Short communication

Boron-doped diamond dual-plate microtrench electrode for generator–collector chloride/chlorine sensing

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ABSTRACT

A novel generator–collector dual-plate boron-doped diamond microtrench sensor is fabricated and its operation demonstrated for chloride/chlorine detection in the harsh anodic potential range. Detection is made sensitive by minimising the inter-electrode gap to ≤10 μm wide and setting the generator and collector potentials to enable repetitive redox cycling. The concentration and potential-dependant impact on the generator and collector currents are reported and optimised conditions suitable for quantitative determination are demonstrated. The diffusional redox cycling currents for chloride in buffer solution are kinetically controlled and first order over a concentration range of 1 to 140 mM.

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1. Introduction

Generator–collector dual-plate sensor electrodes have been pioneered by Anderson [1,2] and Reilley [1–3] and treated theoretically, for example, by Peters and Hubbard [4]. The benefit of mass transport enhancement of redox-active species was recognised early on and applied in particular for the study of reaction kinetics [1,2]. More recently in pioneering work by Lemay, Wolfrum and coworkers [5–7], dual-plate sensor systems have been developed down to the nanoscale opening up the possibility of single molecule detection [8].

Recent applications of dual-plate or microtrench electrodes include femtolitre pH titration [9], ion transport studies [10], pH modulation [11], and analytical detection of dopamine and ascorbate [12] and cysteine/cysteine [13]. A severely limiting factor of current dual-electrodes is surface corrosion and stability under harsh anodic and cathodic potentials. One possibility to overcome this limitation is to employ sp³-hybridised carbon electrodes such as boron-doped diamond (BDD). BDD has been applied in electroanalysis for many years [14,15] due to benefits in particular at extreme anodic conditions where reactive intermediates may be studied, such as hydroxyl radicals, without significant deterioration of the electrode [16,17]. Macpherson and coworkers very recently reported a method for fabricating BDD co-planar dual-electrodes that offers excellent reproducibility and versatility and a minimum feature size of 50 μm [18].

In this work, we describe for the first time a simple and low-cost method for the fabrication of dual-plate or "trench" BDD electrodes with low microscale inter-electrode gap size. Chloride/chlorine detection is demonstrated and the special case of gas evolving electrode processes in microtrench geometries is discussed.

2. Experimental

2.1. Reagents

Sodium chloride (98%), potassium chloride (≥99%), mono-sodium phosphate monohydrate (98–102%), di-sodium hydrogen phosphate heptahydrate (98–102%), sulphuric acid (≥95–98%), hydrogen peroxide (30 wt.% in water), acetone (≥99.5%) and isopropyl alcohol (≥99.5%) were purchased from Sigma-Aldrich, UK. Hexaammineruthenium (III) chloride (Ru(NH₃)₆Cl₃, 99%) and SU-8 2002 negative photoresist were purchased from Strem Chemicals and Microchem Corp., respectively. Aqueous solutions were prepared using ultrapure water at 20 °C (resistivity ≥ 18.2 MΩ cm).

2.2. Instrumentation

Electrochemical measurements were performed at 20 ± 2 °C using an SP-300 bipotentiostat (Biologic, France). A four-electrode cell was employed with a Pt wire counter electrode, saturated calomel electrode (SCE, Radiometer), and the two working electrodes of the microtrench. A PWM32 spin coater (Headway) was used to spin photoresist. Scanning electron microscopy (SEM) images were obtained with a JSM-6480LV (JEOL, Japan).

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2.3. Electrode fabrication

BDD-coated p-doped Si substrates (300 nm BDD, SiO$_2$/Si$_3$N$_4$ interlayer, 8000 ppm doping and resistivity = 10 mΩ cm) were purchased from NeoCoat SA, Switzerland. The 5 mm × 20 mm substrates were first rinsed successively with ultrapure water, acetone and isopropyl alcohol then dried with a stream of nitrogen. Kapton tape (Farnell, UK) was applied on the top of the substrates at one end to define a ≈ 5 mm × 5 mm region for electrical contact. The BDD substrates were subsequently spin-coated with a single coat of SU-8-2002 photoresist using a first step at 500 rpm (15 s) and a second step at 3000 rpm (30 s). Next, the Kapton tape was removed and the two substrates were pressed together face-to-face. The substrates were placed on a hot plate pre-heated to 90 °C for 2 min then heated at 160 °C for 5 min. After cooling to room temperature, the end of the BDD electrode was sliced-off with a diamond cutter (Isomet 1000, Buehler) and polished using decreasing grits of SiC abrasive paper (Buehler). The SU-8 layer was partially etched out using piranha solution (5:1 sulphuric acid:hydrogen peroxide) to form the trench (Fig. 1). SEM images in Fig. 1b and c demonstrate the trench width of approximately 9 ± 1 μm.

3. Results and discussion

3.1. Generator-collector voltammetry at a BDD dual-plate sensor I: aqueous Ru(NH$_3$)$_6^{3+/2+}$

Initial experiments were performed to characterise the reactivity of the BDD electrode and to calibrate the trench depth. Fig. 1d shows a schematic depiction of the Ru(NH$_3$)$_6^{3+/2+}$ redox system. Fig. 1e and f shows voltammograms for the reduction of 1 mM Ru(NH$_3$)$_6^{3+}$ at the generator electrode with the collector potential held at 0.35 V vs. SCE for the back-oxidation (Eq. (1)).

$$Ru(NH_3)_6^{3+}(aq) + e- \rightleftharpoons Ru(NH_3)_6^{2+}(aq)$$
$$E^0 = -0.18 \text{ V vs. SCE [19]} \tag{1}$$
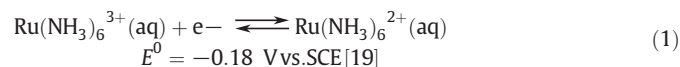
When changing the scan rate, the generator current response is affected but the collector current response remains very stable, free of capacitive current components and sigmoidal in shape (Fig. 1e and f). The collector response is therefore consistent with mass-transport controlled current amplification in the microtrench. Switching the generator and collector electrodes allows the same voltammetric responses to be obtained (Fig. 1f), indicative of a symmetric and well-defined electrode geometry.

The approximate trench depth is obtained by applying the Nernst diffusion layer model [9] and ignoring edge effects (Eq. (2)).

$$\text{Trench depth} = \frac{I_{lim} \times \delta}{nFDwc} = 7 \pm 2 \text{ μm} \tag{2}$$

In this equation I_{lim} is the collector limiting current (see Fig. 1e, i) = 0.33 μA, δ is trench width = 9 ± 1 μm, n = 1 for Ru(NH$_3$)$_6^{3+/2+}$, F is the Faraday constant, D is the diffusion coefficient = 9.1 × 10^{-10} m^2 s^{-1} [19], w is the electrode width = 5 mm and c is 1 mol m^{-3} to give trench depth. The estimated microtrench depth here is 7 ± 2 μm, which suggests a rather shallow trench with an aspect ratio of approximately
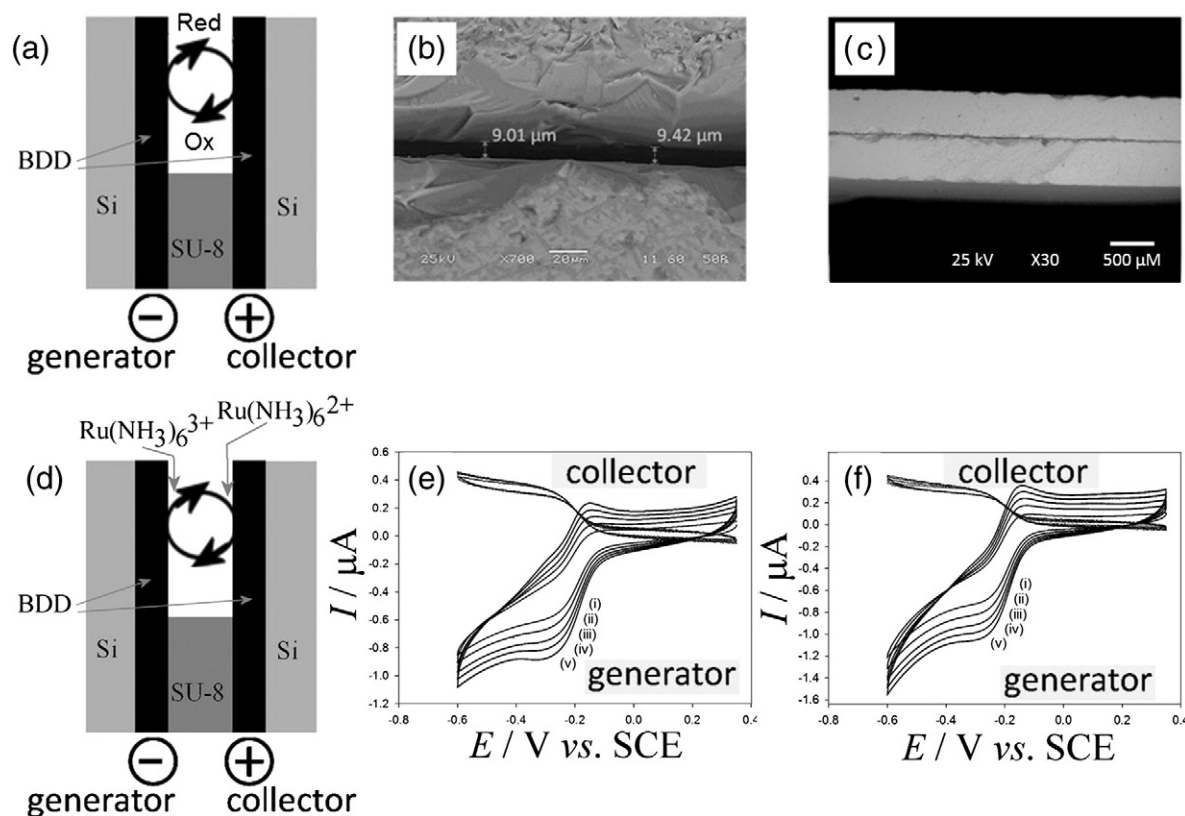

Fig. 1. (a) Schematic drawing of the microtrench sensor in feedback mode. (b, c) SEM images of the BDD dual-plate microtrench with 9 ± 1 μm inter-electrode width. (d) Schematic drawing of the Ru(NH$_3$)$_6^{3+/2+}$ redox cycle in the microtrench. (e, f) Generator and collector voltammograms obtained at a BDD microtrench in 1 mM Ru(NH$_3$)$_6^{3+}$ prepared in 0.01 M PBS pH 7.4 (0.1 M NaCl) with electrode configuration: (e) electrode one and two and (f) electrode two and one as generator and collector, respectively. Scans were recorded at scan rate: (i) 20 mV s^{-1}, (ii) 40 mV s^{-1}, (iii) 60 mV s^{-1}, (iv) 80 mV s^{-1} and (v) 100 mV s^{-1}. Collector potential fixed at 0.35 V vs. SCE.