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Revision

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**A Dual-Plate ITO-ITO Generator-Collector Microtrench Sensor:
Surface Activation, Spatial Separation and Suppression of
Irreversible Oxygen and Ascorbate Interferences**

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Abstract

Generator-collector electrode systems are based on two independent working electrodes with overlapping diffusion fields where chemically reversible redox processes (oxidation and reduction) are coupled to give amplified current signals. A generator-collector trench electrode system prepared from two tin-doped indium oxide (ITO) electrodes placed vis-à-vis with 22 μm inter-electrode gap is employed here as a sensor in aqueous media. The reversible 2-electron anthraquinone-2-sulfonate redox system is demonstrated to give well-defined collector responses even in the presence of oxygen due to irreversible nature of the oxygen reduction. For the oxidation of dopamine on ITO, novel “Piranha-activation” effects are observed and chemically reversible generator-collector feedback conditions are achieved at pH 7, by selecting a more negative collector potential, again eliminating possible oxygen interference. Finally, dopamine oxidation in the presence of ascorbate is demonstrated with the irreversible oxidation of ascorbate at the “mouth” of the trench electrode and chemically reversible oxidation of dopamine in the trench “interior”. This spatial separation of chemically reversible and irreversible processes within and outside the trench is discussed as a potential in situ microscale sensing and separation tool.

Keywords: dopamine, ascorbate, oxygen, interference, electroanalysis, sensors.

1. Introduction

New types of electrochemical sensor electrodes are desirable, in particular for applications in complex media and multi-analyte cases,¹ for example, in blood analysis.^{2,3} Electrochemical methods are attractive as they often allow rapid on-site or point-of-care measurements without the need for separation or off-line laboratory apparatus. Sensitivity and selectivity of electrodes as well as multi-purpose analysis applications are of interest.

Recently, the benefits of “junction electrode systems”⁴ with generator-collector^{5,6} or modulator-sensor⁷ electrode arrangements under bipotentiostatic control have been highlighted. In the extreme limit, as dual-plate nano-gap sensors,⁸ these kinds of electrode systems can be employed down to single molecule sensitivity⁹ and with the opportunity for novel statistical analysis techniques being developed.¹⁰ More generally, the generator-collector configuration with bipotentiostatic control offers benefits due to (i) the steady state nature of analytical responses, (ii) the amplification effect, which is inversely proportional to the inter-electrode gap δ (in first approximation^{11,12}) $I_{feedback} = \frac{nDFAc}{\delta}$ with n , the number of electrons transferred per molecule diffusing to the electrode, D the diffusion coefficient, F the Faraday constant, A the area, and c the concentration), and (iii) the possibility to fill the trench with a “filter” or “separation” material such as cellulose.¹³ A particularly useful sensor geometry is the dual-plate or “trench” electrode system which was initially developed, reported, and treated by Sluyters,¹⁴ Anson,¹⁵ Reilley,¹⁶ and Hubbard,¹⁷ and more recently employed in electroanalysis.^{18,19} Here, further benefits of this type of

electrode system where separated trench “interior” and “mouth” regions can be assigned (see red and green regions in Figure 1C, respectively) are identified in terms of suppression of interference responses and effects.

Figure 1. Schematic drawing of (A) the assembly of the ITO-ITO dual-plate trench electrode system, (B) the operation in generator-collector feedback mode for amplified detection of a chemically reversible redox system, and (C) the “exclusion” of the irreversible redox system (e.g. O₂ reduction) from the trench region. The green region is the “mouth” region and the red region is the “interior” region.

In this report it is demonstrated that ITO-ITO dual-plate electrode systems assembled by placing a thin layer of epoxy between two ITO electrodes (see Figure 1A) can be employed in electroanalytical tasks where interferences from oxygen or other chemically irreversible redox active reagents traditionally cause problems. With two active electrodes, the generator and the collector, one electrode can be polarized to actively remove chemically irreversible redox systems, such as O₂ or ascorbate, from the “trench” region of the dual-plate electrode system. As a result, the collector limiting current reading becomes insensitive to the interfering species. In fact, the

interfering species can be essentially removed from the inter-electrode or “trench” region with potential future applications in nanoscale *in situ* separation and detection.

The redox systems selected for this study are the two-electron reduction of anthraquinone and the two-electron oxidation of dopamine²⁰ to reflect possible problems of interferences during reduction (oxygen) and interferences during oxidation (ascorbate). Both of these systems have been studied for a considerable time. The reduction of anthraquinones is important as redox mediators²¹ and in particular in the catalytic reduction of oxygen to hydrogen peroxide.²² The oxidation of dopamine has been studied particularly for *in vivo* application where signaling mechanisms between cells are investigated.^{23,24}

Although methods reported in this study cannot compete with the wide range of existing methods²⁵ and with the exquisite sub-micro-molar sensitivity achieved for example by graphene-based electrodes,²⁶ the ongoing development of new generator-collector sensing tools²⁷ could be fruitful with both potential for high sensitivity and for suppression of interferences in improved devices. A recent study of the geometry effects for generator-collector sensors for dopamine (in the presence of ascorbate) has highlighted important advantages.²⁸

2. Experimental

2.1. Chemical Reagents

Anthraquinone-2-sulfonic acid sodium salt monohydrate (97 %), L-ascorbic acid (99 %), dopamine hydrochloride, sodium hydroxide (≥ 98 %), phosphoric acid, nitric acid

($\geq 69\%$), hydrogen peroxide (30 wt. % in water), sulphuric acid (95 - 98%), oxalic acid (98%) and tartaric acid (99.5 %) were all purchased from Sigma Aldrich (UK). Aqueous solutions were made with Barnstead Nanopure water ($>18.2\text{ M}\Omega\text{ cm}$ at 20°C). Nitrogen (BOC) was employed to de-aerate electrolyte solutions. Experiments were conducted at $20 \pm 2^\circ\text{C}$.

2.2. Instrumentation

Electrochemical measurements were performed using either a PGSTAT12 biopotentiostat system (Autolab, EcoChemie, Netherlands) with GPES 4.7 software or a CompactStat with biopotentiostat module (Ivium Technologies, Netherlands) with IviumSoft software 2.178. A conventional three or four-electrode cell was employed with a Pt wire counter electrode and Ag/AgCl (saturated KCl) reference electrode (Radiometer). The three-electrode cell employed an ITO glass slide as the working electrode. The four-electrode cell set-up employed an ITO-ITO junction system with generator and collector working electrodes. Scanning electron microscopy (SEM) micrographs were recorded using a JSM-6480LV (JEOL, Japan). A 5 nm layer of chromium was sputter deposited onto the substrate prior to SEM analysis.

2.3. Electrode Fabrication

Tin-doped indium oxide junction electrodes were prepared following a method described previously.¹⁶ Briefly, ITO glass slides (Image Optics, Basildon, UK) were cut into $10\text{ mm} \times 25\text{ mm}$ substrates then masked using Kapton tape (Farnell) to give a masked strip in the centre of the electrode ($5\text{ mm} \times 25\text{ mm}$). The exposed ITO was then etched using a solution of 1 wt.% tartaric acid and 3 wt.% oxalic acid at 35°C

for 20 min. After rinsing and drying, the Kapton tape was removed and the two ITO slides were aligned face-to-face and glued under pressure using epoxy (SP106 multi-purpose epoxy, SP Gurit). After curing, the end of the ITO-ITO electrode was removed using a diamond cutter and the freshly exposed surface subsequently polished flat using SiC paper (P320, Buehler). The epoxy in between the ITO-ITO electrode was etched out using Piranha solution (1:5 hydrogen peroxide: sulphuric acid; WARNING: this solution is highly aggressive) to yield the micro-trench junction electrode (see Figure 2). Piranha solution treatment was also applied to clean micro-trench electrodes as well as bare ITO electrodes (see text) used in voltammetric measurements.

Figure 2. SEM images of the ITO-ITO dual-plate trench electrode system at (A) low and (B) high magnification (The electrode was sputter-coated with chromium prior to imaging).

3. Results and Discussion

3.1. Dual-Plate Microgap Sensor Electroanalysis I.: Reduction of Anthraquinone-2-sulfonate in Aqueous 0.1 M NaOH

The electrochemical reduction of anthraquinone-2-sulfonate occurs in a 2-electron multi-step mechanism²⁹ with cation association exerting strong effects on the reversible potential³⁰ of the electron transfer in step 1 (equation 1a) and in step 2 (equation 1b).

In aqueous 0.1 M NaOH both reduction responses should merge into a single 2-electron reduction which is observed at -0.56 V vs. Ag/AgCl. However, at ITO electrodes further complexity is induced by the presence of oxygen in the electrolyte solution (see Figure 3).

Figure 3. (A) Cyclic voltammograms (scan rate 0.1 Vs⁻¹) for the reduction of 100 μM anthraquinone-2-sulfonate in 0.1 M NaOH at a 1 cm² ITO electrode for (i) a bare ITO electrode and (ii) a Piranha-treated ITO electrode. (B) As above but with (i) oxygen present and (ii) argon atmosphere. A dashed line indicates the approximate reversible potential.

The anthraquinone-2-sulfonate reduction is affected by the presence of oxygen in solution which, in particular at low anthraquinone-2-sulfonate concentration, causes a significant increase in current (and the formation of peroxide^{31,32}). The expected reversible reduction of anthraquinone-2-sulfonate is observed only after de-aeration (see Figure 3B) with a second reduction peak at more negative potentials (ca. -0.85 V vs. Ag/AgCl) dominating all data obtained in the presence of oxygen. The change in reactivity when treating the ITO electrode surface with Piranha solution is insignificant. The negative shift in potential and irreversibility of the voltammetric response for anthraquinone-2-sulfonate reduction in the presence of oxygen may be associated with the formation of an oxygen adduct of the reduced anthraquinone species. However, further mechanistic details of this process are beyond the scope of this study.

Perhaps surprisingly, a considerable change in voltammetric behaviour is observed when using the dual-plate electrode in the presence of oxygen. Data obtained with a dual-plate ITO-ITO micro-trench electrode with 22 μm inter-electrode gap (see Figure 2) is shown in Figure 4. Well-defined steady-state mass transport limited currents at the reversible potential are observed (even in the presence of oxygen), which reflect a fully active trench electrode area as long as both the generator and the collector electrode are set to sufficiently positive and negative potentials (relative to the reversible potential).

Figure 4. (A) Generator-collector cyclic voltammograms (scan rate 0.025 V s^{-1} , $E_{\text{collector}} =$ (i) -0.5 , (ii) -0.25 , (iii) 0.0 , (iv) 0.25 , and (v) 0.5 V vs. Ag/AgCl) for the reduction of $100 \mu\text{M}$ anthraquinone-2-sulfonate in aqueous 0.1 M NaOH . (B) As above with $E_{\text{collector}} = 0.5$ V vs. Ag/AgCl and [anthraquinone-2-sulfonate] = (i) 0.1 , (ii) 0.2 , (iii) 0.3 , (iv) 0.4 , (v) 0.5 , (vi) 0.6 , and (vii) 0.7 mM. (C) Plot of the collector limiting current versus concentration.

Data in Figure 4A demonstrates the generator and collector currents for an anthraquinone-2-sulfonate concentration of $100 \mu\text{M}$. The generator limiting current exhibits a drifting baseline, however, the collector limiting current is well-defined

(apart from a shift in baseline current) and a precise analytical reading is possible (see dashed line in 4Ai and 4Av) even in the presence of oxygen in bulk solution. Changing the applied collector potential does not significantly change the collector limiting current (except for collector potential settings close to the reversible potential, see 4Ai), but it does shift the collector response due to oxygen background processes (outside of the trench region, *vide infra*). Data in Figure 4B and 4C demonstrate a linear dependence of collector limiting current on concentration. The hysteresis effect of ca. 54 mV in the collector current response at a scan rate of 25 mVs⁻¹ is consistent with diffusional delay across the inter-electrode gap. The diffusion coefficient for anthraquinone-2-sulfonate under similar experimental conditions has been reported as $D_{\text{anthraquinone-2-sulfonate}} = 5.7 \times 10^{-9} \text{ m}^2\text{s}^{-1}$.¹⁸ With the diffusion coefficient for anthraquinone-2-sulfonate known, and with the inter-electrode gap determined as 22 μm (see Experimental, Figure 2), the average trench depth can be estimated (see equation 2, this equation is appropriate here and consistent with work by Reilley¹⁶ and Hubbard¹⁷).

$$\text{Trench depth} = \frac{I_{\text{lim}} \times \delta}{nFDwc} = 800 \mu\text{m} \quad (2)$$

Here I_{lim} is the limiting current and w denotes the width of the trench electrode. The sensor therefore has an aspect ratio of approximately 36. In summary, the reduction and back-oxidation of anthraquinone-2-sulfonate at the ITO-ITO dual-plate electrode occurs with good sensitivity and without interference from oxygen in the solution phase presumably due to “pre-electrolysis” (irreversible removal of oxygen at the generator electrode) at the “mouth” of the dual-plate trench electrode (see Figure 1C).

3.2. Dual-Plate Microgap Sensor Electroanalysis II.: Oxidation of Dopamine in Aqueous Phosphate Buffer pH 7

The detection of dopamine in the presence of interferences/co-analytes such as ascorbate,³³ ureate,³⁴ and serotonin³⁵ has been thoroughly studied for application in the investigation of neuron communication³⁶ and detection in urine.³⁷ Amplification of the voltammetric signal based on modified electrodes^{38,39} and on dopamine capture and surface derivatisation has been proposed.⁴⁰ Here, dopamine is employed as a model analyte with ascorbate interference to demonstrate the potential benefits of dual-plate trench electrodes in analysis. Very recently Amatore and coworkers also highlighted the importance of geometry effects in generator – collector sensing for the case of dopamine in the presence of ascorbate.⁴¹

The electrochemistry of dopamine is dominated by the redox active catechol fraction of the molecule. In aqueous buffer media at pH 7 dopamine is present as a cation of overall +1 charge ($pK_{A1} = 8.9$ and $pK_{A2} = 10.4$ ⁴²) which is oxidised initially in a 2-electron process to the 1,2-dione.⁴³ More complex follow-up reactions are known to occur in alkaline media to give dopachrome⁴⁴ (cyclisation and further oxidation) but these are beyond the scope of this study and not relevant for the case of fast inter-electrode diffusion (with $\tau \approx \delta^2/D$ here approximately 0.48 s).

Figure 5. (A) Cyclic voltammograms (scan rate 0.025 Vs^{-1}) for the oxidation of 1 mM dopamine at a 1 cm^2 ITO electrode immersed in 0.1 M phosphate buffer pH 7 with (i) to (iv) indicating different start potentials. (B) As in A, but for scan rates (i) 10, (ii) 25, (iii) 50, (iv) 75, (v) 100, (vi) 125, (vii) 150, (viii) 175, and (ix) 200 mVs^{-1} . (C) As in A, with scan rate 0.025 Vs^{-1} and for [dopamine] = (i) 0, (ii) 0.2, (iii) 0.3, (iv) 0.4, (v) 0.5, (vi) 0.6, and (vii) 0.7 mM. (D) Cyclic voltammograms (scan rate 0.025 Vs^{-1} , first 5 potential cycles) for the oxidation of 1 mM dopamine at a 1 cm^2 “Piranha-activated” ITO electrode immersed in 0.1 M phosphate buffer pH 7. (E) As in D, but for scan rates (i) 10, (ii) 25, (iii) 50, (iv) 75, (v) 100, and (vi) 125 mVs^{-1} . (F) As in D with scan rate 0.025 Vs^{-1} and for [dopamine] = (i) 0, (ii) 0.2, (iii) 0.3, (iv) 0.4, and (v) 0.5 mM.

Figure 5A shows cyclic voltammograms for 1 mM dopamine in 0.1 M phosphate buffer pH 7 at a 1 cm^2 ITO electrode. The oxidation response at $0.95 \text{ V vs. Ag/AgCl}$ is shown to be chemically linked to the reduction process at $0.08 \text{ V vs. Ag/AgCl}$. The considerable gap between oxidation and back-reduction peak is observed due to the bare ITO surface not being kinetically active rather than formation of follow-up

chemical products. This changes dramatically when a Piranha cleaning treatment is applied (see experimental). The effect of Piranha treatment on ITO surface roughness and an increase in surface energy have been reported by Vacca et al.⁴⁵ However, effects observed here of Piranha treatment on the electron transfer to dopamine are new. Figure 5D has been obtained under otherwise identical conditions and a change in onset potential (improved electrochemical reversibility) is clearly evident. When changing the scan rate (see Figure 5B), on bare ITO an additional surface immobilised redox system emerges (at higher scan rate) with midpoint potential 0.62 V vs. Ag/AgCl. This is assigned tentatively to surface immobilised (physically or chemically) dopamine on the ITO electrode surface. For a Piranha treated ITO electrode, the separation between oxidation and reduction responses appears much less pronounced (Figure 5E). Figure 5C and 5F demonstrate the effect of the dopamine concentration on the oxidation and back-reduction peak responses on bare ITO and on Piranha-treated ITO, respectively.

Next, generator-collector processes in the ITO-ITO dual-plate electrode system were investigated. Figure 6A shows cyclic voltammetry data for 0.25 mM dopamine. The oxidation is observed at the generator electrode with a midpoint potential of ca. 0.25 V vs. Ag/AgCl, consistent with a Piranha-activated ITO electrode surface. When the collector potential is set to a potential positive of 0.0 V vs. Ag/AgCl, only insignificant collection efficiencies are observed. Well-defined collector current responses are obtained for $E_{\text{collector}} = -0.5$ V vs. Ag/AgCl. The collector current of ca. 5 μA is in good agreement with the theoretical value of $I_{\text{lim}} = \frac{nFD\Delta c}{\delta} = 5.2 \mu\text{A}$ (with $n = 2$, $D_{\text{dopamine}} = 0.6 \times 10^{-9} \text{ m}^2\text{s}^{-1}$,^{46,47} $A = 800 \mu\text{m} \times 5 \text{ mm}$, and $\delta = 22 \mu\text{m}$, see equation 2). Concentration measurements with optimised collector potential settings

are possible into the lower μM range (see Figure 6B). These measurements were performed without de-aerating the solution. The removal of oxygen occurs in this case at the collector electrode. In order to explore the effects of other interferences with chemically irreversible electrode reaction the addition of ascorbate was investigated next.

Figure 6. (A) Cyclic voltammograms (scan rate 0.025 Vs^{-1}) for the oxidation of 0.25 mM dopamine at a dual-plate ITO-ITO electrode immersed into 0.1 M phosphate buffer pH 7. The generator current is shown and collector responses for $E_{\text{collector}} =$ (ii) 0.5, (iii) 0.25, (iv) 0.0, (v) -0.25, and (vi) -0.5 V vs. Ag/AgCl. (B) Plot of the generator and collector limiting currents as a function of dopamine concentration recorded with $E_{\text{collector}} = -0.5 \text{ V}$ vs. Ag/AgCl.

3.3. Dual-Plate Microgap Sensor Electroanalysis III.: Oxidation of Dopamine in the Presence of Ascorbate

The interference of ascorbate on dopamine is well known. L-Ascorbate represents a chemically irreversible redox system with formation of dehydro-L-ascorbate in a 2-electron process.⁴⁸ When investigated at a 1 cm² ITO electrode immersed into 0.1 mM ascorbate in 0.1 M phosphate buffer pH 7, only an irreversible oxidation commencing at 0.2 V vs. Ag/AgCl is observed for either Piranha-activated ITO or bare ITO (see Figure 7A). When the concentration of ascorbic acid is increased, the anodic signal increases accordingly consistent with ascorbate being oxidised. In the ITO-ITO dual-plate electrode system the oxidation at the generator is still observed, but independent of the collector potential setting, there is no significant collector current response (see Figure 7B). The collector current signal only “shifts” according to the applied potential. That is, under these conditions ascorbate is “consumed” at the generator and not available for back-reduction independent of the choice of the collector electrode potential.

Figure 7. (A) Cyclic voltammograms (scan rate 25 mVs^{-1}) for ascorbate (concentration (i) 0.1, (ii) 0.2, (iii) 0.3, (iv) 0.4, and (v) 0.5 mM in 0.1 M phosphate buffer pH 7) at a 1 cm^2 ITO electrode. (B) Generator-collector voltammograms (scan rate 25 mVs^{-1}) for 1 mM ascorbate for an ITO-ITO dual-plate sensor with (i) generator current and (ii)-(vi) collector currents for $E_{collector} =$ (ii) 0.5, (iii) 0.25, (iv) 0.0, (v) -0.25, and (vi) -0.5 V vs. Ag/AgCl.

When a combination of ascorbate and dopamine is investigated there appears to be a clear separation, with dopamine generator and collector currents relatively unaffected (see Figure 8). Changing the concentration of dopamine in the presence of ascorbate (see Figure 8A and 8B) allows reliable collector current responses to be obtained with an onset potential of ca. 0.25 V vs. Ag/AgCl. The ascorbate is oxidised irreversibly and therefore not adding to the feedback current. A smaller peak feature at ca. 0.6 V

vs. Ag/AgCl in both generator and collector current could be associated with the surface of the electrode being affected by either ascorbate or dopamine, but during these experiments the current signals remain stable without the need for “re-activation” of the electrode in Piranha.

Figure 8. (A) Cyclic voltammograms (scan rate 0.025 Vs^{-1} , $E_{\text{collector}} = -0.5 \text{ V}$ vs. Ag/AgCl) for a dual-plate ITO-ITO electrode immersed in 0.1 M phosphate buffer pH 7 after addition of 0.5 mM ascorbate with (i) 0.1 , (ii) 0.2 , (iii) 0.3 , (iv) 0.4 , and (v) 0.5 mM dopamine. (B) Plot of limiting currents versus sum of concentrations of ascorbate and dopamine. (C) As above but with addition of 0.5 mM dopamine first then addition of (i) 0.1 , (ii) 0.2 , (iii) 0.3 , (iv) 0.4 , and (v) 0.5 mM ascorbate. (D) Plot of limiting currents versus sum of concentrations of dopamine and ascorbate.

A similar experiment conducted by adding 0.5 mM dopamine first followed by stepwise addition of ascorbate gives very similar results (see Figure 8C and 8D) confirming that systematic variation in ascorbate concentration has no significant effect on the collector current response. The limiting current for the dopamine oxidation in both cases is $I_{\text{collector}} = 10 \mu\text{A}$, which based on equation 2 and $D_{\text{dopamine}} = 0.60 \times 10^{-9} \text{ m}^2\text{s}^{-1}$,^{49,50} is in excellent agreement with the anticipated two electron redox conversion of dopamine.

The use of ITO in the dual-plate electrode may have some disadvantages over traditional metal or carbon electrodes due to the sometimes sluggish electron transfer at the oxide surface as well as the tendency for adsorbate attachment. However, in conjunction with the Piranha cleaning process, the ITO-ITO dual plate trench sensor appears much more active and re-usable, at least for the case of dopamine, which is important due to the lack of polishing or other cleaning procedures for micro-trench electrodes.

4. Conclusions

It has been shown that dual-plate or “micro-trench” electrodes offer interesting interference screening effects which allow chemically irreversible redox systems such as oxygen and ascorbate to be “removed” *in situ* by pre-electrolysis at the “mouth” of the sensor electrode. This type of process is dependent on the aspect ratio of trench-width to trench-depth. Considerable future improvements in the observed effects are likely for “nano-trench” electrodes with smaller width. Very interesting for future

applications will be the exploration of new types of electrodes with sub-micrometer gap, either made from ITO or from metal substrates, possibly produced based on readily available lithography technologies.

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