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Pulse Electroanalysis at Gold-Gold Micro-Trench Electrodes: Chemical Signal Filtering

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Abstract

Bipotentiostatic control of micro- and nano-trench sensor systems provides new opportunities for enhancing signals (employing feedback currents) and for improved selectivity (by “chemical filtering”). In this study both phenomena are exploited with a gold-gold micro-trench electrode with ca. 70 μm width and ca. 800 μm trench depth. In “generator-collector mode”, feedback current enhancement is demonstrated for the hydroquinone/ benzoquinone redox system. Next, a “modulator-sensor mode” experiment is developed in which one electrode potential is stepped into the negative potential region (employing the normal pulse voltammetry method) to induce an oscillating pH change locally in the micro-trench. The resulting shift in the hydroquinone/ benzoquinone reversible potential causes a Faradaic sensor signal (employing chronoamperometry). This method provides a “chemical filter” by selecting pH-sensitive redox processes only and by showing enhanced sensitivity in the region of low buffer capacity. The results for the chemically reversible hydroquinone/ benzoquinone system are contrasted to the detection of the chemically irreversible ammonia oxidation.

Keywords: *pulse, pH, ammonia, hydroquinone, buffer, electroanalysis, gold electrodes, sensors, voltammetry, nano-trench, water analysis.*

1. Introduction

Generator-collector electrode systems [1] can be utilised as sensors to detect low concentrations of analyte [2] and may have many more uses in environmental or medicinal analysis [3]. There is considerable interest in particular in micro-gap or nano-gap electrode systems as pioneered by Lemay and coworkers [4,5]. These consist of two closely spaced working electrodes, where one is the generator and one the collector electrode (Figure 1). The purpose of the generator electrode is to perform either an oxidation or reduction upon the redox species. The function of the collector electrode is providing feedback to enhance the current reading and/or to give a much cleaner current response free of capacitive background [6]. Significant enhancements are possible in particular for sub-micron generator-collector gap or trench systems [7].

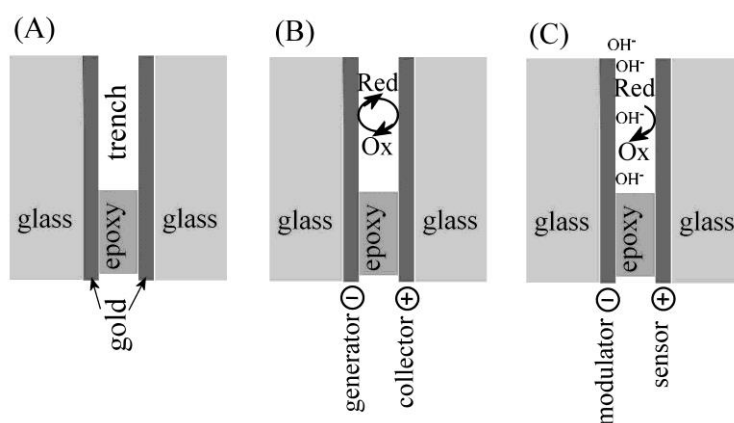


Figure 1. Schematic drawing of (A) the gold-gold micro-trench electrode system, (B) the operation in “generator-collector” mode, and (C) the operation in “modulator-sensor” mode.

A second mode of operation is possible with the first electrode (“modulator”) locally changing the pH in the micro-trench, which then leads to an oxidation at the “sensor”

electrode (Figure 1C). The geometry and the gap-width between the two electrodes is of key importance with smaller gap sizes being beneficial to faster feedback. Gold-gold double-hemisphere electrodes have been suggested [8] but due to the small active area these electrodes are of limited use in electroanalysis. Recently, it has been demonstrated with tin-doped indium oxide (ITO) plate electrodes that ITO – epoxy – ITO micro-trench designs allow excellent collection efficiencies due to the electro-generated species remaining within the confined space between the two electrodes [9]. Here a gold-gold micro-trench electrode is investigated for operation in pulse-mode.

Chronoamperometry and pulse electroanalysis has been studied before with generator-collector electrode systems. Work on “time of flight” studies in chronoamperometry mode has been performed for example at interdigitated electrodes [10] and at paired hemispherical electrodes under bipotentiostatic control [11]. The time it takes for the redox species to diffuse across the gap is determined and the diffusion coefficient of the redox species or charge carrier calculated [12]. Differential pulse voltammetry at hemispherical gold-gold electrode junctions grown by electro-deposition has been reported [13]. In previous work by Rassaei et al. a “modulator-sensor” pulse technique for gradually changing the local pH was reported for glucose detection [3]. The “modulator electrode” was pulsed to negative potentials to reduce water and produce hydroxide ions to increase the pH within the diffusion field. The oxidation of glucose on gold was then detected as Faradaic response at sufficiently high pH with fixed applied potential. Here, this methodology is developed further to demonstrate the “chemical filtering” effect.

In this report a novel gold-epoxy-gold micro-trench electrode with coplanar gold electrodes is formed (by Piranha etching of the epoxy spacer layer; see Figure 1). The co-planar gold-gold micro-trench electrode system with ca. 70 μm gap (by SEM) is investigated for pulse voltammetry electroanalysis. Examples for feedback enhancement (hydroquinone oxidation) and chemical control via localised pH shift (hydroquinone oxidation and ammonia detection) are reported. Feasibility of nano-trench electrode experiments is discussed.

2. Experimental

2.1. Reagents

Hydroquinone, phosphoric acid, sodium hydroxide, nitric acid, hydrochloric acid, sulphuric acid, hydrogen peroxide and ammonium nitrate were all purchased from Sigma-Aldrich (UK) and were used as received without further purification. All solutions were made with ultra-pure water (Barnstead) with a resistivity of not less than 18 M Ω .

2.2. Instrumentation

Electrochemical measurements were carried out on a Biologic SP-300 bipotentiostat. (Biologic, France) A four electrode arrangement was employed where the reference electrode was a KCl-saturated calomel electrode (SCE, Radiometer REF 401), the counter electrode a platinum disk and two working electrodes were the generator and collector of the gold-gold micro-trench electrode. Normal pulse voltammetry was carried out on the generator (or modulator) electrode with a step height of 5 mV, a pulse width of 1 s and a step time of 2 s. The collector electrode was held at a constant

potential and the current recorded every 0.1 seconds. SEM images were obtained with a JEOL SEM6480LV system and samples were coated in 5 nm of chromium prior to imaging.

2.3. Procedure: Fabrication of Gold-Gold Piranha Junction Electrodes

Microscope slides with a 100 nm thick layer of gold were purchased from Sigma-Aldrich (UK) and were sliced into 1.0 cm × 2.5 cm sections using a diamond cutter (Buehler Isomet 1000). Kapton (Farnell) tape was then used to mask off a strip of gold in the centre of the electrode (0.5 cm × 2.5 cm). Gold was then etched from the exposed areas using aqua regia (1:3 v/v nitric acid: hydrochloric acid; *WARNING: this solution is highly aggressive and appropriate precautions are needed*) and the slide dipped into the solution for 3 minutes. Once the slide was removed from the aqua regia solution, rinsed with water and the Kapton tape removed, the slides were put into the furnace for 30 minutes at 500 °C to oxidise the remaining conducting titanium under-layer to make it fully insulating. Two etched gold slides were then stuck together with epoxy (SP106 multi-purpose epoxy system, SP Gurit; a 1 h delay after mixing the epoxy was necessary to avoid short-circuiting of the two gold surfaces) and left in a home-made press overnight to cure. The end of the micro-trench was sliced off to reveal a surface which was then polished flat (SiC paper P320, Buehler). The epoxy in between the electrode was etched out using Piranha solution (1:5 v/v hydrogen peroxide: sulphuric acid; *WARNING: this solution is highly aggressive and appropriate precautions are needed*) to give the trench (see Figure 2).

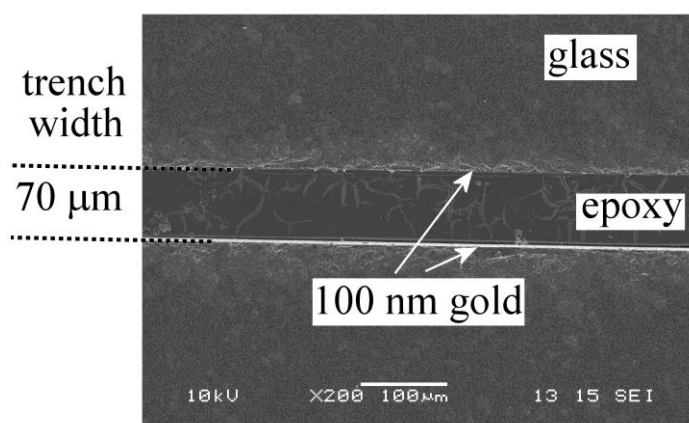
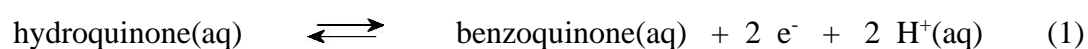


Figure 2. SEM image of the gold-gold micro-trench electrode with trench width 70 μm , electrode length ca. 5 mm, and trench depth ca. 1 mm (estimated from SEM focal planes) used in pulse voltammetry experiments.

3. Results and Discussion

3.1. Gold-Gold Micro-Trench Electroanalysis I.: Generator-Collector Voltammetry for the Oxidation of Hydroquinone

Cyclic voltammetry for hydroquinone oxidation was used as a test system to calculate/confirm the trench depth/width between the two gold plate electrodes. The oxidation of hydroquinone to benzoquinone takes place via a 2-electron 2-proton process (equation 1 [14]) with diffusional transport between the two plate electrodes.



This process is pH dependent [15] with a dependence given approximately by E_{mid} vs. $\text{SCE} / \text{V} = 0.46 - 0.059 \text{ pH}$ under the conditions used in this study. With a buffer pH of 7 the reversible potential should therefore be at $E_{\text{mid}} = 0.05 \text{ V vs. SCE}$. This is confirmed by data in Figure 3.

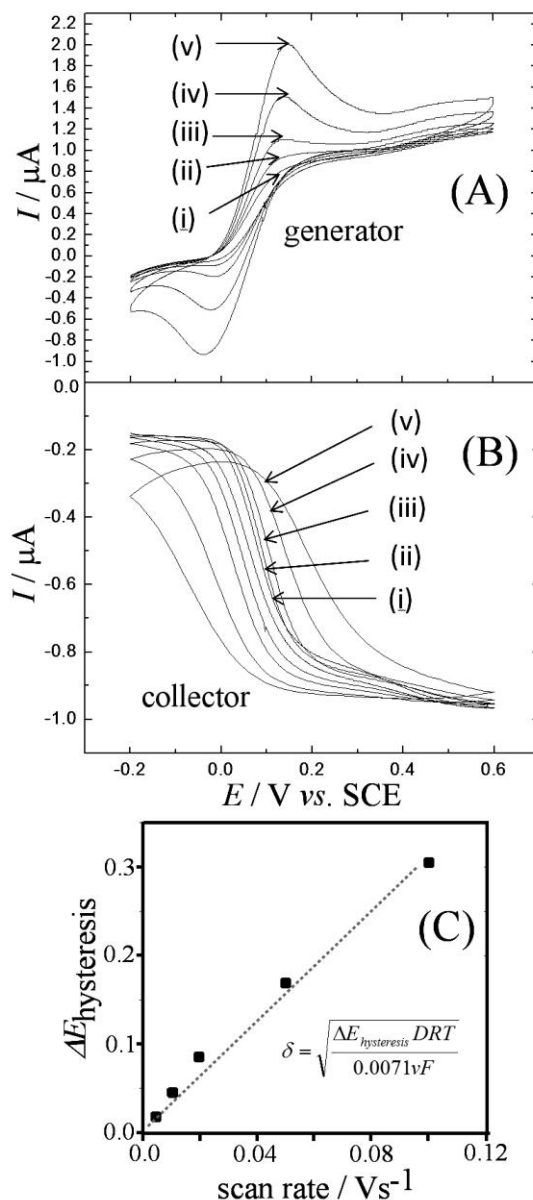


Figure 3. (A) Cyclic voltammety (generator signal, $E_{\text{collector}} = -0.2 \text{ V}$, scan rate (i) 5 mVs^{-1} , (ii) 10 mVs^{-1} , (iii) 20 mVs^{-1} and (iv) 50 mVs^{-1} (v) 100 mVs^{-1}) for the oxidation of 1 mM hydroquinone in 10 mM PBS pH 7 using the gold-gold micro-trench electrode. (B) The corresponding collector current responses. (C) Plot of the collector current hysteresis versus potential scan rate with a dotted line indicating $\delta = 90 \mu\text{m}$ (see text).

Figure 3A shows the cyclic voltammogram for the generator electrode (with $E_{\text{collector}} = -0.2$ V vs. SCE fixed) and the peak at 0.1 V vs. SCE indicating the formation of benzoquinone. A slight peak at ca. 0.5 V vs. SCE is probably due to the surface oxidation of gold. Simultaneous chronoamperometry on the second electrode was carried out with the collector electrode set at a fixed potential of -0.2 V vs. SCE (Figure 3B) and at different scan rates. Hysteresis effects (diffusional lag, see Figure 3C) were observed for the collector signal with the effect becoming more apparent with higher scan rates. The trench depth can be estimated from the steady state limiting current and the approximate Nernst layer equation 1 [16].

$$|I_{\text{generator}}| = |I_{\text{collector}}| = \frac{nFDdwc}{\delta} \quad (2)$$

Here I is the current, n is the number of electrons transferred per molecule, F is the Faraday constant, D is the diffusion coefficient of hydroquinone (ca. $0.74 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ [17]), d is the trench depth, w is the trench width, c is the concentration of hydroquinone, and δ is the inter-electrode gap. From the data ($I = 0.75 \mu\text{A}$) the trench depth is estimated as $800 \mu\text{m}$ (in agreement with SEM data in Figure 2). From the hysteresis effect in the collector current response (see Figure 3C) the trench width is

estimated as $\delta = \sqrt{\frac{\Delta E_{\text{hysteresis}} DRT}{0.0071\nu F}} = 90 \mu\text{m}$ [18], (with $\Delta E_{\text{hysteresis}}$ determined a half

height and ν the scan rate; it is assumed that in first approximation the diffusion coefficients for reduced and oxidised species are equal) which is slightly higher when compared to the value obtained by SEM (Figure 2).

Next, in order to explore the benefits of pulse electroanalysis in micro-trench systems, normal pulse voltammetry was utilised (applied to the generator electrode with the collector electrode in chronoamperometry mode with fixed potential) to study the same hydroquinone/ benzoquinone redox system. The generator was pulsed from -0.2 V to 0.6 V vs. SCE with increments of 5 mV for each pulse, pulse time was 1 second with the step time 2 seconds. Figure 4A shows the generator electrode response, which is independent of the applied potential at the collector over a range of -0.2 V to 0.1 V vs. SCE. Figure 4B shows the collector response (in chronoamperometry mode at fixed potential of -0.2 V vs. SCE), which is dominated by an oscillating current signal (see Figure 4C).

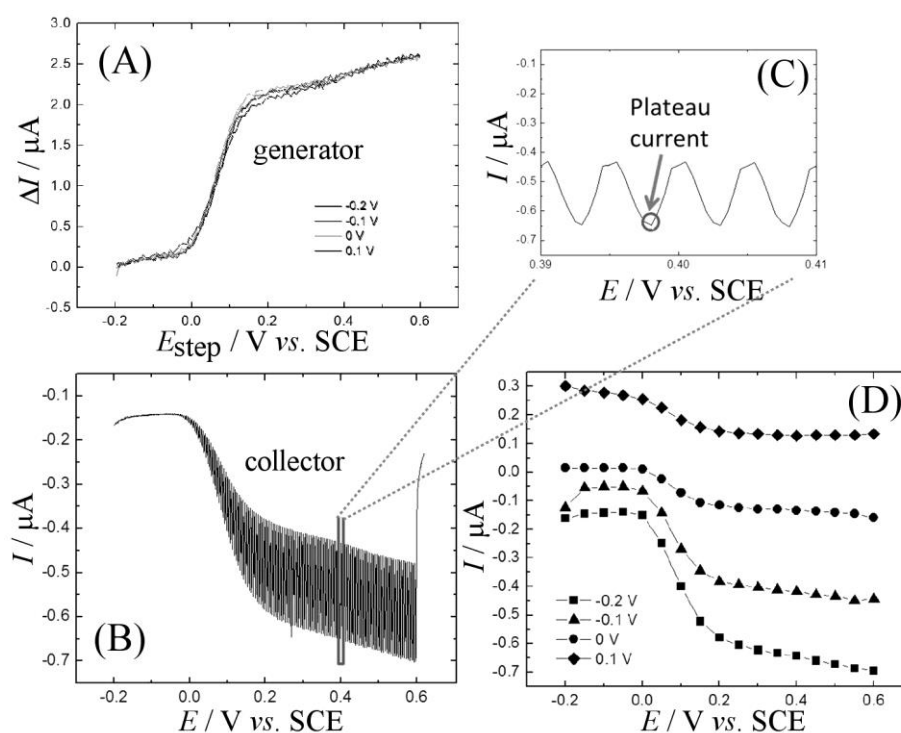


Figure 4. (A) Normal pulse voltammetry generator response (from -0.2 V to 0.6 V, 5 mV steps, pulse time 1 s, step time 2 s, collector at -0.2 V/-0.1 V/ 0.0 V/ +0.1 V vs. SCE) for the oxidation of 1 mM hydroquinone in 10 mM PBS pH 7. (B) Collector current for -0.2 V vs. SCE. (C) Magnified plot of the collector current response. (D) Plot of collector plateau currents taken every 0.05 V for the collector electrode held at -0.2 V/ -0.1 V/ 0.0 V/ 0.1 V vs. SCE.

A plot of the limiting reduction current during pulses (corresponding to close to mass transport limiting conditions) is shown in Figure 4D. Here, the potential applied to the collector electrode clearly matters and the best response is observed at $E_{\text{collector}} = -0.2$ V vs. SCE where the response appears to plateau.

3.2. Gold-Gold Micro-Trench Electroanalysis II.: Modulator-Sensor Voltammetry for the Reversible Oxidation of Hydroquinone

In a different type of measurement mode one electrode (modulator, in normal pulse voltammetry method) can be employed to modulate the micro-trench pH with the second electrode at fixed potential (sensor, in chronoamperometry method) responding to the shift in local pH. This kind of method was suggested recently for the determination of glucose [3] and is investigated here in more detail for the chemically reversible hydroquinone/ benzoquinone system. As the modulator potential is stepped more negative, a shift in pH to more alkaline conditions (depending on buffer type and capacity) is expected, associated with an oxidation at the sensor electrode in cases where the oxidation is pH dependent. A “chemical filter” effect is observed because redox systems that are not responsive to pH variation would remain undetected.

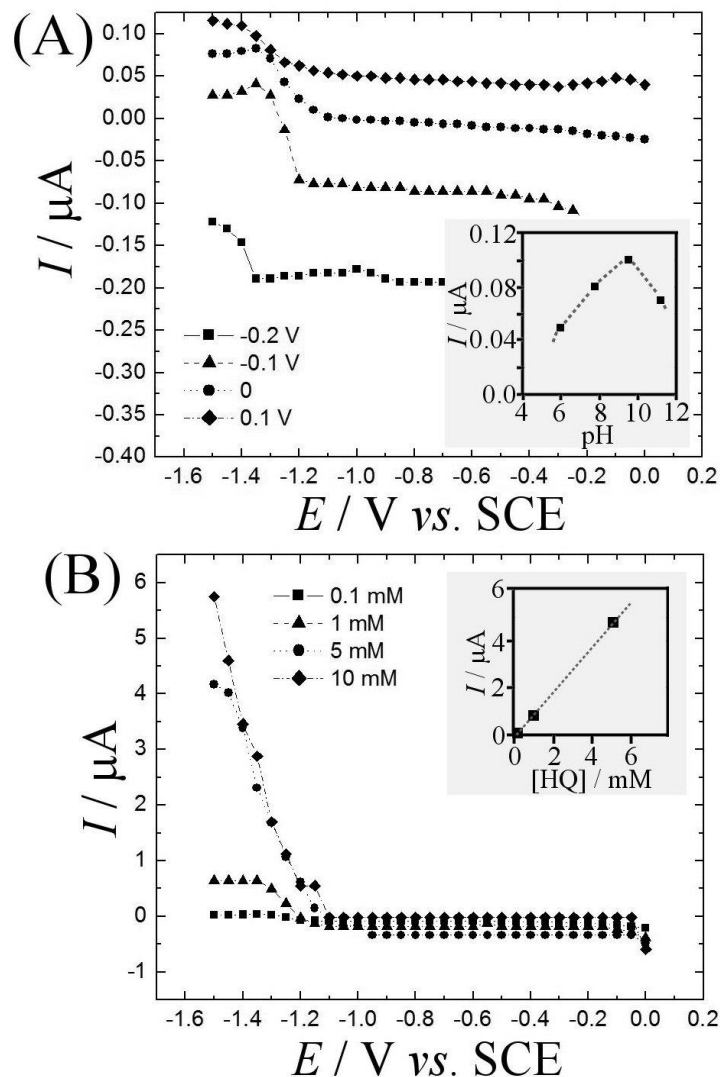


Figure 4. (A) Chronoamperometry signal (plateau currents measured every 0.05 V) for the collector electrode versus generator step potential for the oxidation of 0.1 mM hydroquinone in 10 mM PBS pH 7 held at varying fixed potentials whilst normal pulse voltammetry was applied to the generator electrode to change the trench pH. The inset shows a plot of hydroquinone oxidation current versus midpoint pH (see text). (B) Chronoamperometry signals for the collector at different concentrations of hydroquinone with potential fixed at -0.1 V vs. SCE. The inset shows current signal versus concentration.

The reduction of water (in the presence of buffer) to produce hydroxide ions was achieved through normal pulse voltammetry at the modulator electrode whilst the sensor was held at a fixed potential. Sufficient local pH changes were observed once

the modulator potential had reached -1.2 V vs. SCE (as shown in Figure 4A) by the change in sensor plateau current at this potential (the corresponding generator current is not informative and therefore not shown). Changing the pH means a shift in the midpoint potential with higher pH conditions to more negative potentials. When the sensor potential is held at -0.1 V vs. SCE, there is a large step in the current compared to the other sensor potentials (see inset in Figure 4A). This effect can be understood based on the buffer capacity in relation to the midpoint potential for the hydroquinone/benzoquinone redox system. A midpoint potential of -0.1 V vs. SCE corresponds to a pH 9.5 [15], which is the point of minimum buffer capacity for phosphate buffer (with $pK_{A1} = 2.12$ at 18 °C, $pK_{A2} = 7.21$ at 18 °C, and $pK_{A3} = 12.67$ at 25 °C [19]). Setting the sensor potential to 0.0 V or -0.2 V vs. SCE moves in both cases the hydroquinone/benzoquinone midpoint potential into a more effective buffer regime, and therefore the pH change generated in the trench produces a smaller current response. In the maximum buffer range (and when increasing the buffer concentration) the signal is diminished.

Once the optimum sensor potential has been identified at -0.1 V vs. SCE, the effect of hydroquinone concentration is investigated. The concentration of hydroquinone in the gold-gold micro-trench electrode was varied from 0.1 mM to 10 mM (see Figure 4B) and it was found that current increases linearly with concentration (see inset).

3.3. Gold-Gold Junction Pulse-Electroanalysis III.: Modulator-Sensor Voltammetry for the Irreversible Oxidation of Ammonia

It is interesting to apply the “chemical filter” concept to an irreversible redox system, here the oxidation of aqueous ammonia (equation 3 [20,21]).



The oxidation of ammonia is known to be pH dependent [22] and effective only under alkaline conditions ($\text{pK}_A = 9.23$ at $20\text{ }^\circ\text{C}$ [19]). However, this process is chemically irreversible and therefore not able to give a current feedback effect. Therefore the sensor currents are expected to be lower. Nevertheless, the “chemical filter” effect should still be effective due to pH dependence.

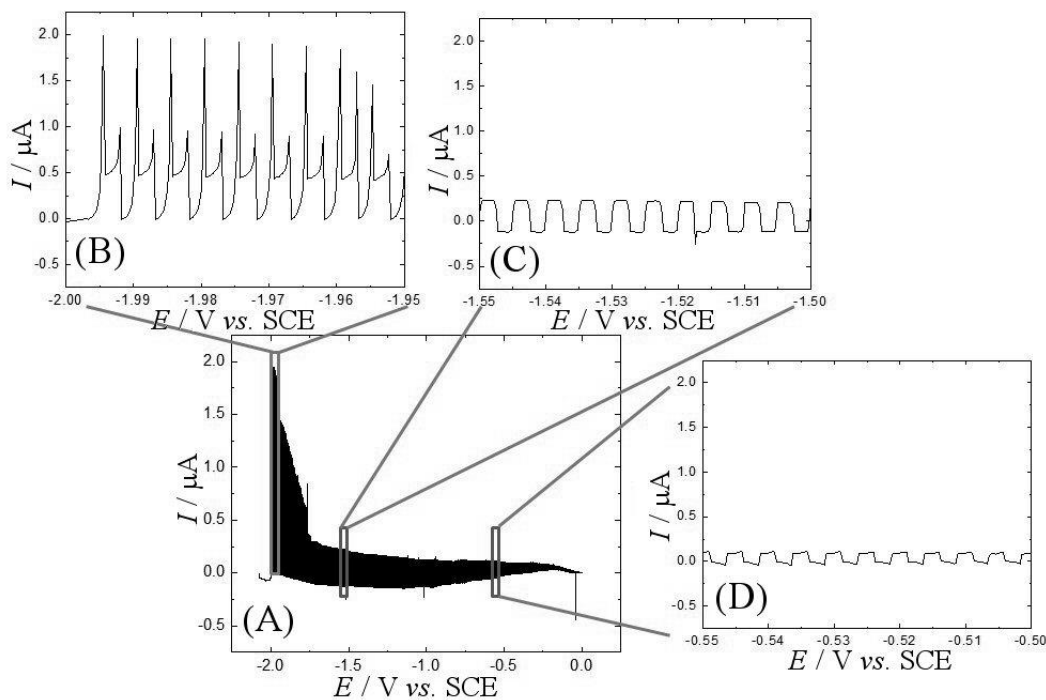


Figure 5. Chronoamperometry data for the collector electrode (modulator electrode in normal pulse voltammetry mode stepping from 0.0 to -1.0 V vs. SCE in 5 mV steps, pulse time 1 s, step time 2 s) held at a potential of 0.4 V in aqueous 10 mM NH_4NO_3 in 10 mM phosphate buffer pH 7 with insets (B), (C) and (D) showing a zoomed in region.

Figure 5 shows typical sensor data for an applied potential of 0.4 V vs. SCE and for the modulator electrode stepping in normal pulse voltammetry mode from 0.0 to -2.0 V vs. SCE. The phosphate buffer pH 7 solution stops the oxidation of NH_3 , which requires more alkaline conditions. Ammonia oxidation was therefore carried out using normal pulse voltammetry on the modulator electrode to create high pH conditions within the micro-trench and the sensor electrode was set at a fixed potential. Figure 5 shows the sensor response when the potential was held at 0.4 V vs. SCE. Clear pulses are seen even at -0.5 V vs. SCE, but as the modulator potential is stepped past -1.7 V vs. SCE, additional current spikes are seen at the start of each pulse segment. It is likely that a low level background process such as the gold surface oxidation (which due to interfacial oxide formation is also pH dependent) at the sensor electrode is

observed in addition to the ammonia oxidation, which appears to be active at -1.7 V vs. SCE.

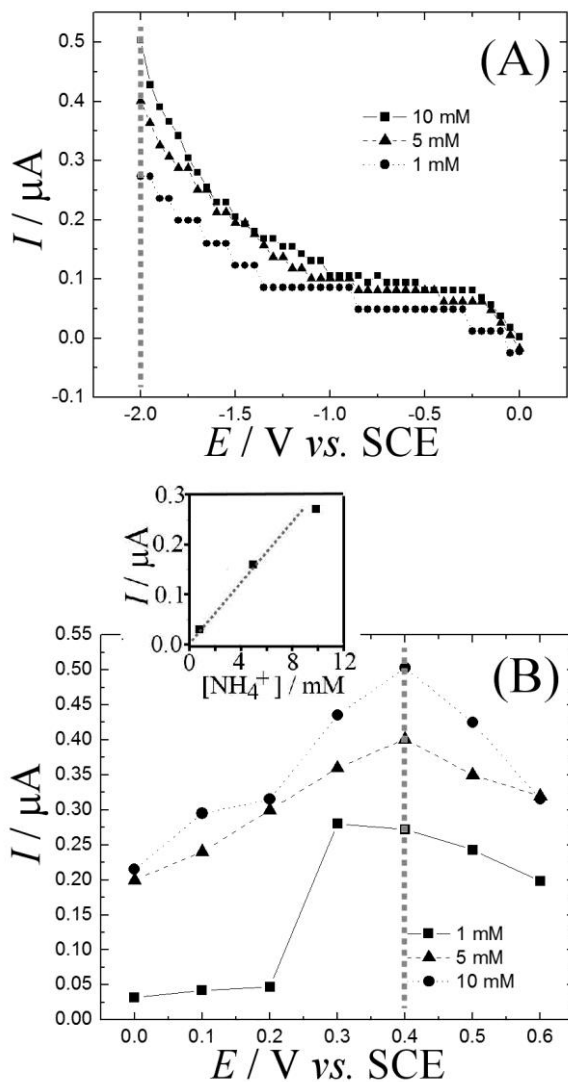


Figure 6. (A) Plateau currents for the sensor (held at 0.4 V vs. SCE) with the modulator being swept negative from 0.0 to -2.0 V vs. SCE using normal pulse voltammetry (5 mV steps, pulse 1 s, step duration 2 s) for different concentrations of NH_4NO_3 . (B) Plateau current for the sensor at generator potential of -2 V vs. SCE for varying sensor potentials and concentrations of NH_4NO_3 . The inset shows a plot of sensor current versus NH_4^+ concentration (see text).

The effect of ammonium nitrate concentration was investigated as shown in Figure 6A. Although the current has not plateaued at -2 V vs. SCE, an increase in current can be seen with increasing ammonium nitrate concentration. Figure 6B shows the plateau current taken for the last pulse at -2 V vs. SCE, where the pH is at its highest and shows the variation in current with collector potential and concentration. A second electrode potential of 0.4 V vs. SCE gives the highest collector current, indicating that this is the optimum potential to oxidise ammonia. The future potential of this modulator-sensor methodology for electroanalytical applications remains to be further investigated and optimised. In particular, work in much smaller trench electrodes with sub-micron gap will be desirable to improve sensitivity and speed. However, it has been demonstrated in this study that by employing a wider gap control of the local pH in the micro-trench is possible and effective in modulating redox chemistry.

4. Conclusions

Bipotentiostatic control of processes in micro-trench electrodes allows (i) feedback enhancement of analytical current responses and (ii) “chemical filter” effects to be exploited. In particular chemically reversible processes for analytes such as hydroquinone are affected where both effects occur simultaneously. However, even for chemically irreversible processes such as ammonia oxidation the methodology can be applied and a concentration dependent current signal can be obtained “in situ” with pH adjustment only locally within the micro-trench electrode system. Currently, the new methodology has many weaknesses in particular due to the gold film electrode being electrochemically active and sensitive to corrosion and degradation. Improved designs will be possible in future, for example with boron-doped diamond [23] micro-

trench electrodes or with flow-through micro-trench electrode systems associated with flow injection analysis.

The use of smaller nano-trench electrode systems will be beneficial in that feedback effects are much more pronounced. The control of pH in the trench will be possible with lower current pulses, which should further improve the methodology. A potential instrumentation problem/limit arises due to the need to control of the two working electrodes simultaneously, which in particular for pulse conditions can lead to short instabilities (capacitive coupling of electrodes). This is expected to become more prominent for narrower and deeper trench systems where slower transients rather than fast pulses are more likely to give good electroanalytical performance. Work towards sub-micron trench systems is in progress.

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