E$_9$

PASSIVATION OF CARBON ANODES DURING THE FLUORINE EVOLUTION PROCESS

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Fluorine is produced by the electrolysis of molten 2HF-KF, at T = 80 to 100°C. It has been proved by E.S.C.A. measurements [1] that a passivating layer of graphite fluoride (CFx) is formed on the surface of the carbon anodes during the electrochemical process. The experiments, in agreement with thermodynamic calculations [2], indicated that CFx was formed even at 2 V vs Pt H_2, i.e. below the fluorine evolution potential.

On the other hand, the insulating and non-wetting properties of CFx when x is > 0.5 are well known and it has been suggested that the mechanism of discharge of fluoride ions, leading to fluorine evolution, involves electron tunneling across the passivating film.

We have studied the electrical properties of the layer generated on the electrode surface by galvanostatic and impedance measurements. The results show that it is necessary to distinguish the formation of two kinds of CFx compounds, depending on the potential E of the graphite working electrode (measured vs a Pt-H_2 reference electrode) :

- If E remains lower than 2.2 V during the oxidation step, the stoichiometric coefficient x_1 is lower than 0.4 and the compound CFx_1 can be completely reduced by means of an inverse electrochemical pulse.
- When a positive current intensity, under galvanostatic conditions, is imposed to the electrode, a sudden increase of E appears after a transition time. This phenomenon corresponds to the irreversible formation of a second kind of graphite fluoride which cannot be reduced subsequently. The electrochemical reaction (1) leads to the formation of a few layers of insulating CFx_2 (x_2 > 0.5) :

$$(x_2 - x_1)\,F^- + CFx_1 \longrightarrow CFx_2 + (x_2 - x_1)\,e^- \qquad (1)$$

In conclusion, during the fluorine evolution, carbon electrodes are covered with a non-homogeneous film. The deep layers (thickness >100Å) which are directly in contact with the carbon substrate are characterized by a good electrical conductivity (x_1 < 0.4). The upper layers form a thin dielectric film (a few Å) through which the current flows by tunneling effect. This carbon fluoride acts as a high potential barrier and is responsible for the large energy loss in the electrochemical process.

1 H. Imoto and N. Watanabe, Bull. Chem. Soc. Jpn., 49 (1976) 1736.
2 D. Devilliers, Thesis, Paris 1984.