Study of the Anodic Overvoltage During the Electrolytic Production of Fluorine Gas

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Much attention have been paid to the electrogeneration of bubbles at gas-evolving electrodes (1-3). The mechanism of bubbles evolution involves usually the formation of a gas-supersaturated solution (with H_2 for example) in the region near the electrode / electrolyte interface. In that region, the formation of small bubble nuclei occurs at nucleation sites which correspond generally to imperfections of the surface.

In the case of fluorine evolution in KF-2HF, a large contact angle (about 120-160°) is usually observed giving rise to strongly adherent bubbles to the carbon anodes surface (1,4-8) due to the presence of a solid carbon-fluorine surface film (denoted C-F) generated during electrolysis.

Recently, we have proposed (1,7) a new description of the electrode/electrolyte interface (Fig. 1) to explain the origin of the anodic overvoltage and also to understand how the current can flow at the electrode/KF-2HF interface even if a complete coating of the electrode by a fluorine gaseous film is observed. In this model, the presence of an intermediate layer called "fluidized" layer sandwiched between the C-F surface layer and the gaseous film (Fig. 1) is suggested. This intermediate layer, which is supposed to be composed of a mixed phase of KF-2HF and dissolved fluorine gas, is characterized by its resistivity, ρ. It was concluded that the total anodic overvoltage, η_T, is the sum of two contributions: the C-F film giving rise to $\eta_{C\text{-}F}$ (activation overvoltage for the fluorine evolution reaction), and the intermediate "fluidized" layer, $\eta_{fluid.}$ (ohmic drop in the "fluidized" layer).

In the present work, the model proposed above is confirmed by SEM observations of the surface of carbon anodes before and after electrolysis. They have shown (Fig. 2) that the electroactive species are mainly consumed at the edge of the electrode and that its centre is rather completely inactive. Finally, the calculation of the contributions (Fig. 3) due to the "fluidized" layer, $\eta_{fluid.}$, and to the C-F film, $\eta_{C\text{-}F}$, to the total anodic overvoltage, η_T, is performed by numerical simulation for various ρ values.

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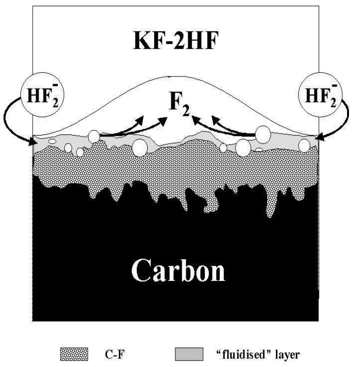

Fig. 1. Schematic representation of C/KF-2HF interface. The electroactive species (HF_2^-) as well as K^+ and HF present in the electrolyte diffuse simulta-neously under the gaseous film *via* the lateral sides of the electrode.

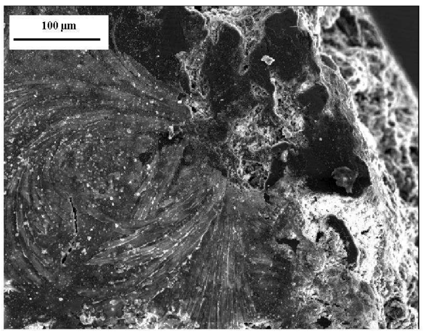

Fig. 2. Scanning electron microscopy image of the surface of carbon anode activated at 40 V in KF-2HF during one minute showing a smoothing and a cleaning of the lateral side of the electrode.

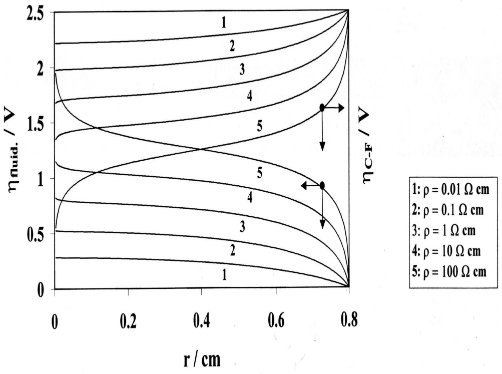

Fig. 3. Variation of the overvoltage in the "fluidized" layer, $\eta_{fluid.}$, in the C-F layer, $\eta_{C\text{-}F}$, *vs* distance, r, for several values of the resistivity ρ of the "fluidized" layer. η_T = 2.5 V, T = 95°C.