

Sol-gel derived Ir-based electrodes for the electrochemical detection of glucose

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INTRODUCTION

As the number of individuals suffering from diabetes is increasing rapidly, efforts to develop a reliable glucose biosensor have intensified [1], with emphasis on electrochemical and optical detection techniques [2-3]. When designing a successful glucose-sensing electrode, issues that must be considered include the stability and biocompatibility of the electrode material, the immobilization process, the stability of the glucose oxidase (GOx) enzyme in the electrode material, etc. Recently, sol-gel (SG) derived materials have received attention as possible matrices for enzyme entrapment [4-5], due to their high surface area (porosity), stability, and easy method of preparation. Glucose sensors based on silicate sol-gel films have been studied extensively, although their poor conductivity leads to the need for an additional electroactive species in the matrix.

In the present work, a sol-gel method has been employed to form a nanoparticulate conducting thin film composed of Ir metal, which is subsequently converted to a nanoparticulate Ir oxide layer. These films are highly porous, conductive, stable, known to be compatible with body fluids [6] and have a high surface area. The goal of this work is to entrap GOx in this matrix, allowing for the possibility of direct regeneration (involving the Ir(III)/(IV) redox chemistry of Ir oxide (IrOx)) of the active FAD site of GOx. Alternatively, glucose detection could take place by the oxidation of H₂O₂, in the presence of oxygen. To our knowledge, no other study of this kind has been carried out using conductive nanoparticles, although some prior work involving glucose detection with IrOx films, formed electrochemically at bulk Ir, has been carried out.

EXPERIMENTAL

The Ir sol was synthesized using an ethanol based procedure, as described elsewhere [7] and was then gradually converted to a predominantly aqueous based solution. GOx immobilization was achieved by mixing the GOx powder with the aqueous Ir sol, and then depositing the mixture onto a Au substrate using the dip-coating method. The films were air-dried for 24 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 to 1.45 V (vs. RHE). Electrochemical signals were obtained in solutions of a range of glucose concentrations, both in the presence and absence of GOx.

RESULTS AND DISCUSSION

Initial experiments involving the deposition of GOx on the surface of an Ir nanoparticulate film, in a two step process and in the absence of oxygen, did lead to a current (at above 1.0 V) proportional to the glucose concentration. While this suggested that a mediated

mechanism could be involved, these results were found to be irreproducible. Therefore, subsequent work was carried out with IrOx/GOx films formed simultaneously, as described in the experimental section. First-round experiments demonstrated that the IrOx redox response was stable in the presence of glucose in solution, and also unaltered when GOx was present in its matrix. In the presence of GOx in the electrode and glucose in solution and when oxygen was present, clear evidence for the formation of H₂O₂ was obtained, in that both the oxidation and reduction of H₂O₂ was seen. However, due to the overlap of the oxygen and H₂O₂ reduction currents, the signal due to H₂O₂ oxidation was tracked at potentials positive of ca. 0.9 V vs. RHE, typically at 1.2 V. Some of the variables examined during IrOx/GOx film construction included the conditions of the drying procedure used and the number of layers of film deposited.

Typical Michaelis-Menton plots were obtained over a range of glucose concentration (0.3 to 100 mM). Km values obtained were in the range of 25 to 35, similar to those reported by Rivas *et al* in studies using Ir-GOx deposition on glassy carbon electrodes [8].

A number of techniques have been employed to determine the amount of GOx entrapped in the electrode matrix, and if possible, to establish its distribution and activity. These techniques include Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Quartz Crystal Microbalance (QCM), Inductively Coupled Plasma Spectroscopy (ICP), and Thermal Gravimetric Analysis (TGA). The results of these studies, as well as a comparison with the characteristics of IrOx based electrodes containing GOx, but formed by the electrochemical growth of IrOx at bulk Ir in a GOx solution, will also be presented.

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