

# EFFECT OF ANIONS ON THE ELECTRO-OXIDATION OF D-SORBITOL AT A PLATINUM ELECTRODE IN ACID MEDIA

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**Abstract:** The influence of anions on the electro-oxidation of D-sorbitol, at a platinum polycrystalline electrode, was studied in HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> solutions. Results show that Pt has a higher activity in perchloric than in sulfuric medium for the oxidation of D-sorbitol. Based on the rates of oxidation of D-sorbitol, the following sequence has been found for D-sorbitol oxidation in presence of adsorbed anions: ClO<sub>4</sub><sup>-</sup> ~ F<sup>-</sup> > HSO<sub>4</sub><sup>-</sup> (SO<sub>4</sub><sup>2-</sup>) >> Cl<sup>-</sup> >> Br<sup>-</sup>.

**Keywords:** Electrocatalysis; Oxidation; D-sorbitol; Platinum; Anions

## INTRODUCTION

The kinetics and mechanism of electrocatalytic reactions, such as the electro-oxidation of organic molecules on noble metals, depend on several parameters, like the nature of the electrode, its potential and the temperature and pH of the electrolytic solution [1].

Recently, the electro-oxidation of D-sorbitol, on a polycrystalline platinum electrode in perchloric medium, has been studied under varying these and other experimental conditions [2]. The role of electrode material [3] and superficial structure of the electrode [4-6] were also considered in previous studies.

It is known that the supporting electrolyte can modify an electrocatalytic reaction rate or even the reaction path by specific adsorption of its constituting anions [7]. Simultaneously, inhibition of the electrocatalytic activity of noble metals by foreign adsorbing anions, like halide ions, is a general feature reported in the literature [8-10].

The aim of this paper is to present voltammetric results concerning the influence of the supporting electrolyte composition on the electro-oxidation of D-sorbitol at a platinum polycrystalline electrode, in acid media.

Perchloric and sulphuric acids were used as electrolytic solutions. Fluoride, chloride and bromide anions were added to the perchloric electrolytic solution. Their bulk concentrations were varied from 10<sup>-5</sup> mol dm<sup>-3</sup> to 10<sup>-3</sup> mol dm<sup>-3</sup>.

## EXPERIMENTAL

The cyclic voltammetric measurements were performed with a computer-controlled Autolab<sup>®</sup> PST10 potentiostat (Eco chemie). All experiments were carried out in a three-electrode three-compartment glass cell, at room temperature.

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The working electrode was constructed from a 0.5 mm diameter Pt wire (Specpure, Johnson Matthey) having a geometric area of 0.238 cm<sup>2</sup>. Before each experiment the platinum electrode was pre-treated using a procedure described previously [2]. A Hg | Hg<sub>2</sub>SO<sub>4</sub> | K<sub>2</sub>SO<sub>4</sub> (sat.) electrode (*sme*) and a platinum grid served as the reference and the counter electrodes, respectively.

Supporting electrolytes were prepared from ultrapure water (Milli-Q Millipore system) and Merck Suprapur<sup>®</sup> products (HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>). D-sorbitol (p.a. grade) was also purchased from Merck. Halide anions were obtained from the correspondent potassium salts (KF, KCl and KBr, purum p.a.). The solutions were deaerated with ultrapure nitrogen (U Quality from L'Air Liquid).

### RESULTS AND DISCUSSION

For comparison, Fig.1 shows the voltammetric curves obtained with the Pt electrode in 0.5 mol dm<sup>-3</sup> HClO<sub>4</sub> and 0.25 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> supporting electrolytes, in presence of 0.1 mol dm<sup>-3</sup> D-sorbitol. Larger peak currents are observed in HClO<sub>4</sub> than in H<sub>2</sub>SO<sub>4</sub> solutions, except for peak R. Peak potentials are also dependent on the electrolyte (see Table I).

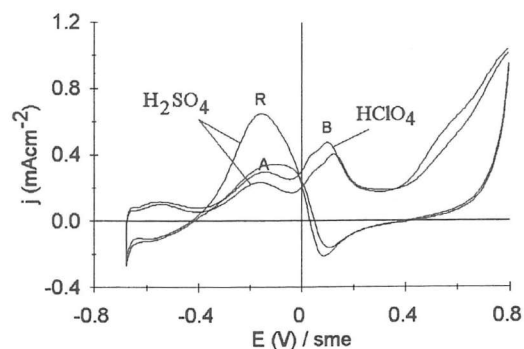


Fig. 1. Typical cyclic voltammetric responses of platinum in 0.5 mol dm<sup>-3</sup> HClO<sub>4</sub> and 0.25 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, 0.1 mol dm<sup>-3</sup> D-sorbitol,  $\nu = 0.050$  Vs<sup>-1</sup>.

Table I. Peak current densities and potentials for peaks A and B

|                                | Peak A        |                         | Peak B        |                         |
|--------------------------------|---------------|-------------------------|---------------|-------------------------|
|                                | E/(V) vs. sme | j/(mAcm <sup>-2</sup> ) | E/(V) vs. sme | j/(mAcm <sup>-2</sup> ) |
| H <sub>2</sub> SO <sub>4</sub> | -0.164        | 0.233                   | 0.122         | 0.402                   |
| HClO <sub>4</sub>              | -0.142        | 0.296                   | 0.100         | 0.473                   |

Fig. 2 shows the influence of chloride concentration on the current densities of the anodic peaks A and B, for both supporting electrolytes.

The magnitude of the chloride inhibition is dependent on the other anions in solution, ClO<sub>4</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup> / SO<sub>4</sub><sup>2-</sup>. The inhibition is more pronounced in HClO<sub>4</sub> solutions ( $[Cl^-] = 10^{-5} M \rightarrow 10^{-4} M$ ).

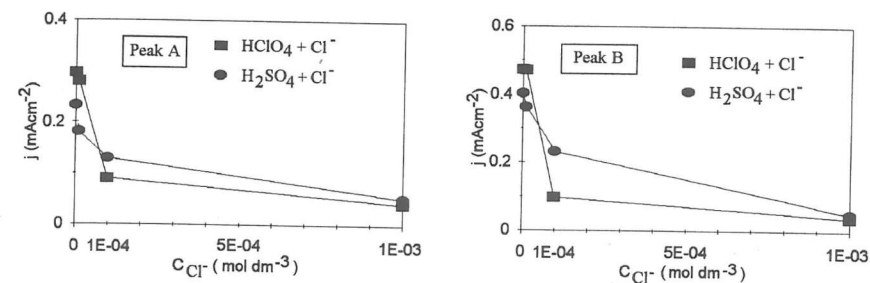


Fig. 2. Influence of chloride concentration on the current densities of peaks A and B, for 0.5 mol dm<sup>-3</sup> HClO<sub>4</sub> and 0.25 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> (Pt / 0.1 mol dm<sup>-3</sup> D-sorbitol,  $\nu = 0.050$  Vs<sup>-1</sup>).

In perchloric medium, the inhibition of D-sorbitol electro-oxidation occurs, even for small traces of Cl<sup>-</sup> and Br<sup>-</sup> anions (Fig. 3). The total inhibition is attained with  $[Br^-] = 10^{-3}$  M.

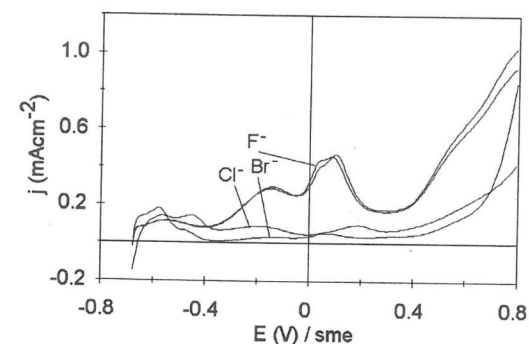


Fig. 3. Anodic sides of the CVs for the Pt / D-sorbitol 0.1 mol dm<sup>-3</sup> + HClO<sub>4</sub> 0.5 mol dm<sup>-3</sup> + X<sup>-</sup> 10<sup>-4</sup> mol dm<sup>-3</sup> systems, with X = F, Cl and Br.  $\nu = 0.050$  Vs<sup>-1</sup>.

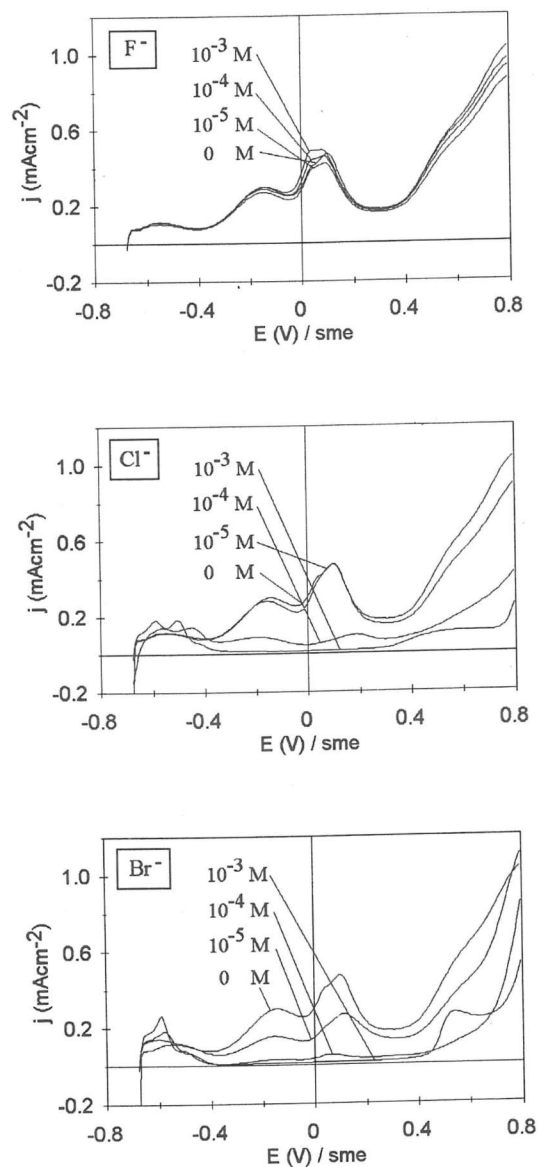


Fig. 4. Anodic sides of the CVs for the Pt / D-sorbitol  $0.1 \text{ mol dm}^{-3} + \text{HClO}_4 0.5 \text{ mol dm}^{-3} + \text{X}^- 10^{-y} \text{ mol dm}^{-3}$  systems, with  $\text{X} = \text{F}, \text{Cl}$  and  $\text{Br}$ ,  $y = 3, 4$  and  $5$ , showing the effect of halide concentration.  $v = 0.050 \text{ Vs}^{-1}$ .

### CONCLUSIONS

Results show that Pt has a higher activity in perchloric than in sulfuric medium for the oxidation of D-sorbitol.

$\text{Cl}^-$  and  $\text{Br}^-$  anions contribute to the inhibition of the electro-oxidation process of D-sorbitol probably by means of competitive adsorption with fragments of the organic species, while  $\text{F}^-$  seems to not significantly affect the process.

On the other hand, the presence of anions ( $\text{Cl}^-$  and  $\text{Br}^-$ ) in solution induces a displacement on the formation of the platinum oxides to more positive potentials. As platinum oxides may participate in the oxidation of organic molecules and/or fragments, thus that may be another reason for the observed inhibition effect.

Based on the rates of oxidation of D-sorbitol, the following sequence has been found for D-sorbitol oxidation in presence of adsorbed anions:  $\text{ClO}_4^- \sim \text{F}^- > \text{HSO}_4^- (\text{SO}_4^{2-}) \gg \text{Cl}^- \gg \text{Br}^-$ .

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