

Article

Electrochemical Performance of Lithographically-Defined Micro-Electrodes for Integration and Device Applications

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Abstract: Small; lithographically-defined and closely-spaced metallic features of dimensions and separation in the micrometer range are of strong interest as working and counter electrodes in compact electrochemical sensing devices. Such micro-electrode systems can be integrated with microfluidics and optical biosensors, such as surface plasmon waveguide biosensors, to enable multi-modal sensing strategies. We investigate lithographically-defined gold and platinum micro-electrodes experimentally, via cyclic voltammetry (CV) measurements obtained at various scan rates and concentrations of potassium ferricyanide as the redox species, in potassium nitrate as the supporting electrolyte. The magnitude of the double-layer capacitance is estimated using the voltammograms. Concentration curves for potassium ferricyanide are extracted from our CV measurements as a function of scan rate, and could be used as calibration curves from which an unknown concentration of potassium ferricyanide in the range of 0.5–5 mM can be determined. A blind test was done to confirm the validity of the calibration curve. The diffusion coefficient of potassium ferricyanide is also extracted from our CV measurements by fitting to the Randles–Sevcik equation ($D = 4.18 \times 10^{-10} \text{ m}^2/\text{s}$). Our CV measurements were compared with measurements obtained using macroscopic commercial electrodes, yielding good agreement and verifying that the shape of our CV curves do not depend on micro-electrode geometry (only on area). We also compare our CV measurements with theoretical curves computed using the Butler–Volmer equation, achieving essentially perfect agreement while extracting the rate constant at zero potential for our redox species ($k^0 = 10^{-6} \text{ m/s}$). Finally, we demonstrate the importance of burn-in to stabilize electrodes from the effects of electromigration and grain reorganization before use in CV measurements, by comparing with results obtained with as-deposited electrodes. Burn-in (or equivalently, annealing) of lithographic microelectrodes before use is of general importance to electrochemical sensing devices

Keywords: biosensors; cyclic voltammetry; microfluidics; lithographic microelectrodes

1. Introduction

Small, closely spaced metallic features of dimensions and separation in the micrometer range are of interest in electrochemical device applications or for integration with optical biosensors, e.g., based on surface plasmon-polaritons (SPPs) [1–3]. Optical biosensors exploiting long-range surface plasmon-polariton (LRSP) waveguides have solicited significant interest because they enable compactness in integrated architectures, and offer

very high sensitivity in an arrayed format [4–7]. LRSPs are supported by a thin metal slab or stripe bounded by dielectrics of similar refractive index [8]. For biosensing, the metal stripe is typically formed of Au and is supported by a cladding of low refractive index, e.g., a fluoropolymer such as Cytop, which has an index close to water and is thus well-matched to the index of aqueous biosensing media [5,6]. Alternatively, Au-sensing waveguides can be fabricated on a multilayer dielectric cladding, behaving optically as a 1-D photonic crystal (1DPC), and supporting Bloch LRSPs within the bandgap of the 1DPC [4,5,7]. Advantageously, the multilayer cladding in such structures can be formed of robust inorganic dielectrics (e.g., SiO_2 , Si_3N_4 , Ta_2O_5), allowing multiple wafer-scale processing steps to be applied thereon, thereby enabling a high degree of integration and conferring strength and resilience to the chips [7].

Prism-coupled surface plasmon resonance (SPR) biosensors have been combined with other sensing techniques, such as mass spectroscopy [9–11], SELEX [12], and electrochemistry [13–27]. An early study on electrochemical SPR reports the use of surface plasmons to probe the electrochemical interface in perchlorate and halide electrolytes [13]. In another study, the SPR response was monitored as the potential on the Au sensing surface was cycled similarly to cyclic voltammetry [14]. Electrochemical SPR was recently used for the label-free detection of the cancer biomarker miRNA-145 [15].

The drive towards compactness and high levels of integration has motivated electrochemical SPR sensing approaches based on Au micro- and nano-structures [16,17]. Electrochemical SPR sensors on optical fibers present another alternative [18], where a gold-coated optical fiber sensor was also used as the working electrode in an electrochemical set-up [19]. In recent work, a flow-injection electrochemical plasmonic optical fiber sensor was proposed, with the sensor inserted into a PDMS flow channel [20].

Other approaches to integrating optical and electrochemical sensing include a gold-coated graded-index optical waveguide sensor, where changes in optical transmittance were measured while cyclic voltammetry was performed in sulfuric or perchloric acid solutions [21]. An electrochemical thin-film chlorine sensor on a planar optical waveguide was also proposed to measure oxidation in the thin-film by monitoring the light transmitted through the waveguide [22]. An electrochemical SPR glucose biosensor was reported, with the ability to detect enzymatic reactions in a conducting polymer/glucose oxidase (Gox) multilayer thin film [23]. In addition to sensing applications, combining electrochemical probes with plasmonic structures is of interest in the investigation of light-induced hot-carrier electrochemical reactions [24–27].

Cyclic voltammetry (CV) plays an essential role in the interrogation of electrochemical sensors in general [28]. Voltammetry can be the fundamental mode of operation of a sensor because the measured current is linearly dependent on the analyte concentration in a well-designed system [29]. Furthermore, a single scan is very rich in information on the chemical and physical behaviors of an electrochemical system, and CV can be inexpensively implemented in a compact form-factor [28,29].

Motivated by the high sensitivity of Au stripe LRSP waveguide biosensors [4–7], along with their suitability for high levels of integration, we investigate microelectrode systems suitable for integration with such optical biosensors, to ultimately enable multi-modal sensing strategies, of strong interest in, e.g., disease detection problems. The use of high-volume wafer-scale manufacturing tools and techniques in the fabrication of the sensors ensures a low chip cost. Electrochemical measurements are performed in the form of CV for different scan rates and concentrations of the redox species (potassium ferricyanide). We also demonstrate the importance of microelectrode burn-in (current annealing) before performing electrochemical measurements. Burn-in is a crucial issue, inducing electromigration and grain reorganization in lithographically-defined and evaporated electrodes, ultimately stabilizing them before use. Peak oxidative currents in the CV measurements are plotted vs. concentration and used as a calibration curve, from which an unknown concentration of potassium ferricyanide in the range of 0.5–5 mM can be determined. The diffusion coefficient of potassium ferricyanide is obtained by fitting our experimental data

to the Randles–Sevcik equation. A comparison of CV measurements with theoretical results computed using the Butler–Volmer equation is done while extracting the rate constant at zero potential of our redox species.

2. Experimental

2.1. Electrode Structures

Figure 1a shows a sketch of a chip bearing a Au LRSP waveguide designed to also operate as a working electrode (WE), a Pt counter electrode (CE), and Pt/Cu electrical contact pads. These structures were arranged in an array along the width of the chip to enable multiple sensing channels. The metal structures are supported by a multilayer dielectric stack consisting of 15 periods of $\text{SiO}_2/\text{Ta}_2\text{O}_5$. Both Au and Pt stripes are lithographically defined and evaporated. Fabrication details and the optical operation of the LRSPs waveguides are reported elsewhere [4,5,7].

Identical dimensions were used for the Au and Pt stripes, as illustrated in Figure 1a. Figure 1b gives a microscope image taken near the top of a chip, showing portions of contact pads to working and counter electrodes (the substrate appears green). An atomic force microscope (AFM) scan of both stripes reveals that their thickness is 35–40 nm (including 3 nm of Ti for adhesion), and that the roughness levels are less than 2 nm (RMS) along the top surface of both. The edge-to-edge lateral separation between them is $l_s = 40 \mu\text{m}$. The contact pads are formed of a Pt/Cu stack, 50/200 nm in thickness. The Pt layer is used to passivate the Cu and provide a more resilient surface for probing. The geometry, dimensions and thickness of the Au working electrodes are constrained by their dual use as Bloch LRSP waveguides [4]. An identical design was adopted for the Pt counter electrodes for simplicity.

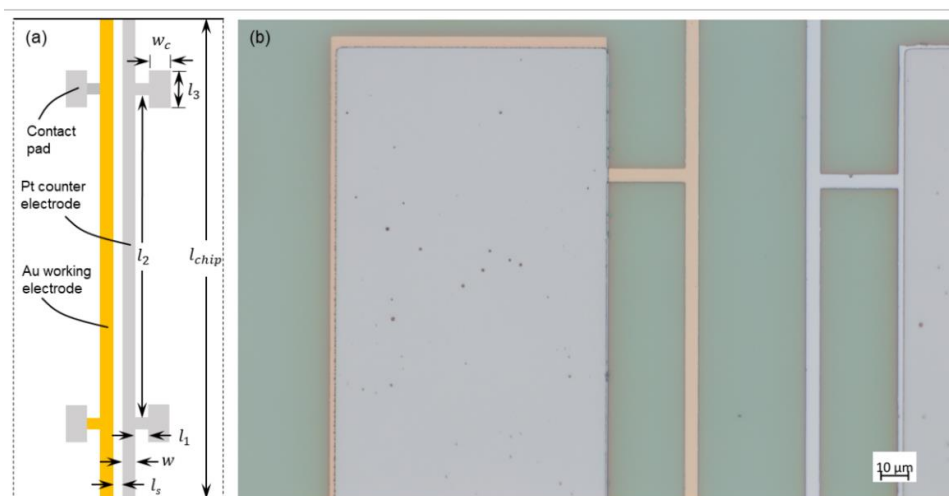


Figure 1. (a) Schematic (not to scale) of a chip bearing a Au LRSP waveguide/working electrode, Pt counter electrode, and electrical contact pads on a multilayer dielectric substrate. The dimensions are: $l_1 = 29 \mu\text{m}$, $l_2 = 2600 \mu\text{m}$, $l_3 = 250 \mu\text{m}$, $l_{\text{chip}} = 3000 \mu\text{m}$, $w_c = 100 \mu\text{m}$, $w = 5 \mu\text{m}$, $l_s = 40 \mu\text{m}$. (b) Microscope image of a fabricated chip.

2.2. Electromigration

Electromigration and grain reorganization may occur initially when a current density flows for the first time through an as-deposited metal nanostructure or stripe [30–32]. Electromigration occurs mainly via the current-induced migration of metal ions along the grain boundaries of a structure, and grain reorganization consists mainly of thermally-driven coalescence of small grains into larger ones. Consequently, metal electrodes should be stabilized, through annealing, or burn-in via the passage of current density, before use in a CV experiment. In the case of burn-in, the injected current density induces electromigration and heating via Ohmic loss leading to grain reorganization, the effects of

which are evident in the evolution of the measured resistance of the structure as a function of current density and time.

A controlled voltage was applied to a metal stripe, via a pair of probes touching its contact pads, and the injected current and resistance were measured. The applied voltage was increased in steps of 0.1 V with each voltage held constant for 10 s. The burn-in process was repeated a few times to determine the burn-out (open-circuit) point of the stripes, which was about 30 V for our Au stripes and 120 V for our Pt stripes. Once these values were known, the burn-in process consisted of cycling the applied voltage several times to just below the burn-out point until electromigration and grain reorganization no longer occurred, as evidenced by a stable measured resistance.

Figure 2 shows typical measured burn-in curves for as-deposited (evaporated) Au and Pt stripes, consisting of cycling the voltage applied between a pair of pads at each end of a stripe, six times (6 runs) while measuring the current and resistance. Run 1 in both cases shows the stripe resistance increasing with voltage up to a threshold, 22 V for the Au stripe (Figure 2a) and 60 V for the Pt stripe (Figure 2b), beyond which the resistance flattens, to then increase again with voltage. The behavior observed in run 1 for both stripes indicates that electromigration and current-induced thermal annealing occurred on the stripes, resulting in grain reorganization and lowered stripe resistance. After cycling a few additional runs, the stripe resistance stabilizes with no further significant grain reorganization. In this regime, the stripe resistance varies with voltage in a manner that is consistent with the dependence of resistivity on temperature, and the electrodes are deemed ready for CV measurements. Using electrodes as-evaporated (not burned-in or annealed) produce inaccurate CV results, as demonstrated and discussed further below.

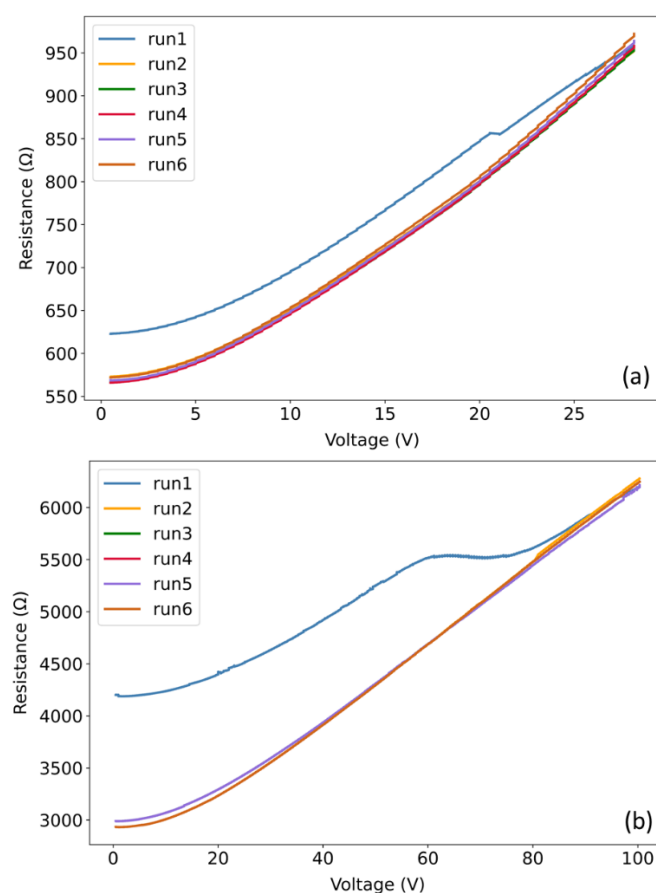


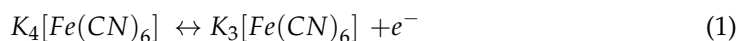
Figure 2. Measured stripe resistance vs. voltage in steps of 0.1 V. Each voltage step was held constant for 10 s. (a) Au stripe over the voltage range from 0.5 to 30 V; (b) Pt stripe over the voltage range from 0.5 to 100 V.

2.3. Materials

Potassium ferricyanide, potassium nitrate, and an external Ag/AgCl reference electrode (double junction PH combination, glass body, BNC connector) were purchased from (Sigma-Aldrich Canada Ltd, Oakville, ON, Canada). The cyclic voltammetry experiments were performed by a WaveDriver 20 BiPotentiostat (basic bundles) from (Pine Research Instrumentation Inc., Durham, NC, USA). A commercial Au electrode (outer diameter 6 mm, inner diameter 1.6 mm) was purchased from London Scientific.

2.4. Setup

CV experiments were performed with a Au stripe operating as the working electrode, and a neighboring Pt stripe operating as the counter electrode, both on chip, as sketched in Figure 1. Potassium ferricyanide (a mediator for glucose detection) was used as the redox species [33,34]. CV measurements were obtained for various potassium ferricyanide concentrations. Specifically, the experiments were carried out using 20 mL of 0.5, 1, 3, and 5 mM potassium ferricyanide, dissolved in 100 mM potassium nitrate as the supporting electrolyte, the latter providing low resistance and high ionic strength, leading to unperturbed near-zero electric fields within the electrochemical cell [35] CV experiments were carried out over the potential range of 0–0.5 V vs. the Ag/AgCl reference electrode using a triangular waveform at scan rates of 5, 10, 20, 50, and 100 mV/s (see Appendix A.1) Applying such a voltage to the system leads to the reversible reaction of potassium ferricyanide ($K_3[Fe(CN)_6]$) to potassium ferrocyanide ($K_4[Fe(CN)_6]$) as a redox couple in a 1-electron transfer process:



The electrochemical cell made of glass consisted of a Petri dish with the chip affixed to the bottom with epoxy. Electrical contacting to the working electrode (Au stripe) and counter electrode (Pt stripe) was achieved using two tungsten needles. The needles were attached to the arms of two precision positioners to align and establish contact to the contact pads. Any possible reaction between the needles and the redox species or the electrolyte was eliminated by coating the body of the needles with PMMA (except for their tips). The chip was then immersed in electrolyte. The Ag/AgCl reference electrode was also immersed in electrolyte to establish a constant and stable reference potential (Appendix A.1).

The tungsten needles, coated with poly (methyl methacrylate)—PMMA—except for their tips, were independently tested to make sure that they have no effects on the CV measurements. A needle was immersed in the solution (1 mM of potassium ferricyanide as the redox species in 100 mM of potassium nitrate) and used as a working electrode. An external Pt wire was used as a counter electrode along with the Ag/AgCl reference electrode. CV experiments were carried out at different scan rates (5, 10, 20, 50, and 100 mV/s). The measured currents produced no discernable patterns and were in the range of nA, which corresponds to the noise floor of our potentiostat. The probing needles therefore do not interact electrochemically in this system.

3. Results and Discussion

3.1. CV Measurements

Figure 3 shows the cyclic voltammograms obtained using the on-chip Au and Pt stripes as working and counter electrodes (Figure 1a), for different scan rates and concentrations of ferricyanide.

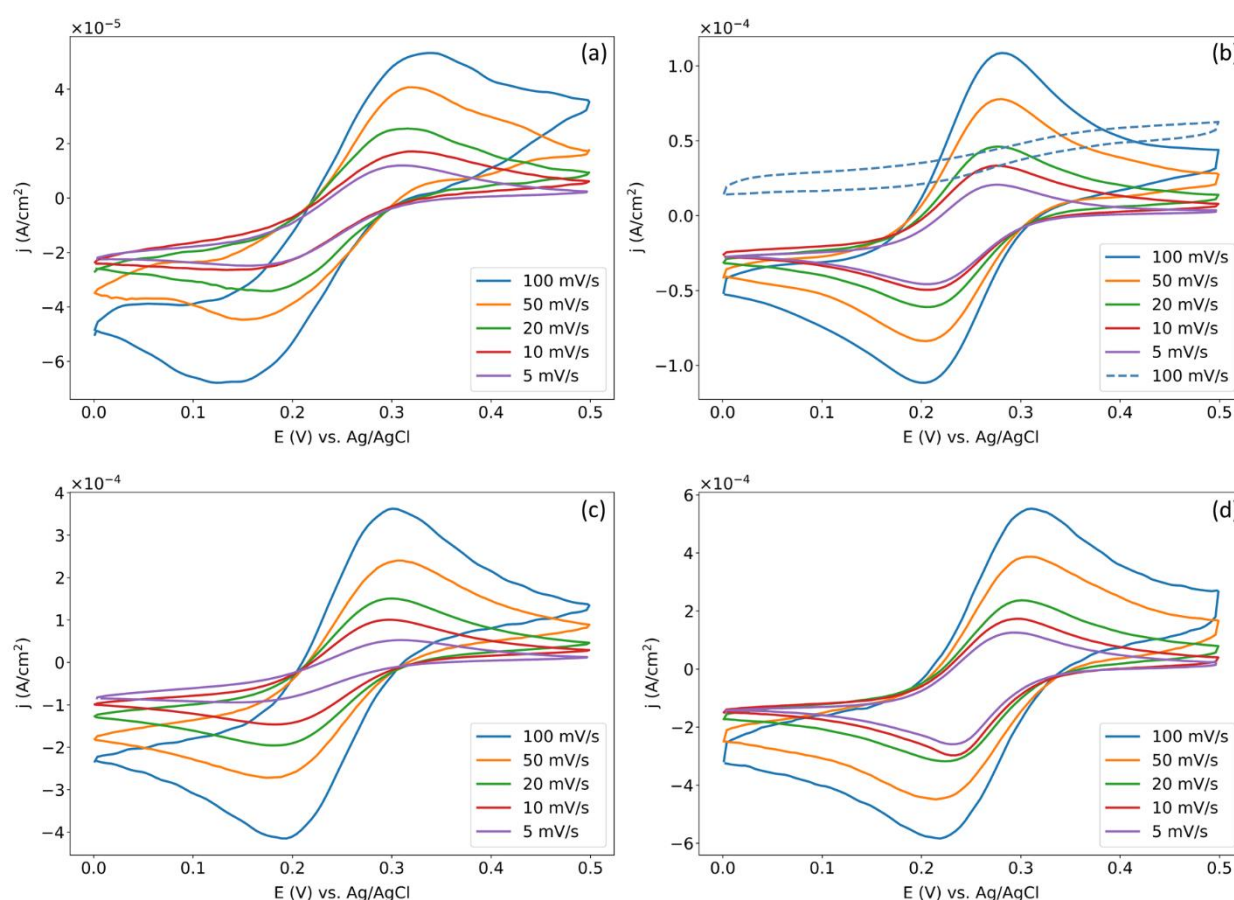


Figure 3. Cyclic voltammograms of Au stripes on chip, at different scan rates (legend), for different concentrations of potassium ferricyanide: (a) 0.5 mM, (b) 1 mM, (c) 3 mM, (d) 5 mM. The dash-dot curve in (b) corresponds to a CV measurement for electrodes that were not burned-in (cf. electromigration section).

The results of Figure 3 were obtained using on-chip electrodes of identical design with different concentrations of the redox species. Comparing the results reveals that the CV curves are very similar, the main difference being the magnitude of the currents measured. As discussed earlier, the measurements were carried out under a high electrolyte concentration, such that the main difference between the experiments is the concentration of the redox species.

Slight differences in the shape of the CV curves are attributed to the use of different chips in gathering the measurements reported in the four panels of Figure 3. Different chips were needed because of accumulated damage caused to the contact pads during repeated probing. However, a complete set of experiments for a specific concentration (e.g., 0.5 mM) involving all scan rates was completed with the same on-chip electrodes.

In cases where the same on-chip electrodes could be used, cleaning between measurements involving different concentrations is required. For cleaning, a chip was placed into a large glass vial of acetone which was then transferred to into an ultrasonic bath for 5 min. Next, the chip was immediately rinsed using pipettes filled with 3–4 isopropyl alcohol (IPA), followed by deionized (DI) water, and then N₂ gas was used to blow dry the chip. Finally, the chip was placed into a UV/ozone chamber with the UV source on for 30 min then off for another 30 min.

Figure 3b also shows a CV measurement at a scan rate of 100 mV/s for electrodes that were not burned-in (dashed-dot curve, cf. electromigration sub-section). As is obvious from this plot, the oxidation and reduction peaks have essentially disappeared. The need to properly burn-in (anneal) micro-electrodes before use in an electrochemical experiment is manifest.

Figure 4 compares the results of Figure 3b with voltammograms obtained using a commercial Au working electrode (outer diameter 6 mm, inner diameter 1.6 mm), and a Pt wire as a counter electrode (the surface area of the Au working electrode on chip is 0.588 mm^2 and the surface area of the commercial Au electrode is 2.010 mm^2 for an area ratio of 3.42).

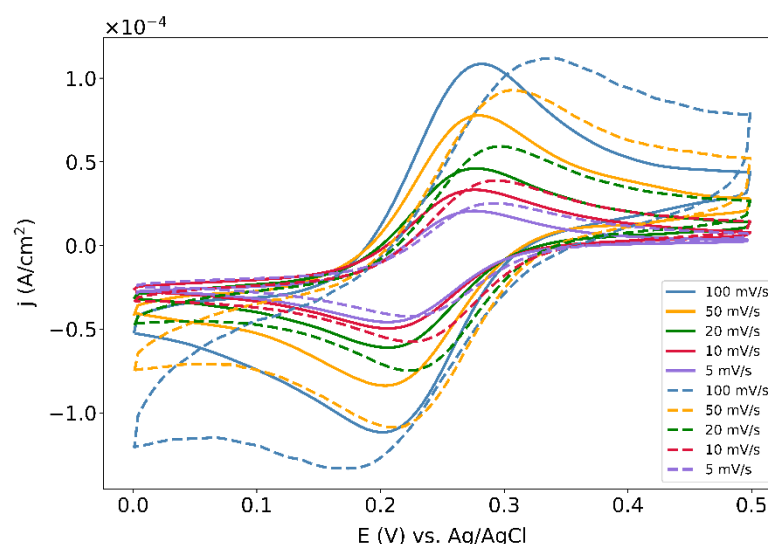


Figure 4. Cyclic voltammograms of Au stripes on chip electrode (solid curves), at different scan rates (legend), compared to measurements obtained using a commercial Au electrode (dashed curves) in 1 mM ferricyanide solution.

As shown in Figure 4, the results obtained using the electrodes on chip are very similar to those obtained using the commercial electrodes. The cathodic and anodic peaks are clearly identifiable in all CV curves and agree well for both sets of electrodes. Referring to the 50 mV/s scan rate, an oxidative current peak at $1.91 \mu\text{A}$ for an oxidative potential of 0.28 V, and a reductive current peak at $-2.23 \mu\text{A}$ for a reductive potential of 0.21 V, are noted for the commercial electrodes (Figure 4, dashed curves). In the case of the electrodes on chip, the oxidative current peaks at $0.495 \mu\text{A}$ for an oxidative potential of 0.280 V, and the reductive current peaks at $-0.513 \mu\text{A}$ for a reductive potential of 0.204 V (Figure 4, solid curves). The mean value of the oxidative and reductive potentials occurs at 0.24 V for both sets of electrodes.

Electrochemical impedance spectroscopy (EIS) can be used to determine the electrolyte double-layer capacitance of electrochemical cells. Another approach consists of using CV measurements, as charging currents (forward segment of CV curve) and discharging currents (reverse segment of CV curve) are observed whenever a potential sweep is applied across a capacitive load. The double-layer charging current (i_{DL}) is related to the potential sweep rate (ν) and the double-layer capacitance (C_{DL}) at the surface of a working electrode by the following equation [36]:

$$i_{DL} = C_{DL} \nu \quad (2)$$

The vertical separation between the two segments at any point along a voltammogram is equal to $2i_{DL}$. Choosing a point and plotting i_{DL} vs. ν yields C_{DL} from the slope of the graph. Using the data plotted in Figure 3 we find a double-layer capacitance of $C_{DL} = 0.29 \mu\text{F}$ for the working electrode on chip, and $C_{DL} = 1.02 \mu\text{F}$ for the commercial electrode.

3.2. Calibration Curves

The magnitude of the current in the CV curves of Figure 3 is directly proportional to the concentration of redox species. Figure 5 plots the peak oxidative current from these CV curves vs. the concentration of redox species for different scan rates. The plots are clearly linear and can be used as calibration curves to determine unknown concentrations of redox species (in this case potassium ferricyanide) after carrying out a cyclic voltammetry experiment using a similar chip.

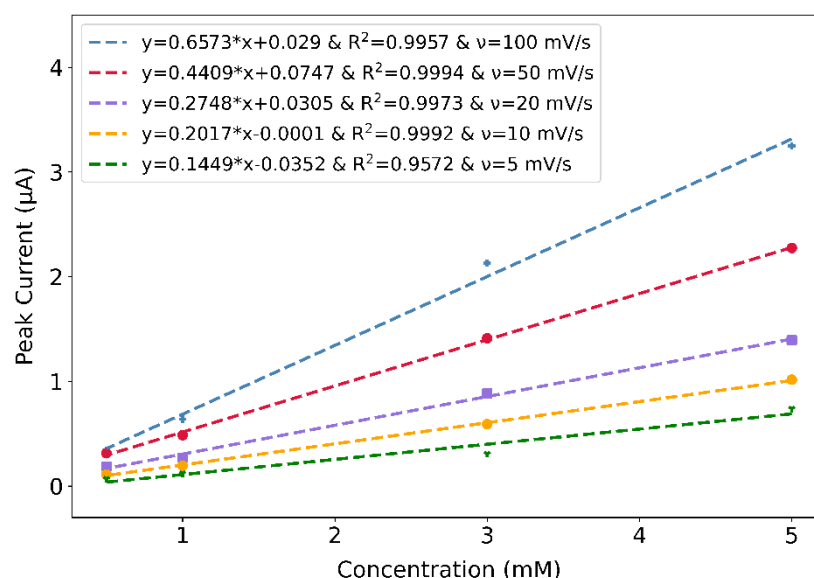


Figure 5. Calibration graphs for various scan rates (legend), taken as the peak oxidative current vs. the concentration of potassium ferricyanide, based on the CV curves of Figure 3, obtained using on-chip Au electrodes.

The intercepts in Figure 5 are not zero as expected when the concentration of redox species is zero. The main cause is noise in the set-up. The noise current of our set-up was measured and found to be in the range of 2–100 nA. This range was obtained using the same setup and electrolyte, but without the redox species.

Blind testing was carried out to ensure that the calibration curves yield the correct concentration of redox species. Electrolyte solutions with three different concentrations of redox species were prepared and given to the experimentalist without communicating the concentrations. The experimentalist performed CV experiments and used Figure 5 to determine the unknown concentration of redox species based on the peak current. The three concentrations measured were 0.5, 2, and 3 mM, corresponding to the prepared concentrations to within 2%.

3.3. Diffusion Coefficient

The diffusion coefficient of a redox species can be obtained from the Randles–Sevcik equation, which describes the relationship between the peak oxidative current, the scan rate, and the diffusion coefficient as follow:

$$i_p = 0.4463 n F A C \left(\frac{n F \vartheta D}{RT} \right)^{1/2} \quad (3)$$

where i_p is the peak oxidative current (A), n is the number of electrons transferred per redox event (here $n = 1$), A is the electrode area (m^2), D is the diffusion coefficient (m^2/s), C is the concentration of the redox species (mol/m^3), ϑ is the scan rate (V/s), R is the gas constant ($\text{J}/(\text{mol}\cdot\text{K})$), T is the temperature (K), and F is the Faraday constant (C/mol). The diffusion coefficient of potassium ferricyanide can be obtained from the slope of the peak

oxidative current plotted against the square root of the scan rate. The diffusion coefficient thus obtained for potassium ferricyanide using our on-chip electrodes is $4.18 \times 10^{-10} \text{ m}^2/\text{s}$, which is in very good agreement with the literature [37].

3.4. Theoretical

A brief synopsis of the applicable theory [38–41] is given in the Appendices A.2 and A.3. The current density passing through the electrode is given by the Butler–Volmer equation (Appendix A.2) [40]:

$$j = Fk^\circ \left\{ c_{red}^s \exp\left(\frac{\alpha F (E - E^\circ)}{RT}\right) - c_{ox}^s \exp\left(-\frac{(1 - \alpha) F (E - E^\circ)}{RT}\right) \right\} \quad (4)$$

c_{red}^s and c_{ox}^s evaluated from the general expressions given in the Appendix A.3, at the electrode position ($x = 0$) (i.e., $c_{red}^s = c_{red}(x = 0, t)$, $c_{ox}^s = c_{ox}(x = 0, t)$). E is the electrode potential as a function of time (e.g., Figure A1a in the Appendix A), and E° is the equilibrium potential which can be obtained from the experimental curves. Thus, the total current density due to both the reduced and oxidized species is:

$$j = Fk^\circ \exp(\mu^2 Dt) \operatorname{erfc}(\mu \sqrt{Dt}) \exp\left(\frac{|\eta|}{b}\right) \left[c_{ox}^b \exp\left(\frac{\alpha F (E - E^\circ)}{RT}\right) - c_{red}^b \exp\left(-\frac{(1 - \alpha) F (E - E^\circ)}{RT}\right) \right] \quad (5)$$

where α is the transfer coefficient. The anodic and cathodic transfer coefficients, α_a and α_c , are defined by the following equations [42]:

$$\alpha_a = \frac{RT}{F} \left(\frac{d \ln j_a}{dE} \right), \quad \alpha_c = \frac{RT}{F} \left(\frac{d \ln j_c}{dE} \right) \quad (6)$$

where j_a and j_c are the anodic and cathodic current densities, respectively. For a 1 electron transfer reaction the transfer coefficient is termed the symmetry factor and could be taken equal to 0.5. Indeed, Figure 3 reveals that the CV curves are symmetric in our case, about the equilibrium potential, E° , so setting $\alpha_a = \alpha_c = \alpha = 0.5$ is justified.

Figure 6 plots the computed current vs. the applied potential E for scan rates of 10 and 100 mV/s. The current was taken as jA where $A = 0.588 \text{ mm}^2$ is the area of the on-chip working electrode and the current density, j , was computed via Equation (4). For potassium ferricyanide as the redox species, in potassium nitrate as the electrolyte, we extract $k^\circ = 10^{-6} \text{ m/s}$ by adjusting the theoretical curves to the experimental results of Figure 3 (re-plotted in Figure 6 for convenience). The theoretical and experimental CV curves are in excellent quantitative agreement.

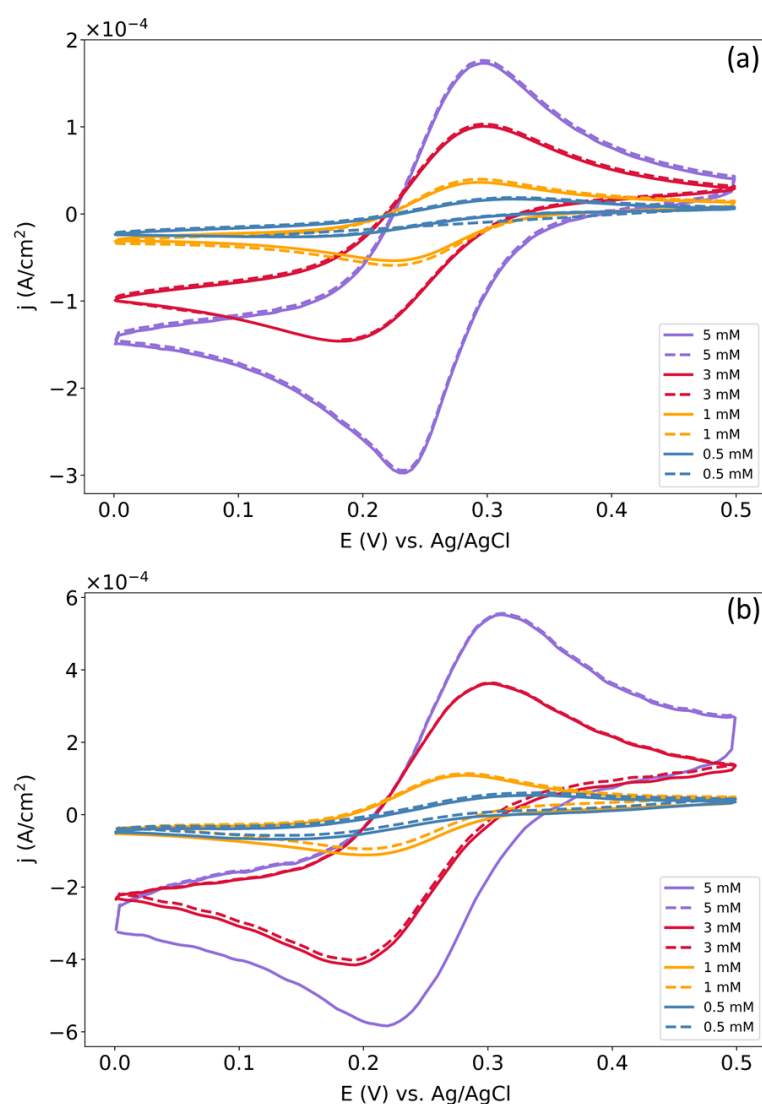


Figure 6. Experimental cyclic voltammogram obtained using Au stripes on chip as working electrodes (solid curve), at a scan rate of (a) 10 mV/s and (b) 100 mV/s, compared to the computed voltammograms (dashed curves). The concentration of potassium ferricyanide (redox species) was set to 0.5, 1, 3, and 5 mM, as labelled in the legend, in 100 mM of potassium nitrate as the electrolyte.

4. Conclusions

Lithographically-defined and evaporated microelectrodes on a substrate are effective structures for electrochemistry as long as they are burned-in, or (equivalently), annealed before use. Micro-electrodes are of strong interest in compact chip-based electrochemical sensing devices. The working electrodes investigated here serve an additional purpose, that of supporting long-range surface plasmons for optical biosensing which constrains its geometry to that of a thin, narrow, and straight stripe. When operated in sufficiently conductive electrolyte, the shape of the electrode has no bearing on the CV measurements, but its area sets the magnitude of the currents involved.

Evaporated gold and platinum micro-electrodes, used as working and counter electrodes, respectively, produced CV measurements in good agreement with commercial (macroscopic) electrodes. Potassium ferricyanide was used as the model redox system, given the reversible nature of the reaction, and its relevance to glucose sensing. Scan-rate dependent concentration curves for potassium ferricyanide were extracted as the peak oxidative currents in the CV measurements. The diffusion coefficient of potassium ferricyanide, extracted by fitting our experimental data to the Randles–Sevcik equation, is

in excellent agreement with the literature. The CV measurements compare very well to theoretical results computed using the Butler–Volmer equation, allowing extraction of the rate constant at zero potential of our redox species.

Micro-electrode systems as investigated here can be integrated with microfluidics and other sensing structures, such as surface plasmon waveguide biosensors, to enable multi-modal sensing strategies.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Appendix A.1. Setup

A triangular voltage wave, as sketched in Figure A1a, was applied within a potential window selected to reveal the redox current peaks.

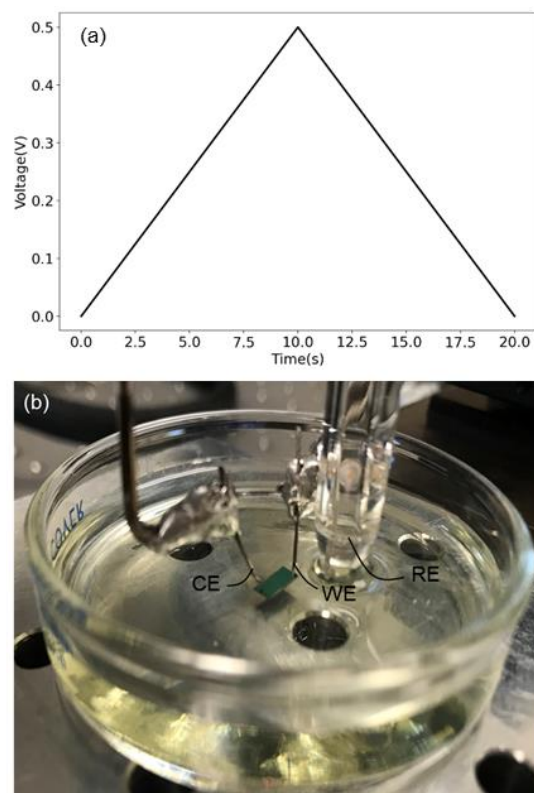


Figure A1. (a) Example triangular voltage waveform applied in the CV measurements (0.5 V peak, 50 mV/s scan rate). (b) Full CV set-up showing probe needles contacting a chip (green) bearing a Au working electrode (WE) and a Pt counter electrode (CE), and a Ag/AgCl reference electrode (RE).

Appendix A.2. Butler–Volmer Equation

Electrode reactions and kinetics describe the relationship between concentration and current density, and the reaction rate depends on the distribution of the species (concentrations and pressures), the temperature, and the electrode potential, E . The net rate of the electrochemical reaction per unit area of electrode, γ_{net} (mol/M·s), equals the rate of oxidation minus rate of reduction:

$$\gamma_{net} = K_{ox}c_{red}^s - K_{red}c_{ox}^s \quad (A1)$$

where $c_{red,ox}^s$ is the concentration at the surface of the electrode of the reduced and oxidized species (mol/m³), and $K_{red,ox}$ is the rate constants of reductant and oxidant (m/s). The rate constants are determined using absolute rate theory:

$$K_{ox} = A \exp\left(-\frac{\Delta G_{ox}^+(E)}{RT}\right) \text{ and } K_{red} = A \exp\left(-\frac{\Delta G_{red}^+(E)}{RT}\right) \quad (A2)$$

where A is a factor (pre-exponential constant in the Arrhenius equation), and $\Delta G_{ox,red}^+(E)$ are the molar Gibbs free energies of activation of the oxidized or reduced species (J·K/mol). The molar Gibbs free energies are expressed in the following forms for anodic and cathodic reactions:

$$\Delta G_{ox}^+(E) = \Delta G_{ox}^+(E^\circ) - \alpha_a F(E - E^\circ) \text{ and } \Delta G_{red}^+(E) = \Delta G_{red}^+(E^\circ) + \alpha_c F(E - E^\circ) \quad (A3)$$

where α_a and α_c are the anodic and cathodic transfer coefficients, which must satisfy $\alpha_a + \alpha_c = 1$. Setting $\alpha_a = \alpha$ and $\alpha_c = 1 - \alpha$, we rewrite Equation (A2) as:

$$K_{ox} = \exp\left(-\frac{\Delta G_{ox}^+(E)}{RT}\right) = k^\circ \exp\left(\frac{\alpha F(E - E^\circ)}{RT}\right)$$

$$K_{red} = A \exp\left(-\frac{\Delta G_{red}^+(E)}{RT}\right) = k^\circ \exp\left(-\frac{(1 - \alpha)F(E - E^\circ)}{RT}\right) \quad (A4)$$

where $k^\circ = A \exp\left(-\frac{\Delta G_{red}^+(E^\circ)}{RT}\right)$.

The observed current density, in units of A/m², of the electrode reaction can be expressed as:

$$j = F\gamma_{net} = F(K_{ox}c_{red}^s - K_{red}c_{ox}^s) \quad (A5)$$

Substituting Equation (A4) into Equation (A5) yields the Butler–Volmer equation (Equation (4) of the main text):

$$j = Fk^\circ \left\{ c_{red}^s \exp\left(\frac{\alpha F(E - E^\circ)}{RT}\right) - c_{ox}^s \exp\left(-\frac{(1 - \alpha)F(E - E^\circ)}{RT}\right) \right\} \quad (A6)$$

Comparing experimental results with theory is useful to validate the electrode designs and the experimental techniques applied, and to extract further information about the redox reactions.

Appendix A.3. Concentration

The Poisson–Nernst–Planck (PNP) equations model a mean-field approximation for ion interactions involving ionic concentration and the electric potential. These equations model ion and charge transport problems in semiconductor devices, electrochemistry and biological systems. In electrochemistry, the PNP model describes the influence of an ionic concentration gradient and of an electric field on the flux of chemical species, specifically ions.

The general form of the conservation of mass equation for an incompressible fluid is combined with the equation for flux density to describe mass transport in a system:

$$\frac{\partial c_i}{\partial t} + \mathbf{u} \cdot \nabla c_i - \nabla \cdot [D(\nabla c_i + u_{m,i} z_i F c_i \nabla \varphi)] = 0 \quad (\text{A7})$$

In the above, c_i is the molar concentration (mol/m^3), $\mathbf{u}$ is the drift velocity vector (m/s), D is the diffusion coefficient (m^2/s), $u_{m,i}$ is the mobility ($\text{s} \cdot \text{mol}/\text{kg}$), F is the Faraday constant (C/mol), z_i is the number of electrons involved in a redox reaction, and φ is the electric potential distribution (V) throughout the electrolyte. Recall that an incompressible fluid implies $\nabla \cdot \mathbf{u} = 0$. Equation (A7) is known as the Nernst–Planck equation.

The subscript i in Equation (A7) identifies a particular ionic species for which the equation is written. Thus, the number of ionic species involved in a reaction directly controls the number of equations to be solved—in general, oxidized and reduced species are involved. Thus, Equation (A7) yields i equations with $i + 1$ unknowns. To solve this system, more equations are needed, so Poisson’s equation is added, which governs the distribution of the electrostatic potential throughout the system. Poisson’s equation relates the potential distribution to the distribution of charged species within a medium:

$$-\nabla \cdot (\epsilon \nabla \varphi) = \sum_i z_i e c_i \quad (\text{A8})$$

where e is the elemental charge and ϵ is the permittivity of the medium. Here the medium is the electrolyte and the only charge carriers involved are the ions (species i). It is assumed that the solvated ions and electric field do not alter the permittivity of the electrolyte. The full set of Poisson–Nernst–Planck (PNP) equations are thus given by Equations (A7) and (A8) written for all ionic species under consideration.

CV experiments are usually performed at a high electrolyte concentration. Under this condition, the resistivity of the solution is sufficiently low that the electric field therein is negligible, and we can assume $\varphi = 0$ throughout the medium. In this circumstance, the PNP equations reduce to:

$$\frac{\partial c_i}{\partial t} + \mathbf{u} \cdot \nabla c_i - \nabla \cdot [D(\nabla c_i)] = 0 \quad (\text{A9})$$

For zero convection ($\mathbf{u} = 0$, no flow), no reaction (null electrode potential), and a constant diffusion coefficient, the simplified PNP Equation (A9) becomes Fick’s second law of diffusion:

$$\frac{\partial c_i}{\partial t} = D \nabla^2 c_i \quad (\text{A10})$$

This is a partial differential equation that describes how the concentration of ionic species, i , evolves over time. For our case under consideration, where the electrolyte concentration is high, reactions are limited to the direction normal to the electrode surface and near the latter. As a result, the model simplifies further to one spatial dimension, x , over the domain $x = 0 - L$, the maximum extent of the diffusion layer. Boundary conditions are needed to obtain particular solutions to Equation (A10). For the case of one spatial variable x and time t , two boundary conditions in space at $x = 0$ (electrode position) and $x = L$ (bulk) are required, along with an initial condition at $t = 0$.

$$L = 6\sqrt{Dt_{max}} \quad (\text{A11})$$

A conservative value for L is set by the Cottrell equation to greatly exceed the mean diffusion layer thickness:

Where t_{max} is the period of the cyclic voltammogram. Thus, at $x = L$ we have:

$$c_i(x = L, t) = c_i^b \quad (\text{A12})$$

where c_i^b is the bulk concentration of ionic species i .

At $x = 0$, Fick's first law, which describes the relationship between the diffusive flux and the concentration under steady-state conditions, must be satisfied for all t . In one spatial dimension, this law is written in the molar basis as:

$$\frac{k^\circ}{D} \exp\left(\frac{|\eta|}{b}\right) c_i^s = -\frac{\partial C_i}{\partial x} \Big|_{x=0} \quad (\text{A13})$$

where $c_i^s = c_i(x = 0, t)$ is the concentration of ionic species, i , at the electrode surface (mol/m^3), k° is the rate constant at zero potential (m/s), η is the overpotential, and $b = RT/F$ is a constant. The potential E of the electrode through which a current flows differs from the equilibrium potential E° established when no current flows. The difference between these potentials is the overpotential $\eta = E - E^\circ$. To simplify the notation, the parameter μ is defined as $\mu = \frac{k^\circ}{D} \exp\left(\frac{|\eta|}{b}\right)$. Thus, Equation (A13) can be rewritten as:

$$\mu c_i^s = -\frac{\partial C_i}{\partial x} \Big|_{x=0} \quad (\text{A14})$$

The last boundary condition required is the initial condition applicable at $t = 0$ (before application of the potential), which holds for all x :

$$c_i(x, t = 0) = c_i^b \quad (\text{A15})$$

Equation (A10) subject to boundary conditions (A12), (A14), and (A15) can be solved using the Laplace transform. Thus, considering a redox reaction involving one oxidized and one reduced species ($i = ox, red$), the concentration function of the oxidized species, $c_{ox}(x, t)$, has the following form:

$$\frac{c_{ox}(x, t)}{c_{ox}^b} = 1 - \operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}}\right) + \exp(\mu x + \mu^2 Dt) \cdot \operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}} + \mu \sqrt{Dt}\right) \quad (\text{A16})$$

The concentration of the reduced species, $c_{red}(x, t)$, has a similar form.

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