

A Large-Scale, Wireless Electrochemical Bipolar Electrode Microarray

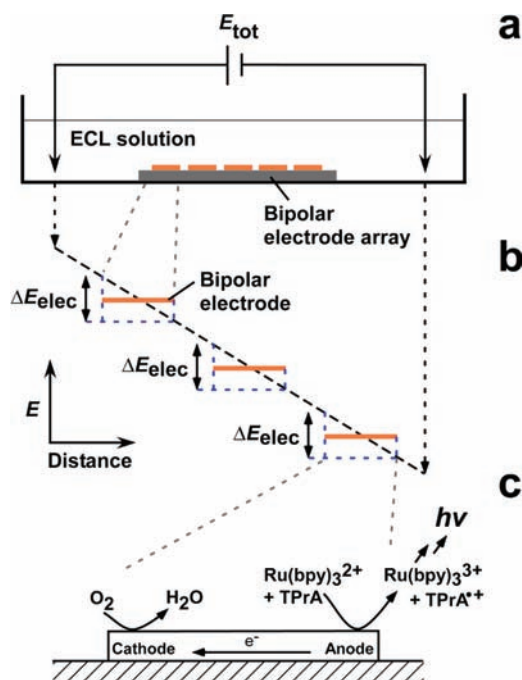
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Here we report a microelectrochemical array composed of 1000 individual bipolar electrodes (Figure 1a) that is controlled with just two driving electrodes and a simple power supply. The system is configured so that faradaic processes occurring at the cathode end of each electrode are correlated to light emission via electrogenerated chemiluminescence (ECL) at the anode end. This makes it possible to read out the state of each electrode simultaneously. The significant advance reported here is that the electrode array is fabricated on a glass microscope slide and is operated in a simple electrochemical cell. This eliminates the need for housing the bipolar electrode array within a microfluidic channel,^{1,2} provides a fabrication route to arbitrarily large electrode arrays, and will make it possible to place sensing chemistries onto each electrode using a robotic spotter.

Scheme 1



Typical electrochemical experiments utilize a three-electrode configuration.³ However, using this approach for electrode array technologies requires running a separate wire to each electrode one at a time. Because the time scale for electrochemical methods is slow compared to optical- or field-driven processes, it may be impractical to use this approach for very large arrays of electrodes. However, we recently reported a method for overcoming these limitations. Specifically, we showed that when a microfabricated wire on the order of 100–1000 μm in length is confined within a microfluidic channel, the potential difference between the electrode

and the contacting solution can be controlled via a pair of driving electrodes situated at the ends of the channel.^{1,2} In contrast to a normal three-electrode configuration, where the potential of the electrode is controlled, this approach relies on controlling the potential of the solution. One obstacle with using bipolar electrodes as sensors is that there is no convenient method to directly read the current. However, we have shown that this impediment can be circumvented using ECL reporting.^{1,2}

The principles of bipolar electrochemistry have been rigorously described in several publications.^{1,2,4–7} Scheme 1a illustrates how these principles are exploited in a microarray. A voltage applied between two driving electrodes (E_{tot}) creates a linear potential gradient through the solution above the bipolar electrodes. Each bipolar electrode floats to an equilibrium potential whose value is governed by the potential gradient in solution (Scheme 1b). The potential difference at the electrode/solution interface will vary across the length of the electrode according to the potential gradient applied to the solution. For a linear potential gradient, the potential difference across each electrode (ΔE_{elec}) will be identical, and both anodic and cathodic overpotentials will exist on a single electrode. When the anodic and cathodic overpotentials are larger than the onset potentials for the oxidation and reduction of species in solution, then both reactions will occur simultaneously at the ends of the bipolar electrode. Due to charge neutrality, an electrochemical process at one pole of the bipolar electrode must be accompanied by an equal and opposite process at the other pole (Scheme 1c). In the experiments reported here, O_2 is reduced at the cathode, and $\text{Ru}(\text{bpy})_3^{2+}$ and tri-*n*-propylamine (TPrA) are oxidized to emit ECL at the anode.^{8,9} Our group has previously quantified the ECL intensity at the anode and found that it is directly related to the rate of the cathodic reaction.²

Figure 1a is an optical micrograph of the microelectrode array design used in these experiments. The array consists of 1000 Au bipolar electrodes microfabricated on a glass slide. Each electrode is 500.0 μm long by 50.0 μm wide, and the electrodes are separated horizontally by 200.0 μm and vertically by 50.0 μm . The electrochemical cell was constructed of Teflon (29.0 cm \times 4.0 cm) and filled with 5.0 mL of 5.0 mM $\text{Ru}(\text{bpy})_3^{2+}$ and 25.0 mM TPrA in 0.10 M phosphate buffer (pH 6.9) (Scheme 1a). Two stainless steel plate electrodes were placed 18.0 mm apart with the microarray situated between them. Figure 1b is a luminescence micrograph of the region shown in Figure 1a after application of 85.0 V to the driving electrodes. Using geometrical arguments, an E_{tot} of 85.0 V translates to a ΔE_{elec} of ~ 2 V. This voltage is sufficient to initiate the reduction of O_2 and simultaneous oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ and TPrA at opposite ends of the bipolar electrode. Therefore, light is emitted from the anodic surface of every bipolar electrode in the array.

Figure 1b illustrates the uniformity of the position and area of ECL emission for each electrode. This luminescence micrograph indicates that each electrode has been subjected to an acceptably

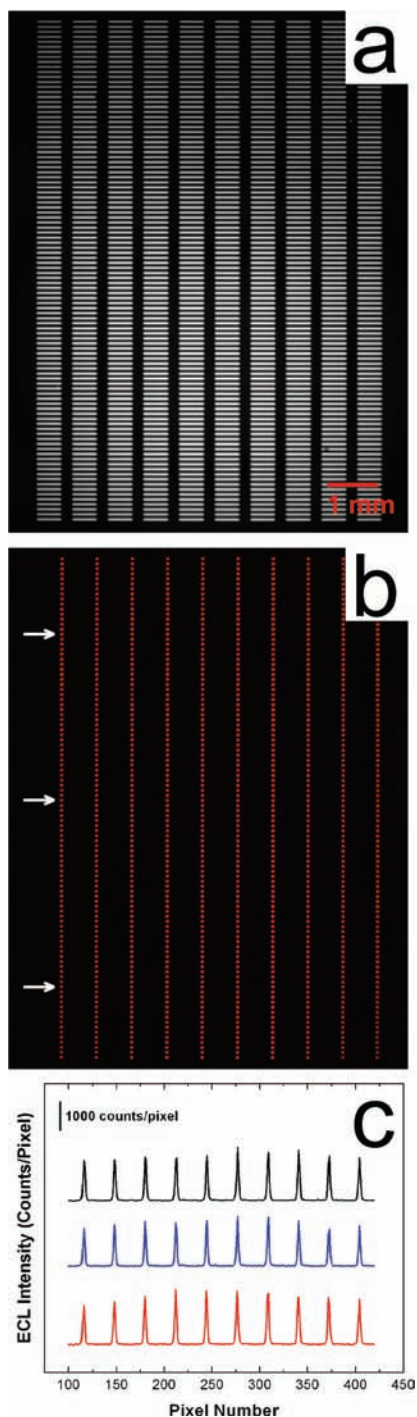


Figure 1. (a) Optical micrograph of the bipolar electrode array. (b) ECL intensity emitted at $E_{\text{tot}} = 85.0$ V. (c) ECL intensity profile obtained from the three rows indicated by arrows in frame b.

uniform electric field. Accordingly, every electrode in the array has a nearly identical anodic and cathodic overpotential. Figure 1c corroborates these assumptions by showing the ECL intensities from several different rows of electrodes. This plot indicates that the ECL intensity, and hence the current flowing through each electrode, is nearly the same: 3877 ± 374 counts.

Faradaic reactions on a bipolar electrode have been shown to induce a local decrease in the electric field, and the magnitude of this decrease depends on a competition between the electronic conductivity of the electrode and the ionic conductivity of the solution.⁵ In our design, the solution height above the electrodes (4 mm) is large and the buffer concentration is high (0.10 M). These conditions prevent faradaic reactions on the bipolar electrodes from significantly distorting the electric field. In other words, the electrical current flowing through the bipolar electrodes is kept negligibly small compared to the ionic current flowing through the solution.

The cell design used for these experiments is not optimal, because products produced by electrochemical reactions at the driving electrodes contaminate the electrolyte solution in contact with the electrode array. This limits the operation of the array to just a few seconds before the luminescence is quenched by electrogenerated impurities.⁹ This time is sufficient for most sensor applications; however, and in any event the gold electrodes remain fully intact throughout the experiment and the array returns to its fully operational condition if the buffer solution is replaced. We are currently exploring the use of simple conductive partitions, constructed of agarose or cellulose, to separate the driving electrodes from the array to prevent electrogenerated contaminants from reaching the electrode array.

The array presented here has a density of ~ 2000 sensing elements/cm². A typical density for a fluorescence-based microarray is ~ 5000 spots/cm²,¹⁰ and commercial electrochemical arrays¹¹ may have densities as large as 18 000 electrodes/cm². We believe it will be possible to increase the absolute number of bipolar electrodes in an array, and hence the number density, by using smaller, more closely spaced electrodes. Our present studies are aimed at that objective and at demonstrating that this approach can be used for quantitative sensing applications. The results of those studies will be reported in due course.

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Supporting Information Available: Information about materials and fabrication procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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