

SHORT COMMUNICATION

Potentiodynamic E/I profiles of Pt electrodes in molten KHSO_4 in the hydrogen electrode region

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The cathodic evolution of hydrogen and its electrooxidation on platinum in molten KHSO_4 have been studied over a wide range of temperature¹⁻⁴. The former reaction was mechanistically interpreted in a simple way by assuming that on platinum black the hydrogen discharge step is followed by the recombination of hydrogen atoms as the r.d.s. The cathodic reaction is inhibited by sulphide species formed at high cathodic current densities⁵.

On the basis of previous results one would expect that potentiodynamic E/I curves would give pseudo-capacitance peaks. These have been well established on platinum in aqueous solutions, at potentials positive to the commencement of significant hydrogen evolution. Previous attempts⁴, however, in molten KHSO_4 failed to separate the component currents due to hydrogen-atom adsorption and ionization at potential sweep rates below 10^3 V s^{-1} . The present results indicate that these current peaks can be easily recorded if inhibition of the hydrogen electrode reaction is prevented by working at a cathode potential less than 0.1 V with respect to the hydrogen electrode reaction in the melt.

Figure 1 exhibits a series of potentiodynamic E/I curves run at 0.5 V s^{-1} and 309°C , obtained with application of a linear potential sweep with ohmic drop compensation. Each voltammogram was started from an initial potential towards anodic potentials. The initial potential was more cathodic in going from Fig. 1a to Fig. 1d although covering the same potential amplitude. Potentials are referred to the hydrogen electrode in the KHSO_4 melt. This potential is clearly defined in the voltammograms covering the largest cathodic limit of the amplitude swept (Figs. 1d and 2e). This figure coincides with the hydrogen electrode potential extrapolated²⁻⁵ from e.m.f. measurements from 180 up to 270°C . Within this potential range the E/I display comprises the region of the hydrogen electrode reaction at low potentials and at high potentials that of the electrochemical formation and dissolution of platinum-oxide monolayer. The voltage range between the faradaic reactions certainly is smaller than that in water⁶.

At the lowest cathodization (Fig. 1a and 1b) the anodic sweep exhibits one complex but well defined anodic current peak related to the electrooxidation of hydrogen at *ca.* 165 mV and at *ca.* 580 mV the anodic current maximum corre-

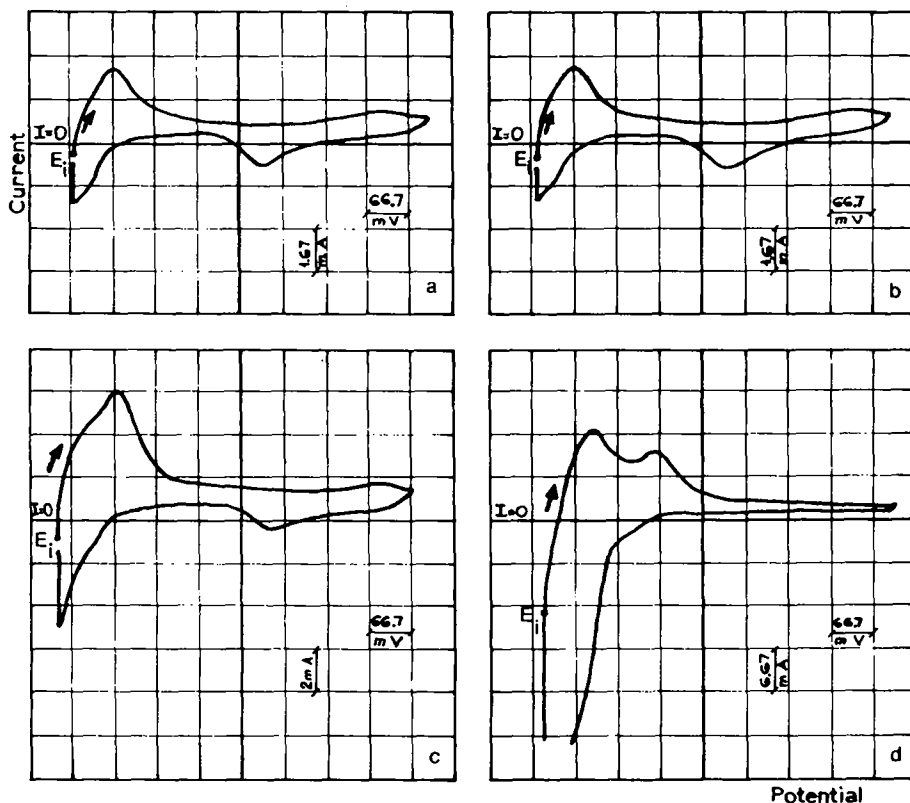


Fig. 1. Single sweep voltammograms started from E_i towards anodic potentials at 0.5 V s^{-1} . (a) $E_i = -25 \text{ mV}$ and 15 s cathodization time; (b) $E_i = -25 \text{ mV}$ and 30 s cathodization time; (c) $E_i = -50 \text{ mV}$; (d) $E_i = -150 \text{ mV}$ (net hydrogen evolution).

sponding to platinum surface oxide formation. The returning potential sweep shows the cathodic current peak related to the electroreduction of platinum surface oxide at *ca.* 397 mV. At the highest cathodization (Figs. 1d and 2e) at least two anodic current peaks are seen at *ca.* 55 mV and 160 mV, related to hydrogen electrooxidation and also two cathodic current peaks appearing rather poorly defined at *ca.* 150 mV, and the other as a shoulder at *ca.* 60 mV. Both current peaks are presumably related to the formation of atomic hydrogen. These voltammograms exhibit also a shift of the baseline towards anodic currents due to the continuous oxidation of molecular hydrogen during the course of the complete run. This reaction, under certain conditions, is a molecular diffusion-controlled process, as discussed elsewhere⁵. This effect is more marked when the cathodization time increases (Fig. 1b to 1d). Under these circumstances the hydrogen oxidation current peaks become clearer, suggesting that the experimental one is the overlap of at least one due to molecular hydrogen electrooxidation and the other related to the electrooxidation of adsorbed hydrogen atoms. Furthermore, complementary cathodic current peaks of the latter exist as shoulders in the cathodic E/I profile (Fig. 1d). Figure 1d exhibits a minor contribution to platinum surface oxidation and reduction because the anodic limit of the potential amplitude is smaller than those shown in the

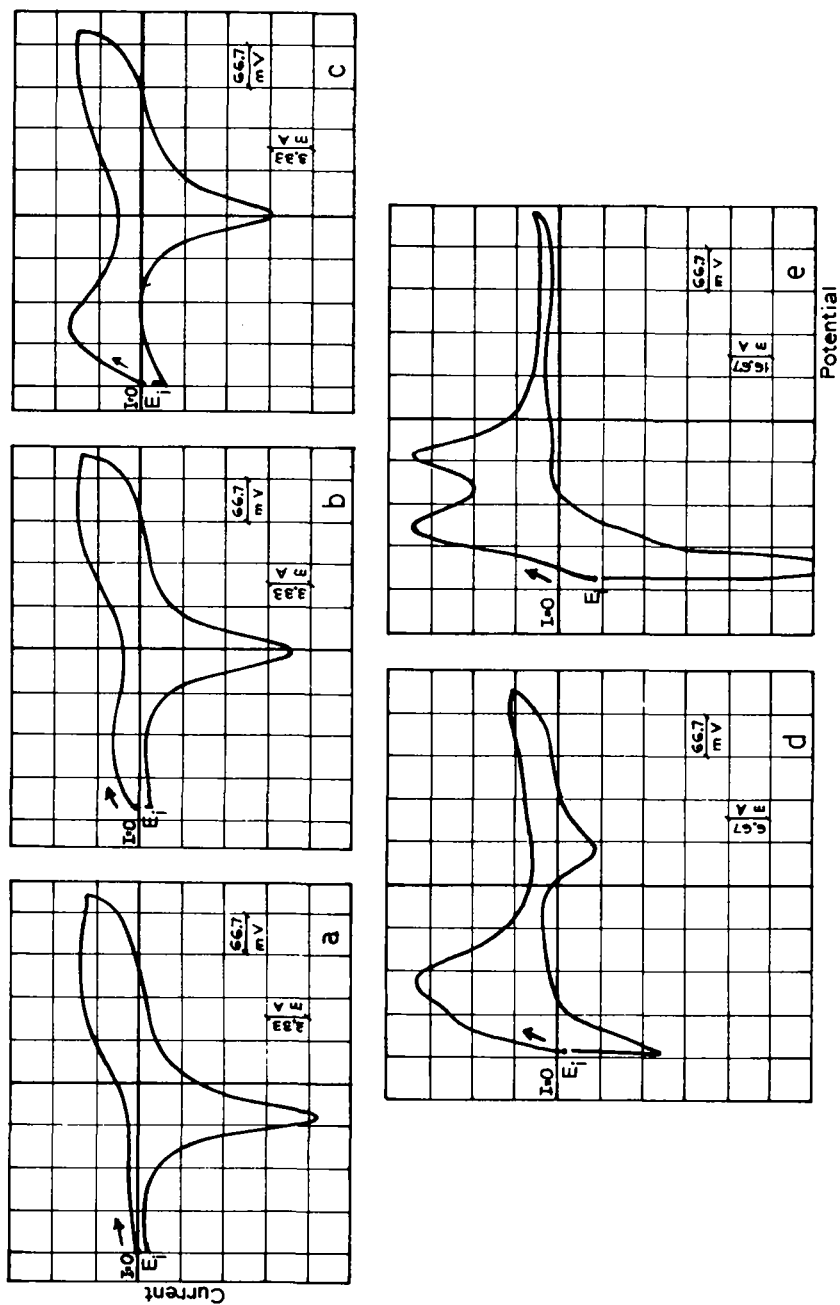


Fig. 2. Single sweep voltammograms started from E_i towards anodic potentials at 5 V s^{-1} . (a) $E_i = 50$ mV; (b) $E_i = 25$ mV; (c) $E_i = 0$ mV; (d) $E_i = -50$ mV; (e) $E_i = -150$ mV.

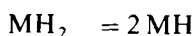
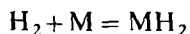
preceding E/I curves.

Figure 2 corresponds to a set of voltammograms run at 5 V s^{-1} , covering a constant potential amplitude with an initial potential which becomes more cathodic from Fig. 2a to Fig. 2e. The first E/I display is run from an initial potential which is more anodic than the hydrogen electrode potential. Under these circumstances, the E/I characteristics correspond to those of electrochemical surface oxide formation and reduction on platinum. When the initial potential becomes more cathodic, the anodic current peaks related to the electrooxidation and hydrogen discharge are better depicted. Simultaneously, the initial baseline at potentials more anodic than the electrooxidation of hydrogen shifts again upwards due to the continuous electrooxidation of molecular hydrogen dissolved in the melt. The E/I characteristics are therefore, very reproducible either at low or high potential sweep rate.

The amount of anodic charge involved during the electrooxidation of hydrogen largely exceeds that of a monolayer when there is a molecular hydrogen contribution, as shown by comparing it with the charges corresponding either to platinum surface oxide formation or electrodisolution⁷. For instance, at 0.5 V s^{-1} the anodic charge covers from $524 \mu\text{C cm}^{-2}$ in Fig. 1a to $1640 \mu\text{C cm}^{-2}$ in Fig. 1d. At 5.0 V s^{-1} it is $334 \mu\text{C cm}^{-2}$ in Fig. 2a and $1.2 \times 10^4 \mu\text{C cm}^{-2}$ in Fig. 2e.

The preliminary results show then, the occurrence of a separate current component of the hydrogen electrode reaction on platinum in molten KHSO_4 at 309°C if both ohmic drop distortion and inhibition effects are prevented.

The shape of the voltammograms are in this case very much like those already known in aqueous solutions^{8,9}. The E/I display can be interpreted in terms of the reaction mechanism involving for the anodic process the following steps:



as earlier suggested for aqueous solutions⁹. The hydrogen atom electrooxidation presumably involves energetically different adsorbed species as assumed for aqueous systems⁸ on the basis of the different anodic peaks appearing at potentials more anodic than the hydrogen evolution reaction during the potential sweeps, both from cathodic to anodic potentials and *vice versa*.

These results presumably are also affected by the electrooxidation of hydrogen partially dissolved into the metal. A more extended report on the quantitative aspects of the hydrogen electrode reaction and its inhibition will be published soon¹⁰.

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