Glucose detection at sol-derived nanoparticulate Ir oxide films

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INTRODUCTION

The importance of glucose biosensors in the lives of diabetics' patients has attracted many scientists over the past 40 years, with emphasis on the development of electrochemical and optical glucose detection techniques. Ideal glucose biosensors should exhibit long-term stability and good biocompatibility, as well as a lack of response to common interfering species.

In the present work, nanoparticulate conducting thin films composed of Ir/IrOx, exhibiting high porosity and surface area, excellent conductivity, long-term stability, and known compatibility with body fluids, have been formed The primary goal of this work is to entrap glucose oxidase (GOx) in this matrix, allowing for the possibility of direct regeneration (involving the Ir(III)/(IV) redox chemistry) of the active FAD site of GOx.

The Michaelis-Menten (MM) model describes the behavior of enzymes that are free in solution. Applying this model to immobilized enzyme systems is highly simplistic and the kinetic parameters deduced describe only *apparent* reaction rates and not the *intrinsic* catalytic activity of the enzyme. Consequently, a modified version of the MM model is employed here, which accounts for mass transfer processes at the surface. The results were also analyzed kinetically, using a computer algorithm, and were then compared to the case of IrOx/GOx formed on bulk Ir wires[1].

EXPERIMENTAL METHODS

The Ir sol was synthesized using $IrCl_3$ and Na ethoxide, employing an ethanol based procedure, as described elsewhere[2]. The amount of EtOH was then reduced by 50% and replaced with water. GOx immobilization was achieved by mixing the GOx powder with the H_2O/EtOH Ir sol, and then dip-coating the mixture onto a Au substrate at a constant withdrawal rate. The films were air-dried at room temperature for 48 hours. The Ir sol was converted to IrOx by cycling the potential of the dip-coated substrate in neutral phosphate buffer between 0.0 V and 1.45 V (vs. RHE). Electrochemical signals were obtained at a range of glucose concentrations, both in the presence and absence of GOx.

RESULTS AND DISCUSSION

The response of IrOx/GOx electrodes to glucose addition in the presence of oxygen was readily observed, evidenced by the reduction and oxidation of H_2O_2. When the response was tracked again in the absence of oxygen, oxidation currents only were observed, and no sign of H_2O_2 was detected, indicating that redox mediation by the IrOx film is taking place. The resulting IrOx/GOx electrodes showed long-term stability towards glucose up to 35 days. A number of other variables were also examined, such as the concentration of GOx in the Ir sol, the number of IrOx/GOx coatings employed, and solution agitation. As well, the effect of common interfering species, such as ascorbic acid and uric acid, on the response to glucose in the presence and absence of Nafion was also studied.

In order to determine the amount of GOx entrapped in the electrode matrix and its distribution, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Quartz Crystal Microbalance (QCMB) and Inductively Coupled Plasma Spectroscopy (ICP) were employed. The results of these film characterization studies will also be presented.

Michaelis-Menten plots with *apparent* kinetic parameters, Km and Vm, were obtained, using the sol-gel derived Ir-GOx electrodes (Type II-porous IE, Figure 1). A computer algorithm was used to numerically solve the second order partial differential equation describing the Type II-porous IE system, similar to what was reported by Miyakawa *et al*[3]. From the results obtained, the intrinsic values of the kinetic parameters were calculated, as well as the effectiveness factor describing the degree of diffusion limitations on the reaction rate.

For comparison purposes, a kinetic analysis was also carried out for IrOx films formed on bulk Ir wires, with glucose oxidase (GOx) immobilized on the outer surface (Type I-surface IE, Figure 1). Intrinsic kinetic parameters were obtained from the same plots by graphically removing the external mass transfer effects[3]. Both the apparent and intrinsic values are compared and the modified Thiele's modulus describing the degree of external mass transfer effects are reported.

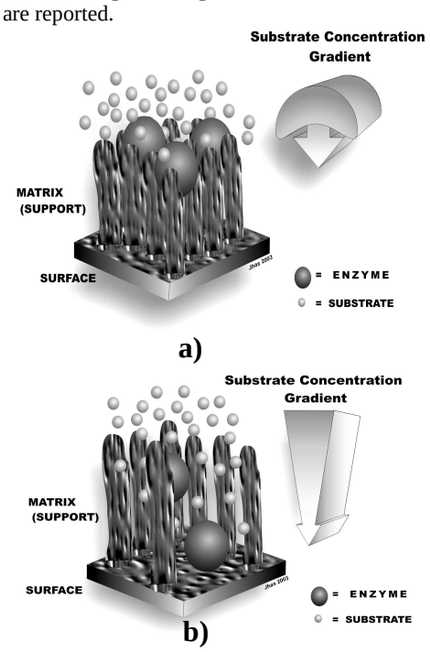

Fig. 1: *Illustration of enzyme, (a) adsorbed on the surface of the electrode (Type I-surface IE); (b) immobilized within a porous matrix (Type II-porous*

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