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SOME VOLTAMMETRIC OBSERVATIONS IN CONNECTION
WITH ELECTROCHEMICAL FLUORINATION

Fluorination of the disc Ni anode in the HF solution has been carried out by means of the voltammetric method.

It has been stated that a layer of Ni oxide is produced on the surface of the electrode as the result of water trace presence in the HF. The produced oxide layer influences electrochemical reaction of fluorination to a great extent.

INTRODUCTION

Although the anodic fluorination of organic compounds in HF on a Ni anode has been an electrochemical process of industrial importance since its discovery, its details are not yet sufficiently well known for the phenomena involved to be understood. Thus, it is not clear (i) whether the process follows an ionic or radical mechanism, (ii) what role is played by the surface layer formed on the anode in the reaction, (iii) what role is played by adsorption of the organic substrate in the overall reaction, and (iv) what the source of the peculiar voltammetric behaviour is.

After a long period of investigation well documented in [1], two thorough studies were published on some aspects of the phenomena involved, although the approaches and the conclusions were quite different. Haruta [2] stresses the importance of the role of the surface layer and the reaction between the fluorine and the substrate, while Rozhkov [3], on the basis of investigations of the partial fluorination of organic compounds, suggests an ionic mechanism.

Since the question of the interpretation has not yet been an-

swered, the phenomena have been investigated in our laboratory. This paper presents some data on the voltammetric behaviour.

EXPERIMENTAL

The experimental details were reported in [4]. The HF handling system and electrochemical cell were made of teflon. A rotating Ni disc and Pt ring were used for voltammetric investigations, while a Cu/CuF_2 electrode was applied as reference.

The potential was controlled with a double potentiostat (AFKEL 414) and an EMG 1500 digital recorder and analyzer were used for data handling.

RESULTS

In liquid HF, a surface layer is formed on a Ni anode as the current is switched on. The formation can be followed via the change in current during the potentiostatic polarization (Fig. 1). An initial drop in current is a clear indication of formation of the layer. The layer contains not only fluoride, but oxide as well [5], due to the water content of the liquid HF. The build-up

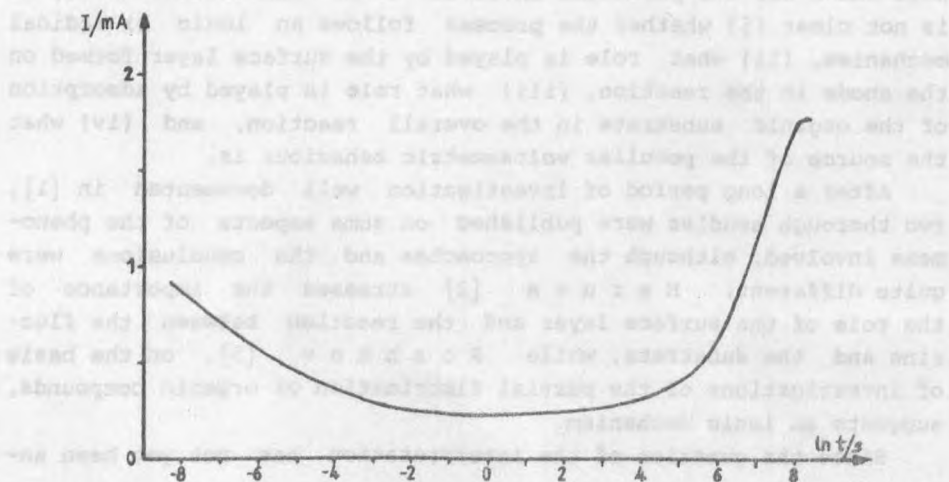


Fig. 1. Change in current with time at 4500 mV

of the surface layer is followed by a period during which the current is temporarily stabilized at a low level. This state is not final: after a certain time, which depends on the potential, the current starts to increase again, and after a long period of time it reaches a steady state. This behaviour is typical for valve metals [6] and indicates that the conductivity of the layer is changing. Thus, the electrochemical behaviour of a Ni anode in HF is strongly influenced by the oxide layer formed on its surface. This is shown by the detection of fluorine evolution. In Fig. 2,

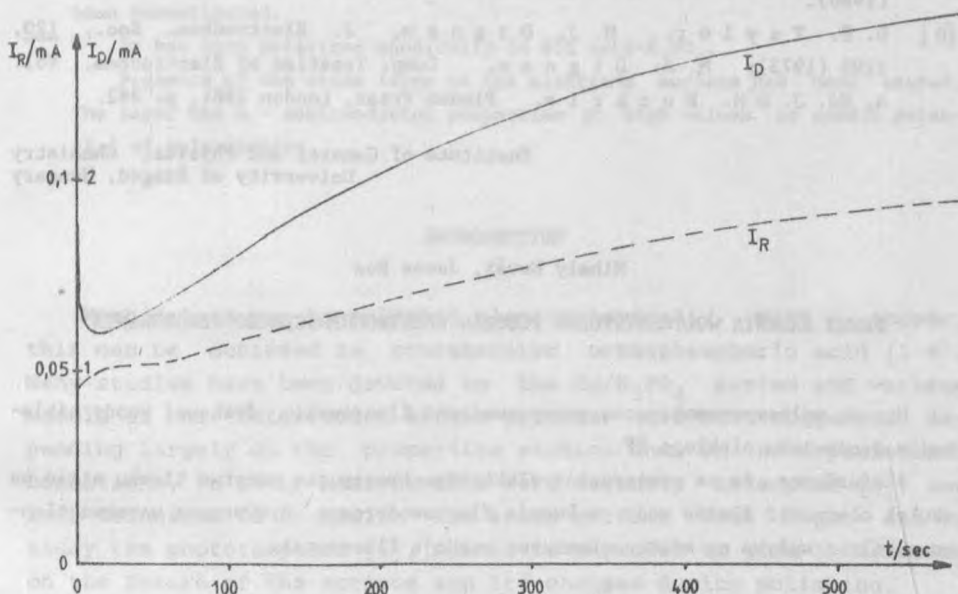


Fig. 2. Disc and ring current in the first period of polarization at 4500 mV

the disc and ring currents are given for the early period of electrolysis. The change in current indicates that fluorine evolution increases as the surface layer forms. It might therefore be assumed that the reaction takes place through the oxide layer.

Since the voltammetric features and the formation of fluoride are strongly connected with the presence of the oxide, further study is in progress to elucidate its role in the process of electrochemical fluorination.

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PEWNE BADANIA WOLTOMETRYCZNE PODCZAS ELEKTROCHEMICZNEGO FLUOROWANIA

Metodą woltamperometryczną przeprowadzono fluorowanie dyskowej anody niklowej w środowisku ciekłego HF.

Stwierdzono, że na powierzchni elektrody tworzy się warstwa tlenku niklu na skutek obecności śladów wody w kwasie fluorowodorowym. Wytworzona warstwa tlenkowa silnie wpływa na elektrochemiczną reakcję fluorowania.