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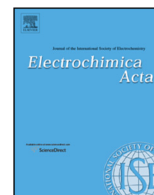

Practical Implications of using Nanoelectrodes for Bioanalytical Measurements

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ABSTRACT

The performance of a 50 nm thick nanoband electrode structure which forms an array of nano-scale electrodes has been investigated for bioelectrochemical applications, specifically the performance related to the detection of three common bioelectrochemical redox species, ferrocene carboxylic acid, hydrogen peroxide and 4-aminophenol. The detection limits were established to be 89, 2 and 36 $\times$ 10^{-9} mol dm^{-3} respectively, which is consistent with the increased sensitivity of nanoelectrode systems compared to larger electrodes. The limit of detection determined for H_2O_2 is comparable to those previously obtained by using both nanowires and modified electrodes for enhanced detection suggesting these arrays are highly suited for use in bioanalysis. This relatively simple nanoband electrode architecture is shown to be capable of fast scan cyclic voltammetric detection up to 10 V s^{-1} while at the same time being relatively insensitive to hydrodynamic perturbations. The paper considers the implications of these enhanced performance characteristics within bioanalytical measurement systems and their practical benefits in the development of electroanalytical devices.

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1. Introduction

Nanoelectrodes have been of intense interest for the past two decades in the field of bioelectrochemistry. The potential benefits of nanoelectrodes compared to electrodes of larger dimensions have been demonstrated by numerous workers and they are very well understood from a theoretical perspective. Such benefits include enhanced mass transport, increased signal-to-noise ratio, greater sensitivity and increased immunity to hydrodynamic perturbations [1–4]. However, there still remain considerable challenges in the production of robust, reproducible nano-scale devices and the extent to which these theoretical benefits can be realised experimentally. This arises, at least in part, from the complexities involved in nanoelectrode fabrication and the verification of electrochemical performance post fabrication [2]. More recently, the fabrication of reproducible nanoelectrode arrays with highly controlled electrode geometry, array spacing and quantifiable response has been achieved by taking advantage of processes and equipment more readily associated with semiconductor fabrication technology [5–8].

One of the key potential applications of nanoelectrodes is in bioanalytical measurement systems e.g. for healthcare applications. In principle, the theoretical benefits of nanoelectrodes can be exploited to give enhanced Limits Of Detection (LOD) for a range of physiologically relevant redox active biomolecules, especially as the critical dimension of the nanoelectrode approaches the molecular scale [2]. A key area of interest would be to improve the overall performance of bioelectroanalytical devices through this enhanced sensitivity. The objective of this paper is to demonstrate the practical feasibility of this approach.

1.1. Nanoband electrode characterisation

Previously, we have described the precise semiconductor processes employed to produce a model nanoband electrode structure (the Microsquare Nanoband Edge Electrode (MNEE) array system [5]) and the enhanced performance benefits observed compared to a single microdisc electrode of comparable electrode area under similar experimental conditions [5–7]. In the previous papers the characterisation of these structures for several electrode geometries and dimensions has been undertaken in detail [6]. This work demonstrated good agreement between finite element

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simulations and experimental measurements of the nanoarray response, giving, under conditions when each electrode in the array behaves independently with no neighbouring diffusion field overlap, steady-state limiting (mass transport controlled) currents, I_L, consistent with the following equation:

$$I_L = BNnFDc_\infty L \quad (1)$$

where B is a constant based on the electrode geometry, N is the number of microsquare apertures with nanobands in them, n is the number of electrons transferred, F is Faraday's constant, D is the diffusion coefficient of the redox species, c_∞ is the bulk concentration of the redox species and L is the microsquare edge length. The value for B obtained for single microsquare [8] and nanoarray systems were shown to be comparable (with $B = 0.96$ for MNEE, 41% of the microsquare current with only 2% of the effective electrode area). This was taken to indicate that the performance of the contribution of edge diffusion to the limiting current in microsquares is such that the MNEE (which from impedance and voltammetric measurement appears to correspond with good approximation to an array of microsquare edge electrodes) produces a comparable mass transport limiting current (signal) to the equivalent microelectrode array, whilst markedly decreasing the electrode area and hence the non-Faradaic electrode response (the noise) [6]. Furthermore, the observed time, t, at which deviation of the response from equation 1 occurs in experiment and modelling in stagnant solution, due to onset of diffusion field overlap between the neighbouring array electrodes was shown [6,7] to be consistent as expected with that predicted from equation 2, calculated using the diffusion coefficient, D, of the redox species and the distance, l, between electrodes:

$$l = 2(Dt)^{1/2} \quad (2)$$

There was also a demonstrated insensitivity of response to forced convection [6,7]. These enhanced characteristics observed using standard redox couples motivates this study.

In this paper the response of the model nanoband electrode structure to common bioelectrochemical redox species, ferrocene carboxylic acid (FCA), hydrogen peroxide (H_2O_2) and 4-aminophenol (4AP) is determined to assess the achievable performance of a nanoelectrode system. The reported data (the measured LODs, the potential modes of interrogation, the temporal characteristics when conducting Fast Scan Cyclic Voltammetry (FSCV) and the effects of hydrodynamic perturbations) are discussed in terms of the breadth of applications for such nanoband electrode structures and their potential benefits in the development of electroanalytical devices for enhanced bioanalytical measurements.

2. Experimental

2.1. Materials

Ferrocene carboxylic acid (FCA, >97%, Sigma Aldrich, UK), sodium citrate dihydrate (>99% ACS grade, Sigma Aldrich UK), citric acid (ACS grade, Sigma Aldrich, UK), potassium nitrate (99%, Arcos Organics, Belgium), potassium hydroxide (Lab Grade, Fisher Scientific, UK) and potassium chloride (99% Fisher Scientific, UK), 4-aminophenol (4AP, 97%, Arcos Organics, Belgium), Dulbecco's Phosphate Buffered Saline (PBS) (MP Biomedicals LLC, USA) aqueous hydrogen peroxide (H_2O_2, 30% in water, Fisher Scientific, UK), sulfuric acid (99.999% purity, Sigma Aldrich, UK) were used without further purification. All solutions were prepared using deionised water with a measured ionic resistivity of 18.2 MΩ cm and N_2 was passed through all solutions for 15 minutes prior to experimentation to ensure complete sparging of oxygen. Prior to experimentation, the glassware was rinsed in concentrated sulfuric acid and then thoroughly rinsed in deionised water.

2.2. Instrumentation

Electrochemical experiments were carried out in a Faraday cage using a DY2322 digital bipotentiostat (Digi-IVY, USA) or an Autolab PGSTAT128 N (Metrohm Autolab, NL). The instruments were controlled and the data collected using the appropriate proprietary control and data acquisition software provided, DY2300EN (Digi-IVY, USA) and NOVA version 1.9 (Metrohm Autolab, NL) respectively. An electrochemical cell of 120 ml total volume was used with a 10 cm length, 0.5 mm diameter platinum (Pt) wire as counter electrode (Fisher Scientific Ltd, UK) and a 12 mm diameter Saturated Calomel Electrode (SCE) as the reference electrode (Scientific Laboratory Supplies, UK). All potentials, E, are quoted with respect to the SCE unless otherwise stated. Electrochemical experiments were carried out at 293 K with temperature control being achieved using a GA100-S5 circulating water bath (Grant, UK).

2.3. Working electrode

2.3.1. 50 nm nanoband electrode system

A 50 nm Pt nanoband electrode (also referred to as the MNEE [5,6]) was used as the working electrode (CAVIARE^{TM} Nanoelectrode Substrate, Platinum 303D, NanoFlex Ltd, UK). The electrode consisted of an array of 30×30 μm edge length square apertures with a 120 μm pitch producing 42×42 square elements. Within each aperture there is a 50 nm thick layer of exposed Pt, which forms a nanoband electrode positioned halfway up the vertical walls (1.05 microns high in total) of each aperture (Fig. 1). The aperture array occupies a 5×5 mm footprint with a total of 1764 electrodes and a total exposed Pt area of 0.0106 mm^2. The architecture is described in detail elsewhere [5,6]. The substrate was electrically connected via the contact pad using a commercial nanoelectrode substrate holder (NanoFlex Ltd, UK) which enabled the substrate to be immersed into the solution and to be interrogated by commercial potentiostat systems. Electrochemical conditioning of the electrode was carried out using cyclic voltammetry in 0.1 mol dm^{-3} aqueous potassium chloride using a scan rate of 0.1 V s^{-1} between potentials of -0.5 and 1.9 V with respect to the SCE.

2.4. Cyclic voltammetry

Cyclic voltammetry was conducted to determine the electrochemical behaviour of each bioelectrochemical redox species, FCA, H_2O_2 and 4AP using the 50 nm nanoband electrode.

2.5. Chronoamperometric measurements

Serial additions of typically 10 μl aliquots of the analytes, FCA (0.16 mmol dm^{-3}), H_2O_2 (0.1 mmol dm^{-3}) and 4AP (0.1 mmol dm^{-3}) were added to 50 ml aqueous electrolyte solution and the solutions stirred for 30 seconds to ensure thorough mixing. The stirrer was then stopped immediately after 30 seconds and chronoamperometric measurements (5 replicates) were recorded with the 50 nm nanoband electrode at fixed potentials with respect to the SCE. The steady state current was analysed immediately after the potential pulse (estimated to be after 100 μs), at 1.5 and at 3 s. Longer timescales were not used due to the onset of diffusion field overlap between neighbouring elements of the array after 3 s [7]. A 10-point calibration curve was generated to demonstrate the change in the measured current (I) as a function of the analyte concentration.

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