



Use of interelectrode material transfer of nickel and copper-nickel alloy to carbon fibers to assemble miniature glucose sensors



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ARTICLE INFO

Keywords:

Non enzymatic glucose sensor
Anodic dissolution
Nickel nanoparticles
Copper nickel alloyed nanoparticles
Carbon fiber microelectrode

ABSTRACT

Electrochemical deposition of the material released by anodizing nickel and copper nickel alloy in pure water onto carbon fiber microelectrodes was used to assemble miniature glucose sensors. The composition and morphology of the deposits was investigated by scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. The deposition of anode-derived materials proceeded by two consecutive mechanisms, which are explained in detail. The electrochemical properties of the designed electrodes were subsequently investigated by cyclic voltammetry and electrochemical impedance spectroscopy. The different Ni- and mixed CuNi-modified microelectrodes were examined as glucose sensors and the best performing electrodes based on the alloyed deposit exhibited very high sensitivity ($5720 \mu\text{A mM}^{-1} \text{cm}^{-2}$), low detection limit ($0.3 \mu\text{M}$) and ability to quantify glucose in blood serum.

1. Introduction

The determination of carbohydrates is highly relevant in the fields of biochemistry and food chemistry [1–5]. Carbohydrates, despite of their great significance, are regarded as difficult-to-determine compounds and have been subject of concern to many researchers for decades. Electrochemical techniques represent a mainstream analytical approach to detect carbohydrates in general and glucose in particular due to the difficulty to use other techniques e.g. spectroscopic (lack of chromophores for UV/VIS and fluorophores for fluorimetry, structural similarities for IR/Raman and mass spectrometry etc.) [6]. Generally, electrochemical methods for detecting and quantifying glucose fall into two categories: enzymatic [7,8] and non-enzymatic [9,10]. The former is glucose specific due to the use of glucose oxidase enzyme whereas the latter is broadly adaptable and may be used to detect not only glucose, but also an assortment of other carbohydrates.

It is generally accepted that the performance of glucose non-enzymatic sensors is based on the reaction of glucose with highly valent solid state Cu(III) [9] or Ni(III) oxides/hydroxides [11] generated in situ at the working potential (typically 500–600 mV vs. Ag/AgCl), in alkaline environments, despite some debate concerning the exact

identity of the Cu(III) species [11]. However, the properties of the Cu, Ni and CuNi based sensors strongly depend on the composition of the modifying layer, its morphology, adherence to the underlying substrate etc. This is reflected on the figures of merit of the assembled sensors where especially the sensitivity exhibits large variability. The sensitivities of the Cu-based sensors reported in the last decade vary greatly from 79 [12] to 3643 [13] $\mu\text{A mM}^{-1} \text{cm}^{-2}$. Even broader range from 62 [14] to 7320 [15] $\mu\text{A mM}^{-1} \text{cm}^{-2}$ can be found in the literature for Ni-based sensors. The application of mixed CuNi materials leads to improvement in response stability and noise while maintaining approx. the same sensitivities as the Ni-based sensors [16]. This effect can be explained by the suppression of unstable $\gamma\text{-NiOOH}$ phase formation in the CuNi sensing layer [17]. Recent examples of the use of mixed CuNi materials for glucose sensing include nickel-copper oxide nanowires yielding the sensitivity of $5610 \mu\text{A mM}^{-1} \text{cm}^{-2}$ [18], Cu-Ni nanocomposites synthesized via the polyol reduction method ($64 \mu\text{A mM}^{-1} \text{cm}^{-2}$) [19] and two sensors based on N-doped graphene decorated with CuNi nanoparticles. The sensitivity of $1847 \mu\text{A mM}^{-1} \text{cm}^{-2}$ was reported for solvothermally prepared hybrid of CuNi nanoparticles and N-doped graphene [20] while a highly sensitive sensor ($7143 \mu\text{A mM}^{-1} \text{cm}^{-2}$) was prepared by heating the

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<https://doi.org/10.1016/j.jelechem.2018.03.039>

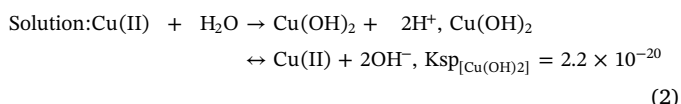
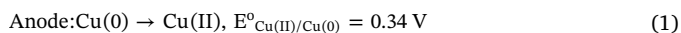
Received 22 January 2018; Received in revised form 16 March 2018; Accepted 20 March 2018

Available online 21 March 2018

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mixture of graphene oxide, urea, nickel and copper nitrate at 900 °C [21].

The procedures and protocols of sensors' assembly are being continuously developed and optimized. Currently, an effort is being made to develop “green and facile” procedures which are fast and robust and do not require high consumption of toxic and/or expensive chemicals, multiple steps, etc. Our previous works [22–24] have demonstrated that nanostructured deposits of silver and copper can be prepared by in situ cathodic reduction of the material released during the anodization of silver or copper in ultrapure water. According to our observations, silver and copper deposits are formed by electrochemical reduction of their free cations, which exist in equilibrium with insoluble anode-derived material, for example of copper [23]:



The restriction of the maximum concentration of free copper ions imposed by solubility equilibrium and the benefits of working in unsupported medium ensure that the nucleation prevails over particle growth, providing metal-nanostructures rather than smooth or larger particles containing deposits [25]. In this work we demonstrate that the technique can be further developed to allow for material depositing formed by anodization of Ni and even mixed material, such as copper-nickel alloy. Nickel and copper-nickel alloys are known to form compact oxide layers upon anodization and only a low amount of anodic material is released into the interelectrode space [26]. The amount of the material obtained in both cases was found to be sufficient to modify carbon fiber microelectrodes in the time interval of approx. 20–40 min during which time two different modes of the deposition process operate. Initially, nanoparticulate deposits are formed by electrochemical reduction. After certain threshold time, thicker deposits of oxidic nature are formed, presumably due to electrophoretic deposition (i.e., deposition of colloidal particles suspended in the electrolyte that migrate under the influence of the applied electric field). These layers are shown to serve as excellent electrocatalytic surfaces for the anodic oxidation of glucose in alkaline medium, permitting to construct miniaturized glucose sensors.

2. Experimental

2.1. Reagents

Sodium hydroxide, ascorbic acid, uric acid, potassium chloride, paracetamol, potassium hexacyanoferrate (II) were Sigma-Aldrich compounds. D-glucose was purchased from Penta, Czech Republic. All reagents were of p.a. purity and stock solutions were prepared using ultrapure water, produced by Millipore Smart Direct Q-3 UV system.

2.2. Carbon fiber microelectrodes (CFMEs)

Individual polyacrylonitrile-based carbon fibers (Sigrafil C30, 7 µm in diameter) were glued onto copper wires (d = 0.4 mm) using Epotek H20E (Polytec, Germany) conductive epoxy. Glass electrode bodies were fabricated by pulling hematological capillaries (Keraglass, Czech Republic) using Narishige PC10 capillary puller. Each fiber with attached copper contact was heated to 120 °C for 30 min in order to cure the epoxy and then fitted into a glass electrode body so that about 5 mm of the fiber was left protruding from its tapered end. Both ends of the capillary were sealed using epoxy resin (L-200, Havel Composites Inc., Czech Republic). The fiber end of the electrode was briefly sonicated in dichloromethane in order to clean the electroactive surface.

2.3. CFME modification by interelectrode material transfer

For CFME modification, a NRP-3630 (Manson, Hong Kong) power supply was used. CFME was connected to its negative pole, while nickel wire (99.99%, 0.5 mm diameter, Alfa Aesar, Germany) or copper-nickel wire (0.5 mm diameter, composition, Cu:Ni 55:45 wt%, Alfa Aesar, Germany) was connected to the positive pole. The CFME and the metal anode were placed 1 cm apart into a quartz beaker filled by ultrapure water, which was used as “electrolyte”, and CFME modification was attained by applying voltage of 20 V (optimized value) for 30 min, unless stated otherwise.

2.4. Electrochemical experiments

Voltammetric and amperometric measurements were performed using the Nanoampere electrochemical workstation (L-Chem, Czech Republic) in a single compartment, three-electrode electrochemical cell. A leak-free Ag/AgCl electrode (LF-2, Innovative Instruments, Inc., USA) was used as a reference electrode; this all-plastics electrode offers stable operation in alkaline solutions used in glucose sensing experiments. Platinum wire served as auxiliary electrode and bare or modified CFMEs were connected as working electrodes. Amperometric experiments were performed in stirred solutions (300 r.p.m.) using MIX1 eco (2mag, Germany) magnetic stirrer. The analyte (glucose) was dosed by Titronic® basic (Schott Instruments, Germany) automatic burette interfaced to a PC and controlled by dedicated software (L-Chem, Czech Republic). Voltammograms and amperograms were processed using ElchemViewer software [27]. Electrochemical impedance spectroscopy spectra were recorded with the electrochemical analyzer PGSTAT12/FRAII (Metrohm Autolab BV) over the frequency range 10^{-1} – 10^5 Hz, using a sinusoidal excitation signal, superimposed on i) +0.200 V and ii) +0.700 V DC potential values. Excitation amplitude of 10 mV (rms) was used throughout. All measurements were conducted in 0.1 M NaOH at room temperature.

2.5. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX)

SEM images were obtained with a Vega 3 microscope (Tescan, Czech Republic) at 10 kV. The individual coated carbon fibers were cut off from the CFMEs and placed onto conductive carbon discs. EDX data were collected using the Quantax EasyEDS module (Bruker, U.S.A.)

2.6. X-ray photoelectron spectroscopy (XPS)

XPS studies were carried out with the PHI VersaProbe II XPS system (Physical Electronics, U.S.A) with monochromatic Al-Kα source (15 kV, 50 W) and photon energy of 1486.7 eV. All the spectra were measured in the vacuum of 1.3×10^{-8} Pa at 20 °C. The analyzed areas on each sample were spots of 10 µm in diameter. The energy resolution for high-resolution spectra was set to 0.2 eV and the photoelectron take-off angle was 45° with respect to the surface normal. The dual beam compensation was used for all measurements. All values of binding energy were referenced to C 1s peak at 284.80 eV. The obtained spectra were evaluated with the MultiPak software (version 9.4.0.7; Ulvac – PHI, Inc., Japan). Spectral analysis was carried out under the conditions of Shirley background and mixed Gaussian–Lorentzian functions.

3. Results and discussion

3.1. Anodic dissolution of Ni and CuNi in pure water

The technique under study combines anodic dissolution and electrochemical deposition of the released material. It is well known that nickel and copper nickel alloys exhibit resistance against anodic dissolution in aqueous solutions in a broad pH range by forming a

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