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BUBBLE EFFECT AND INTERFACIAL CAPACITANCE BEHAVIOUR IN ANODIC F_2 EVOLUTION AT CARBON ELECTRODES

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The role of a) F_2 bubble adherence and detachment and b) passivating 'CF' film formation in the anodic F_2 evolution reaction (FER) in KF.2HF melt has been evaluated by means of steady-state polarization, potential-decay and a.c. impedance measurements at a carbon rotating cone electrode (RCE)

Use of the RCE technique enables the role of F_2 bubble adherence in determining the observed high polarization and "anode effect" in the FER to be determined, since at the cone electrode, contrary to the situation at a rotating disc electrode, bubbles are spun upward and away from the surface. At the carbon RCE, bubble detachment is greatly facilitated and the bubble effect diminished or eliminated. Then reliable measurements of the real electrode kinetic polarization behaviour can be made, especially the significance of high Tafel slopes (b) that are commonly observed.

The polarization behaviour is then characterized by 2 abnormally high slope Tafel relations: $b = 0.3 - 0.5$ V at low c.d. and $b = 0.8 - 0.9$ V at high c.d. For a given electrode, the slopes depend on prehistory of the melt. Rotation of the RCE facilitates F_2 removal and extends the high-b region to larger c.d.s.

A.c. impedance and potential-decay measurements agree in giving abnormally low interfacial capacitance (C) values of ca. 1 or <1 $\mu F\ cm^{-2}$. The low C is attributed to a small dielectric capacitance, C_f, due to CF film formation, in series with the double-layer capacitance so that the low C_f determines the measured C.

In the present work, studies were made by our recent [1] new procedure for potential-decay measurement, and enabled C to be evaluated as a function of anodic potential over a wide range of potentials (V) and currents. C decreases with increasing V, corresponding to thicker 'CF' film formation. Complementary measurements were made over a wide frequency range (0.1 to 10 kHz), enabling the impedance of the FER process to be represented in the complex plane. One semicircle is found, as also in the results of Chemla et al. [2] in their work from 5 to 1000 kHz.

1 B.E. Conway and Lijun Bai, J. Chem. Soc., Faraday Trans. I, 81 (1985) 1841.

2 M. Chemla, D. Devilliers and F. Lantelme, Proceedings of the First International Symposium on Molten Salt Chemistry and Technology, Kyoto, Japan, April, 1983; see also Ann. Chim. Fr., 9 (1984) 633.