Journal of Fluorine Chemistry, 33 (1986) 133 - 147

Chapter 6

MODERN FLUORINE GENERATION

J. F. ELLIS and G. F. MAY

Technical Department, British Nuclear Fuels plc, Springfields Works, Salwick, Preston PR4 0XJ (U.K.)

Introduction

As one of the strongest oxidising agents, elemental fluorine is prepared only by electrochemical methods. It is produced commercially by the electrolysis of the fused salt $KF{\cdot}2HF$. The fluoride ion is oxidised at the anode to liberate fluorine gas, and the hydrogen ion is reduced at the cathode with consequent hydrogen evolution. Electrolytic cells for the generation of fluorine were used on a laboratory scale for many years before increased usage demanded industrial production. Production of fluorine began on an industrial scale in the 1940s in the U.S.A. and Europe for the manufacture of uranium hexafluoride, halogen fluorides and specialised fluorocarbon compounds. Cells of three different types were developed, characterised by their operating temperature. Those operating between 15 - 50 °C based on $KF{\cdot}xHF$ electrolyte are classed as low temperature, between 70 - 130 °C as medium temperature ($KF{\cdot}2HF$) and from 245 - 310 °C as high-temperature cells ($KF{\cdot}HF$). A type of low-temperature cell was used by Moissan [1] to isolate fluorine in 1886 and other developments are mentioned in Chapters 3 and 5. Post-war studies in the U.S.A. on all three types resulted in the selection of the medium-temperature cell as the most practical source of fluorine. It has the advantages of relatively low rates of corrosion of components and a low vapour pressure of hydrogen fluoride over the molten $KF{\cdot}2HF$ electrolyte. In addition, reasonable variations in electrolyte composition can be tolerated with little change in operating temperature. Large-scale fluorine cells are currently operated in North America, Europe and Japan, either associated with the nuclear industry or in the production of specialist fluorine chemicals.

For a detailed description of the early years of fluorine cell development, the reader is referred to a number of excellent reviews covering the formative years of their development [2 - 6].

Commercial cell designs

Operating and material data for four designs of commercial fluorine cells used in the world today are presented in Table 6.1.

0022-1139/86/$3.50

TABLE 6.1

Operating and material data for four types of commercial fluorine cell

	I.C.I.	Union Carbide	Pierrelatte	Montecatini
Operating data				
nominal current capacity/A	5000	6000	<6000	5000
F_2 output/kg h^{-1}	3.3	3.47	3.47	3.3
current efficiency/%	95	90 - 95	95	90 - 95
voltage at normal load/V	10 - 11	12	8.5 - 10	8.5 - 9.5
anode current density/mA cm^{-2}	180	100 - 150	130	70
electrolyte temperature/℃	80 - 90	88 - 104	85 - 100	95 - 105
HF concentration/% w/w	39 - 41.5	40 - 42	~40	39 - 41
Constructional details				
cell body dimensions/mm	3100 × 710 × 585	2260 × 965 × 1040	—	2000 × 1000 × 600
cell body material of construction	mild steel	monel	monel	monel
cathode	mild steel	mild steel	steel	iron
anode	porous carbon	graphite-free carbon	carbon	amorphous carbon
gas separation skirt	monel	monel	—	monel
diaphragm	none	monel	monel	monel
anodes in cell	24	32	32	32

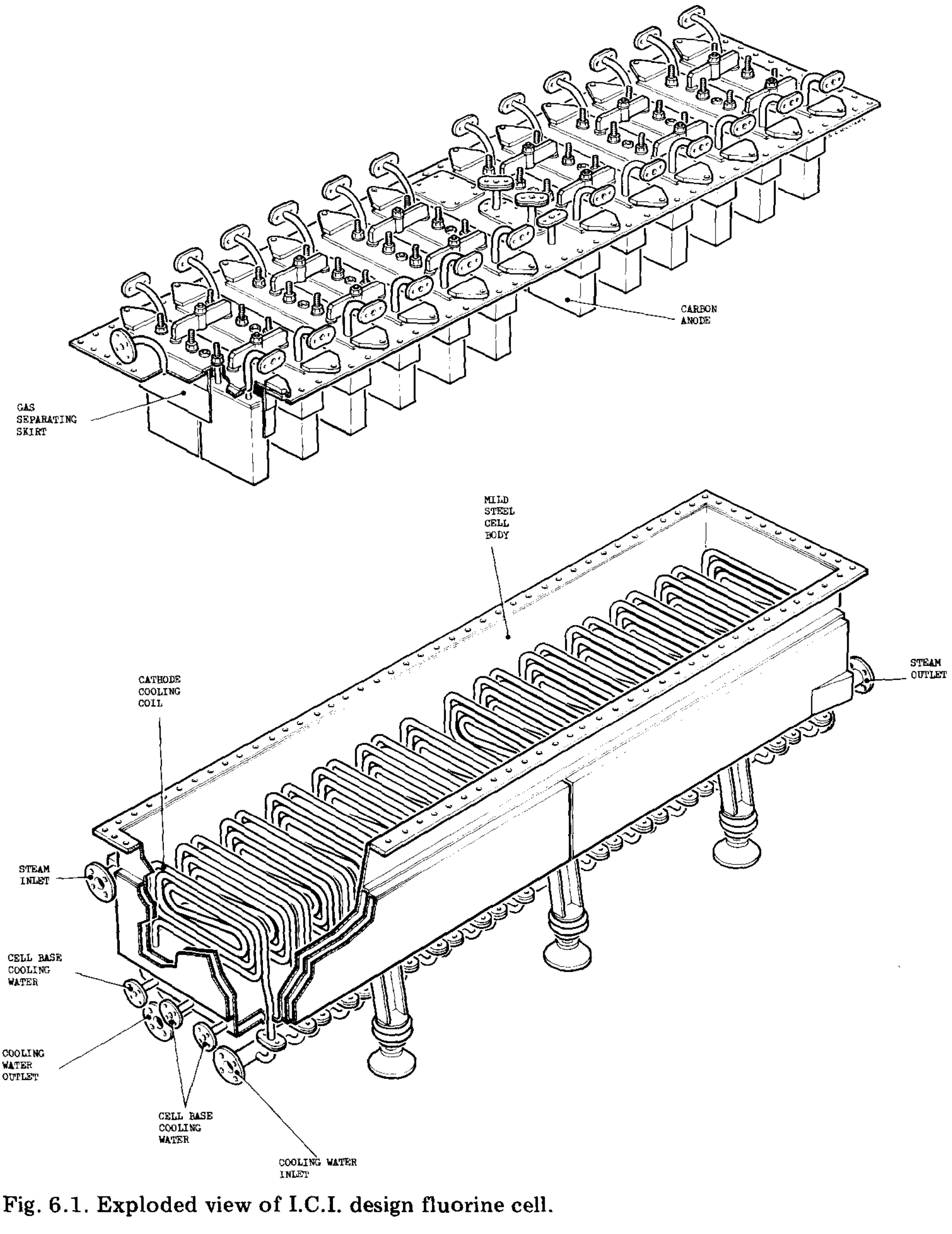


Fig. 6.1. Exploded view of I.C.I. design fluorine cell.

All manufacturers have facilities for continuously replenishing the HF supply to maintain a constant composition of KF•2HF. In the U.K., cells operated by British Nuclear Fuels plc are based on the I.C.I. design [5, 7] and are rated at a nominal 5 kA capacity, although upscaled 11 kA cells are in regular use. The cell body (Fig. 6.1) consists of a welded mild steel tank jacketed on the sides and separately on the bottom. Steam heating is applied to the side jackets when the cells are not in production or operating at low currents to prevent the electrolyte solidifying (m.p., 71 °C). Twenty-four coils connected to inlet and exit headers divide the cell transversely and function as water-cooled cathodes. The cell lid has 12 rectangular openings into which anode assemblies fit, so that they are interposed between pairs of cathode coils. Each assembly consists of a flat plate of mild steel to the underside of which is attached a rectangular monel gas separating skirt inside which are located a pair of anode blocks. The anodes are insulated from the skirt assembly and the cell top by means of neoprene or fluoro-elastomer gaskets depending on the duty. To ensure no mixing of the gaseous products, each skirt protrudes a short distance into the electrolyte, thus dividing the cell into 12 fluorine compartments and one hydrogen compartment. Fluorine from the anode assemblies is collected in a common manifold while the hydrogen leaves at an offtake located at one end of the cell. By deliberately cooling the base of the cell, a solid electrolyte layer is formed. This prevents hydrogen being generated on the cell base, which would otherwise have access to the anode compartment. Provision is made in the cell lid for a liquid hydrogen fluoride feed pipe, electrolyte sample dip pipe, electrolyte thermocouple wells, and a nitrogen purge to both the hydrogen side and each individual anode compartment. Electrical contact to each anode is provided by a mild steel/nickel hanger secured to the block by means of a nickel oversprayed coating. The hanger, which has a nickel base plate, has two mild steel vertical threaded studs which protrude through the top of the gas separating skirt.

Electrical connections from the pairs of anodes are made to a positive busbar running the length of the cell. The negative busbar is connected to the cell body which is thus at the same potential as the cathodes. A pilot installation using external electrolyte cooling has been operated which allowed for operation of cells up to 15 kA [8]. A general view of the fluorine cell room in the UF_6 plant at British Nuclear Fuels' Springfields Works is given in Fig. 6.2.

The majority of modern American cells [9 - 11] are based on designs, C-type and E-type, developed over many years by the Union Carbide Nuclear Company for the American Atomic Energy Commission. The E-type cell body (Fig. 6.3) consists of a welded monel tank with a monel water jacket for cooling and heating, incorporated to overcome the corrosion problems encountered with the steel jacket of the C-type cell. Additional heat-transfer capacity is provided by baffles in the water jacket and water recirculation tubes in the centre of the tank.

The cell lid consists of a steel plate with fluorine and hydrogen compartments, monel gas separating skirts, externally threaded packing glands for the anode and cathode supports, fluorine and hydrogen offtake pipes, nitrogen purge and hydrogen fluoride feed lines, and electrolyte thermocouple and sampling wells. The lid is attached to the cell body with a bolted flange and sealed with a synthetic rubber gasket.

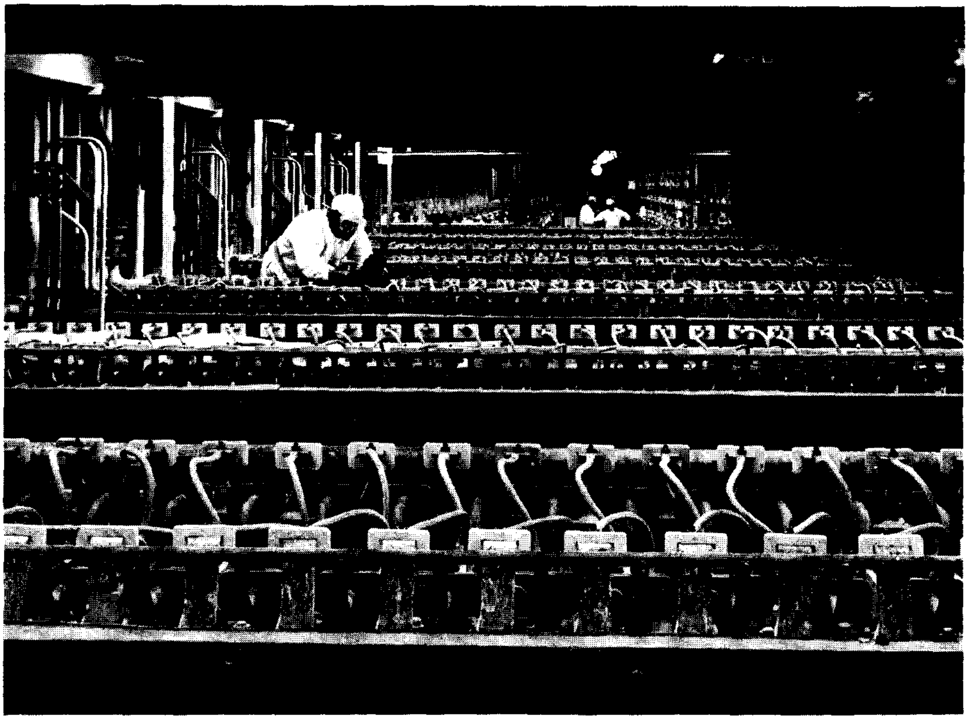


Fig. 6.2. A general view of the fluorine cell room in the uranium hexafluoride (UF_6) plant at the Springfields Works, near Preston, of British Nuclear Fuels Limited. (Copyright: British Nuclear Fuels plc.)

The anode assembly contains 16 anodes arranged in two parallel rows of eight each. Two assemblies totalling 32 anodes are used in each cell. A recessed bolt sealed with a carbon plug fastens the anodes to a copper support bar. This design gives improved cell life over the C-type design which uses a copper pressure plate and steel anode support bar. Copper rods are projected through insulating packing glands in the cell lid to serve as electrical connectors.

The cathodes comprise three vertical parallel steel plates welded to cross-members at the end and suspended through the cell cover by steel rods which pass through insulating packing glands. A six-mesh woven monel diaphragm is attached to an angle frame and bolted to the gas separation skirt through a Teflon gasket. The diaphragm acts to divert the hydrogen gas into the hydrogen compartment of the cell and also prevents broken anodes shorting out the cell. The maximum current rating of this cell design is 6000 A. Gaseous hydrogen fluoride is fed continuously to the electrolyte at a rate based on the operating amperage. As with U.K. cells, hydrogen fluoride content is checked by electrolyte level measurements and periodic analysis of electrolyte samples.

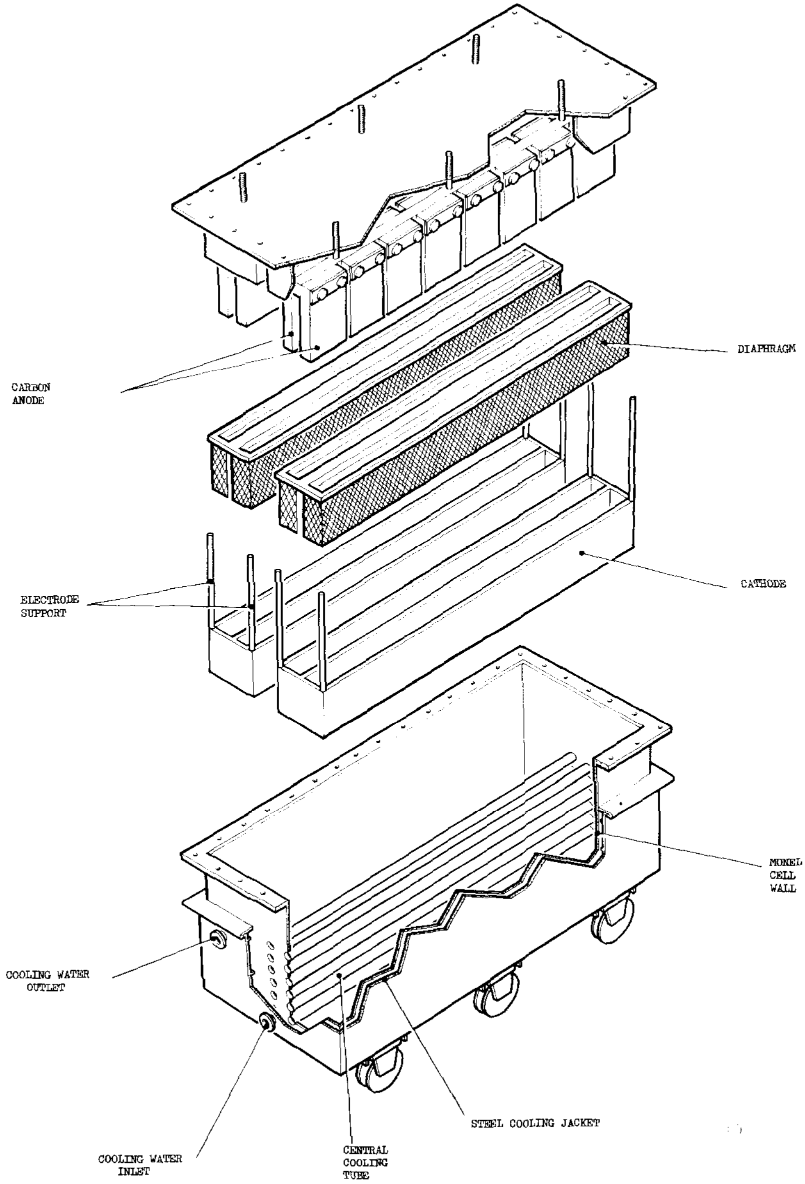


Fig. 6.3. Exploded view of Union Carbide design fluorine cell.

The other cell type used in the U.S.A. has a reported capacity of 5000 A [5] and was developed by the Allied Chemical Corporation. Few details are available about this cell other than that it has a steel body which acts as the cathode and uses a magnesium alloy combined lid and skirt. Unlike the Union Carbide cell, it does not employ a diaphragm.

Published information in the open literature on other cell designs is limited, that which is available [12 - 14] indicating that, outside the U.K., fluorine manufacturers use cells based on American designs.

Anode materials

Initially anodes were made of nickel, but corrosion problems and low current efficiency led to carbon being adopted and to date this has remained the preferred choice of anode material in all medium-temperature fluorine cells. The type of carbon used should provide low electrical resistance, good physical strength, resistance to degradation, stability of electrical contact and resistance to polarisation. Deterioration of the carbon anode is one of the major causes of operating problems with fluorine cells, and many types have been tried in order to improve cell performance.

A major difference between cells used in the U.K. and those used elsewhere is in the composition of the anode. In the U.K., porous carbons having higher permeability are employed whilst other fluorine producers use hard, dense carbons. Both systems use non-graphitised carbon. The hard carbon has the advantage that it is mechanically stronger than a more porous carbon but it can suffer severely from a phenomenon common to fused-salt electrolytic processes known as polarisation. In this context polarisation is defined as the condition under which at a fixed voltage a sudden or gradual decrease occurs in the current flowing through the cell to a value which is a small fraction of that passing when the cell is operating normally.

Before discussing polarisation further, a brief description of the accepted mechanism of fluorine generation on carbon anodes is presented. Despite the significant effects of anode polarisation, the only published work which adequately explains the mechanism of fluorine evolution and hence anode polarisation is that of Rudge and co-workers in the U.K. and Watanabe and co-workers in Japan.

Mechanism of fluorine evolution at carbon anodes

The effect of a large contact angle at the electrode/electrolyte/gas interface of a working carbon anode, and the subsequent effect of this on the mechanism of fluorine evolution at the anode surface was described by Rudge in 1947 [15]. In this situation, Rudge suggested that when lenticular bubbles are produced on a low permeability non-wetted electrode surface, bubble breakaway cannot readily occur. Gas transport to the electrolyte surface takes place by the bubbles slipping up the electrode under the influence of buoyancy forces, or by a process of coalescence. A contact angle as high as 140° was reported by Rudge [16] and later by Watanabe [17], verifying much earlier observations made of the non-wetting characteristics of carbon anodes in high- [18] and medium-temperature [19] cells.

However it was noted that if carbon is not polarised anodically it is wetted by the electrolyte. Both Rudge and Watanabe proposed that this change in the anode surface is the result of the formation of carbon monofluoride $(CF)_n$. Later Watanabe [20] confirmed the presence of $(CF)_n$ using ESCA (XPS) spectroscopy.

Anode polarisation

Anode polarisation has been attributed to the mechanism of fluorine evolution at the surface of the anode. A number of workers [17, 21] have proposed that the condition of electrolysis is determined by the rates of adsorption of fluorine gas on the electrode surface and subsequent desorption of fluorine from the surface. The rate of adsorption of fluorine depends directly on the applied current density and the current efficiency. The desorption rate on the other hand is influenced by the contact angle, *i.e.* wettability at the anode surface, the ease of desorption decreasing as the contact angle increases. Watanabe also demonstrated that the contact angle is a function of current density, increasing as the current density increased. Polarisation occurs at a limiting current density when the rate of adsorption is greater than the rate of desorption of fluorine. Rudge [5] suggested that at a constant value of the contact angle, growth of bubbles on a low permeability carbon results in a reduction in the area of the anode in contact with the electrolyte. This causes an increase in current density at the areas not covered by fluorine. At this increased current density, fluorine accumulates on the available anode area. Any further increase in the current reduces the effective anode surface unless the fluorine generated can travel through the pores of the carbon anode.

In 1978 Watanabe [22], following studies on carbon and pyrolytic graphite anodes, proposed an alternative explanation for polarisation which involved the decomposition of edge-plane CF_2 groups. Under certain circumstances, as the anode potential is increased, the layer planes become less active until only the edge planes pass current. Thus the small apparent current density, does not reflect the true current density, which passes only through the small edge-plane regions.

Methods of overcoming polarisation

In U.K. cells

U.K. cells use porous carbon anodes, as a direct result of the work of Rudge, who established that the use of porous high-permeability anodes eliminated the problems of polarisation. This type of carbon allows fluorine to escape to the electrolyte surface via interconnected pores in the carbon anode and can eliminate the formation of bubbles on the anode surface. Rudge clearly established the relationship between anode permeability and resistance to polarisation. An additional feature of operation with high-permeability anodes is that rigid controls of electrolyte composition and the impurity levels in the hydrogen fluoride feed are not required to maintain the resistance of the anodes to polarisation. In 1966 Rudge [16] proposed that nickel salts were effective in reducing the electrode/electrolyte contact angle if the nickel was in a high oxidation state. He showed the effects of water and nickel to be interdependent, the presence of water in electrolyte reducing any high-oxidation-state nickel present, thereby inhibiting the depolarising action of nickel. The role of nickel at the anode surface was further demonstrated by its concentrating effect at anode surfaces during electrolysis. Rudge also found that a 2% addition of water prevented polarisation until the water was completely consumed, and proposed that water acted to oxidise the carbon or carbon fluoride to maintain a rough and more wetting surface. The use of porous carbons and the beneficial presence of adventitious nickel resulting from corrosion of monel from the gas-separating skirt has overcome polarisation problems in modern U.K. fluorine cells.

In American cells

Polarisation is prevented in American cells by the addition of lithium fluoride to the electrolyte. Other fluoride salts were tried, but only aluminium fluoride and sodium fluoride were found to be nearly comparable in performance. Lithium fluoride was first added to the electrolyte with the intention of reducing its melting point and consequently its losses of hydrogen fluoride by vaporisation [23]. Its observed ability to reduce polarisation was discovered by chance in 1951 [24]. The beneficial effects of lithium fluoride, often demonstrated by operating experience, were confirmed by Watanabe *et al.* [25] who found that the addition of lithium fluoride to the electrolyte in sufficient quantities (<1.0%) formed a colloidal dispersion which was effective in preventing anode polarisation. Special techniques for the elimination of polarisation have been developed which rely on the manipulation of the operating voltage of the cell [11]. Low current conditioning of this type has also been used in conjunction with the addition of lithium fluoride [9].

Cathode polarisation

Polarisation of the cathode is uncommon, but can occur if the electrolyte is allowed to solidify on the cathode and consequently introduce an effective insulating film on its surface. Widespread precipitation may occur if the bulk electrolyte becomes HF-deficient, or locally if a blockage to free electrolyte circulation is introduced. In certain cases deposition of impurities can aggravate the polarisation. Cathode polarisation in American cells has also been observed as a result of the bipolarity of the monel diaphragm [3]. By careful consideration of design features cathode polarisation can be eliminated from modern fluorine cells.

Energy efficiency and cell working voltage

Amongst commercial electrolytic processes fluorine generation is one of the most energy consuming. At about 15 000 kWh t^{-1} the energy consumption of a fluorine cell is pro rata about five times that of cells used in the chloralkali industry. The power efficiency of an electrochemical cell is defined as the product of the voltage efficiency and the current efficiency. The current efficiency of a fluorine cell is typically 95%, any losses in efficiency for electrolyte having a low water content being attributed to hydrogen and fluorine recombination. For a fluorine cell operating at 10 - 11 V and with the reversible decomposition voltage of HF being 2.9 V [26], the power efficiency is calculated to be about 26%.

The operating voltage is made up of the reversible decomposition voltage for the electrolyte, the anodic and cathodic overvoltages, and the voltage drop due to electrolyte ohmic resistance with smaller contributions from electrode ohmic resistance and external losses, for example in busbars. Typical values of the components of a fluorine cell operating voltage measured against a palladium hydrogen reference electrode in a laboratory cell [27] are shown in Table 6.2.

TABLE 6.2

Typical values of cell parameters

Current efficiency	95%
Cell voltage components	
thermodynamic decomposition voltage	2.9 V
anode overvoltage	3.0 V
cathode overvoltage	1.0 V
ohmic drop	3.0 V
average cell voltage	10.0 V
Operating conditions	
anode current density	150 mA cm^{-2}
temperature	85 °C
electrolyte	$KF \cdot 2HF$

Fundamental studies of fluorine generation

Despite its many interesting aspects, the fluorine evolution reaction has not been the subject of many publications and only a few of these attempt to explain the kinetics of fluorine evolution. Watanabe *et al.* [28] carried out studies in $KF \cdot 2HF$ at temperatures that are not reported, but probably in the range 80 - 100 °C. Arvia and Bebczuk de Cusminsky [29] have carried out studies in $KF \cdot HF$ at temperatures in the range 251 - 256 °C. Both sets of workers employed open-circuit decay techniques with both carbon and graphite electrodes. Watanabe *et al.* also used steady-state polarisation data.

A range of kinetic parameters were evaluated by each set of workers. It is apparent from the findings of these workers that fluorine evolution from carbon electrodes is an unusual reaction in electrochemical terms. Steady-state polarisation data lead to the conclusion that the fluorine evolution reaction is inhibited in some manner. Large overvoltages are observed and the reaction is relatively insensitive to potential. Based on the reported results, there is no change in the mechanism of fluorine evolution over the temperature range 80 - 260 °C with electrolytes ranging in composition from $KF \cdot 2HF$ to $KF \cdot HF$. Both sets of workers proposed similar general mechanisms for the reaction involving discharge of the bifluoride ion HF_2^-. However, each set of authors has implied that there is insufficient evidence to give conclusive proof.

Based on work using alternative electrolyte systems, Pourcelly and Rolin [30] have published details of electrochemical studies in an electrolyte comprising a mixture of ammonia and hydrogen fluoride. Electrolysis was carried out at ambient temperature, the principal advantage claimed for this system. The most recent publications in the field are those of French and Canadian workers. Devilliers *et al.* [31] calculated the decomposition potential of hydrogen fluoride from thermodynamic data, using the partial pressure of HF(g) over solutions of potassium fluoride in hydrofluoric acid and the free energy of HF formation, deduced from spectral data. Subsequently steady-state current–voltage plots were used to determine electrochemical kinetic constants for the evolution of fluorine on a carbon anode at 85 °C.

In 1983 Novak and Hough [32] and Devilliers *et al.* [33] published the results of studies into the inhibiting effects of $(CF)_n$ on fluorine evolution. Novak and Hough characterised the fluorine evolution reaction on carbon electrodes using a range of electrochemical diagnostic techniques. They observed that after potential cycling, or after successive polarisation runs, an anodically formed $(CF)_n$ film developed on the anode surface and this film strongly inhibited fluorine evolution. They noted a change in state of the film occurring above an applied potential of 4.5 V.

Similarly, Devilliers *et al.* showed the behaviour of carbon anodes to be related to the growth of an insulating layer of $(CF)_n$. They investigated the kinetics of film growth using chronoamperometry. Interfacial impedance measurements showed that film thickness increased as the potential of the anode was made more positive. A further paper dealing with measurements of the thickness of $(CF)_n$ films was published by the same workers in 1984 [34].

Devilliers *et al.* [35] compared the mass spectra of several graphite fluorides with those of samples obtained from the surface layers of carbon electrodes used as anodes in fluorine generation to confirm the formation of a $(CF)_n$ passivating surface film. They estimated the stoichiometric ratio, n, to be *ca.* 1.1. Analysis of the anodic gases evolved from a laboratory fluorine cell showed that gaseous fluorocarbons are evolved at a potential lower than that of fluorine evolution.

Recent advances in fluorine cell technology

The majority of recent publications on fluorine cell operations are related to improvements in the operating performance of the carbon anode. Most of this work appears in patent publications emanating from Japan. These have included developments in electrode manufacturing techniques [36, 37], and the use of additives either incorporated in the electrode [36, 38] or added to the electrolyte [39]. In the latter case a great variety of additives have been tried, specific success being claimed in the use of nickel salts. The general aim of most of this work has been in the suppression of the onset of anode effect. Anode effect is an extreme case of polarisation where, as a result of raising the voltage and hence driving the current through an anode, arcing or sparks are produced on the surface.

Some recent work [40] has gone into studying the effect of the application of a short duration high-voltage pulse to the anode as a means of preventing polarisation. The problems of deterioration of carbon/metal contact in cells employing hard carbon anodes was the subject of study by Italian workers [41]. By locating the contact above the cell lid they obtained a fourfold increase in cell operating time. A method for the reduction of gas-separating skirt corrosion involving the addition of barium and strontium salts to the electrolyte was patented by German workers in 1975 [42]. Two recent U.K. patent publications have dealt with the problems of anode supports for porous carbons [43] and the development of a composite electrode [44]. Composite electrodes have also been investigated by U.S. workers in the development of the Phillips Petroleum ECF process [45].

The most advanced cell design so far published is described in a patent for a bipolar plate and frame cell, published in the U.K. in 1978 [46]. The cell was adapted from a water electrolyser design following experiments with a double tank arrangement. Claims in the patent deal with bipolar electrodes made of carbon or a carbon–metal duplex structure, and an electrolyser suitable for a mixture of HF, NH_4F and KF, with walls made of or lined with a plastic insulating material. The use of this alternative electrolyte system was pioneered in Japan for the preparation of NF_3 [47] and further developed in France [48] in the early 1970s. It is claimed that such an electrolyser can operate at a voltage of 6 V per element at a current density of 150 mA cm^{-2} giving rise to a 40% reduction in energy consumption. The maximum operating temperature for an acrylic cell is 37 °C and electrolyte cooling is effected by circulation through external tanks.

Continuing the subject developments in cell design, a recent Japanese patent [49] dealt with the use of louvred or mesh cathodes having the ability to channel the hydrogen produced away from the interelectrode region. It is claimed that increased current efficiency and lower operating voltages were obtained with cells fitted with these types of cathode.

The use of a segmented anode assembly has recently been described in an American patent [50]. It comprises a stack of dense carbon anode plates fitted to a central conductor. The plates are provided with a combination of horizontal grooves and vertical holes forming internal passages for directing the fluorine generated away from the anode surface.

References

1 H. Moissan, *C.R. Acad. Sci.*, *102* (1886) 1534; *ibid.*, *103* (1886) 202, 256.
2 H. R. Neumark, *Trans. Electrochem. Soc.*, *91* (1947) 367.
3 C. Slesser and S. R. Schram (eds.), *Preparations, Properties and Technology of Fluorine and Organic Fluorine Compounds, National Nuclear Energy Series,* Div. VII, Vol. 1, McGraw Hill, New York, 1951.
4 J. H. Simons (ed.), *Fluorine Chemistry,* Vol. 1, Academic, New York, 1951.
5 A. J. Rudge, in A. T. Kuhn (ed.), *Industrial Electrochemical Processes,* Elsevier, Amsterdam, 1971, p. 1.
6 R. J. Ring and D. Royston, *A Review of Fluorine Cells and Fluorine Production Facilities,* Australian A.E.C., AAEC/E281, 1973.
7 A. J. Rudge and A. Davies, *Br. Pat. 861 978*(1961) (to I.C.I.).
8 A. E. Grant and S. Wainwright, *Br. Pat. 1 570 004*(1980) (to B.N.F.L.).
9 J. Dykstra, S. Katz, C. B. Clifford, E. W. Powell and G. H. Montillon, *Ind. Eng. Chem.*, *47* (1955) 883.
10 S. P. Valvalides, R. E. Cable, W. K. Henderson and C. A. Powell, *Ind. Eng. Chem.*, *50* (1958) 178.
11 A. P. Huber, J. Dykstra and B. H. Thompson, 'Multi ton production of fluorine for manufacture of uranium hexafluoride', Paper presented at *2nd UN Int. Conf. Peaceful Uses of Atomic Energy,* A/CONF 15/P/524, June 1958.
12 A. Level, *Chim. Ind. Genie Chim.*, *102* (1969) 1077.
13 M. Bergeret, *Energ. Nucl. (Paris)*, *7* (1965) 93.
14 D. Sianesi, *Chim. Ind. (Milan)*, *46* (1964) 883.
15 A. J. Rudge, W. N. Howell and H. Hill, *Nature (London)*, *160* (1947) 504.
16 A. J. Rudge, *Chem. Ind. (London)*, (1949) 247; *ibid.*, (1962) 482; *The Manufacture and Uses of Fluorine and its Compounds,* Oxford University Press, London, 1962.
17 N. Watanabe, M. Ishii and S. Yoshizawa, *J. Electrochem. Soc. Jpn.*, *29* (1961) 110.
18 K. Fredenhagen and O. T. Krefft, *Z. Elektrochem. Angew. Phys. Chem.*, *35* (1929) 670.
19 G. H. Cady, D. H. Rogers and C. A. Carlson, *Ind. Eng. Chem.*, *34* (1942) 443.
20 H. Imoto, T. Nakajima and N. Watanabe, *Bull. Chem. Soc. Jpn.*, *48* (1975) 1633.
21 W. H. Wilson and H. Hill, *Br. Pat. 731 066*(1955) (to I.C.I.).
22 H. Imoto, S. Koyama and N. Watanabe, *Denki Kagaku*, *46* (1978) 680.
23 W. C. Schumb, R. C. Young and K. J. Radimer, *Ind. Eng. Chem.*, *39* (1947) 244.
24 S. Katz, *USAEC Rep. AECD 4230*, (1951).
25 N. Watanabe, M. Ishii and S. Yoshizawa, *J. Electrochem. Soc. Jpn.*, *29* (1961) 177.
26 O. R. Brown, *Electrochim. Acta*, *25* (1980) 367.
27 A. Marshall, private communication.
28 N. Watanabe, M. Inoue and S. Yoshizawa, *J. Electrochem. Soc. Jpn.*, *31* (1963) 168.
29 A. J. Arvia and J. B. de Cusminsky, *Trans. Faraday Soc.*, *58* (1962) 1019.
30 G. Pourcelly and M. Rolin, *J. Chim. Phys. Phys.-Chim. Biol.*, *74* (1977) 401.
31 D. Devilliers, F. Lantelme and M. Chemla, *J. Chim. Phys. Phys.-Chim. Biol.*, *76* (1979) 428.
32 D. M. Novak and P. T. Hough, *J. Electroanal. Chem.*, *144* (1983) 121.
33 D. Devilliers, F. Lantelme and M. Chemla, *J. Chim. Phys. Phys.-Chim. Biol.*, *80* (1983) 267.
34 M. Chemla, D. Devilliers and F. Lantelme, *Ann. Chim. Fr.*, *9* (1984) 633.
35 D. Devilliers, M. Vogler, F. Lantelme and M. Chemla, *Anal. Chim. Acta*, *153* (1983) 69.

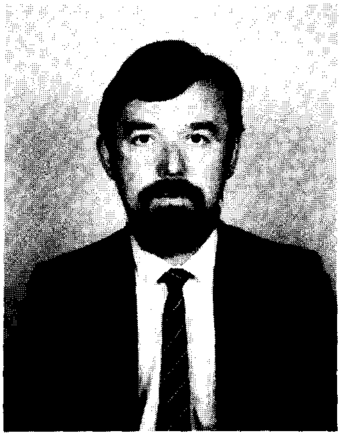
36 N. Watanabe, M. Aramaki and Y. Kita, *UK Pat. Appl. 2 054 650A* (1981).
37 *Jpn. Pats. 82 200 584*(1982) and *82 200 585*(1982) (to Nippon Light Metal Research Laboratory Ltd.).
38 *Jpn. Pat. 83 67 877*(1983) (to Asahi Glass Co. Ltd.).
39 *Jpn. Pat. 83 81 981*(1983) (to Asahi Glass Co. Ltd.).
40 *Jpn. Pat. 82 54 286*(1982) (to Central Glass Co. Ltd.).
41 A. Tricoli, A. Battarra, G. Rebua and L. Bestetti, *UK Pat. 1 354 314*(1974) (to Montecatini Edison).
42 P. Kaudewitz and H. Friedrich, *UK Pat. 1 407 579*(1975) (to Kali-Chemie Fluor.).
43 A. Marshall, *UK Pat. Appl. 2 135 355A*(1984).
44 A. Marshall, *UK Pat. Appl. 2 135 354A*(1984).
45 W. V. Childs, in N. L. Weinberg and B. V. Tilak (eds.), *Technique of Electroorganic Synthesis*, Part 3, Wiley, New York, 1982, p. 341.
46 F. Faron and A. Cathala, *UK Pat. 1 498 306*(1978) (to Produits Chimiques Ugine Kuhlmann).
47 N. Watanabe, A. Tasaka and K. Nakanishi, *Denki Kagaku, 36* (1968) 685.
48 M. Caron, P. Coste, C. Coquet and M. Rey, *UK Pat. 1 303 389*(1973) (to Société des Usines Chimiques de Pierrelatte).
49 *Jpn. Pat. 83 100 688*(1983) (to Asahi Glass Co. Ltd.).
50 A. M. Saprokhin, D. J. Friedland, R. M. Baran, J. T. Kim and L. E. McCurry, *U.S. Pat. 4 511 440*(1985) (to Allied Corporation).

BIOGRAPHIC NOTES

J. F. Ellis

Dr. J. F. Ellis graduated in 1949 from the University of Durham, where in 1952 he was subsequently awarded the degree of Ph.D. for a thesis on the reaction of chlorine trifluoride with organic compounds. In 1952 he took up an appointment as a research chemist with the U.K.A.E.A. at their Capenhurst Works, and was involved in the chemistry of uranium fluorides and their interaction with other fluorochemicals. In the late 1950s he was responsible for founding the technique of corrosive gas analysis by gas chromatography. Since 1961 he has worked at the Springfields Works, originally of U.K.A.E.A. and subsequently of B.N.F.L., where he is now Acting Technical Manager (Chemical Processes Development) covering a spread of activities in uranium and uranium oxide nuclear fuel manufacture.

Dr. G. F. May graduated in 1975 from Liverpool Polytechnic and subsequently obtained a Ph.D. from the University of Newcastle-upon-Tyne in 1978 for a thesis on the anodic behaviour of iron in acidic solutions of liquid ammonia. He joined B.N.F.L. in 1978 and was subsequently appointed to the post of Senior Development Chemist (Chemical Processes Development) where he is responsible for the activities of a section whose major duties involve fluorine cell development.



G. F. May