

Electrochemical Oxidation of Methanol on Platinum Electrodes Modified by Tin Atoms Deposited at Underpotentials

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Received: August 15, 1991

Estudou-se a oxidação eletroquímica do metanol em eletrodos de platina modificados por átomos de estanho depositados a sub-potencial, à temperatura de 60 °C. A energia de ativação aparente para a oxidação do álcool varia de 38,3 kJ mol⁻¹, na ausência dos adátomos de estanho, a 14,6 kJ mol⁻¹, quando presentes os adátomos.

Electrochemical oxidation of methanol on platinum electrodes modified by tin atoms deposited at underpotentials was studied at 60 °C. The apparent activation energy of oxidation changes from 38,3 kJ mol⁻¹ in the absence of tin adatoms to 14,6 kJ mol⁻¹ when those adatoms are present.

Key Words: Methanol; tin adatoms; electrocatalysis.

Introduction

The activity of a platinum electrode for the oxidation of a number of technologically important organic substances can increase with the presence of tin adatoms deposited at underpotentials.^{1,2} Tin adatoms are one of the more promising catalysts and have been the subject of several studies^{1,3-7}. The published papers, however, refer to room temperatures.

In the present paper the results obtained for the electro-oxidation of methanol on platinum electrodes modified by tin adatoms at a temperature of 60 °C are related. The effect of the adatoms on the apparent activation energy of oxidation is discussed.

Experimental

A PAR Model 370-4 electrochemical system was used to perform the electrochemical experiments. A Houston RE OO74 recorder, a PAR Model 4102 signal recorder and a Tektronix 5115 storage oscilloscope were employed for recording the potentiodynamic curves. The electrochemical cell, 60 cm³, consisted of a three-electrode arrangement with a platinized platinum working electrode or, alternatively, a platinum working electrode modified by adsorbed tin atoms, prepared according to the procedure described by Furuya and Motoo.⁸ The underpotential deposition of tin atoms on the platinum electrode was achieved by holding the potential at 0.2 V for 5 min in the sulphuric acid solution containing Sn²⁺ ions. Then the electrode was washed with oxygen-free background solution, while the electrode potential was kept constant. Subsequently, the methanolic solution, 0.1 M methanol and 0.5 M H₂SO₄, was introduced into the cell and the polarization measurements performed. The real surface area of the electrode, 0.05 cm², was determined by Gilman's procedure.⁹ A helical platinum wire,

having a great area, was used as the auxiliary electrode. All the potentials were measured vs. the reversible hydrogen electrode.¹⁰ Analytical grade reagents, H₂SO₄ (Merck) and SnSO₄ (Merck) and triply distilled water were used in preparing the solutions. The concentration of methanol was maintained at 0.1 M, and that of H₂SO₄ at 0.5 M.

Results and Discussion

Figure 1 illustrates the potentiodynamic profile obtained for methanol. Two anodic current peaks are observed dur-

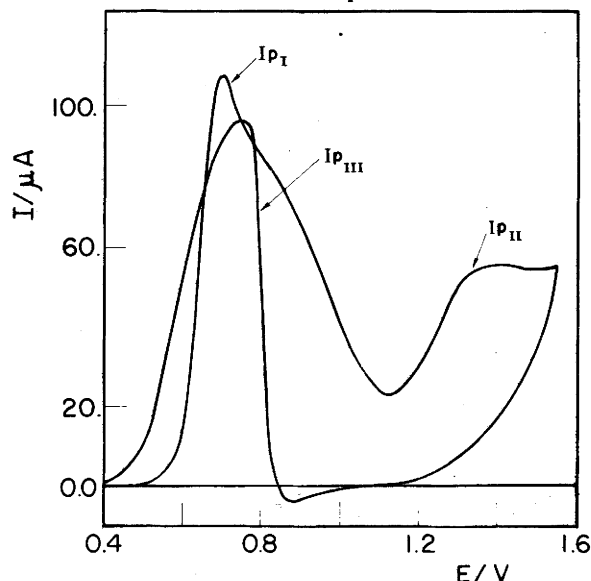


Figure 1. The potentiodynamic E/I profile for 0.1 M methanol at 0.05 V s⁻¹, 60 °C; 0.5 M H₂SO₄, E_{AD} = 0.4 V, t_{AD} = 3 min.

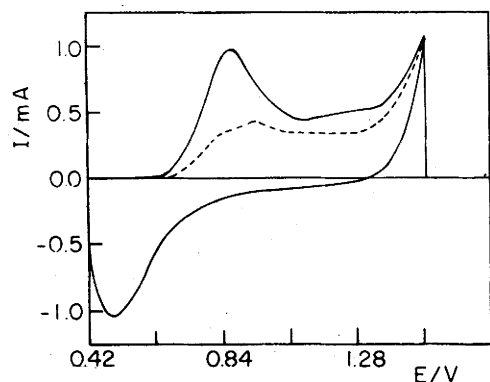


Figure 2. The potentiodynamic E/I profile for 0.1 M methanol at 10 V s^{-1} , 60°C ; $0.5 \text{ M H}_2\text{SO}_4$, $E_{AD} = 0.4 \text{ V}$, $t_{AD} = 3 \text{ min}$.

ing the potential sweep towards higher potentials and one anodic current peak appears on the reverse scan. All these peaks refer to the electrooxidation of the adsorbed alcohol. For sweep rates, ν , higher than 9 V s^{-1} the third peak disappears indicating that it corresponds to oxidation of the molecules which adsorb on the platinum surface originated by the reduction of the oxygen layer (Fig. 2). Since the second cycle coincides with the curve recorded for the blank,

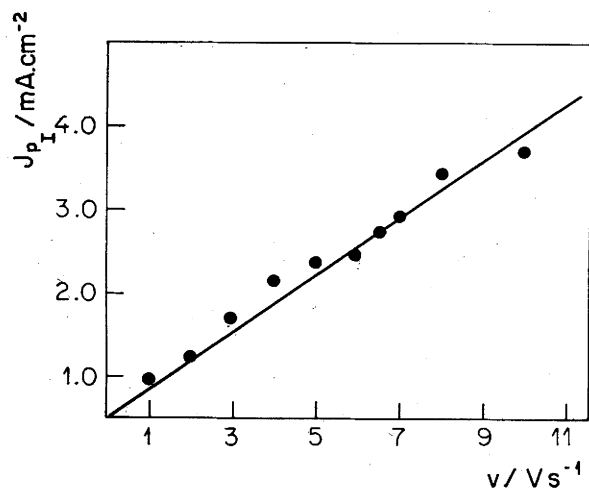


Figure 3. Plot of the current peak density versus the potential sweep rate; $E_{AD} = 0.4 \text{ V}$, $[\text{Methanol}] = 0.1 \text{ M}$, 60°C .

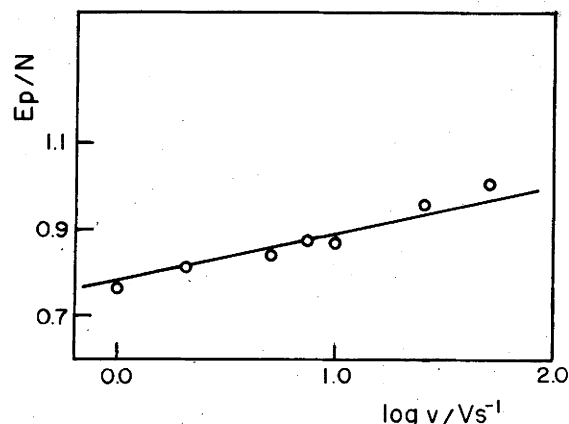


Figure 4. Plot of the current peak potential versus the logarithm of potential sweep rate; $E_{AD} = 0.4 \text{ V}$, $[\text{Methanol}] = 0.1 \text{ M}$, $t_{AD} = 3 \text{ min}$, 60°C .

all the adsorbed methanol reacted during the first potential sweep.

Figures 3 and 4 show that the dependence of the current peak, I_p , on ν and that of the peak potential, E_p , on $\log \nu$ is linear. According to the model developed by Srinivasan and Gileadi¹¹ those results characterize a surface reaction with the rate-determining step being an irreversible charge transfer associated with the electroadsorption or electrooxidation of intermediary species. From the straight line which represents E_p vs $\log \nu$, the value 0.10 V dec^{-1} is obtained.

The adsorption isotherm is shown in Fig. 5. The surface coverage corresponds to the ratio between the charge needed for the oxidation of the monolayer adsorbed at a given methanol concentration and the charge related to the oxidation of the monolayer formed at saturation conditions.

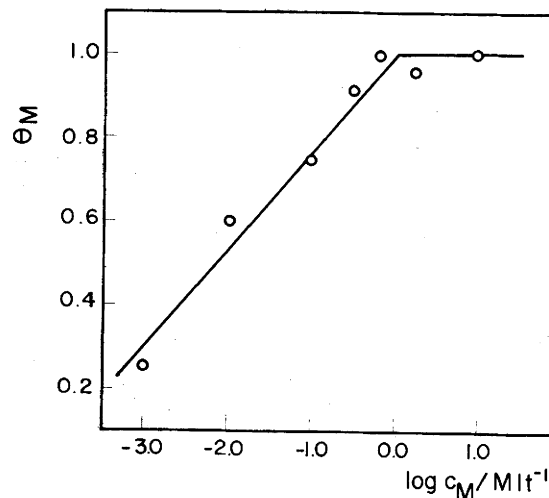


Figure 5. Dependence of θ_M on the logarithm of methanol concentration; $E_{AD} = 0.4 \text{ V}$, $t_{AD} = 3 \text{ min}$, 60°C .

The result is a Temkin-type isotherm with a heterogeneity factor of 12.0, a value in good agreement with that found in the literature,¹² and very close to the heterogeneity factor of ethanol. According to Bagotzky and Vassiliev,¹³ this fact indicates that the adsorption isotherm of these alcohols is determined by the surface heterogeneity of the platinum electrode rather than by the interaction between the adsorbed particles.

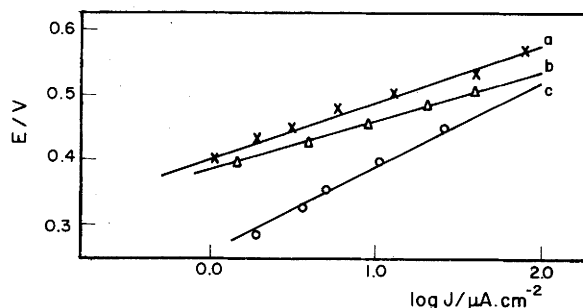


Figure 6. Tafel plots for methanol electrooxidation, $[\text{Methanol}] = 0.1 \text{ M}$, $E_{AD} = 0.4 \text{ V}$, $t_{AD} = 3 \text{ min}$; (a) without tin adatoms, (b) with $\theta_{Sn} = 0.5$ and (c) with $\theta_{Sn} = 0.65$.

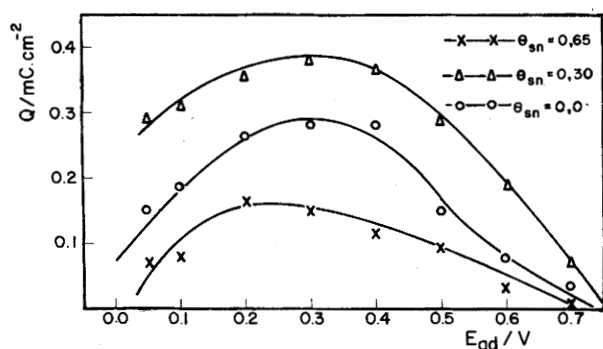


Figure 7. Dependence of the oxidation charge of adsorbed methanol on the adsorption potential at several values for θ_{Sn} , $[Methanol] = 0.1 M$.

In Fig. 6 the Tafel plots for the oxidation of methanol on the unmodified and modified platinum electrodes are compared. It can be observed that the oxidation current increases with increasing coverage by tin adatoms. This effect tends to disappear for potentials higher than 0.6 V, and the Tafel coefficient varies with θ_{Sn} (95 mV dec⁻¹, 80 mV dec⁻¹ and 120 mV dec⁻¹ for θ_{Sn} equal to 0.0, 0.5 and 0.65, respectively).

Figure 7 compares the oxidation charge of methanol on the platinum electrode for several coverages by tin adatoms when the bulk concentration of methanol is 0.1 M and $v = 10 V s^{-1}$. The oxidation charge related to the adsorbed methanol reaches its maximum value around 0.3 V when $\theta_{Sn} = 0.3$. At higher potentials the oxidation of the adsorbed species simultaneously with adsorption causes a decrease in the value of that charge. For $\theta_{Sn} = 0.65$ the oxidation charge diminishes possibly due to an interaction between tin ions and the oxygen layer on the platinum with the consequent inhibition of the adsorption of methanol molecules.

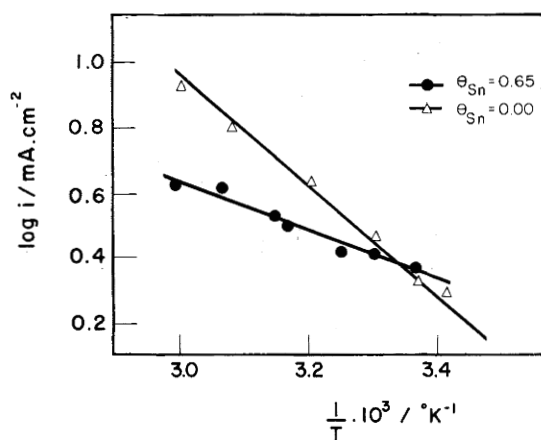


Figure 8. Variation of the logarithm of the current peak density, j_p , with the inverse of absolute temperature; $[Methanol] = 0.1 M$, $E_{AD} = 0.4 V$, $t_{AD} = 3 min$, $v = 10 V s^{-1}$.

Table 1. Activation energies for methanol electrooxidation on Pt/Pt electrodes in the absence (Pt/Pt) and in the presence (Pt r/Pt/Sn) of tin atoms adsorbed on the electrode; $E_{AD} = 0.4 V$, $t_{AD} = 3 min$.

Potential / V	Activation energy / kJ mol ⁻¹ Pt/Pt	(Pt/Pt/Sn)
0.84	38.5	14.6
0.95	17.7	10.6
1.25	15.2	9.3

The apparent activation energy can be estimated from the values of the oxidation current at a given potential for different temperatures (the peak potential varies with temperature). From the straight lines obtained for 0.84 V, Fig. 8, the values 14.6 kJ mol⁻¹ and 38.3 kJ mol⁻¹ are calculated for s_n equal to 0.65 and 0.0, respectively. In Table 1 values of the apparent activation energy for the oxidation of methanol are given at several potentials.

Acknowledgements

Financial support from FINEP, FAPESP (Procs. 82/746-2, 89/3488/-2), and from CNPq (Proc. 30.1426/79) are gratefully acknowledged.

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