluss des Sauerstoffs bei den bekannten Passivitätsercheinungen an Eisen elektroden, doch reichen unsere bisherigen Versuche zur Aufstellung einer ungehenderen Erklärung nicht aus."

Dennis, Feeder and Rochow (6) make a similar observation:

"When pure $\text{KF} \cdot \text{HF}$ is thoroughly pulverized and is dried at about 130° for forty-eight hours, fluorine is evolved at once when the electrolyzing current is passed through the molten salt.

If the electrolyte has not previously been freed from water, it is necessary to employ a current of high voltage (100 V) at the beginning of the electrolyses to prevent polarization by the oxygen evolved at the anode".

Bigelow (7) recommends that the electrolyte be dried at 150°C with dry air at reduced pressure followed by fluorine gas. Then the charge is melted. It is extremely difficult to dry the electrolyte after melting. In regard to the operation of the electrolyte, Bigelow commented:

"Perhaps the greatest difficulty encountered in its use was the tendency of less skilled operators to cut short the rather tedious dehydration

process, which could not be completed within the cell because the maximum current capacity of about 10 amp. was too low.---

The regeneration of the melt by passing commercial anhydrous hydrogen fluoride directly into it is now a universally accepted procedure, but care must be taken that the gas is really anhydrous, or much trouble may result."

Otto Ruff (8) does not attribute the polarization or passivity of the carbon electrode to an oxygen film but rather to the initial formation of $(CF)_X$, catalyzed by the oxygen present:

"Verwendet man aber eine frische Elektrode in wasserhaltiger Schmelze, so entwickelt sich an ihrer Oberfläche bei einer Spannung von ~ 6 volt zunächst nur Sauerstoff, bis der Wassergehalt unter $\sim 0.7\%$ gesunken ist; danach beobachtet man eine allmählich immer stärkere Passivierung derart, dass selbst Spannungen von 40 - 50 Volt kaum noch den Stromdurchgang gestatten. Wahrscheinlich ist die Ursache der Spannungserhöhung auch in diesen Fall die Einwanderung von Fluor in die Oberfläche unter Bildung von $(CF)_X$, trotz der in diesem Fall nach verhältnismässig niedrigen Temperatur von beispielsweise 250° , denn die Gegenwart von Sauerstoff erleichtert den Angriff des Fluor auf Graphit."

More extensive information on the formation of carbon-fluoride compounds was given by Walter and Gerda Rudorf (9).

Simons (10) dried his electrolyte by a preliminary electrolysis in order to avoid damage to the operating electrodes:

"As the greatest amount of corrosion of the anode occurred at the time the last traces of water were being removed this method saved the anode of the generator. ---- When most of the water had been removed, the cell had a tendency to polarize with arcing around the anode. This persisted until all the water had been removed."

Nickel anodes have been used by many operators to "condition" the electrolyte, for example, the Hooker Company used nickel anodes for 30,000 ampere hours before operation with carbon electrodes.

In similar fashion the duPont Company (11) during the start-up period used auxiliary nickel electrodes which carried most of the current

even though connected in parallel with the carbon anodes. The cells were operated with the nickel electrodes for two days, after which the carbon anodes were placed in service with the nickel rods still connected in parallel. If the voltages were then normal the nickel was disconnected and the cell was considered to be conditioned. If the cell continued to have a high anode-ground voltage drop indicating polarization at the carbon anode it was then cured by continued use of the nickel treater rod.

The Harshaw Company used auxiliary nickel anodes in a similar manner.

A preliminary electrolysis may remove other impurities than water.

Emeleus (12) makes the following observation:

"Simplification of the cell so as to allow a rapid interchange of anode made it possible to overcome the difficulty arising from the formation of a glassy silicate coating on the anode. This arises from silicates contained in acid potassium fluoride and its removal by a preliminary electrolysis followed by the insertion of a fresh graphite anode, greatly simplifies the production of fluorine from the salt $KF \cdot 3HF$." (Some observers claim that magnesium helps to form the silicate coating.)

The effect of impurities was noted also in Germany. A manufacturer of HF states that the HF for electrolysis must contain no SO_2 or SO_3 since these would corrode the electrodes. Furthermore, the cell operators removed the small amounts of impurities through reaction with hot copper, iron or fluorine (13).

Further work was carried out at this plant on the effect of impurities on the anode polarization. In several experiments a preliminary electrolysis was carried out but polarization was still encountered. However, in this procedure both the electrolyte and the electrodes were exposed to

moist air during assembly. In a modification of this experiment the anodes on only one side of a cell were run at high current density and voltage to condition the electrolyte. After the polarization was removed by continued operation at high voltage, the other side of the cell was started without polarization.

With a number of cells polarization has set in after initial operation. As pointed out by Bigelow (7) and others, (2), and (5), impurities from the commercial HF may cause trouble. Analyses of the HF cylinders indicate that the impurities were variable, and for part of the time exactly in the range associated with the most severe polarization conditions.

It should be noted that polarization with carbon anodes is dependent upon the current density (2), (5). At low current densities the carbons do not polarize. For operation at higher current densities it appears that impurities must be removed or steps taken to increase the effective anode area. Both of these measures have been successful. The use of a dry electrolyte and higher purity HF has given cells which did not polarize. On the other approach, a roughened anode has operated at a higher current density than a smooth anode, but polarized in the region of 25 - 50 amp/sq. ft.

In order to study a further increase in surface area, porous carbon anodes were used in a laboratory cell containing the usual impurities in the electrolyte. The porous anodes polarized at several hundred amp/sq. ft. After the removal of impurities by electrolysis the anode did not polarize at 1000 amp/sq. ft. After running for a short time at 1500 amp/sq. ft., the anode connections burned off. The electrolyte used with the porous anodes did not contain LiF.

Corrosion and Impurities

Corrosion is an important item in the cost of fluorine. A cell operating for a year or two without maintenance should go a long way toward bringing down the cost of fluorine production to the region of chlorine production costs.

The effect of impurities on anode corrosion was pointed out in the above discussion of anode polarization. The impurities may have similar effects on the corrosion of metal parts.

Mathers (5) made the following observations:

"If copper apparatus is used in the Moisson method the hydrofluoric acid must be very concentrated. If not almost anhydrous the copper in contact with the anode dissolves and is reprecipitated as a sponge upon the cathode whereby a short-circuit is soon produced. The protecting or insulating film is formed on the copper only where the concentration of the hydrofluoric acid is high."

Dennis (6) made a similar observation:

"When the impure electrolyte was used and the salt was removed from the cell after a run of some hours, the discoloration of the $KF \cdot HF$ showed that the inner walls of the cell had been seriously attacked during the electrolysis. With the pure electrolyte no such corrosion results. The salt is quite colorless when removed from the cell."

The following observations on corrosion are made in Simon's book on fluorine chemistry (3).

"Copper is, of course, below hydrogen in the replacement series and so in the absence of oxygen or oxidizing agent is not attacked. In the presence of oxygen, copper is rapidly attacked."

"The most annoying feature of the laboratory technique is the corrosion of vessels, tubing, fittings, valves, etc. that occurs when the apparatus contaminated with hydrogen fluoride is allowed to stand open

to the air. The acid catalyzes air oxidation. This corrosion does not occur during the experiments. The difficulty can be avoided by cleaning all equipment immediately after use."

"The condenser should be kept tightly closed at all times, when not in use, as hydrogen fluoride adheres strongly on metal surfaces, and water is condensed from the air upon them. This adds water to the condenser and promotes corrosion as well as contaminating the next sample."

"As all commercial hydrogen fluoride contains some water and other impurities the rate of gas evolution from the cylinder decreases as the cylinder is emptied and the impurities concentrated in the remainder."

The above citations indicate that the corrosion of both metal and anodes are dependent upon the amount of impurities in the cell. The corrosion is also dependent upon the type of impurities and the corrosion currents. Iron, for example, is protected from corrosion by either anodic or cathodic films, but is destroyed by bi-polar conditions. The cell diaphragm has been insulated to facilitate measurements of some of the corrosion currents and provide a direct measure of impurity concentrations.

Explosions and Impurities

Explosions in the cell may cause damage by cracking off the carbon anodes. A description of cell explosions is given by Cady (3) as follows:

"A variety of kinds of explosions occurs within a fluorine cell. As the last traces of water are being removed by electrolysis, crackling noises which seem to be caused by many rising bubbles of gas may be heard. These are harmless. If a mixture of hydrogen and air collects in the cathode compartment, it may suddenly explode, perhaps because of ignition by a bubble of fluorine. At times explosions occur within the anode chamber. Perhaps some of these are caused, as already explained, by hydrogen. If for any reason small particles of carbon are present in the anode compartment, they may form an explosive product by combining with fluorine. The writer has had explosions of this type result from impurities in the technical KHF_2 used in the electrolyte. Upon removal of dark scum from electrolyte, the explosions stopped. If one of the lines for carrying the gases becomes blocked, fluorine and hydrogen may be forced to mix with a consequent explosion."

Concerning the preparation of electrolyte, Cady writes as follows:

"Electrolytes prepared as just described need further treatment. If the surface of the liquid is dark (owing, perhaps, to carbon or organic matter), the black solid should be removed by skimming. This precaution may avoid explosions as the cell operates."

Since the carbon anode is extremely unreactive with fluorine, it would seem more likely that the explosive material would be an organic compound or carbon-oxygen complex in which the oxygen would catalyze the combination with fluorine. The reaction of an oxygen-carbon complex with fluorine has been described by Ruff and Bretschneider (14) as follows:

"Wir haben folgendes festgestellt: Gewöhnlicher, d.h. sauerstoff - bzw. luft-und wasserhaltiger Norit (die Kohlenstoffform geringster kristalliner Ordnung) fängt in Fluor z.b. in einem Kupferrohr ohne weiteres Feuer and verbrennt zu einem gemisch verschiedener Fluorid, ----- Sauerstoffrie d.h. bei etwa 1000°C in Hochvakuum 2 Stunden lang entgaster Norit Kann in Fluor von etwa 25 mm Druck bis 280° erhitat werden, ohne sich zu entzunden; -----."

It is unlikely that Ruff prepared pure carbon by the method described, but purification was sufficient to indicate the effect of impurities on the reaction rate of carbon with fluorine.

Explosions may result from a number of impurities in the cell, notably: air, H_2 , O_2 , SO_2 , and H_2S . The mixing of hydrogen with the fluorine may be remedied by better design for gas separation. Particular care may be needed to avoid contamination of the cell with oxygen compounds, for example, the water removed from air by adsorbed HF as noted earlier. In large scale operations even the minor impurities in the HF may be concentrated in fractions which may reach explosive conditions.

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The concentration of impurities by distillation may account for a number of the difficulties encountered in large scale operation. The following observation was made by one operator (15):

"Carbon anode cells have operated continuously for months without any polarization when installed with individual temperature control and continuous hydrofluoric acid feed from cylinders on scales. All water was removed from the electrolyte at the beginning by nickel anodes, and any sludge was removed from the bottom of the cells every few months. On the other hand, when a considerable number were installed as a series circuit, with a common and not very satisfactory cooling system and batchwise hydrofluoric acid feed every six hours, periodic polarization was encountered. There is little doubt that this is due to departing from the optimum temperature and hydrofluoric acid concentration..... If close to optimum conditions are maintained, the cells will not polarize, provided the anode contacts are in good condition and the electrolyte is not too dirty."

No polarization was found in the small scale operation with a continuous feed, but the batchwise feed was accompanied by polarization. The authors attribute the polarization to "departure from the optimum temperature and hydrofluoric acid concentration." (15) No measurements are given to support this contention. In view of their other difficulties with corrosion it seems likely that inadequate care was taken to avoid impurities and the cells became polarized in the manner described by Fredenhagen (2) or Bigelow (7). Also, it seems likely that the introduction of the impurities which might be concentrated in this manner could well cause explosions. Our experience has indicated that explosions have followed the batchwise introduction of HF vaporized from large tanks.

Cathode Polarization and Impurities

In discussing cathode polarization, Cady (3) has made the following observation:

"When a large cathode is used, the tendency for the occurrence of the abnormally great overvoltage is small. The fact that most cells of the intermediate temperature type have used low cathode current densities is probably responsible for the fact that the high overvoltage phenomenon has caused little trouble."

It has been our observation that cathode polarization is associated with a lack of good circulation and with the deposition of impurities over the cathode surface. The impurities deposited on the cathode appear to be derived partly from the electrolyte and partly from the corrosion of metal parts. Here it would be of interest to know how much of these corrosion products resulted from reaction with impurities. In our experience, successful operation at higher cathode current densities has been associated with electrolyte of greater purity.

Anode Stability and Impurities

In general the fluorine evolved at a carbon anode is contaminated with CF_4 . Fredenhagen has claimed (2) that very pure fluorine can be made if the electrolyte is kept sufficiently dry. Bigelow (7) questions this claim as follows: "The product may have been free of oxygen compounds, but undoubtedly it contained a small but unknown amount of carbon fluoride." Bigelow's statement seems to leave out of consideration the observations of

Ruff (8) on the role of oxygen as the catalyst for the combination of carbon with fluorine. If it is conceded that the electrolyte is free of oxygen it could then follow that the fluorine would be free of carbon fluorides. Accordingly, the formation of the carbon fluorides may prove a useful tool in working out the reactions at the anode surface.

Impurities and the Anode Contact

The anode contact apparently fails through corrosion of the copper and the carbon. Accordingly, the impurities may bring about the corrosion that causes the anode contact to fail. Our experience indicates that the contact may be protected by the use of impregnated carbon, by copper plated contacts, and by Karbate cement in joints.

A copper-plated contact apparently provides protection by interaction with impurities before corrosion reaches the actual contact points. The exposed copper is corroded off gradually, but in the joint itself, corrosion products build up and are held tightly about the actual contact points. Protection by a copper plate was demonstrated in the Hooker cell: Copper-plated contacts were in good condition over a period of time in which unplated contacts failed. Protection by copper was further demonstrated in the modified Hooker cell by two methods: First, areas of carbon under copper plate were in good condition but adjoining areas were severely attacked. Second, the carbons on one side of a cell were protected with a copper spray which preserved the carbon while the unprotected and exposed carbon on the other side of the cell was eroded at some anodes clear down to the bolts.

The sprayed copper gave protection to the carbon but did not give a permanent contact. The copper spray upon exposure in the fluorine cell swelled so much that several of the bolts were snapped off. Despite the increased pressure of swelling, few of the other contacts remained good after operation for several weeks.

In another cell the copper-sprayed electrodes were compared with copper-plated electrodes. After removal from the fluorine cell the copper-plated contacts were still good but the contacts through the copper spray were poor. To explain this situation, it is supposed that a copper spray is porous and reacts readily with impurities which catalyze its combination with fluorine. On the other hand, the copper plate is solid so that the actual contact points remain in contact and surround themselves with a tough, adherent, and protective layer of fluoride. Other factors may be involved, for example, the plated copper may be saturated with hydrogen while the sprayed copper may be covered with copper oxide which reacts rapidly with HF or F₂ to form an insulating layer.

Removal of Impurities

Several years ago the cell operation here was modified by the substitution of a more impure grade of HF. Trouble with cell operation was experienced until this HF was replaced with a material of greater purity. In a similar manner the use of an electrolyte (KF.HF and HF) of higher purity has greatly improved the cell operation over the period of the preceding months.

With the use of higher purity (or conditioned) electrolyte and HF, less trouble has been experienced with polarization, the cells have operated at higher current densities, less maintenance has been required because of cell corrosion, and cell explosions have decreased in frequency. The specification for the HF in the plant design called for a purity of 99.4%; $99.8 \pm 0.1\%$ is now being used.

Further measurements are needed to determine the most economical degree of purification. In this regard it may be noted that large lots of HF with a purity of 99.9% are quoted at a lower price than that recently asked for 99.4% HF. Accordingly, only a small amount of impurities remain to be removed. At the present time further economies of cell operation might be achieved by using HF of still higher purity for it may be cheaper to react impurities with copper and iron outside of the cell rather than add them to the cell where they corrode out anodes, contacts and cell body.

A method for the "Purification of Anhydrous Hydrogen Fluoride" has been described by Shenk and Pellon (16) of the Harshaw Company, as follows:

"The anhydrous hydrogen fluoride of commerce -- contains substantial quantities of water, SO_2 and H_2S , and sometimes also contains small quantities of organic sulfur compounds, -----"

"It is known that pure anhydrous HF is very inert with respect to steel such as steel shipping drums and steel equipment as well as to other metals such as nickel and copper. It is known, also, that an increase in water content and SO_2 content reduce the inertness and render the product more corrosive. It is obvious, then, that if the anhydrous hydrogen fluoride of commerce could be freed of its water and sulfur content, it would be improved with respect to its -- use. It has been proposed heretofore to purify the anhydrous hydrogen fluoride of commerce by redistillation for the reduction of the content of moisture and sulfur; but it has been found that even after redistillation, there still remains a small portion of the SO_2 or H_2S and moisture as well as "traces of the organic sulfur compounds."

"---SO₂ and H₂S are fluorinated to produce the very stable sulfur-fluorine compounds SO₂F₂ and SF₆ which are exceedingly inert as is well known. Fluorination at the same time converts the moisture content to hydrogen fluoride and oxygen, and the sulfur in the organic sulfur compounds, which may be present in trace quantities, is converted to SO₂F₂ or SF₆."

"----the desired fluorination can be accomplished by --- trifluoride. ----Only AgF₂ and CoF₃ have been found effective to reduce active sulfur to or below .001% by weight."

"The combined SO₂, H₂S, SO₃ and organic sulfur content of anhydrous HF, which is convertible to sulfate by HNO₃ and which is hereinafter referred to as "active sulfur" in contradistinction to the inert sulfur compounds SO₂F₂ and SF₆, is readily determined by passing the anhydrous HF containing small proportions of such sulfur compounds into nitric acid."

In the operation of the German fluorine cells the removal of impurities was described as follows (13):

"The purification of the HF is of prime importance for smooth operation of the fluorine cell. The most objectionable impurities in the HF are sulfur compounds and water. -----The sulfur removal can be accomplished by passing the acid over copper and iron filings. ---- for large scale commercial production --- the sulfur and water removal is accomplished by passing the gas, together with elemental fluorine, through a nickel furnace at 300°C. The sulfur is converted to gaseous fluorine compounds and the water to HF and O₂."

Experiments Proposed to Select Anodes

It should seem that the reactions of various impurities and LiF on a few typical carbon anodes should be observed with care before extensive studies are undertaken on the properties of carbon as anode. Typical anodes might be GA, YAA, and porous carbons, AGX and chlorine purified graphite. The value of a carbon anode may be described in terms of its electrical resistance, physical strength, "limiting current density", contact stability and general aging quality.

The "limiting current density" is the current at which the anode polarizes. The values run from 5 to 15 amperes/sq. ft. for YAA carbon in a commercial electrolyte, and 100 to 200 amps/sq. ft. for YAA anodes in an electrolyte purified by fluorination and electrolysis. In general, GA carbon anodes will carry a higher current without polarization than YAA anodes, and a porous carbon carries 1000 amp/sq. ft. or more without polarization.

The limiting current density is a function of temperature, circulation, electrolyte composition, and cell construction as well as the concentration of impurities. As an example of the relationship between these variable factors the electrical resistance of the carbon may be noted. With a high resistance in a carbon the current density near the contact may be much greater than the current density at a distance because the anode current may double with an increase in the anode potential of a few tenths of a volt. Accordingly, only a portion of the anode may reach the limiting current density and thereby polarize. The polarization may then proceed over the whole electrode, or, on the other hand the electrode may become depolarized along with some chemical attack on the carbon. Successive polarization and depolarization may lead to the complete decomposition of the carbon near the contact. Effects of this kind would be minimized in a cell with a low resistance anode or in a bi-polar connection.

After excluding gross effects of cell construction like the example above we may examine the type of surface needed for efficient fluorine evolution: the carbon structure, crystal orientation, degree of graphitization, point of ion discharge, electron work functions of surface atoms,

migration of ions, combination of ions, formation of gas bubbles, the adherence of gas bubbles and the movement of gas bubbles.

In the study of impurities, particular care should be taken to observe the effect of concentration. For example, a cell containing one percent of water gives off oxygen; with 0.1 percent or so the cell polarizes. It may well be that 0.01 or 0.001 percent of water would be effective either in blocking off all of the surface in time or in eroding only certain areas leading to the development of the surface and more efficient evolution of fluorine.

The development of surface was demonstrated with a gray YAA anode. A gray layer on the surface reacted with oxygen impurities to form a carbon powder which fell off readily and collected on the surface of the electrolyte. The explosive properties of this powder were not tested.

Care should be taken to find out whether the wetting of the surface is a function of capillary size resulting from surface development or a change in chemical composition of the carbon surface or an attribute of the diameter of the lithium ion in LiF. Observations are needed to determine whether wetting of the anode is an advantage or whether it is a preliminary step in anode failure and decomposition.

Experiments on the effect of impurities and LiF should be fairly straightforward. Adequate methods of analysis should be developed for following these impurities. For example, Fredenhagen used the electrical conductivity of the HF as a measure of its purity. Harshaw determined the "active sulfur" compounds to distinguish these from the harmless sulfur compounds formed by fluorination.

The claims made for NaF, AlF_3 and LiF in wetting the anode and avoiding polarization warrant investigation from a number of viewpoints if the observation is found to be correct. It should be noted that these compounds are markedly insoluble in the electrolyte. Only 0.01% of LiF was found in the electrolyte after operation of a cell which started with 2% LiF. In a similar manner the AlF_3 precipitated from the electrolyte. It is, therefore, to be determined whether these elements have a specific action or whether they act as a scavenging precipitate that removes harmful impurities.

Other experiments are closely associated with the question of LiF. For example, Pinkston added LiF to reduce the operating temperature of the melt, but was unsuccessful because of the insolubility of the LiF. For this purpose it would be appropriate to follow the work of Mathers and Stroup (17) who used CsF to lower the temperature of the cell. The addition of various amounts of CsF may permit operation at the lower temperature and achieve the purpose which the addition of LiF failed to accomplish.

Studies on the addition of CsF and other compounds should include a careful study of the discharge potential. Valuable evidence may be obtained on the nature of electrode behaviour and the mechanism of the discharge process which could be utilized in the design of better electrodes and cells. For this purpose, a better reference electrode is needed than the diaphragm screen which is used at present. The diaphragm is not accurately positioned and its potential is subject to wide variation since either a fluorine or a hydrogen atmosphere may predominate.

Reactions at an electrode are associated with catalytic effects which are usually described in terms of the catalyst itself and one or two promoters. A description of a typical catalytic reaction has been given by Simons (p. 284, Ref. 3):

"The use of fluorosulfuric acid as a catalyst for the alkylation of isoparaffins with olefins is probably the catalytic action of either hydrogen fluoride or sulfuric acid or one of them promoted by the other, as fluorosulfuric acid is a most powerful dehydrating agent and reacts violently with water to form sulfuric acid and hydrogen fluoride. ----- As used commercially for the catalytic conversion of hydrocarbons or in condensation reactions, the hydrogen fluoride is never completely anhydrous. The presence of this small amount of water is not detrimental. It acts as a powerful promoter. It is only when larger amounts of water are present that the catalytic action is retarded."

The catalyst - promoter action of the fluorosulfuric acid - water combination is analogous to the action of "active sulfur compounds" and water in causing polarization and decomposition of carbon electrodes. Catalytic effects of this kind may be followed by the anode potential and by cell products such as O_2 , CO_2 and CF_4 .

Catalyst Addition

It is obvious that we should have "catalysts" that bring about the evolution of fluorine at a low potential. From a consideration of other cells we may suppose that the addition of such metals as iron, nickel, cobalt, manganese, thorium, cesium, aluminum or boron may have catalytic effects. These may have a specific effect on the discharge potential or might work through a secondary action. For example, Cady (3) suggests the impregnation of the electrode with nickel to improve the contact and prevent polarization.

Impregnation of the carbon with copper is carried out by the Harshaw Company in order to make a better contact and a sinking electrode. It is suggested, however, that copper may have a secondary action through reaction with and the removal of the impurities which cause polarization.

The action of catalysts is usually dependent upon structure, for example, platinum black may be a catalyst for a reaction in which the effect of solid platinum is negligible. Again catalysts may play a part in determining the structure and degree of graphitization of the carbon in the process of anode manufacture. Accordingly, it is planned to observe the effect of a large number of manufacturing variables including raw materials, baking temperatures, atmospheres, rebaking, particle sizes, time and location of catalyst addition in both base and impregnant. For example, what would be the effect of varying proportions of iron, aluminum, and boron using various proportions of anthracite and petroleum cokes, baked at varying temperatures for base and impregnant, and cooled in varying atmospheres? The selection of the best anode from among the variables of cell operation, impurities, LiF, catalysts and carbon manufacture adds up to a problem of some difficulty.

The history of anode selection has been marked by the errors of testing so that often times the best electrodes have been rejected. For example, if anodes are connected in parallel the best electrodes may carry the bulk of the current and fail while inferior electrodes come through the test in good condition. Variations of this behaviour may well take place in a fluorine cell. The best electrode may start with a large current, reach a

limiting current density, polarize and decompose while inferior electrodes are inactive and remain in good condition.

Two types of tests are available for which round anodes have been selected because of convenience in manufacture and testing as well as to avoid the numerous electrochemical problems which arise at square corners. In one type of test a single anode is used in an individual cell so that large variations in cell operation can be studied without interference between two electrodes.

However, a comparison of a large number of electrodes may be carried out more accurately by use in a single cell. A preliminary experiment has indicated that one hundred or so round electrodes may be run in a modified Hooker cell. Accordingly, with the installation of individual connections a large number of the variables of carbon manufacture could be tested in a single cell. In a typical experiment some 5 of 10 electrodes of one type could be interspersed so that each group of electrodes is tested in each section of the cell.

Anode Improvement and Cell Design

With better removal of impurities from the electrolyte and the HF, the cells are operating better at 3300 amperes than in previous runs at 1200 amperes. Then why should the current not be doubled again or what is the economical balance point for the anode current density and cell size? Fluorine costs are on the order of \$0.75 to \$1.00 per pound while electrolytic chlorine costs only a few cents per pound. A comparison of fluorine with chlorine production indicates that, excluding raw material and current costs, the two electrolytic methods should have comparable costs of production.

An anode of long life and high current density would go a long way in making fluorine production costs comparable with chlorine costs. In a laboratory cell a porous carbon anode ran at 1000 amps/sq. ft. or a current density corresponding to 30,000 amperes in the modified Hooker cell. In the direction of economy through long life, the studies on corrosion indicate that the cell life may well be extended to two years by better management of corrosion currents and impurities.

In order to achieve a production cell with high current densities suitable modifications should be made in the design, (18). For example, with porous carbon anodes a metal-backed or bi-polar connection might be an advantage. Any such development should provide for adequate liason between laboratory measurements and engineering design.

Summary

The experimental work has indicated that the current density at the fluorine cell anode may be increased from two to twenty times by better control of impurities and the development of anode surfaces. A large increase in cell life should also be possible through better control of impurities and corrosion currents.

A testing program for the selection of anodes is proposed. As a preliminary step it is suggested that GA, YAA, graphite and porous anodes would be compared in cells from which such known impurities as active sulfur compounds, water, and oxygen were removed so far as possible. As a second step, observations

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would be made on the effect of addition agents in the electrolyte and of variation in the manufacture of carbon anodes. A third step would be to tie in the results of anode tests with a suitable electrochemical cell design.

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