

**ON THE STUDY OF CATALYTIC SULPHUR ADLAYERS TO THE OXIDATION
OF SO₂ AT POLYORIENTED PLATINUM ELECTRODES**

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1. Introduction

Over the last years a number of papers have been published which deal with the electrochemical behaviour of dissolved sulphur dioxide (or related sulphur-oxygen compounds) using platinum as electrode material [1, 2, 3].

The study of sulphur adlayers originated upon reduction of adsorbed SO₂ on Pt has also attracted large interest [4, 5, 6] owing to the influence of such an adsorbate in the course of many electrochemical reactions, like oxidation of small organic molecules [7, 8] and reduction of nitric oxide [9]. Likewise, the catalytic effect of sulphur adlayers on the oxidation of SO₂ is well established [3, 10].

The aim of this paper is to gain further insight into the properties of sulphur adlayers generated from SO₂ and to correlate these properties to the catalytic capability of the adlayer towards the SO₂ oxidation reaction on Pt.

2. Experimental

The electrochemical behaviour of sulphur adlayers was studied by means of cyclic voltammetry. The experimental set-up for cyclic voltammetry consisted of a standard three-electrode potentiostatic assembly described elsewhere [11]. The working electrode was a bead-shaped polyoriented Pt single crystal and the counter-electrode was a coiled polycrystalline Pt wire. All potentials are given with reference to the reversible hydrogen

scale. Cyclic voltammograms were recorded at room temperature and at a sweep rate of 50 mV·cm⁻¹.

The test solution (10 % vol./vol. H₂SO₄) was prepared from ultrapure water (Millipore Milli-Q) and suprapur sulphuric acid (Merck). Sulphur adlayers were generated by reduction of irreversibly adsorbed SO₂ or after a single voltammetric sweep (at 50 mV·cm⁻¹) from 0.65 V to 0.2 V in a 0.1 M SO₂ + 10 % H₂SO₄ solution [10, 11]. Distinct sulphur coverages were obtained by varying SO₂ concentration or by partial oxidative desorption of a thicker layer. The preparation of sulphur dioxide solutions has been described earlier [11]. The voltammetric behaviour of adsorbed sulphur was studied in an SO₂-free test solution.

3. Theoretical considerations

The so-called number of electrons per site (*eps*) involved in the oxidation of an adsorbate can constitute a useful indication about the average surface distribution of the adatom. *Eps* of adsorbed sulphur on Pt can be determined from the existing linear relationship between the overall oxidation charge of sulphur and the fractional coverage, θ_s (expressed as the fraction of Pt sites blocked by sulphur):

$$Q_{ox}^S = n_s \textit{eps} e_0 = Q_H^0 \textit{eps} \theta_s \quad (1)$$

where n_s is the number of Pt sites blocked by sulphur adatoms, e_0 is the electron charge and Q_H^0 is the charge classically associated with the formation of a monolayer of adsorbed hydrogen (210 $\mu\text{C}\cdot\text{cm}^{-2}$).

Sulphur oxidation charges were computed for different surface coverages by following the methodology suggested by earlier authors [4, 5].

4. Results and discussion

Figure 1 shows the voltammetric behaviour of a sulphur adlayer when the platinum electrode is subjected to potential excursions up to 1.50 V. The adlayer was formed during a single negative sweep from 0.65 V to 0.20 V in a 0.1 M SO₂ sulphuric acid solution. The resulting sulphur adlayer imparts a near-to-maximum catalytic activity towards oxidation of dissolved SO₂ [10]. The layer exhibits all the voltammetric properties frequently attributed to adsorbed sulphur [4, 5, 11]: gradual oxidative desorption with competitive oxygen adsorption and the occurrence of an additional reduction process in the so-called hydrogen adsorption region (satisfactorily accounted for the reduction of an S-O-like adsorbed intermediate formed during the oxidation of sulphur). Sulphur layers originated from reduction of irreversibly adsorbed SO₂ display the same voltammetric features [11], but improve the electrocatalysis of SO₂ oxidation to a lesser extent [10]. At first glance, it appears that the difference between both types of sulphur layers is merely quantitative. Nevertheless, the profile of the plot $Q_{ox}^S = f(\theta_s)$ reveals the existence of qualitative divergences (fig.2).

In fig. 2, the presence of a linear relationship between Q_{ox}^S and θ_s becomes evident in the range $0 < \theta_s < 0.9$, in close agreement with Contractor and co-workers [5, 8]. The slope of the linear plot amounts to 620 $\mu\text{C}\cdot\text{cm}^{-2}$, which nearly corresponds to an *eps* of 3. This implicates an average surface distribution with each sulphur adatom occupying two Pt sites (*i.e.*, bridge-bound sulphur), assuming that sulphur desorbs in a six-electron process to yield sulphate or bisulphate. Contractor *et al.* reported an *eps* of 3.8, which was interpreted assuming an heterogeneous adlayer with 70 % of the occupied sites involving two-site adsorption and the remaining 30 % involving one-site adsorption of sulphur. The different surface structure of the electrode materials employed

can account for the encountered discrepancies. Contractor *et al.* utilized a platinized Pt electrode, with a rough and heterogeneous surface, composed of randomly oriented crystallites. In contrast, we used a smooth polyoriented Pt single crystal, which shows higher surface homogeneity.

At coverages above 0.9, the sulphur oxidation charge is higher than that expected for a full monolayer of doubly bonded sulphur and it no longer lies along the straight line. According to Contractor's view, high charge densities observed at $\theta_s > 0.9$ may be satisfactorily explained by the deposition of additional sulphur atoms on top of the first layer, this is, by the build-up of a sulphur bilayer, which is not yet complete under the adsorption conditions of fig. 1.

5. Concluding remarks

In the range $0 < \theta_s < 0.9$, adsorbed sulphur lies on a Pt surface in such a way that each sulphur atom occupies two adsorption sites, and a linear relationship is found in the plot Q_{ox}^S vs. θ_s . This distribution may reflect that of the SO_2 layer from which sulphur is derived. At higher coverages, $\theta_s > 0.9$, the linearity breaks down and the formation of second sulphur layer – yet incomplete in the example shown herein – upon the first monolayer is adduced to explain this fact.

A full monolayer of bridge-bonded sulphur presents a relatively poor catalytic effect on the oxidation of SO_2 at Pt. A complete bilayer would also be detrimental to catalysis [10]. Only an incomplete sulphur bilayer seems to exhibit good catalytic performance. The special properties of such a sulphur deposit cannot be inferred from voltammetric measurements.

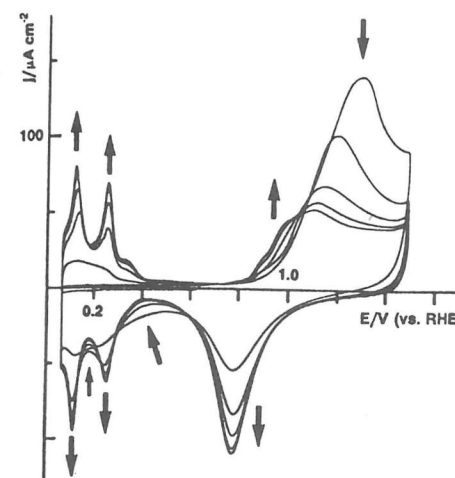


Fig. 1 Oxidation of a sulphur part-bilayer during potentials excursions up to 1.5 V. The arrows indicate the evolution of the various voltammetric features.

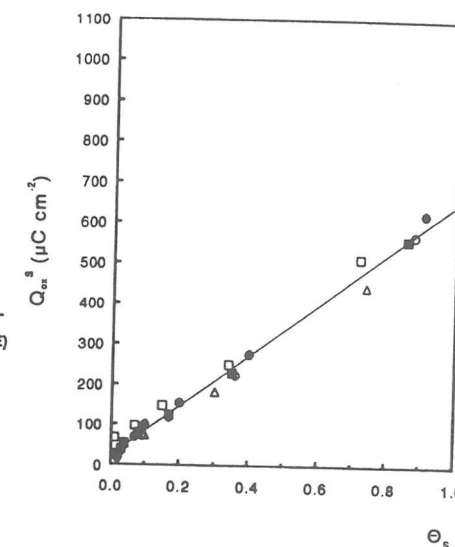


Fig. 2 Plot of Q_{ox}^S versus θ_s . Adlayer formed during reduction of irreversibly adsorbed SO_2 : (□) 10^{-4} M; (■) 10^{-2} M; (○) 0.1 M; (●) 1 M. Sulphur adlayer shown in fig. 1 (Δ).

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