

The conditioning of the DNA-modified electrode is very important. Effectively, as demonstrated in Fig. 2, the reversibility of the electrode reaction becomes better after applying higher potentials to the electrode. In the cyclic voltammograms obtained after conditioning the electrode at +0.8 V the difference between anodic and cathodic peak potentials  $\Delta E_1 = E_{p,a} - E_{p,c} = 290$  mV whereas in those performed after conditioning the electrode at +1.4 V the difference was  $\Delta E_2 = E_{p,a} - E_{p,c} = 80$  mV, which represents significantly faster electrode kinetics. This can be explained as the consequence of the formation at higher potentials of an interwoven hydrogen-bonding network within the DNA double helix that stabilises the contacts between the bases enabling a much easier electron transfer.

#### CONCLUSIONS

A DNA-modified electrode will prove of great interest in the future for the development of microelectronic sensors [2] and for the detection of biological compounds and antigens [3] and their mode of interaction with DNA, either for treatment purposes such as explaining the action of and quantifying anticarcinogenic drugs, or for investigating the consequences of the abuse of toxic pesticides that originate chemical modification of DNA. This mutagenesis is the cause of many human cancers.

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#### ELECTROPOLYMERIZATION OF PHENOL IN DIFFERENT AQUEOUS MEDIA

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#### INTRODUCTION

The electrochemical phenomenon of "selective inhibition" of electrode reactions by organic compounds has been studied by Bejerano et al. [1,2]. They have shown that the oxidation of iodide and bromide ions on a Pt electrode in  $\text{HClO}_4$  could be inhibited by the presence of small amounts of phenol and some of its derivatives. However, the electrooxidation of water to oxygen is essentially unaltered under the same experimental conditions. This behaviour is due to the formation of a polymeric film on the surface electrode.

More recently Mengoli et al. [3,4] have shown that polymerization of phenols dissolved in hydroalcoholic solutions, containing ammonium compounds, is a method for effectively protecting against corrosion, when an appropriate choice of monomers and supporting electrolyte is made.

In this work the polymeric film formation by anodic polarization of phenol on platinum electrode in alkaline and acid media has been studied by voltammetric technique. Scanning Electron Microscopy (SEM) has been used to study the surface morphology of the polymeric films.

#### EXPERIMENTAL

The supporting electrolytes were 0.1M  $\text{Na}_2\text{CO}_3$ , 0.1M NaOH and 0.5M  $\text{H}_2\text{SO}_4$

(Merck suprapur). The phenol was purchased from Merck p.a. and used without further purification. The water used for the preparation of the solutions was from a Millipore-Milli-Q system. The solutions were degassed by bubbling Ar for at least 20 min.

A standard experimental set up was used to record the cyclic voltammograms, which were obtained in all cases at a sweep rate of 50 mV/s. All potentials are referred to the reversible hydrogen electrode (RHE) immersed in the same solution. A Jeol JSM-840 scanning electron microscope was used for surface observations.

The polyorientated platinum electrode used was a spherical and has been obtained by melting of a wire of platinum in an oxygen+gas flame. The electrode was cleaned by a thermally treatment [5].

## RESULTS AND DISCUSSION

The oxidation of phenol on platinum electrodes has been studied in different aqueous media (0.1M NaOH, 0.1M Na<sub>2</sub>CO<sub>3</sub> and 0.5M H<sub>2</sub>SO<sub>4</sub>).

Fig. 1 shows the voltammogram for a platinum electrode in a 0.1M NaOH + 6x10<sup>-4</sup>M C<sub>6</sub>H<sub>5</sub>OH solution. It can be observed a progressive deactivation of the oxidation of phenol with the number of sweeps up to 1.6V. This deactivation could be associated to the formation of a polymeric film on the electrode surface. Fig. 2 shows the behaviour of this electrode covered with polymer, created as in Fig. 1, in 0.1M NaOH free of phenol. It can be observed that this polymeric film shows a good ionic conductivity with respect to H<sup>+</sup> and OH<sup>-</sup> together with a good water permeability (Fig. 2). Oxygen and hydrogen evolutions and the oxidation and reduction of surface oxide on the platinum electrode have not been practically modified with respect to the obtained in a platinum electrode clean of polymer.

A different behaviour is obtained when 0.1M Na<sub>2</sub>CO<sub>3</sub> solution is used. Fig. 3

shows the voltammogram of the oxidation of phenol on a platinum electrode in a 0.1M Na<sub>2</sub>CO<sub>3</sub> + 6x10<sup>-4</sup>M C<sub>6</sub>H<sub>5</sub>OH solution. This figure shows a deactivation with the number of sweeps up to 1.6V more drastic than the obtained in the case of NaOH solution, as consequence of the formation of a polymeric film on the platinum surface. Fig. 4 shows the behaviour of a platinum covered with polymer, created as in Fig. 3, in a 0.1M Na<sub>2</sub>CO<sub>3</sub> solution free of phenol. This voltammogram indicates that the polymeric film shows a smaller ionic conductivity and water permeability than the obtained in a 0.1M NaOH solution.

Fig. 5 shows the voltammogram of a platinum electrode in 0.5M H<sub>2</sub>SO<sub>4</sub>+6x10<sup>-4</sup>M C<sub>6</sub>H<sub>5</sub>OH solution. In this case, the deactivation of the oxidation of phenol with the number of sweeps up to 1.6V is very similar to that obtained in the case of Na<sub>2</sub>CO<sub>3</sub> solution. Fig. 6 shows the voltammogram of a platinum electrode covered with polymeric film, created as in Fig. 5, in a 0.5M H<sub>2</sub>SO<sub>4</sub> solution free of phenol. This figure shows a good ionic conductivity and water mobility as in the case of NaOH solution.

The SEM images of the polymeric films created in alkaline and acid media no present significative differences and the polymeric surfaces are populated by small wrinkles. More pronounced wrinkles are observed when the anodic potential is very positive (within oxygen evolution) in 0.5M H<sub>2</sub>SO<sub>4</sub> and 0.1M NaOH solutions.

## CONCLUSIONS

The oxidation of phenol on a platinum electrode shows a progressive deactivation with the number of sweeps. This deactivation is associated to the formation of a polymeric film on the surface electrode. The nature and characteristic of this polymeric film depend on the electrolyte used, the monomer concentration, the upper potential limit

used in the voltammetry, and if a controlled potential is used instead of a cyclic voltammetry.

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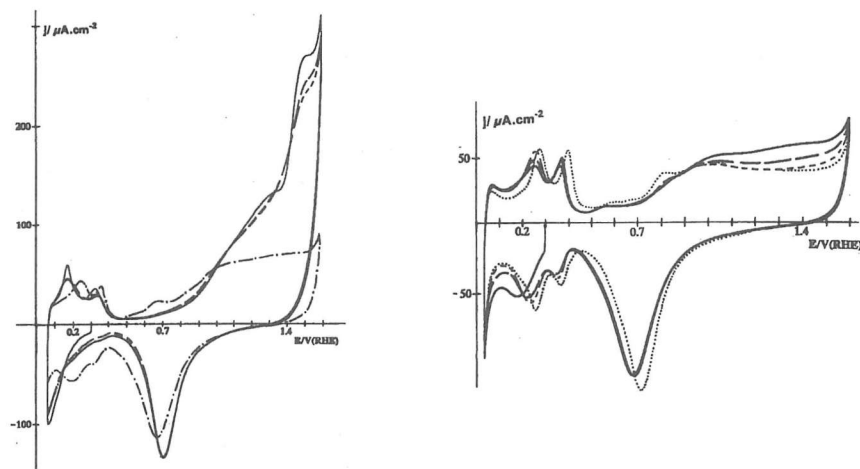


Fig. 1. Voltammogram of a platinum electrode in 0.1M NaOH +  $6 \times 10^{-4}$ M  $C_6H_5OH$  solution.  $v=50$ mV/s. (—) first, (- - -) second, (-----) fifth and (-·-·-) twentieth cycles up to 1.6V.

Fig. 2. Voltammogram of a platinum electrode covered with a polymeric film, created after 20 cycles up to 1.6V in 0.1M NaOH +  $6 \times 10^{-4}$ M  $C_6H_5OH$  solution, in 0.1M NaOH solution,  $v= 50$ mV/s.

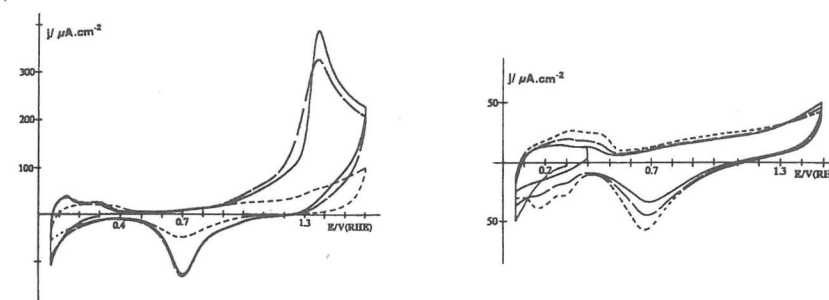


Fig. 3. Voltammogram of a platinum electrode in 0.1M  $Na_2CO_3$  +  $6 \times 10^{-4}$ M  $C_6H_5OH$  solution.  $v= 50$  mV/s.(—) first, (- - -) second, (-----) fifth cycles up to 1.6V.

Fig. 4. Voltammogram of a platinum electrode covered with a polymeric film, created after 5 cycles up to 1.6V in 0.1M  $Na_2CO_3$  +  $6 \times 10^{-4}$ M  $C_6H_5OH$  solution, in 0.1M  $Na_2CO_3$  solution,  $v= 50$ mV/s.

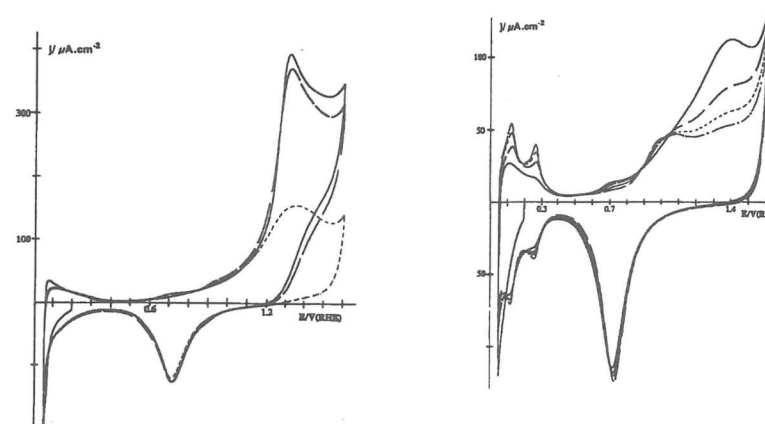


Fig. 5. Voltammogram of a platinum electrode in 0.5M  $H_2SO_4$  +  $6 \times 10^{-4}$ M  $C_6H_5OH$  solution.  $v= 50$  mV/s.(—) first, (- - -) second, (-----) fifth cycles up to 1.6V.

Fig. 6. Voltammogram of a platinum electrode covered with a polymeric film, created after 5 cycles up to 1.6V in 0.5M  $H_2SO_4$  +  $6 \times 10^{-4}$ M  $C_6H_5OH$  solution, in 0.5M  $H_2SO_4$  solution,  $v= 50$ mV/s.