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New products from the carbon electrode reaction

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The author's first interest in fluorine chemistry was the carbon-anode reaction, especially the peculiar phenomenon of the anode effect in the fluorine cell. Anode effects have been studied in aluminum smelting, however, since the end of the 19th century and many mechanisms have been proposed.

The author started from a study of the anode effect in both fluorine and aluminum cells and proposed a new mechanism from results common to the two systems. The main anode reaction in both systems may be described by Eqs. (1) or (2):

$$2F^-(l) \longrightarrow F_2(g) + 2e^- \quad (1)$$

$$2O^{2-}(l) + C(s) \longrightarrow CO_2(g) + 4e^- \quad (2)$$

However, a new step in the mechanism is the formation of graphite fluoride (CF) on the anode surface via the side reaction expressed in Eq. (3):

$$F^-(l) + C(s) \longrightarrow CF(s) + e^- \quad (3)$$

Graphite fluoride was assumed to be a low surface energy compound, but it was not possible to detect the compound at that time. (It was subsequently detected by ESCA analysis.) The step subsequent to that of Eq. (3) would be the chemical reaction

$$4CF(s) \longrightarrow CF_4(g) + 3C(s) \quad (4)$$

In accordance with this suggestion, the formation of carbon tetrafluoride and carbon powder increased during the onset of the anode effect. However, the above propostion was mainly hypothetical and so it was necessary to study the formation and reactions of graphite fluoride in order to clarify the new anode effect mechanism. Some interesting new compounds and new processes have been established as a consequence of this work.

The author wishes to express his gratitude to Professor Cady for his introduction to this field of research, particularly his useful suggestions and warm encouragement. The following has been established [1]:

(1) A new analysis of two kinds of overpotential due to the carbon anode reaction in molten fluoride systems by the introduction of a new thermodynamically induced wettability equation.

(2) The proposal of a new anode effect mechanism due to the formation of graphite fluoride with an extremely low surface energy.

(3) The establishment of the characteristic properties of two kinds of graphite fluoride, CF and C_2F, both new materials.

(4) The preparation of a super hydrophobic composite of metal and graphite fluoride by direct fluorination of PTFE. The contact angle of a water drop on the composite at 173° is the highest known.

(5) The development of a new electrolytic process using the hydrophobic electrode instead of a metal one. The current efficiency was greatly increased and the electrolytic voltage decreased by application of the new process in the electrolytic oxidation from amines to nitriles.

(6) The discovery of the first fluorine or lithium battery combined with metal lithium and graphite fluoride which exhibits the same electrochemical activity as fluorine.

(7) The discovery of some new graphite intercalation compounds of fluorine whose interlayer spacings are much higher than that of the original graphite. The compounds are stable in air and water.

(8) The development of a unique carbon anode for the fluorine cell. The new anode shows very low polarization with no onset of the anode effect even at high current density, as well as a long life.

(9) The development of isotropic graphite as a new carbon material by analysis of the carbon electrode reaction of each plane of HOPG. The material has a high density and a high mechanical strength.

Reference

[1] For more details, see N. Watanabe, T. Nakajima and H. Touhara, *Studies in Inorganic Chemistry*, Vol. 8, *Graphite Fluoride*, Elsevier, Amsterdam, 1988.

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