

ELECTROCHEMICAL BEHAVIOUR OF CARBON IN THE ELECTROLYTIC EVOLUTION OF FLUORINE

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The electrolytic generation of fluorine is characterized by very high overpotentials at the carbon anodes, and a tendency for the carbon to passivate, thereby limiting the sustainable current density. This blockage phenomenon prompted a study of the effect of surface texture on the current-voltage behaviour of industrial carbon anodes. Potentiodynamic cyclic voltammetry measurements conducted in the potential range 0 to 9.5 V show that the fluorine evolution reaction is an irreversible one with initiation of the reaction at 4.5 V. Using standard carbon electrodes, and a linear increase in potential, the current associated with fluorine evolution increases, but drops markedly in the 6.0-6.5 V region. Subsequent repetitive sweeps show lower peak currents than the initial sweep, until a reproducible voltammogram is obtained. Such curves have been reported by others, most notably Watanabe (Battery Materials Symposium, Brussels, 1983), Chemla [Journal de chimie physique, 80, 267, (1983); Annales de chimie, 9, 633, (1984)] and Tasaka [Nippon Kagaku Kaishi, 1795, (1985)]. Fluorination of the carbon surface has been proposed by these authors as the reason for the fluorine evolution process becoming inhibited. However, the use of the same carbon, having a modified surface texture, in the same electrolyte, results in much greater currents being attained than with the standard carbon at the same potentials. The potentiodynamic *i*-*E* curves obtained with electrodes having modified surfaces show that passivation does not occur. Instead, the irreversible Faradaic process is the only apparent process at all potentials up to 8.5 V. Repetitive sweeps do not result in any dramatic drop in the currents attained at given potentials. Discontinuous repeated cycling of the potential, over a period of several weeks, shows that this enhanced surface activity of the modified carbon is maintained. Visual observation of the carbon surfaces (through the use of transparent cells) shows that, at the standard electrode surface, bubbles form in the 4.0 to 4.5 V region and then coalesce into a vein-like film covering much of the surface; at the modified carbon surface, bubbles form in the same potential region but these tend to disengage easily rather than forming a coherent gas film. New bubbles then immediately reform at the same sites. A variety of techniques and procedures have been used to obtain the modified surface of the carbon and all have resulted in similar enhanced current densities during potentiodynamic sweeps.