

SHORT COMMUNICATION

Ageing and dissolution processes affecting the electroreduction of monomolecular oxide films formed on platinum electrodes in molten sodium bisulphate–potassium bisulphate melts

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An oxygen film, either oxide or chemisorbed oxygen, can be formed electrochemically by anodising a platinum electrode in aqueous electrolyte solutions. Many fundamental questions regarding the mechanisms of anodic film formation and dissolution, as well as the nature of the film, are still unresolved^{1–6}.

In an attempt to contribute to the understanding of the behaviour of oxide monolayer formation and dissolution on polished platinum electrodes, those processes were studied in molten sodium bisulphate–potassium bisulphate at 184°C, using linear single-sweep voltammetry with different potential–time profiles. The electrode roughness factor, as obtained from the charge related to the hydrogen reduction in aqueous sulphuric acid, was 1.6.

The single-sweep voltammograms run at constant potential sweep rates and covering the anodic range of potential where the oxide monolayer is formed, exhibit net oxidation and reduction current peaks rather similar to those already described for aqueous electrolytic solutions^{1–4}. The anodic charge, Q_a , is nearly equal to the cathodic charge, Q_c . The Q_a/Q_c ratio approaches one as the potential sweep rate increases from 10 mV s⁻¹ to 3 V s⁻¹. The anodic charge decreases as the sweeping rate increases, but the Q_a/Q_c ratio remains nearly equal to one. Both current peaks divided by the charge involved, follow approximately a linear relationship with the potential sweep rate. Under these conditions no simple dependence of the potential related to the maximum anodic current with the potential sweep rate is observed, although that corresponding to the cathodic current approaches a linear logarithmic dependence with the latter.

The potential of the cathodic current peak becomes more negative as the anodic charge passed is increased. It depends linearly on the anodic charge passed. The height of the cathodic current peak increases also with the anodic charge passed, but the ratio current peak height/charge is not constant as expected for a simple electrochemical reaction. At constant anodic charge, the height of the cathodic current peak approaches a nearly linear dependence on the rate of the cathodic potential sweep, v_c , and shifts towards negative potentials as v_c increases.

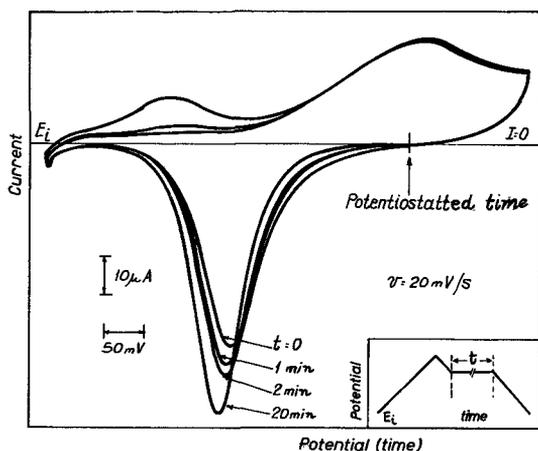


Fig. 1. Single potential sweep voltammograms started from E_i covering a constant potential amplitude. Potential/time profile shown in the figure. Cathodic reduction proceeds after potentiostating the system during t min at the zero net current potential.

Figure 1 comprises different voltammograms run at the same potential sweep rate within a fixed potential amplitude. After the anodic potential sweep and when the cathodic potential sweep had reached the zero net current potential, the system is potentiostatted during a fixed time, which is different for each voltammogram, and afterwards the cathodic potential sweep is continued. The constancy of the charge involved in these experiments is within 7%. These voltammograms exhibit both a shift of the cathodic current peak towards negative potentials and an increase of its height as the time elapsed at the anodic potential corresponding to the zero net current is increased. Correspondingly, more symmetric reduction voltammograms are recorded.

Figure 2 corresponds to voltammograms run in the same way as described for those exhibited in Fig. 1, but once the cathodic sweep has reached the zero net current potential, the working electrode is switched off for a fixed time and simultaneously the open circuit potential decay is measured, and when the latter attains E_i , then the cathodic potential sweep is reinitiated. Under these circumstances the height of the cathodic current peak increases linearly with v_c and its potential depends linearly on $\log v_c$. The slope of the latter is equal to the $RT/2F$ ratio. Furthermore, these cathodic curves are highly symmetric in shape, their initial polarisation being practically the same. A plot of the initial portion of the voltammogram as $E/\log I$, approaches a straight line with a slope equal to $RT/2F$.

If the voltammograms are made at different current interruption times t , counted from the time corresponding to zero net current, the cathodic charge decreases as t increases, which corresponds to the dissolution of the species anodically formed. A shift of the cathodic current peak towards more negative potentials with the interruption time is observed and the voltammograms turn into a more symmetric shape.

After interruption of the current the open circuit potential/time dependence of the potentiostatically oxidized platinum anode involves a net transition time. A zero order rate law for the dissolution process is obtained from the Q_a/t plot. The

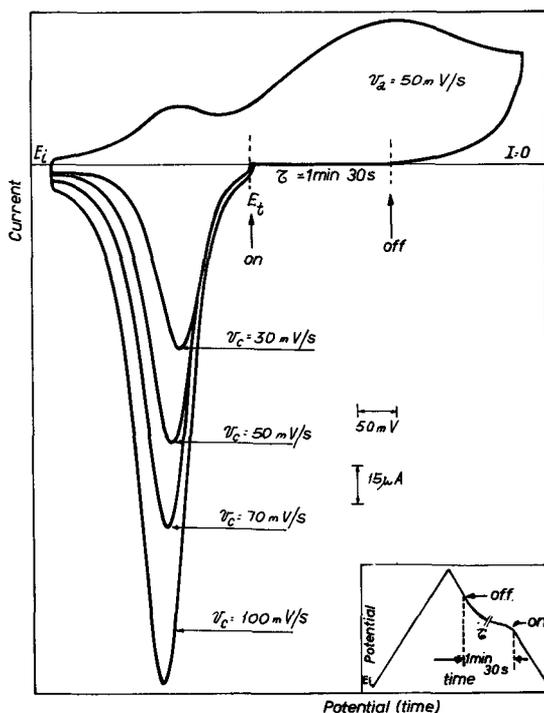


Fig. 2. Effect of current interruption at the zero net current potential on the reduction process. Potential/time profile shown in the figure.

product of rate constant and the transition time gives a charge which coincides with those obtained voltammetrically within the same potential amplitude.

Figure 3 shows the effect of the potential amplitude on the anodic charge passed for a fixed interruption time and a constant cathodic potential sweep rate. The shift of the cathodic peaks fits reasonably well to a logarithmic dependence on charge corresponding to the amount of oxide left on the electrode surface. The symmetry of the curves implies a constant Tafel slope equal to $RT/2F$, and the larger the interruption time the better the coincidence of the initiation of the cathodic E/I curves. If the interruption time is not large enough, then a crossing of the curves occurs as shown for the two runs covering the largest potential amplitudes. This can be explained in terms of a decreasing interaction between species left on the surface⁷.

These results present a clear evidence for the occurrence of at least four processes during a complete voltammetric cycle, namely, the electrochemical oxide formation, a film dissolution process, an ageing process and the electroreduction of the film anodically formed. Therefore, the existence of the ageing and dissolution processes must be taken into account for a reasonable kinetic interpretation of the voltammetric data as well as of the data obtained by any other perturbation experiments. This conclusion should also be extended to experiments made in aqueous electrolytic solutions where the above-mentioned processes, under lower temperature conditions, must occur, though at a lower rate. A quantitative analysis and mechanistic discussion about all these processes will be given in a forthcoming publication⁷.

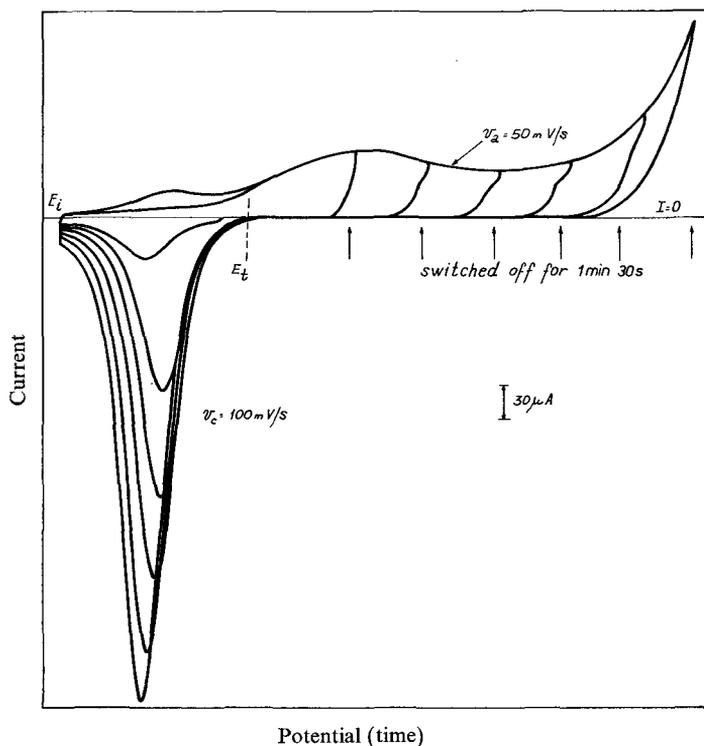


Fig. 3. Single potential sweep voltammograms covering different potential amplitudes. Current interruption at the zero net current potential for 1 min 30 s.

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