DNA-MODIFIED ELECTRODES

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ABSTRACT

The functioning of a DNA-modified glassy carbon electrode was evaluated using the electrochemical system ferricyanide/ferrocyanide, after different electrode conditioning in the absence or presence of the free bases adenine and guanine, and at different applied potentials. The results were compared with those obtained at the bare glassy carbon electrode.

INTRODUCTION

The structure of DNA (deoxyribonucleic acid) is an open one and the two helical polynucleotide chains are joined together by hydrogen bonds. Consequently, in the DNA double helix there are two grooves, the major and the minor groove, Fig.1

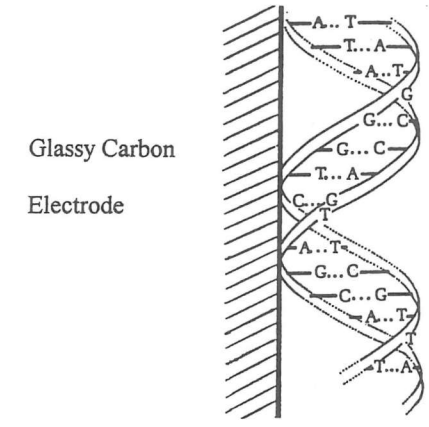

Fig.1 Schematic diagram of a DNA-modified electrode.

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This fact is very important for modifying an electrode with DNA since the distances between the electroactive groups, the bases adenine and guanine, and the surface of the electrode vary.

During the transfer of genetic information the interaction between DNA and divalent ions such as those of manganese, magnesium, cobalt, copper, zinc, nickel, cadmium and lead play an essential role in promoting and maintaining nucleic acid functionalities. The last four ions have been recognized for their carcinogenicity since they damage DNA molecules and alter the fidelity of DNA synthesis. The development of a DNA-modified electrode that could help identifying changes in the DNA structure and predict the action of drugs or pollutants and prevent their utilization of being spread would be most interesting and valuable.

EXPERIMENTAL

Chemicals and solutions

Calf thymus DNA (sodium salt, type I) was obtained from Sigma Chemical Co. and was used without further purification. All other chemicals were commercially supplied and were analytical grade. Acetate buffer solutions of ionic strength 0.1 M were used in all experiments at pH 4.5, and were prepared using purified water from a Millipore Milli-Q system. Single stranded DNA (ss DNA) was prepared by the following procedure. An accurately weighed sample of approximately 4 mg of DNA was treated with 0.5 mL of pure perchloric acid. After dissolution, 0.5 mL of 9M NaOH was then added to neutralize the solution followed by 49 mL of pH 4.5 of acetate buffer. All experiments were done at room temperature ($t \cong$ 19-22° C).

Apparatus and procedures

The working electrode was glassy carbon (Tokai, GC, area 0.07 cm^2) modified by adsorbed DNA, the counter electrode was a Pt wire, and the reference electrode was a SCE which were used in a one-compartment cell. The DNA modified electrode was prepared by covering a glassy carbon electrode with DNA dissolved in pH 4.5 acetate buffer and leaving the electrode to dry. After drying, the electrode was held at different

values of applied potential in acetate buffer solution. Voltammograms were recorded using a μAutolab potentiostat/galvanostat running with model GPES version 3 software, from Eco-Chemie, Netherlands. The potential range studied was from 0 V to +1.6 V *vs.* SCE, cyclic voltammogram scan rate 100 mV s^{-1} and differential pulse voltammetry conditions were: pulse amplitude 50 mV, pulse width 70 ms and scan rate 5 mV s^{-1}.

RESULTS AND DISCUSSION

The DNA-modified glassy carbon electrode was characterized using the electrochemical system ferricyanide/ferrocyanide. Results obtained were compared with those obtained at the bare glassy carbon electrode under the same conditions. Cyclic voltammograms are shown in Fig.2.

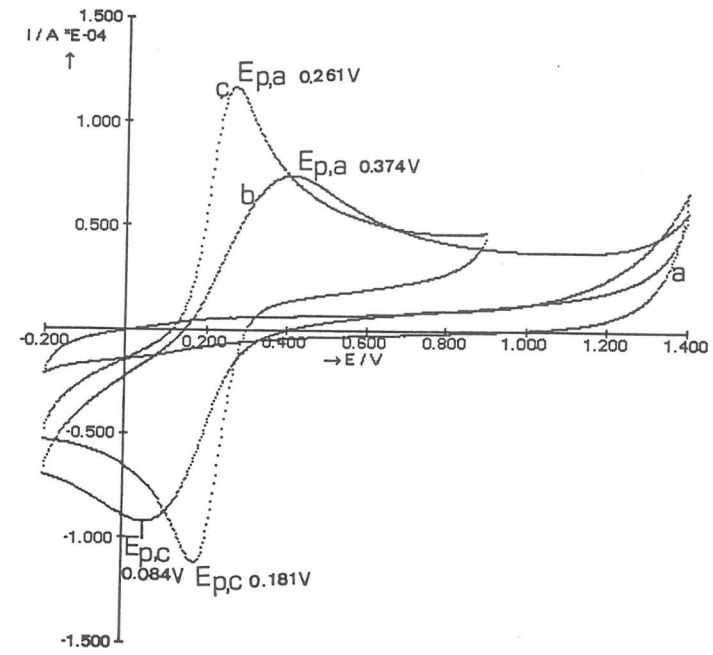

Fig. 2 Cyclic voltammograms, scan rate 100 mV s^{-1}, using a DNA-modified electrode: a) 0.4 M K_2SO_4; b) 2 mM ferricyanide, electrode conditioned at +0.8V; c) 2 mM ferricyanide, electrode conditioned at +1.4V.

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 $HClO_4$ 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 appropiate 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 polimeric films.

EXPERIMENTAL

The supporting electrolytes were 0.1M Na_2CO_3, 0.1M NaOH and 0.5M H_2SO_4

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