

*Supporting Information for*

**Signal Amplification in a Microchannel from Redox Cycling with Varied Electroactive Configurations of an Individually Addressable Microband Electrode Array**

Penny M. Lewis, Leah Bullard Sheridan, Robert E. Gawley, Ingrid Fritsch\*

University of Arkansas, Department of Chemistry and Biochemistry, Fayetteville, AR 72701

Phone: 479-575-6499; Fax: 479-575-4049; E-mail: ifritsch@uark.edu

**Abstract of Content in Supporting Information**

This Supporting Information document contains procedures of microfabrication of electrodes and BCB insulating layer of the device, photograph of the microelectrode array chip with dimensions, a figure of masking PDMS to create a hydrophilic region, plots comparing generator current for different numbers of generator electrodes (collectors off), plots comparing generator current at one generator electrode having different numbers of collector electrodes, and calibration curves from CA and CV with redox cycling for the 7g/7c configuration in the closed microchannel.

## **Details of Microfabrication of Microelectrode Array Device**

**Fabrication of microelectrode arrays.** Microelectrode arrays were fabricated using standard photolithography techniques on 5” silicon wafers. Wafers were coated with a 7.5 nm chromium adhesion layer followed by 100.0 nm gold using a BOC Edwards 306 Auto thermal evaporator (Wilmington, MA).

In a class 100 cleanroom environment, wafers were spin-coated with 1.25  $\mu\text{m}$  of positive photoresist AZ4110 (Clariant Corporation, Charlotte, NC) and cured for 2 min at 110 °C using an MTI TargetTrack spincoater. Wafers were then exposed to UV light using a SUS-4 Karl Suss Mask Aligner through a positive field photoplot contact mask printed with the image of the electrode array. (Photoplots were drawn in AutoCAD and high resolution photoplots (6.35  $\mu\text{m}$ ) were printed by Advanced Reproductions (North Andover, MA).) Exposed AZ4110 was developed for 90 s in AZ400K developer diluted 1:3 with deionized water. Gold and chromium were removed by etching for approximately 2 min in gold etchant (Transene Company, Inc.), then approximately 20 s in chrome etchant (MicroChrome Technology). Finally, patterned photoresist was removed by rinsing with acetone and, if necessary, 3 min of exposure to high-energy oxygen plasma (250 mtorr, RF = 250 W, O<sub>2</sub> flow = 80 sccm) using an Automatic Plasma Equipment APE110 (LFE Plasma Systems). Wafers were diced into individual chips, each patterned with the 20-electrode array, using a Model T1100 Micro Automation dicing saw equipped with a resin-bonded diamond dicing blade.

**Fabrication of BCB microchannels.** The spincoater used for coating BCB is compatible only with 5” wafers, and the thickness of the BCB features required that each chip be patterned individually. Therefore, individual electrode array chips were glued to individual 5” silicon

wafers using a small amount of Cyclotene resin XU35075 (Dow Chemical) as adhesive. To prevent a rim of polymer from building up on the edges of the electrode array chip due to surface tension effects, fragments of silicon wafer were glued flush along the edges of the chip. The BCB was cured in a Blue M Oven (New Columbia, PA) using the following program: 15 min ramp to 100 °C, hold 15 min; 15 min ramp to 150 °C, hold 15 min; 15 min ramp to 250 °C, hold 40 min; and 2 h cool to 25 °C.

Using a MultiFab<sup>TM</sup> spincoater (Machine Technology Inc.), wafers were coated with VM652 adhesion promoter followed by Cyclotene XU35075 Resin, which was spincoated for 5 s at 500 rpm then 60 s at 1000 rpm to create a 30 µm thick layer. BCB was soft-baked for 90 s at 110 °C and exposed to UV light through a dark-field photoplot mask (drawn in AutoCAD and printed by Advanced Reproductions) using a Karl Suss Mask Aligner. Wafers were then puddle-developed in DS2100 development solvent (Dow Chemical) for approximately 175 s (90 s development and a 85 s overdevelop time) and rinsed vigorously with developer for 30 s while spinning at 500 rpm. Patterned BCB was cured in a Blue M oven as described above. Residual BCB in the microchannel was removed using a 208 W O<sub>2</sub>/SF<sub>6</sub> plasma (32 and 8 sccm, respectively) at 250 mtorr in a PlasmaTherm SLR Series reactive ion etch (RIE) before dicing.

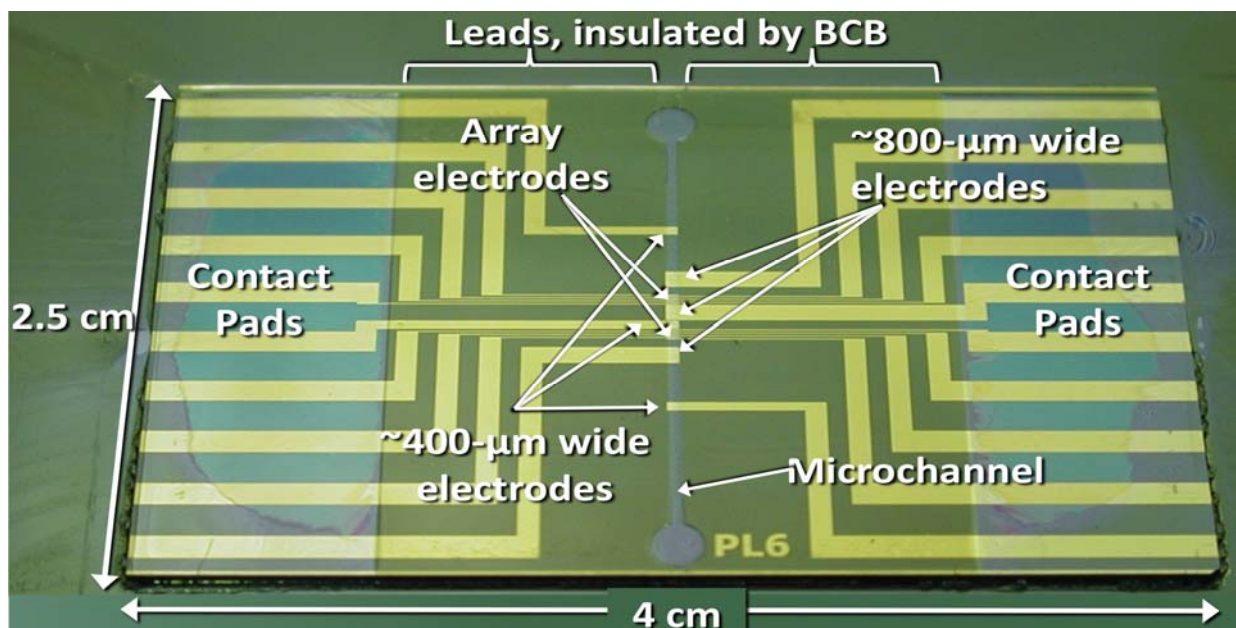


Figure S-1. Photograph of the microelectrode array chip (without the lid), indicating location of the gold arrays (two sets, each with seven,  $\sim 50\text{-}\mu\text{m}$  wide microbands, separated by  $\sim 25\text{-}\mu\text{m}$  gaps),  $\sim 800\text{-}\mu\text{m}$  wide electrodes (three), and  $\sim 400\text{-}\mu\text{m}$  wide (three) electrodes. BCB insulator-covered regions are also shown. Openings in that layer define the microchannel's horizontal length (19 mm, with two 2-mm diameter circles at the ends) and width ( $600\ \mu\text{m}$ ). The microchannel width also defines the electrode length to  $\sim 600\ \mu\text{m}$ .

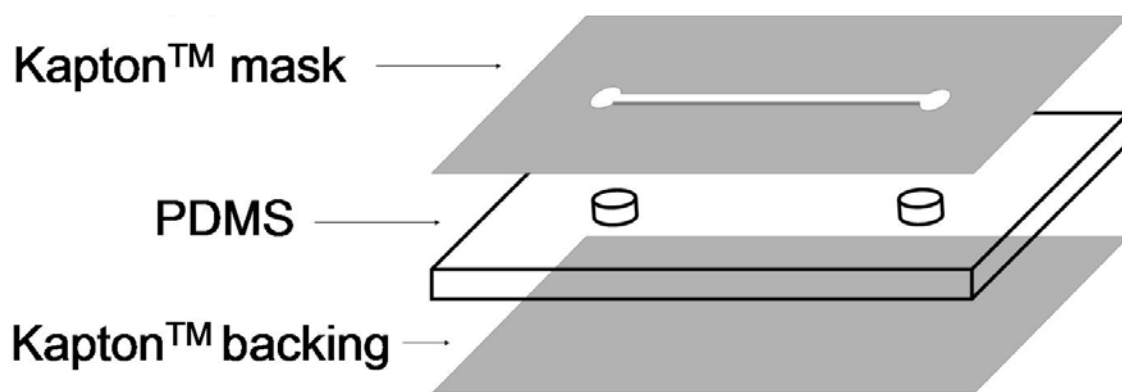
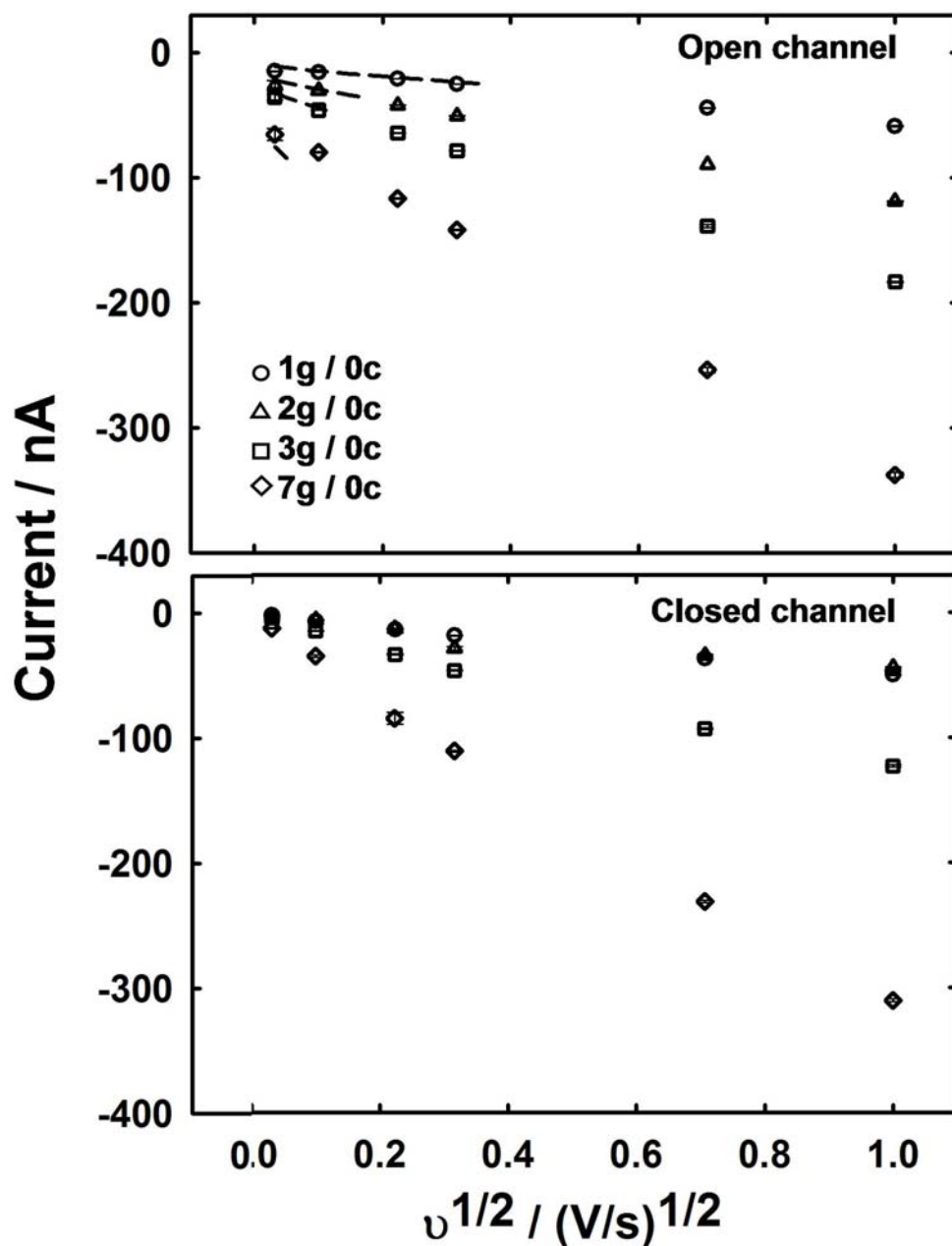
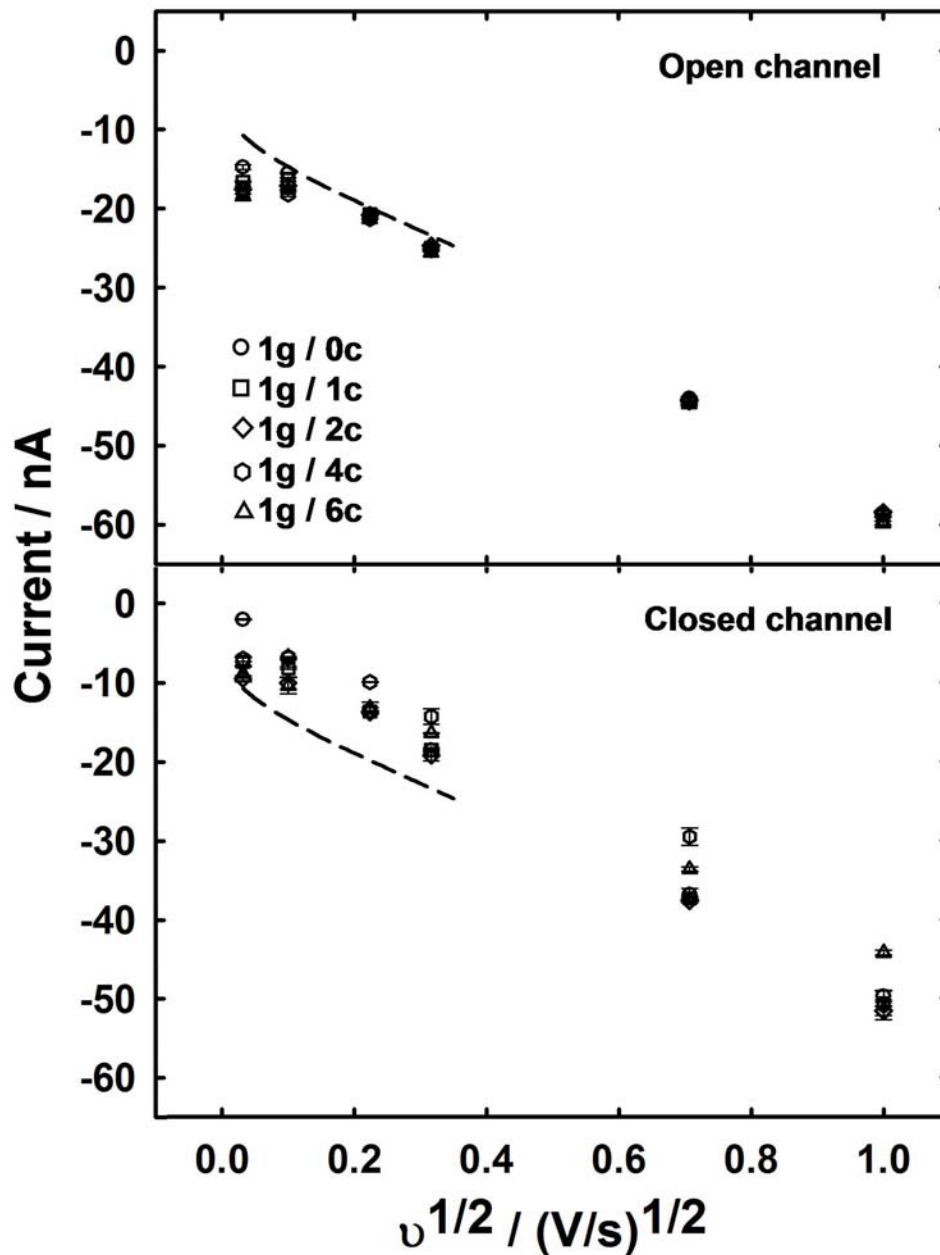


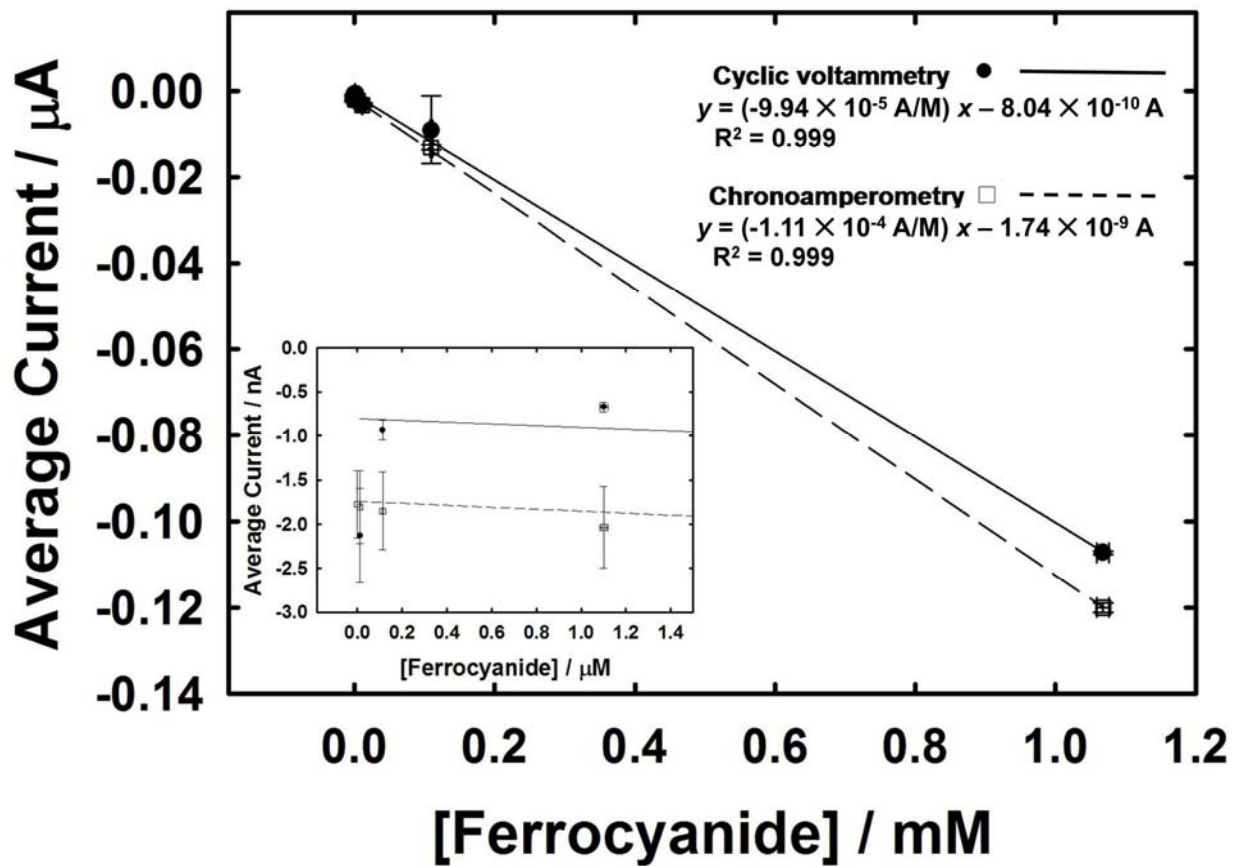
Figure S-2. Schematic of Kapton™-masked PDMS. Layers of Kapton™ film are used to mask solvent-extracted PDMS, exposing only a small strip of PDMS to oxygen plasma. A hydrophilic surface is generated only on the exposed PDMS.



**Figure S-3.** Comparison of electrochemical responses for different numbers of generator electrodes for the open (top figure) and closed (bottom figure) microchannel, using the internal electrode set-up. Observed current (either peak current or plateau current from the cyclic voltammetry (CV) response, whichever is higher) is plotted as a function of square root of scan rate. Current predicted from eq 2 in the main paper is shown by the dashed curves. Error bars represent  $\pm 1$  standard deviation ( $N = 3$ ) and are included, although they fall within the size of the markers. The solution consisted of 0.4 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl.



**Figure S-4.** Comparison of electrochemical responses for electrode configurations involving one generator electrode and different numbers of collector electrodes (held at -0.10 V) for the open (top figure) and closed (bottom figure) microchannel, using the internal electrode set-up. Observed current at the generator electrode (either peak current or plateau current from the CV response, whichever is higher) is plotted as a function of square root of scan rate. Current predicted from eq 2 in main paper is shown by the dashed curves. Data points are averages from three experiments. Error bars represent  $\pm 1$  standard deviation ( $N = 3$ ) and are included, although they fall within the size of the markers. The solution consisted of 0.4 mM  $K_4Fe(CN)_6$  in 0.1 M KCl.



**Figure S-5.** Calibration curves of generator current as a function of the concentration of the model redox compound  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.1 M KCl using chronoamperometry (CA) and CV with redox cycling for the 7g/7c electrode configuration in the closed microchannel, using the internal set-up. Least squares best-fit lines are shown for results from CA (dashed) and CV (solid). The limit of quantification for both techniques is 10  $\mu\text{M}$ . The inset shows an expansion of the region from 10 nM to 1  $\mu\text{M}$  ferrocyanide. The seven collector electrodes were held at -0.10 V while the seven generator electrodes were swept at 0.010 V/s (CV) or stepped (CA) from -0.10 V to +0.30 V. Data points are averages and error bars represent  $\pm 1$  standard deviation (N = 3 for CV and N = 6303 for CA).