Short communication

THE POTENTIODYNAMIC BEHAVIOUR OF IRIDIUM ELECTRODES IN NaHSO$_4$—KHSO$_4$ MELTS

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Noble metal electrodes in aqueous solutions under a triangular potential sweep display current peaks due to the electrosorption and electrodesorption of hydrogen and oxygen species [1—7]. In molten bisulphate electrolytes these characteristics were previously observed for platinum [8—11] and are also common for iridium.

The electrochemical behaviour of iridium (1 mm diameter wire, Johnson Matthey, 1.0 cm^2 apparent area) was studied in the NaHSO$_4$—KHSO$_4$ melts at 180—300°C using a conventional three compartment electrolysis cell. Its potential was referred to a Pt/H$_2$(1 atm)/KHSO$_4$(melt) electrode.

The rest potential, E_{rest}, of an iridium electrode in a H$_2$-free melt is 0.390 V at 212°C, a value comprised between the regions of oxide electroformation and oxide electroreduction. That rest potential value can be achieved just by leaving the electrode in contact with the melt for several hours or by a potentiodynamic anodisation. The iridium electrode dipped in a H$_2$-free melt, after its rest potential has been attained, exhibits a cathodic current corresponding to the electroreduction of a surface oxide species spontaneously formed. The rest potential very likely corresponds to a corrosion potential of the metal in the bisulphate melt. The corrosion of the metal is easily visible after leaving it in contact with the melt for several weeks. When H$_2$ is present at the metal/electrolyte interface, $E_{rest} \approx 0$, and no spontaneous oxide formation is observed.

To obtain reproducible potentiodynamic E/I profiles, firstly the electrode was potential cycled during 5 min at 0.05 V s^{-1}, within the regions where the surface oxide species are electroformed and electroreduced, but avoiding the H$_2$ accumulation at the metal/electrolyte interface. Afterwards the single triangular potential sweep voltammogram run between —0.150 to 0.735 V and vice versa (Fig. 1), exhibits, at the lowest potentials, the hydrogen evolution region, including at least one current peak related to hydrogen adatom formation. At the highest potentials O$_2$ evolution takes place and over a wide intermediate potential range, surface oxide species are electroformed and electroreduced. One observes that there is an appreciable interference of the hydrogen electrode reaction with the electroreduction of the oxygen con-
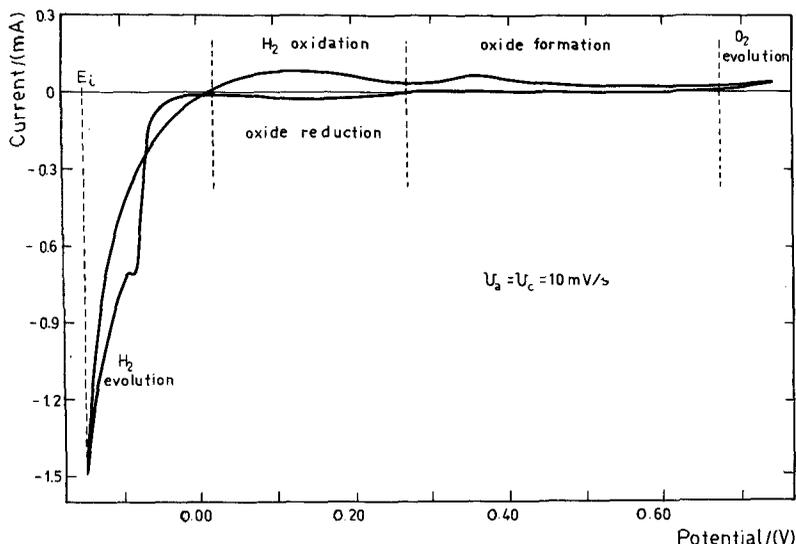
Fig. 1. Potentiodynamic triangular E/I display run from E_i.

taining surface species. Furthermore, one observes that the electrodesorption
of the latter is bound to the formation of a layer of hydrogen adatoms and,
under these circumstances, the hydrogen evolution reaction extends to a more
anodic potential region. For iridium electrodes in the acid melts, the H_2 and
O_2 evolution regions are closer together than in acid aqueous solutions, as it
occurred for platinum.

In the potential range where the oxygen species are either electroformed
or electroreduced, the Q_a/Q_c charge ratio is unity only when the single trian-
gular potential sweep at 0.05 V s^{-1} is run between −0.05 V and 0.640 V. For
lower anodic potential limits that ratio is smaller than one and vice versa.
Although the oxide species formed on iridium are not well established yet in
terms of simple metal/oxygen stoichiometries, however, the cyclic voltammo-
grams run between −0.025 and 0.575 V (Fig. 2) are mainly related to the
electroformation and electroreduction of a surface film whose thickness is of
the order of a monolayer of oxygen atoms. The shape of the voltammograms
in this potential region depends on the limits of the potential excursion, on
the rate of potential scan and on the shape of the potential/time program. The
shape of the cathodic E/I profiles depends also to a large extent on the time
spent at the open circuit potential after the electroformation of the oxygen
containing film (Fig. 3). The amount of cathodic charge slightly increases
with the time elapsed between the anodic and the cathodic scans and simulta-
neously, the cathodic current peak potential becomes more cathodic. These
changes, at 212°C, attain a limiting situation after about 30 min. This evidences
the oxygen containing film undergoes-to some extent an ageing process such
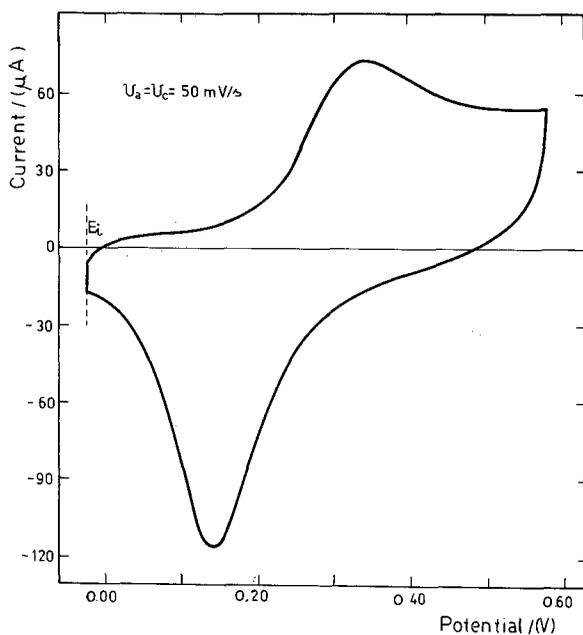as that already described for platinum in the same electrolyte.

Fig. 2. Potentiodynamic triangular E/I display run from E_i covering the potential range where $Q_a/Q_c \approx 1$. $T = 220°$ C.
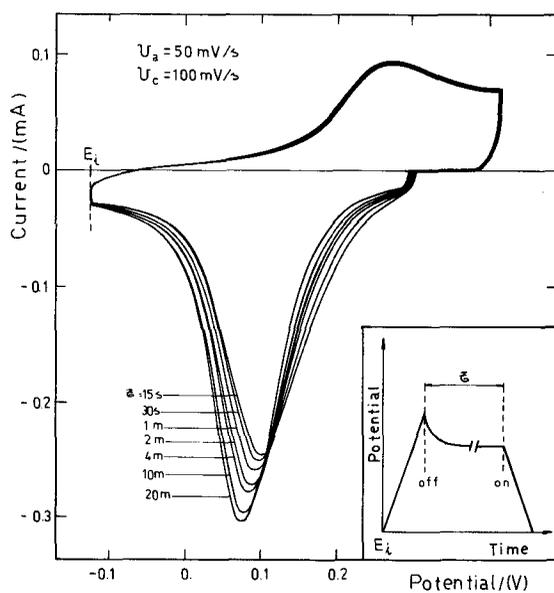

Fig. 3. Potentiodynamic E/I displays run according to the E/t program indicated in the Figure, with $v_a = 0.05$ V s^{-1} and $v_c = 0.1$ V s^{-1}. The electrolysis interruption times between the anodic and the cathodic scan are 15 and 20 min.

The shape of the cathodic voltammogram depends also whether the oxygen containing film was formed electrochemically or chemically. For the latter the reduction current peak is wider. Presumably, the potential of the cathodic current peak depends on the amount of hydrogen adsorbed on the metal.

Using a constant amount of electroformed oxygen containing species and a constant ageing time spent at the rest potential (Fig. 4), the cathodic current peak height increases linearly with v, the potential sweep rate, while its potential shifts linearly with $\log v$.

The existence of an ageing process and the broad appearance of the cathodic E/I profiles, particularly at large v and without ageing, suggest the participation of different species in the overall reactions probably involving OH containing species and O surface atoms. The more reactive species undergoes a chemical transformation (probably involving the OH containing species) to a more stable one (assigned to an O-containing species).

The product initially formed during the electro-oxidation process can be electroreduced when a fast potential perturbation function is employed, as is the case of modulation voltammetry (Fig. 5). The corresponding anodic and cathodic current peak potentials are then very close, suggesting the occurrence of a relatively fast electrochemical redox couple. The anodic and the cathodic charges involved there, obtained after correction for the d.l. effect, are practically the same and any chemical dissolution of the metal under these circumstances is negligible.

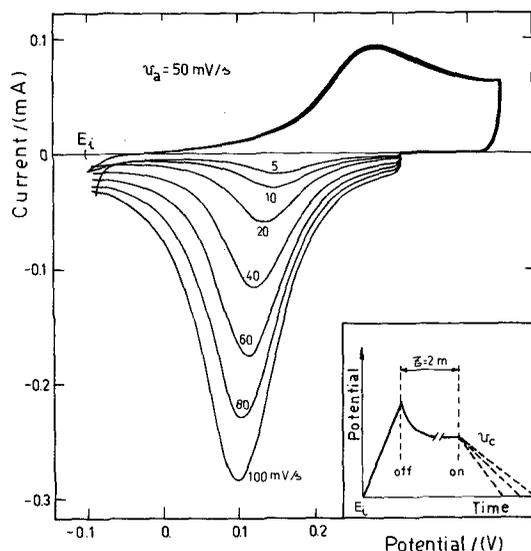In conclusion, the processes occurring on iridium electrodes in molten bi-

Fig. 4. Potentiodynamic E/I displays run according to the E/t program indicated in the Figure, with a constant v_a and different v_c. After the anodic scan the electrolysis is interrupted for 2 min before running the cathodic scan.
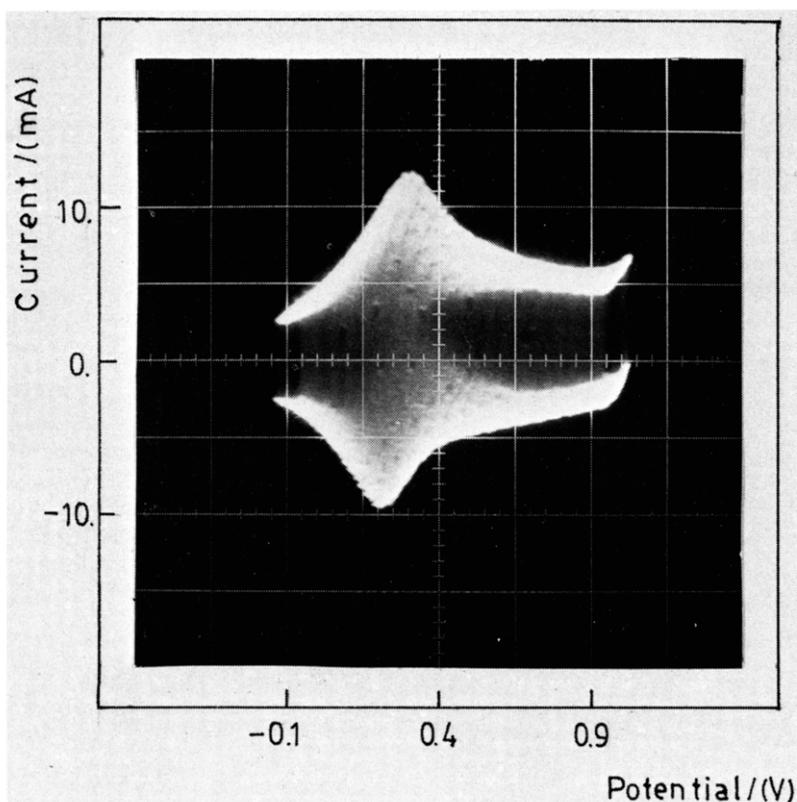
Fig. 5. Single triangularly modulated linear anodic potential sweep display. Base linear potential sweep rate at 3 V s^{-1}; superimposed linear potential sweep at 9 V s^{-1}. E_i = -0.132 V. T = 225°C.

sulphates seem to be those already described for platinum in the same melt [8—11], which included both a chemical transformation of the initial reaction product and an ageing process. For iridium, however, a larger interference of the hydrogen electrode reaction in the oxide formation region is found.

The mechanistic interpretation of the electrochemical processes just described can be attempted following the basic reaction models which apparently explain the reactions of most noble metal electrodes both in aqueous solutions and in molten bisulphates [10—13].

Acknowledgements

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