

Electrochemical Reduction of Mesoxalic Acid on Polycrystalline Platinum Surfaces

Rosa Albalat*, Josep Claret, Carlos Müller, and Maria Sarret

Departament de Química Física, Facultat de Química, Martí i Franquès 1, E-08028 Barcelona, Catalunya, Spain

Abstract. The electrochemical reduction of mesoxalic acid on polycrystalline platinum surfaces has been studied in acid medium. The reaction proceeds through the interaction with adsorbed hydrogen atoms. Malonic acid is proposed as final reaction product.

Keywords. Electrocatalysis; Platinum; Mesoxalic acid.

Elektrochemische Reduktion von Mesoxalsäure auf polykristallinen Platinoberflächen

Zusammenfassung. Die elektrochemische Reduktion von Mesoxalsäure auf polykristallinen Platinoberflächen wurde in saurem Medium untersucht. Die Reaktion verläuft über die Wechselwirkung mit adsorbierten Wasserstoffatomen, wobei als Endprodukt Malonsäure entsteht.

Introduction

The electrochemical reduction of carbonyl compounds on polycrystalline platinum surfaces has been studied and reviewed [1, 2]. The experimental results show that the main reduction products are the corresponding alcohols and saturated hydrocarbons, the ratio between them depending on experimental conditions and electrode pretreatment.

The aim of this paper is to present the characteristics of the electrochemical reduction of a highly oxidized carbonyl compound, mesoxalic acid $\text{COOH-C(OH)}_2\text{-COOH}$, on a polycrystalline platinum electrode in aqueous acid medium ($0.5\text{ M H}_2\text{SO}_4$). The adsorption and the electrochemical oxidation of this organic compound under these experimental conditions have been previously studied [3]: the slow chemisorption rate and the involvement of surface platinum oxides in the irreversible oxidation reaction to form CO_2 are the most relevant facts of the electrochemical behaviour of this compound.

Experimental conditions and surface coverage measurements have been reported elsewhere [3]. Potentials are referred to a potassium sulphate saturated mercury-mercurous sulphate electrode (mse).

Experimental Results

When a polycrystalline platinum electrode is put in contact with a mesoxalic acid solution at a potential corresponding to the double layer range (-200 mV mse)

and then cycled between this potential and -625 mV mse, the charge involved in the negative scan (Q_c) is always higher than the corresponding one for the positive sweep (Q_a). This behaviour is also observed when the experiment is performed with a mesoxalic acid covered electrode in a blank solution (0.5 M H_2SO_4). In this case, successive cycles show a gradual diminution of cathodic charge whereas the anodic one remains constant, and after 3–4 cycles both charges coincide and remain unchanged (Fig. 1). These experimental results indicate that a net cathodic charge (Q_r) appears when the electrode is cycled in the hydrogen zone ($Q_r = Q_c - Q_a$), attributable to the mesoxalic acid reduction in this potential range. In fact, more conclusions can be drawn from the last experiment: i) the reduction product remains adsorbed on the electrode surface, ii) the number of adsorption sites occupied by one molecule of mesoxalic acid and its reduced form is the same and iii) the reduction process is a slow surface reaction.

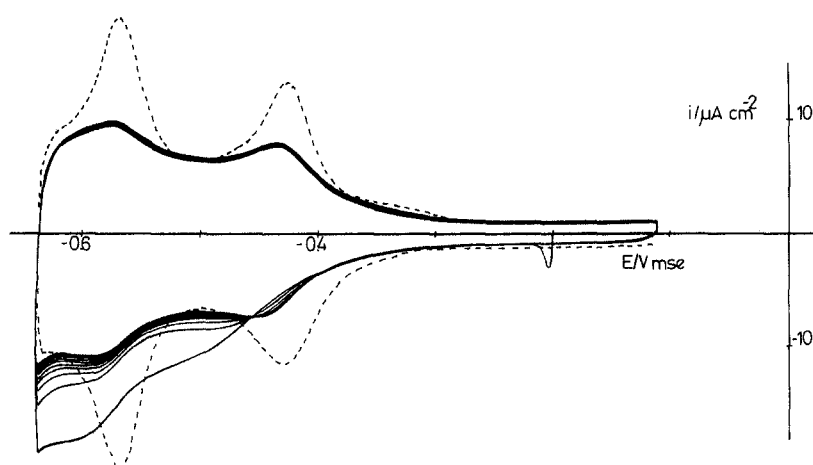


Fig. 1. Successive voltammetric cycles of a mesoxalic covered electrode in H_2SO_4 (0.5 M). $E_{\text{ads}} = -200$ mV mse, $t_{\text{ads}} = 3$ min, $c_{\text{ads}} = 10^{-2}$ M, $v = 105$ mVs $^{-1}$ (—); voltammetric profile of Pt electrode in H_2SO_4 0.5 M (---)

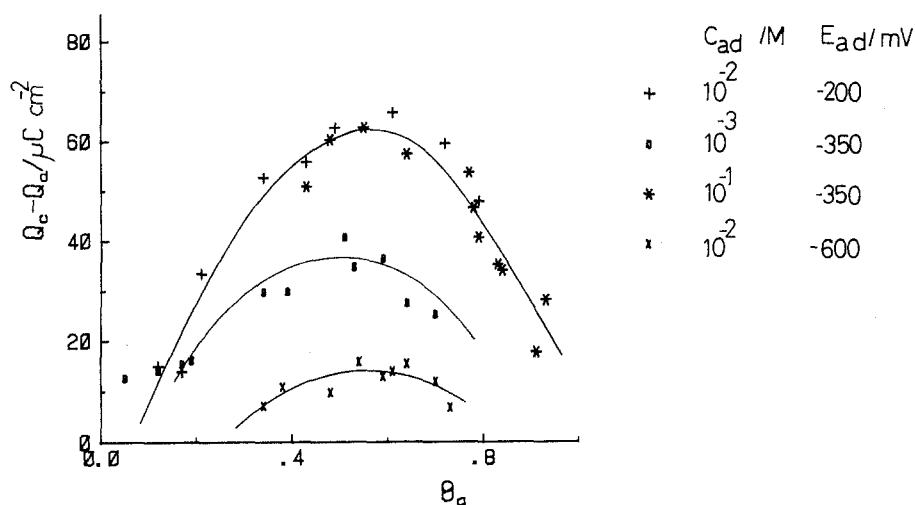


Fig. 2. Plot of Q_c in front of $\Theta \cdot Q_a$, obtained from voltammograms of a mesoxalic acid covered electrode in H_2SO_4 (0.5 M). Different t_{ads} at every c_{ads} and E_{ads} values

The existence of a reduction reaction may also explain the dependence of cathodic charge (Q_c) from the sweep rate, and the different oxidation current-potential profile, when the electrode has been previously cycled to negative potentials. In the first case, the cathodic charge decreases when the sweep rate is increased before attaining a constant value for sweep rates higher than 150 mVs^{-1} . This behaviour cannot be explained if we consider that the cathodic charge is only due to hydrogen adsorption, because a charge increase is expected as it happens in the anodic scan. The cathodic charge decrease is due to the diminution of the readorption processes of mesoxalic acid which implies a diminution of the net reduction charge. The behaviour shown in the second case is easily explained considering that the adsorbed mesoxalic acid has been totally or partially replaced by its reduced form.

Many electrochemical reductions on platinum surfaces have been interpreted by mechanisms involving hydrogen atoms adsorbed on the electrode surface. It can be checked by plotting the net reduction charge (Q_r) in front of the mesoxalic acid surface coverage (Θ). Different surface coverages have been achieved by means of suitable adsorption times and adsorption potentials in the double layer potential range: adsorption potentials more negative than -300 mV msec leads to very low values of Q_r , because mesoxalic acid reduction is already taking place during the adsorption process [3]. The results are shown in Fig. 2. We can observe that Q_r increases at low coverages, reaching a maximum at intermediate coverage values ($\Theta \simeq 0.5$); at higher coverages it decreases and vanishes when the electrode is totally covered by mesoxalic acid. Some conclusions can be deduced from this behaviour: i) the presence of hydrogen atoms on the electrode surface is essential for the reduction process, and ii) the symmetry of this dependence suggests that this surface reaction shows the same order with respect to adsorbed hydrogen and adsorbed mesoxalic acid. This means that the number of hydrogen atoms involved in the reaction is the same as the number of adsorption sites occupied by one mesoxalic acid molecule adsorbed on the electrode surface. In a previous work [3] we have reported that four sites are occupied by one molecule of mesoxalic acid, therefore four hydrogen atoms are involved in this reduction process.

The same conclusion is achieved from the slope of the linear dependence of Q_r against Θ at low mesoxalic acid coverages. Measuring Q_r values from the total net reduction charge, after applying successive cycles in the hydrogen potential range to a mesoxalic covered electrode in a blank solution until a stationary voltammogram is attained in which both anodic and cathodic charge are the same, we have also obtained the number of electrons (= number of hydrogen atoms) involved in the reaction equal to four per one mesoxalic acid molecule.

Discussion

The experimental results indicate that four hydrogen atoms are involved in the electrochemical reduction of mesoxalic acid, and that therefore this reaction leads to the formation of the corresponding saturated hydrocarbon under exhaustive reductive conditions. This means that malonic acid can be proposed as the final product of the mesoxalic acid electrochemical reduction on polycrystalline platinum surfaces.

This conclusion agrees with the fact that malonic acid is not electroactive on platinum surfaces [4], and that the intermediate alcohol, tartronic acid (hydroxymalonic acid), is electroactive under the same experimental conditions and shows a reduction behaviour very similar to that of mesoxalic acid [5]. In fact, mesoxalic and tartronic acids are reduced in the hydrogen potential range and their reduction products remain adsorbed on the electrode surface until enough positive potentials are applied to oxidize them. The adsorption behaviour of the reduced product does not agree with the reported one for malonic acid; in this case, a reversible adsorption has been found from radiotracer measurements [4] which is different from the irreversible chemisorption observed for both reduction products. This result points out the different adsorption behaviour of a malonic acid molecule on polycrystalline surfaces coming from the bulk solution or being formed from a strongly chemisorbed molecule of mesoxalic or tartronic acid. We have to notice that we have not observed chemisorption processes for malonic acid in agreement with Horanyi's results [4].

Finally, we would like to comment the different reductive behaviour of mesoxalic acid on different platinum surfaces. We have previously studied the electrochemical reduction of this compound on the three basal platinum single crystal electrodes [6]. These surfaces show different behaviour: mesoxalic acid is not reduced on Pt(110) electrodes, but its reduction takes place on Pt(100) and Pt(111) through two different mechanisms. In the first case, a mechanism involving the splitting of the mesoxalic acid molecule and giving rise to the formation of strongly bonded CO on the platinum surface, is clear to occur, whereas on Pt(111) a reduction process without splitting of the organic molecule is observed.

The absence of CO formation on polycrystalline platinum surfaces can be attributed to the absence of Pt(100) terrace sites in this electrode surface: splitting reaction takes place mainly on these adsorption sites [6]. So, the mesoxalic acid electrochemical reduction on polycrystalline platinum proceeds through a non-breaking reaction, similar to that taking place on Pt(111) single crystal surface, giving rise to malonic acid as the most probable reaction product. This behaviour emphasizes the high sensitivity of the behaviour of mesoxalic acid towards the surface structure.

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