SHORT COMMUNICATION

On the potentiodynamic E/I profile at platinum electrodes in molten NaHSO_4 – KHSO_4

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The stationary electrolysis of molten NaHSO_4 – KHSO_4 eutectic on Pt electrodes at 185°C yields hydrogen at the cathode and oxygen at the anode with current efficiencies close to 100%^{1,2}. Although the kinetics of the cathodic reaction have been interpreted in terms of the conventional hydrogen electrode mechanisms, it changes apparently according to the potential region where the reaction takes place, since the steady Tafel slope at low overvoltages is equal to $RT/2F$ and at high overvoltages it coincides with the $2RT/F$ ratio. This effect appears when either platinized Pt or bright Pt electrodes are used.

As the apparent change of mechanism depends on the potential applied to the cathode it is interesting to investigate the response of the hydrogen electrode reactions in Pt/bisulphate melts under potentiodynamic conditions, to attempt an explanation of the above mentioned change of mechanism.

The potentiodynamic E/I profile at $v=100\text{ mV s}^{-1}$ (Fig. 1) in the potential range from 1.050 to 0.100 V (*vs.* a Ag/Ag^+ 0.06 *M* reference electrode), exhibits in addition to the already known current peaks related to the formation of a platinum oxide monolayer (I) and to its electrochemical reduction (II) at 0.875 and 0.555 V respectively³, two anodic current peaks (V and VI) at 0.235 and 0.150 V in the hydrogen electrode region. Anodic peaks III and IV are related to the oxidation of hydrogen and cathodic peaks (V and VI) to the evolution of hydrogen. Therefore, as in the case of acid aqueous solutions, it is also possible to produce readily observed pseudocapacitance peaks in cyclic voltammetry experiments using the bisulphate melts. However, the potential difference between the hydrogen electrode region and the platinum oxide formation and electro-reduction is smaller in the molten bisulphate than in the aqueous acid solutions.

The anodic charge related to the current peak (IV) is very close to one half the charge involved in the cathodic reduction of the platinum oxide monolayer. The height of the current peak IV is independent of the cathodization time. Thus it should correspond very closely to one monolayer of hydrogen atoms. This is not the case for the charge involved in the anodic current peak III which depends, principally, on the amount of cathodic charge passed. It is related to the electro-oxidation of molecular hydrogen.

Fig. 1. Potentiodynamic E/I profile at 185°C on Pt electrodes (0.5 cm^2) in molten $\text{NaHSO}_4\text{-KHSO}_4$. Sweeping from 1.05 to 0.10 V at 100 mV s^{-1} . The numbers correspond to the order of the repetitive cycles.

Each small cathodic current peak occurring prior to the abrupt increase of the cathodic faradaic currents is related to the hydrogen evolution reaction. These peaks involve a charge which is also close to one monolayer of hydrogen atoms.

If the electrolysis proceeds at potentials lower than 0 V no stationary current is observed and the potentiodynamic runs show a continuous cathodic current decrease. Simultaneously, the heights of the anodic current peaks III and IV decrease. The shape of the E/I profile changes quite markedly in the region of the anodic oxidation of hydrogen (Fig. 2) when the system is cathodized at potentials lower than 0 V for several minutes. Under these circumstances a new complex anodic E/I contour is observed which is principally related to the oxidation of products formed at the electrode during cathodization. These products which exhibit the chemical characteristics of inorganic sulphides, inhibit the hydrogen evolution reaction. The activity of the electrode is, however, recovered after anodic potential cycling in the range 0.200 to 1.050 V.

These results, therefore, suggest that the change of kinetic behaviour of Pt in molten bisulphates with potential within the region of the hydrogen evolution reaction, is principally related to the state of the Pt electrode surface. Thus, when the cathodic potential is below 0 V, the hydrogen evolution reaction follows the already known reaction pathway in aqueous acid solutions, involving the initial electron transfer followed by the hydrogen adatom recombination as rate determining step. However, at high cathodic potentials a reduction of the melt at the

Fig. 2. Potentiodynamic E/I profile at 185°C , on Pt electrode (0.5 cm^2) at 100 mV s^{-1} , showing the inhibition effect on the anodic hydrogen current peaks. Sweeping initiated at E_i with a clean electrode which is cathodized during 5 min at 0 V before cycling. Potential-time program indicated in the Figure.

electrode surface takes place simultaneously with the hydrogen evolution reaction. Although the current efficiency of the former is much lower than that of the latter, the sulphide-type products change the properties of the electrode. Then, the hydrogen electrode reaction on the poisoned electrode surface follows a different reaction pathway. The corresponding Tafel slope, which is equal to $2RT/F$ is probably related to a reaction mechanism involving the initial electron transfer as rate determining. The two potential regions have actually been observed and are separated by a transition region in which hysteresis occurs⁴.

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