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Direct electrochemical assay of glucose using boron-doped diamond electrodes

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Abstract

We report linear sweep and square wave voltammetric studies on glucose oxidation at boron-doped diamond (BDD) electrodes in an alkaline medium in efforts to evaluate the techniques for electrochemically assaying glucose. The bare BDD electrode showed good linear responses to glucose oxidation for a concentration range from 0.5 to 10 mM glucose, which well encompasses the physiological range of 3–8 mM. The BDD electrodes did not experience interferences from ascorbic acid or uric acid during glucose detection. This method, when applied to real blood samples, gave results similar to those obtained by a commercial glucose monitor.

Keywords: Boron-doped diamond electrodes; Non-enzymatic glucose analysis

1. Introduction

Electrochemical oxidation of glucose has gained a great deal of interest over the years due to its application to glucose detection [1–7] and glucose fuel cells [8]. Electrochemical glucose sensors fall into two major types, i.e., enzymatic [1] and nonenzymatic sensors [2–7]. The majority of enzyme-based sensors utilize glucose oxidase (GOx), which oxidizes glucose and produces hydrogen peroxide. The amount of hydrogen peroxide is quantitatively measured electrochemically to indirectly determine the amount of glucose. Nonenzymatic electrochemical sensors include direct amperometric ones [2–7] utilizing the current response of glucose oxidation directly at the electrode surface and that utilizing competitive host–guest complexation [9]. Metal electrodes including platinum [2,3], gold [4], copper [5], and nickel [6] have been used in past amperometric sensor studies both as electrodes and catalysts. Although enzymatic sensors offer reliable results, the difficulties in miniaturization and instability of the enzymes at body temperature present problems in application to lab-on-a-chip and in vitro glucose assay. Metal electrodes are easy to miniaturize and apply to in vitro analysis, but there are still a few problems associated with direct electrochemical glucose oxidation. First, oxidation of glucose requires a large overpotential [7]. The required potentials sometimes fall beyond the range of electrode and/or solution stability, making it difficult to carry out the oxidation of glucose. Second, the oxidized products can remain adsorbed on the electrode surface, causing a decrease in activity and poisoning of the electrode [7]. The oxidized products form a passive film on the electrode surface, and prevent further oxidation/detection of glucose. Finally, the metals used as electrodes and catalysts tend to be unstable, and experience dissolution at normal operation conditions [5]. This results in decrease in electrode activity along with irreproducible current responses. Even though direct amperometric sensors remain popular due to their simplicity in operation and instrumentation, these problems must be solved in order to fabricate an accurate and durable amperometric glucose sensor.

Boron-doped diamond (BDD) electrodes have gained interest from electrochemists in the past decade, especially

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in the field of electroanalytical chemistry. BDD electrodes have been used for the amperometric detection of several compounds such as metal ions [10], aliphatic polyamines [11], organic acids [12], and nucleic acids [13]. Among their many properties, low capacitive background current, wide potential window in both aqueous and organic solutions, and resistance to electrode fouling [14–17] make them possible electrodes for direct amperometric detection of glucose. BDD electrodes have been studied in the past as glucose sensors, both in enzyme-based and amperometric methods. Su et al. [18] studied a glucose sensor with GOx immobilized on BDD electrode by cross-linking method, while Olivia et al. [19] used a BDD microfiber electrode modified with overoxidized polypyrrole and GOx for glucose monitoring. Fujishima and co-workers [20–22] also investigated BDD electrodes implanted with metal particles such as nickel and copper, which acts as catalysts for electrochemical glucose oxidation, for glucose detection.

In the present study, we demonstrate that bare BDD electrodes can be used to directly assay glucose without any modification with enzymes or metallic catalysts when they are appropriately treated. Bare BDD electrodes seem to be a promising candidate for glucose sensors due to their wide potential window, resistance to fouling, chemical inertness, mechanical stability, and absence of toxic metals.

2. Experimental

2.1. Chemicals and reagents

β-D(+)-glucose and KOH were purchased from Sigma and Aldrich, respectively, and used as received. Doubly distilled, deionized water was used for the preparation of all solutions. All solutions were purged with nitrogen before each experiment.

2.2. Electrochemical experiments

Electrochemical measurements were made using an EG&G/PAR model 263A potentiostat/galvanostat controlled by a PC. All measurements were taken at room temperature without further temperature control. BDD electrodes were purchased from Swiss Center for Electronics and Microtechnology, Inc. (Neuchatel, Switzerland). The electrodes were annealed with a hydrogen flame before use. The effect of hydrogen flame annealing is described later. The electrochemical cell was a single-compartment cell made of Teflon, with the surface of the BDD working electrode (area = 0.19 cm^2 if otherwise stated) exposed at the bottom of the cell through an O-ring supported opening. The counter electrode was a platinum foil, and the reference electrode was a homemade Ag/AgCl (in saturated KC1) electrode. All potentials mentioned in this paper are in reference to this electrode unless otherwise stated.

2.3. X-ray photoelectron spectroscopy

Ex situ X-ray photoelectron spectroscopy (XPS) spectra were obtained with a VG ESCALAB 220i equipped with an Mg anode (Mg Kα radiation, 1253.6 eV) run at 15 kV and 20 mA. The instrument was typically operated at a pressure near 1×10^{-8} Torr in the analysis chamber.

2.4. Glucose monitoring

A commercial blood glucose monitor (Glucotrend 2) from Roche Diagnostics GmbH (Mannheim, Germany) was used to compare and verify the new method with real blood samples.

2.5. Electrode preparation/treatment

BDD electrodes were cleaned using a two-part acid-washing procedure [23]. First, the electrodes were immersed in hot aqua regia for 30 min and rinsed with deionized water to remove metallic impurities. Second, the electrodes were immersed in warm H_2O_2 for 30 min to remove nondiamond carbon impurities from the electrode surface. The electrodes were rinsed again with deionized water and annealed with a hydrogen (99.99%, BOC Gases, Korea) flame. A continuous sweeping motion was used to anneal the entire electrode surface with the hydrogen flame for 10 min. The electrodes were then left to cool down to room temperature in air. Before electrochemical experiments, the electrodes were cycled in 1 M NaOH between 0 and 0.8 V versus Ag/AgCl until a reproducible background voltammogram was obtained. This usually required 5–10 cycles.

3. Results and discussion

3.1. Potentiodynamic glucose oxidation

Fig. 1 shows a series of cyclic voltammograms (CVs) for the oxidation of glucose at various concentrations in a 1.0 M NaOH solution. The CVs show an oxidation peak corresponding to the oxidation of glucose at about 650 mV versus Ag/AgCl. It can be seen that glucose is easily oxidized at BDD electrodes. For each CV, the upper curve represents the oxidation (forward) scan, while the lower curve represents the reduction (reverse) scan. An interesting feature of the CVs is that an anodic peak also appears during the reverse scan. This indicates that glucose is strongly adsorbed on the electrode surface, and is continuously oxidized during the reverse scan. The shape of the CVs are similar to those of polyamines and organic acids at BDD electrodes, described by Koppang et al. [11] and Chailapakul et al. [12], respectively. The reaction mechanism involves anodic oxygen transfer reaction between adsorbed OH radicals and adsorbed polyamines. The oxidation of aromatic organic compounds also follows a very similar reaction pathway [24–26]. The