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A COMPARATIVE STUDY ON THE ELECTROCATALYTIC ACTIVITY OF Pt, Pt-Ir AND Ir ELECTRODES TOWARDS THE OXIDATION OF D-SORBITOL

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Abstract- The electro-oxidation of D-sorbitol in aqueous perchloric medium was used as a test of the electrocatalytic activity of platinum, platinum-iridium and iridium electrodes. Cyclic voltammetry was the main technique used in this study. Results have shown almost no activity for Ir electrodes and similar activities for Pt and Pt-Ir, slightly higher for Pt-Ir (90:10) electrodes.

Key words - electrocatalysis, electro-oxidation, D-sorbitol, noble metals

INTRODUCTION

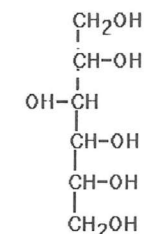
The electrocatalytic activity of noble metals towards the oxidation of various organic molecules, especially those derived from biomass like alcohols and polyols, has been studied for a long time because of the potential interest of these systems in the development of electrochemical generators (fuel cells) [1 and 2 and references therein].

It is well known, that the mechanism and kinetics of those electrocatalytic reactions are influenced by several parameters, such as temperature, pH, concentration of the electroactive species, nature of the electrolyte and structure and composition of the electrode material. The role of the nature and structure of electrode materials in electrocatalysis has been quite well demonstrated [1, 2 and 3 and references therein]: the substrate affects the reaction kinetics, mainly through the adsorption of reactants, reaction intermediates and products [2].

The influence of the molecular structure of the reactant molecule (length of carbon chain, position of OH groups) on the adsorption and electro-oxidation of polyols on Pt has been comparatively examined by Enea and Ango [4].

D-sorbitol is a promising fuel for a clean production of energy, but also a rather large molecule with six OH groups, with one OH group opposite to the others, i.e.:

The electrochemical oxidation of this molecule in perchloric medium at a polycrystalline (poly) and on platinum single-crystals, namely Pt(100), Pt(110) and Pt(111) has been considered [5]; significant structural effects have been observed in acid medium. A quantitative study on the electroadsorption of D-sorbitol on Pt(poly) and Pt(100) electrodes in perchloric medium has also been performed



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[6]: results have shown that the dissociative adsorption of D-sorbitol on platinum leads to the formation of poisoning species with a number of electrons *per site* around 3, decreasing to about 2 after long adsorption times. By Electromodulated Infrared Reflectance Spectroscopy (EMIRS), linearly bonded CO species have been identified as the main poisoning species [6,7]. Other kind of adsorbed species, i.e., (R-COOH), (R-CO-R') and/or (R-CHO), have also been identified by EMIRS [7]. Studies on the electrochemical oxidation of D-sorbitol on gold single-crystal electrodes have been performed by Sottomayor [8].

The final aim of this work is to compare the electrocatalytic activity of platinum, platinum-iridium (90:10) and iridium polycrystalline electrodes, towards the oxidation of D-sorbitol, under the same experimental conditions.

Here, we present some preliminary voltammetric results obtained in acid medium. The effect of sweep rate on peak currents and peak potentials was recorded and the corresponding data is analysed.

EXPERIMENTAL

Cyclic voltammetry was employed as the experimental method. Plots were obtained from a computer controlled electrochemical data acquisition system AUTOLAB³/GPES 3.2, from Echo Chemie BV, Holland.

All electrochemical measurements were made using a three-electrode, three-compartment glass cell. The experiments were carried out at room temperature.

Working electrodes, Pt (99.9%), Pt-Ir (90:10) and Ir (99.9%), were constructed from wires of the corresponding materials (Johnson Matthey, UK). Their geometric areas are, respectively, 0.238 (Pt and Pt-Ir) and 0.196 cm². Current densities were normalized for the geometric area of the corresponding electrode.

A platinum counter electrode and a mercury/mercurous sulphate reference electrode (MSE, +656 mV vs. SHE) were used. The MSE reference electrode was placed in an external compartment and separated from the working electrode by a Luggin capillary.

Electrolytic solutions were prepared from ultrapure water, obtained with a Millipore Milli-Q system and from Merck reagents ("Suprapur" for perchloric acid and "pro-analysis" for D-sorbitol). The solutions were deoxygenated by bubbling pure nitrogen through the cell.

Before each experiment the Pt and Pt-Ir electrodes were pre-treated chemically by immersion in an H₂SO₄/HNO₃ solution and then electrochemically by the application of a repetitive triangular potential sweep between +0.70 and -0.68 V vs. MSE in 0.5 M HClO₄, in order to obtain a clean surface and a reproducible response.

The Ir electrode was generally cleaned (oxide removed) by placing it into the reducing part of a gas/air flame for few seconds.

RESULTS AND DISCUSSION

Figure 1 shows typical cyclic voltammetric responses of the Pt and Pt-Ir electrodes. Correspondent responses of Ir electrodes, covered with thin and thick films of iridium oxides, grown electrochemically in the base electrolyte, are given in Figure 2.

Iridium electrodes in both states, (Fig. 2. a and b), show almost no activity.

On the other hand on Pt and Pt-Ir (90% Pt + 10% Ir) electrodes, the general shape and the number of peaks, due to the electrochemical oxidation of D-sorbitol, is not significantly affected by the 10% of Ir on Pt, however current intensity and peak potentials are slightly different (see values in Table I). The development of a shoulder (B1) preceding peak B is also evident. The reoxidation peak (R) observed during the reverse sweep is more symmetric on Pt-Ir than on pure Pt electrodes.

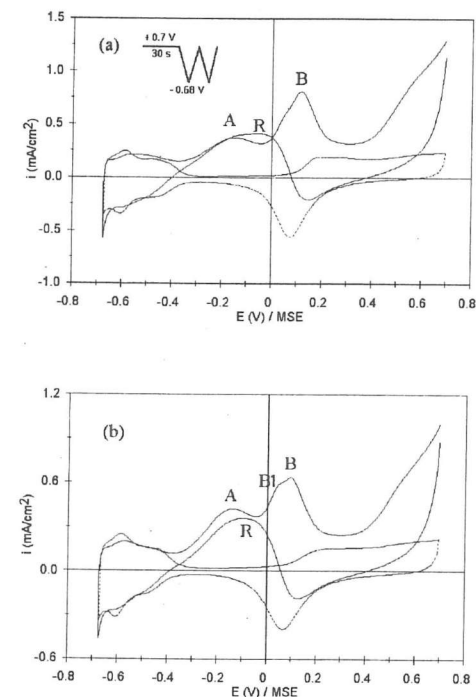


Fig. 1. Typical cyclic voltammograms of Pt (a) and Pt-Ir (b) electrodes in HClO₄ 0.5 M (---) and HClO₄ 0.5 M + D-sorbitol 0.1 M (—); room temperature; $\nu = 0.1$ V/s.

On Pt-Ir electrodes the oxidation of D-sorbitol starts at less anodic potentials. Surprisingly, the 10% of Ir increases the electrocatalytic activity of the Pt electrode towards the oxidation of D-sorbitol (both in terms of potential and current density for peak A).

The effect of varying the potential sweep rate is exemplified on cv's in Figures 3 and 4, for both Pt and Pt-Ir electrodes. The sweep rate was varied from 0.010 to 0.500 V/s.

Plots of $\log i_p$ vs. $\log \nu$ and E_p vs. $\log \nu$ are shown in Figures 5 and 6, respectively. Slopes of the corresponding straight lines are given in Tables II and III.

Table I. Peak currents and potentials for peaks A and B from cv 's recorded at 0.1 V/s.

Electrode material	Peaks					
	A		B		B1	
	$E_p / (V)$	$i_p / (mAcm^{-2})$	$E_p / (V)$	$i_p / (mAcm^{-2})$	$E_p / (V)$	$i_p / (mAcm^{-2})$
Pt	-0.157	0.383	0.114	0.682	—	—
Pt-Ir	-0.139	0.424	0.095	0.636	0.051	0.595

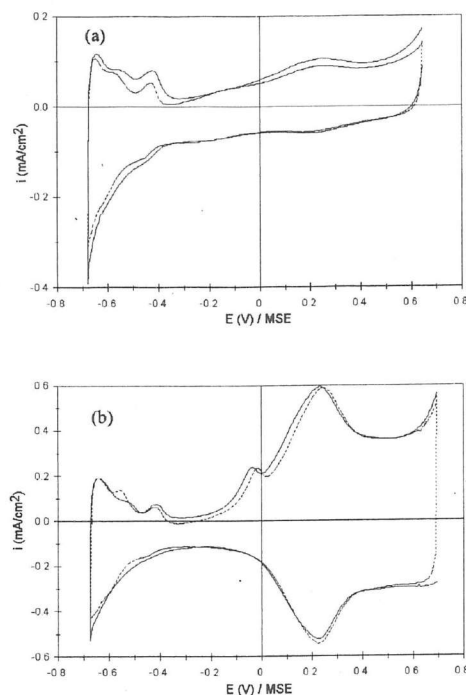


Fig.2. Typical cyclic voltammograms of Ir electrodes with thin (a) and thick (b) films of iridium oxides in $HClO_4$ 0.5 M (---) and $HClO_4$ 0.5 M + D-sorbitol 0.1 M (a) and 0.01 M (b) (—); room temperature; $\nu = 0.1$ V/s.

On Ir electrodes either covered with thin or thick oxide films, (Figure 2.a and b respectively), a minor increase on the anodic charges were obtained due to presence of D-sorbitol.

A similar behaviour has been found for formic acid oxidation under analogous experimental conditions [9-11]. Iridium has also shown no significant activity for the oxidation of saccharose in alkaline medium [12]. But, on the other hand, Ferrer and Victori [13] have recently reported results showing various degrees of activity depending on the experimental conditions, namely: potential limits, sweep rate, concentration of the electroactive species, pH, etc.

A definitive conclusion about the electrocatalytic activity of Ir electrodes towards the oxidation of D-sorbitol requires a more systematic study.

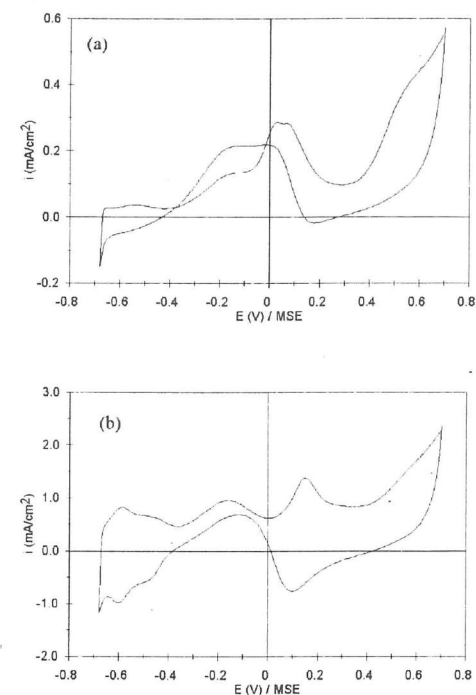


Fig.3. Cyclic voltammograms of the Pt electrode in $HClO_4$ 0.5 M + D-sorbitol 0.1 M, recorded at low (a) and intermediate (b) sweep rates: (a) $\nu = 0.020$ V/s, (b) $\nu = 0.350$ V/s.

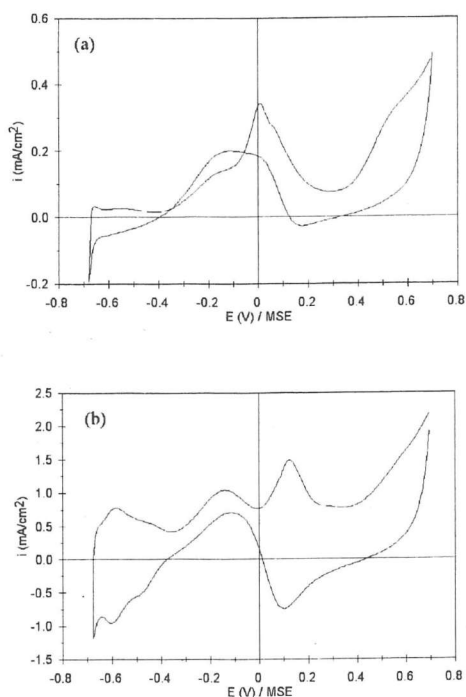


Fig.4. Cyclic voltammograms of the Pt-Ir electrode in HClO₄ 0.5 M + D-sorbitol 0.1 M, recorded at low (a) and intermediate (b) sweep rates: (a) $\nu = 0.020$ V/s, (b) $\nu = 0.350$ V/s.

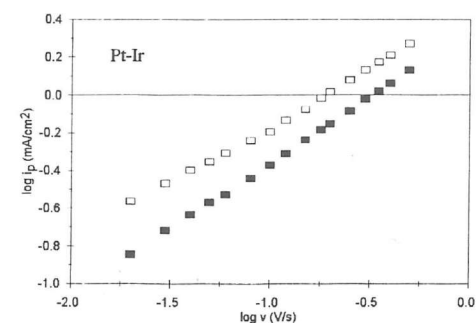
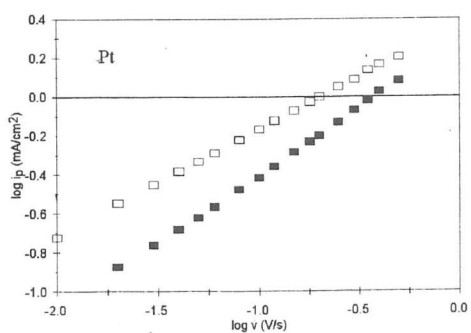
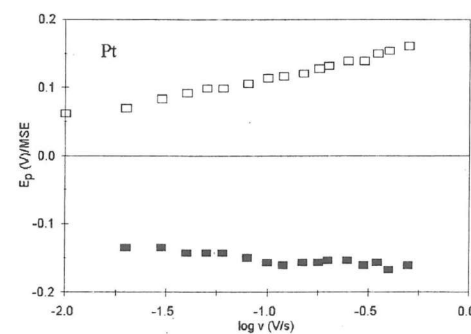


Fig.5. Plots of $\log i_p$ (mA/cm²) vs. $\log \nu$ (V/s), for the oxidation of 0.1 M D-sorbitol, in 0.5 M HClO₄ on Pt and Pt-Ir electrodes, peaks A (■) and B(□).

Table II. Slopes of the straight lines $\log i_p$ vs. $\log \nu$ (Fig.5), and respective correlation coefficients, r .

Peaks	Pt			Pt-Ir		
	<i>slope</i>	<i>r</i>	<i>sweep rate, (V/s)</i>	<i>slope</i>	<i>r</i>	<i>sweep rate, (V/s)</i>
A	0.70	0.999	0.03-0.5	0.70	0.999	0.03-0.5
B	0.55	0.999	0.03-0.5	0.62	0.997	0.03-0.5



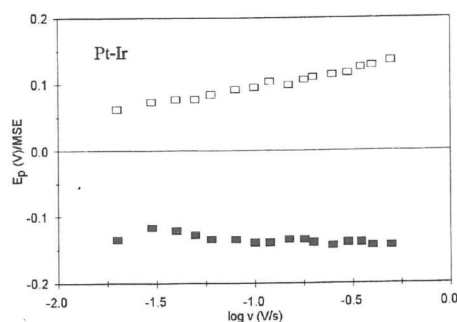


Fig.6. Plots of peak potentials E_p vs. $\log v$ (V/s), for the oxidation of 0.1 M D-sorbitol, in 0.5 M HClO_4 , on Pt and Pt-Ir electrodes, peaks A (■) and B(□).

Table III. Slopes (V/decade) of the straight lines E_p vs. $\log v$ (Fig.6), and respective correlation coefficients, r .

Peaks	Pt			Pt-Ir		
	slope	r	sweep rate, (V/s)	slope	r	sweep rate, (V/s)
A	*	—	—	*	—	—
B	0.067	0.998	0.02-0.5	0.050	0.993	0.03-0.3

* No linear relationship.

Application of the diagnostic criteria used in cyclic voltammetry [14], allow us to conclude that peak B corresponds, to a diffusion-controlled process on Pt (for sweep rates between 0.03 and 0.5 V/s, $i_p \propto v^{0.5}$), while for the case of Pt-Ir, the kinetics of the process leading to peak B is mixed controlled by diffusion and adsorption ($i_p \propto v^{0.6}$). In both electrode materials the process leading to peak A seems to be controlled by a rate determining step, r.d.s., involving both adsorption and diffusion ($i_p \propto v^{0.7}$).

For both electrode materials, potential of peak B varies linearly with the logarithm of sweep rate, with slopes of about 60 mV/decade. This indicates that the r.d.s. of the electro-oxidation process appears to be irreversible.

Accordingly to the diagnostic criteria valid for irreversible electron transfer processes, at 25°C,

$$E_p = K - (30/\alpha_a n \alpha_c) \log v \quad (1)$$

The comparison of values in Table III with eq (1), leads to $n_c = 1$ and α_c equal to 0.45 and 0.60 respectively for Pt and Pt-Ir electrodes.

In both electrode materials, peak potentials of peak A do not follow any regular variation with the sweep rate: its value oscillates between -0.135 and -0.168 V vs. MSE for Pt and between -0.135 and -0.143 V vs. MSE for the Pt-Ir electrode.

Peak A on pure Pt(poly) electrodes have been attributed to the oxidation of D-sorbitol molecules on the surface available for direct bulk oxidation. While peak B has been attributed to the oxidation of species previously adsorbed in the hydrogen adsorption/desorption region. Peak R, observed during the reverse sweep, just after the reduction of the oxides, has been attributed to the oxidation of the organic molecule on a "clean" electrode surface [5,6].

At lower sweep rates ($v < 0.060$ V/s), in the case of the alloy, peak B1 is predominant over peak B. For Pt this feature occurs at even lower sweep rates ($v < 0.030$ V/s). Raising the temperature of the solution, at 45°C, has produced a similar effect [15].

CONCLUSIONS

Voltammetric responses of Pt, Pt-Ir and Ir electrodes, in perchloric aqueous solutions 0.1 M in D-sorbitol, recorded under potentiodynamic polarization between +0.70 and -0.68 V vs. MSE, at sweep rates ranging between 0.01 and 0.5 V/s, have allowed the direct comparison of the activity of the electrode materials under study. The activities are in the following order:

$$\text{Pt-Ir} > \text{Pt} \gg \text{Ir} (\approx 0)$$

The poor catalytic activity of Ir may be related with the acid-basic characteristics of the electrode surface. According to Pickup and Birss [16], in acidic solutions, the reduced form of Ir is cationic, while the oxidized form is neutral or slightly anionic. Probably, as a consequence of that, the hydrogen adsorption/desorption region as well as the oxide region of Ir when compared with the corresponding ones of Pt, under the same experimental conditions, show significant differences, i.e.: the oxide formation starts at more negative potentials on Ir. This fact may be one reason why the oxidation of D-sorbitol do not takes place: in the relevant literature it is generally demonstrated that the formation of oxides on noble metals prevents the oxidation of organic species [1,2].

On the other hand it has also been demonstrated that the oxidation of either small or large organic molecules, namely alcohols and sugars is initiated by a dissociative adsorption step, which in general occurs for noble metals in the hydrogen adsorption/desorption region, by interaction or simple displacement of H_{ads} species. Peaks due to H_{ads} species are well visible on the cv's from Pt but not on Ir cv's, probably due to the presence of other remaining species that do not allow free sites for H_{ads} . As a consequence of that, adsorption of D-sorbitolic species do not takes place and oxidation do not starts.

The reasons presented here to explain the low activity of Ir compared to Pt may be considered a bit speculative. For a better explanation it would be necessary to know the exact reaction pathway for the oxidation of D-sorbitol, which is not a simple one. With this purpose systematic studies on Pt have been performed and others are in progress [5-7, 15].

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THE ELECTRICAL CONDUCTIVITY OF SOME ORGANIC SALTS IN METHANOL-NITROBENZENE MIXTURES AT 25 °C, 35 °C and 45 °C

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ABSTRACT :

Conductance measurements of S-n-butyliothiuronium bromide,-iodide and -picrate (S-n-Buis Br, S-n-Buis I and S-n-Buis Pi) in methanol-nitrobenzene mixtures at approximately 0.25, 0.5 and 0.75 mole fractions of methanol were studied at 25 °C, 35 °C and 45°C respectively. The data were analyzed using Fuoss' equation⁽¹⁾ (1980) to derive the molar conductance at infinitesimal concentration, Λ_0 , the association distance R and the association constant K_A corresponding to minimum standard deviation σ_A . The discussion was based on the variation of anionic size, the mole fraction of methanol and with varying temperature taking into account ionic solvation and viscosity effect. Thermodynamic parameters ΔG /(kJ/mole), ΔH /(kJ/mole) and ΔS /(J mol⁻¹ K⁻¹) were calculated and interpreted according to the variation of temperature and the mole fraction of methanol.

Key words: Electric conductivity, Ion-solvent interactions, Temperature dependence on the conductance, Thermodynamic parameters.

Introduction

Previous conductance studies of S-alkyliothiuronium salts⁽²⁻⁷⁾ [$\begin{matrix} \text{NH}_2 \\ \diagdown \\ \text{C-S-R} \\ \diagup \\ \text{NH}_2 \end{matrix} \text{X}$] show that they are considered as a good example of electrolytes with large solvophobic cations and can be used as an important source of information concerning the behaviour of ions in their solutions.

Binary solvent mixtures have a real behaviour upon ionization, dissociation or association and acid-base equilibria of some electrolytes that take place in a solution of two cosolvents. Recently, increasing attention was focused on non-