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ANODE OVERVOLTAGE IN FLUORINE CELLS

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In situ techniques show that films can be formed at electrode potentials considerably negative to the reversible fluorine potential and they are electrochemically reducible. The ease of reduction is greater on graphite than on vitreous carbon but is kinetically reversible on neither. Films formed on vitreous carbons subjected to fluorine evolution under mild conditions behaved rather similarly but fluorination at high electrode potentials ($>6V$) produced films which exhibited lower capacitances, higher series resistances and increased inhibition of charge transfer processes, all associated with the formation of higher fluorides of carbon and with thicker films. These films are also reducible electrochemically, either in the melt or in aqueous or organic electrolytes.

A comparison of steady-state and pseudo-steady-state polarisation data for fluorine evolution show that fluorine bubbles cover all but some 1% of the anode surface in the former case. However the major cause of the abnormally high overvoltages and Tafel slopes observed experimentally for this reaction is the increasing severity, with increasing electrode potential, of the inhibition of the electron transfer from fluoride ions. Furthermore the anodic film formed at potentials above 6V introduces a series resistance which gives rise to a significant ohmic overvoltage.

Pseudo-steady-state polarisation data were acquired using a potential double step. From a base value of 0V vs. the palladium-hydrogen reference electrode, the electrode potential was stepped to 3.0V for a period of 5s. These conditions were severe enough to fluorinate the carbon surface but were insufficient to generate molecular fluorine. Fluorine formation, which occurred during the second potential step to a potential in the range 4.0V to 5.6V for 0.2s was thus uncomplicated by a significant contribution due to surface oxidation. Currents recorded immediately after the second step are thought to arise from fluorine evolution at a gas-free surface.

The inhibiting effect of the solid film was studied by transferring carbon electrodes, following fluorine evolution in the $KF \cdot 2HF$ melt at 85°C, to other electrochemical systems using aqueous or organic electrolytes at room temperature, where electrode kinetic studies were made of redox reactions (ferrocene/ferrocinium and hexacyanoferrate II/III). Kinetic data were compared with those obtained with unfluorinated carbon surfaces. Rates fell by at least two orders of magnitude in the presence of a film formed by polarising the carbon at 6.0V in the melt.

XPS spectra of carbon anodes fluorinated at 5.0V or at 9.0V and then etched by argon ions show that, with distance from the surface, carbon bound to fluorine is replaced by other carbon whereas fluorine of higher carbon fluorides gives way to fluorine of lower fluorides. SIMS spectra showed a rapid fall-off in fluorocarbon ions with etching.

Both capacitance measurements and kinetic studies of redox reactions indicated that the film became progressively thicker as the potential of the fluorine anode was raised. Estimates of film thickness on vitreous carbon from depth profiling by ion etching, from interfacial capacitance data and from cyclic voltammetry are consistent and lie in the range 1nm at 3.5V to 10nm at 9V polarisation.