



Electrochemical redox cycling in a new nanogap sensor: Design and simulation



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ABSTRACT

We propose a new geometry for nanogap electrochemical sensing devices. These devices consist of two closely spaced side-by-side electrodes which work under redox cycling conditions. Using finite element simulations, we investigate the effects of different geometric parameters on the redox cycling signal amplification to gain insight into the electrochemical sensing performance of the device design. This will allow optimizing the sensor performance of devices to be fabricated in the future.

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1. Introduction

Micro/nanoelectrode systems have been extensively studied for electrochemical (bio)sensing applications due to their fast response time, small capacitive currents and steady-state voltammetric response, which compare favorably to macroelectrode systems [1]. However, the small surface area of these electrodes limits their sensitivity, in particular at low analyte concentrations, due to the limited sensitivity of electronic instrumentation [2]. One way to circumvent these limitations is to configure the electrodes in a dual mode, thereby taking advantage of redox cycling between them. In this way, the concentration profiles of both species overlap, allowing the species generated at one electrode to be efficiently collected at the other electrode. Such successive oxidation and reduction of analyte molecules as a result of the inter-diffusion between two closely spaced electrodes lead to current amplification and, thus, the detection limit of electrochemical sensors is lowered [3–5]. These systems are a modified version of rotating ring disc electrodes operating in generator–collector mode which were in particular developed by Albery and Hitchman [6,7] followed by the development of numerous electrode geometries and techniques such as double-band channel electrodes [8], micro-ring-disc electrodes [9], micro-electrode arrays [10], interdigitated electrodes [11], dual microdisc electrodes [12], and junction electrodes [13]. A summary of the variety of geometries and applications can be found in reference [14].

The advantages of the redox cycling devices are not only limited to an improvement of the sensor sensitivity by amplification of faradic currents [11,15]; they are also powerful tools for determining diffusion coefficients of redox species [8,16] and monitoring the lifetime of electrogenerated intermediates [17,18]. One widely used type of redox cycling devices is thin layer cells which consist of two planar electrodes separated by a thin layer of liquid [19]. Recently, Marken *et al.* developed a simple method for the preparation of dual-plate electrode systems with a micrometer gap *via* etching a thin epoxy layer between the two electrodes [20–22]. Despite the advantage of a simple and innovative fabrication methodology, the gap size is limited to the micrometer length scale, and the method is not compatible mass fabrication needed for many practical applications. The sensitivity of any thin layer cell sensor is increased by reducing the gap size between the two electrodes [21]. However, reducing the gap size to the nanometer range requires cleanroom facilities and multi-step photo or e-beam lithography techniques [19] as demonstrated in pioneering works by Lemay *et al.* [23,24]. In this approach, nanogap devices are fabricated layer-by-layer. Subsequent to the microfabrication, a sacrificial chromium layer separating to metal electrodes is wet-etched, creating a nanochannel and completing the formation of the nanogap sensor. The sensitivity of these nanogap devices allows even single-molecule detection [25,26], and they have been used for a variety of applications [24,27,28]. Considering the need for more sensitive sensing devices, there exists a demand for new nanogap sensors which are simpler to fabricate. Various geometries and fabrication method have been suggested in last few years [4,29]. We currently aim at the fabrication of a new type of nanogap sensor consisting of two closely spaced side-by-

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side electrodes. Comparable redox-cycling sensors with side-by-side electrodes have been realized by a variety of fabrication methods using different electrode materials [30–32]. All of these sensors employ side-by-side electrodes in interdigitated geometries. However, they operate in a microscale regime with gap sizes above 1 μm and, thus, do not benefit from the unique advantages of nanoscale sensors such as highest amplification factors. Side-by-side interdigitated electrodes with sub-micrometers distances have been fabricated, but only employed for impedance sensing [33].

In the present work, we employ numerical finite element simulations to study the electrochemical sensing behavior in a new nanogap design. By evaluating the influence of geometric parameters as well as electrode potentials on the sensor performance an understanding of design rules is gained for future device fabrication.

2. Methods

2.1. Sensor geometry

The nanogap sensor consists of two closely spaced electrodes positioned next to each other (see Fig. 1). The top sides of both electrodes are passivated to avoid a contribution to the electrochemical signal.

COMSOL Multiphysics (version 4.4) was employed to simulate the electrochemical processes and mass transport of analytes in the nanogap sensor. We assume an unstirred solution (with the exception of Section 3.5) and a high supporting electrolyte concentration. Therefore mass transport is diffusive, and convection and migration are not considered. The effects of various design parameters, namely the gap size, the thickness of the top isolating layer, the electrode thickness, the collector potential and the flow rate (see Section 3.5) were studied, and their influence on the current signal and the signal amplification factor was determined.

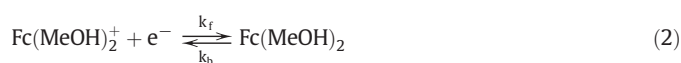
The geometry of the device allows simplifying the simulation to a two-dimensional geometry. Fick's second law describes diffusion of species:

$$\frac{\partial C_j}{\partial t} = D_j \nabla^2 C_j. \quad (1)$$

C_j and D_j are the concentration and diffusion coefficient of a redox species j . For simplicity, we consider equal diffusion coefficients for both oxidized and reduced species (see Table 1).

2.2. Electrochemical reactions

The archetypical redox reaction



was simulated at the electrode surfaces. k_f and k_b are as the forward (reduction) and backward (oxidation) rate constants. The current was defined based on Butler–Volmer kinetics as [34].

$$i = nF[c_0 k_b - c_R k_f] \quad (3)$$

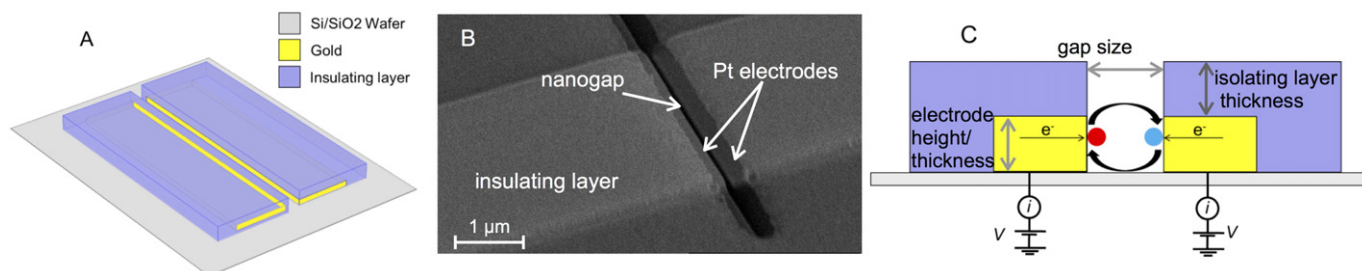


Fig. 1. (A) Schematic of the proposed nanogap sensor, (B) scanning electron micrograph of a precursor of a device acquired at a 30° angle, and (C) schematic side view.

Table 1

Constants used in the current simulation processes [23,29].

D_O	$6.7 \times 10^{-10} \text{ m}^2/\text{s}$	α	0.49
D_R	$6.7 \times 10^{-10} \text{ m}^2/\text{s}$	F	96,485 C/mol
k_0	0.06 m/s	R	8.31 J/K
E_{std}	0.251 V vs. Ag/AgCl	T	298 K

$$k_f = k_0 \exp\left[\frac{-\alpha F (E - E_{std})}{RT}\right] \quad (4)$$

$$k_b = k_0 \exp\left[\frac{(n - \alpha) F (E - E_{std})}{RT}\right] \quad (5)$$

Here, k_0 is the 'standard electrochemical rate constant', α : 'transfer coefficient', F : Faraday constant, E : electrode potential, E_{std} standard potential of the redox couple, n : number of electrons transferred in the redox reaction, c_O and c_R concentration of the oxidized and reduced species, respectively.

2.3. Model geometry

In our simulation, two electrodes are considered with variable thicknesses and a 3 μm width (*i.e.*, the length of the gap in the third dimension which is not simulated explicitly). The electrodes are located at close distance next to each other. An isolating layer is considered above each electrode with a defined thickness. Finally, a solution containing 1 mM $\text{Fc}(\text{MeOH})_2$ in fills the gap and a reservoir above the device. All potentials are defined versus a Ag/AgCl reference electrode.

Table 1 lists the value of the constants used in the simulation based on experimental values reported in the literatures [23,29]. However, the choice of the electrolyte as well as the electrode material and electrode surface conditions can affect these constants [23,35]. In all dual mode studies, the right electrode (generator) was swept in the potential range of 0–0.5 V vs. Ag/AgCl, while the left electrode (collector) was kept constant at a cathodic potential (0 V, except for studying the effect of varied collector potentials, see Section 3.4). Under these conditions, the oxidized species are produced at the generator electrode, the majority of this species is reduced again at the collector electrode and then diffuses back to the generator electrode for re-oxidation.

3. Results and discussion

3.1. Study of the gap size

One important feature in the design of nanogap sensors is the distance between the two electrodes [28,36]. Reducing the gap size enhances the current amplification due to a shorter diffusion time between the two electrodes [23,37]. Thus, we studied this effect on the current amplification factor, which we defined as the ratio between the generator limiting current in dual mode to the current in single mode. (As shown in the cyclic voltammograms in Fig. 2B, the single-

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