

Supporting Information

6 March, 2014

Ms. ID: ac-2014-004294

**Wire, Mesh, and Fiber Electrodes for Paper-based
Electroanalytical Devices**

Stephen E. Fosdick, Morgan J. Anderson, Christophe Renault, Paul
R. DeGregory, James A. Loussaert, Richard M. Crooks

(10 pages)

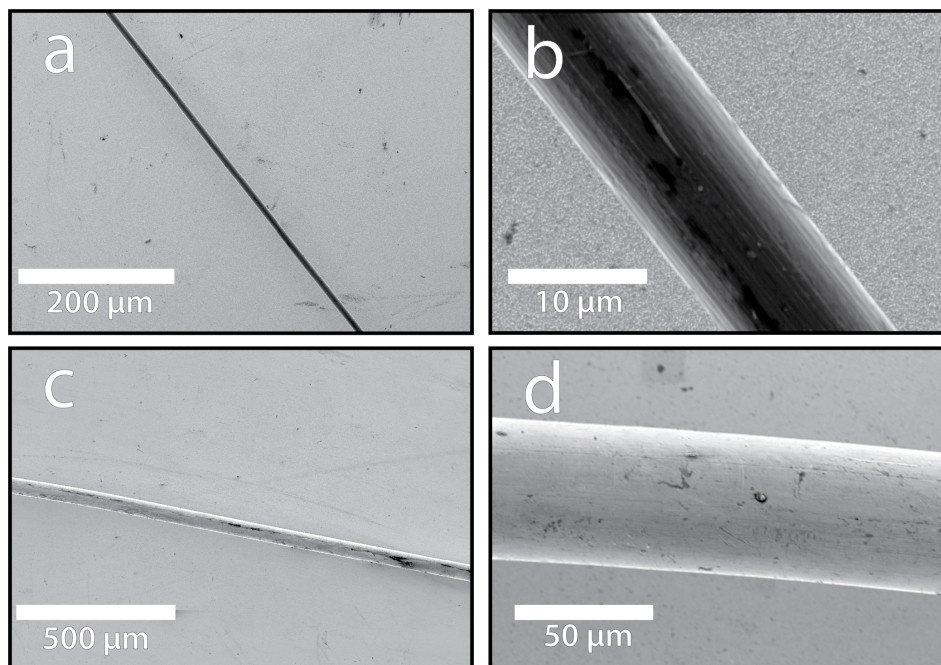


Figure S1. Scanning electron micrographs of the carbon fiber and Au wire electrodes used in this study. The SEM used in this study was a Quanta 650 FEG ESEM system. (a and b) Micrographs of C fiber. (c and d) Micrographs of Au wire. The measured diameter of the Au wire was $51.3 \pm 0.2 \mu\text{m}$ and the measured diameter of the C fiber was $10.0 \pm 0.2 \mu\text{m}$.

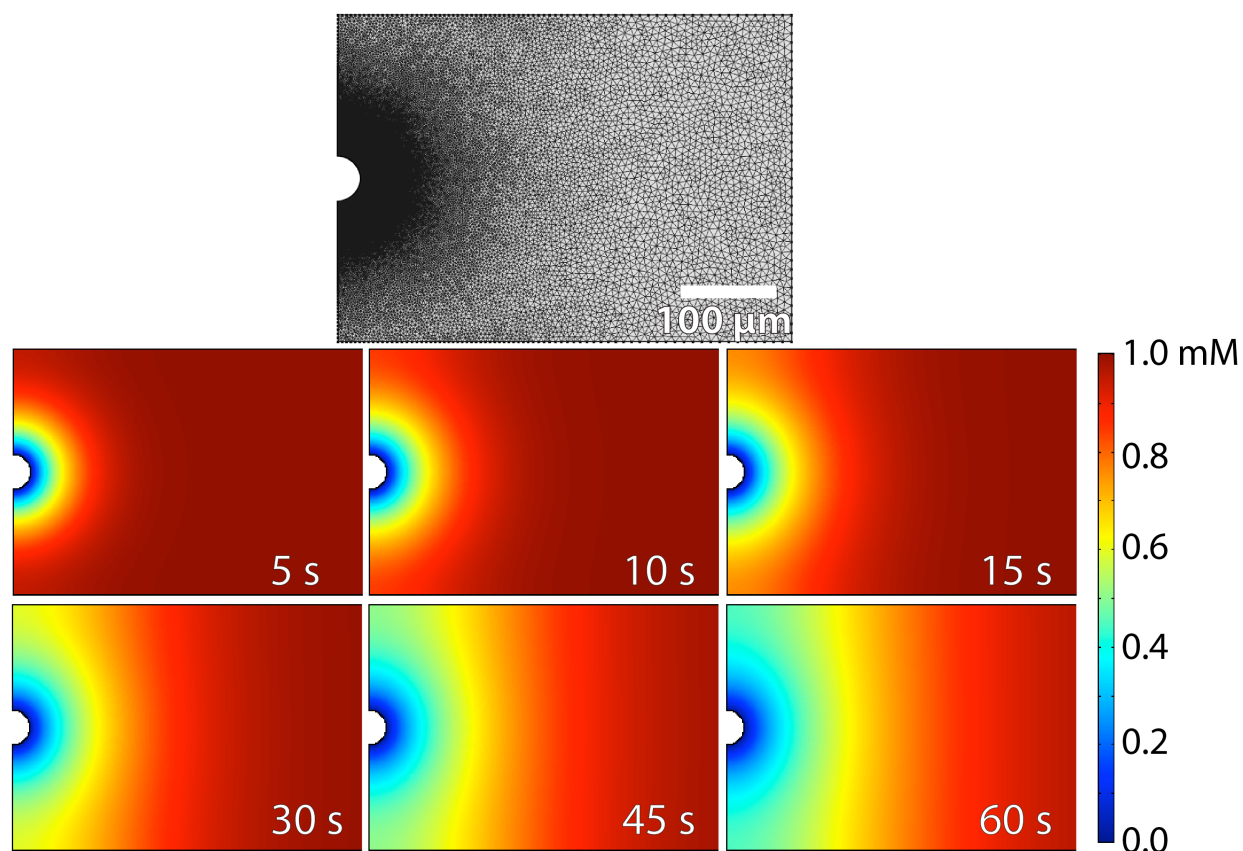


Figure S2. Finite element simulation of a single potential step experiment obtained using a 51.3 μm electrode. The top frame is an image of the simulation geometry and mesh (360 μm tall, 500 μm wide, wire placed at center of height of channel, and the left edge representing a plane of symmetry). The remaining frames show the concentration profiles of the redox probe at the indicated times during the potential step. Note that the diffusion profile of the redox active species begins to reach the top and bottom walls of the simulation in ~ 10 s, breaking the symmetry of the 1D semi-infinite mass transport of the redox probe to the wire. Note that uncompensated resistance, present in the experimental measurements, was not taken into account in the simulations.

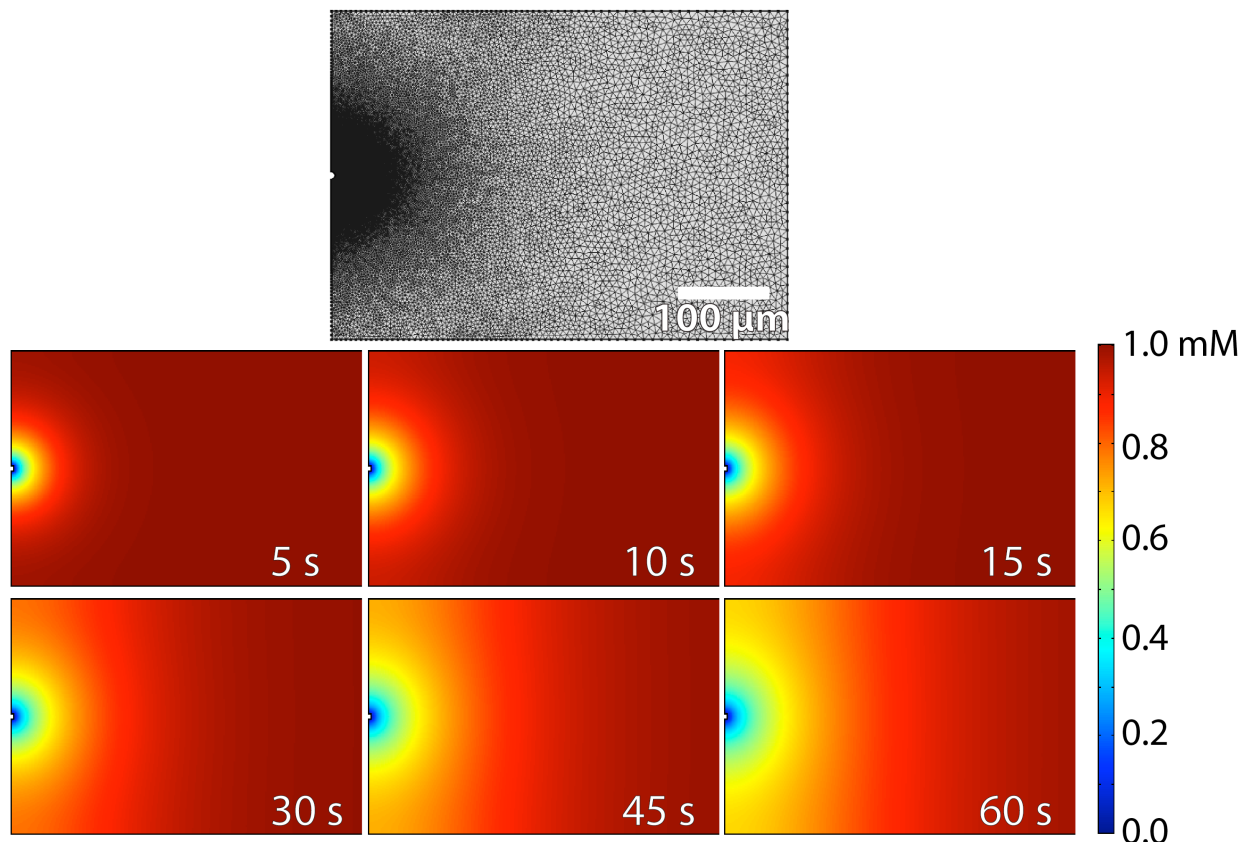


Figure S3. Finite element simulation of a single potential step experiment obtained using a $9.95\ \mu\text{m}$ electrode. The top frame is an image of the simulation geometry and mesh ($360\ \mu\text{m}$ tall, $500\ \mu\text{m}$ wide, wire placed at center of height of channel, and the left edge representing a plane of symmetry). The remaining frames show the concentration profiles of the redox probe at the indicated times during the potential step. Note that the diffusion profile of the redox active species begins to reach the top and bottom walls of the simulation in $\sim 15\ \text{s}$, breaking the symmetry of the 1D semi-infinite mass transport of the redox probe to the wire. Note that uncompensated resistance, present in the experimental measurements, was not taken into account in the simulations.

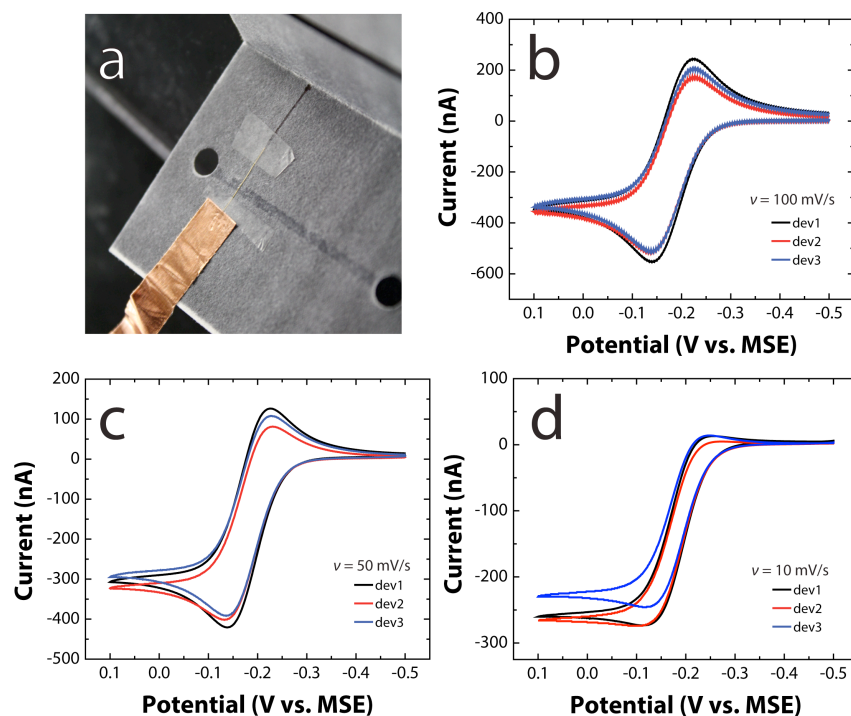


Figure S4. (a) Photograph of a HC-oPAD where the Au wire is placed on the bottom of Layer 1 instead of between Layers 3 and 4. (b-d) CVs obtained using three independently fabricated oPADs like that shown in (a). The scan rates are indicated in the individual frames. The solution contained 1.0 mM FcMeOH in 0.10 M KNO_3 . At $v = 100 \text{ mV/s}$, $i_{p,a}$ and $i_{p,c}$ varied by $\pm 4.3\%$ and $\pm 5.1\%$. At $v = 50 \text{ mV/s}$ $i_{p,a}$ and $i_{p,c}$ varied by $\pm 3.9\%$ and $\pm 3.8\%$, respectively. The variation at $v = 10 \text{ mV/s}$ was more substantial, the shape of the CVs somewhat different, possibly due to a small amount of unintentionally added flow. The reference electrode was a mercury/mercurous sulfate (MSE) ($\text{Hg}/\text{H}_2\text{SO}_4$, $E = 0.64 \text{ V vs. NHE}$) and the counter electrode was a Pt wire. The reference and counter electrodes were placed in the outlet reservoir.

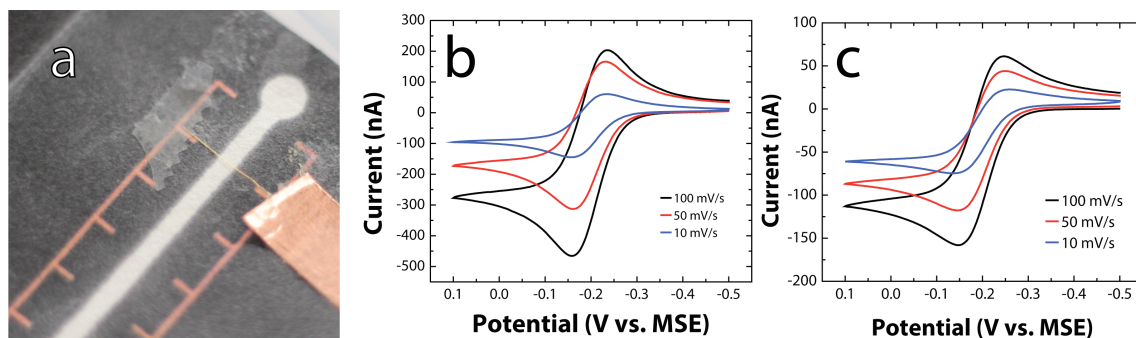


Figure S5. (a) Photograph of an oPAD having a cellulose-filled paper channel (i.e., not a hollow channel). The working electrode was placed in contact with the paper channel on top of Layer 3. The reference (MSE) and counter electrodes (Pt wire) were placed in the outlet reservoir. (b and c) CVs of 1.0 mM FcMeOH as a function of scan rate using the oPAD shown in (a). In (b) the working electrode was a 51.3 μm Au wire and in (c) it was a 10.0 μm C fiber. The pink lines in (a) are alignment features for folding and wire placement.

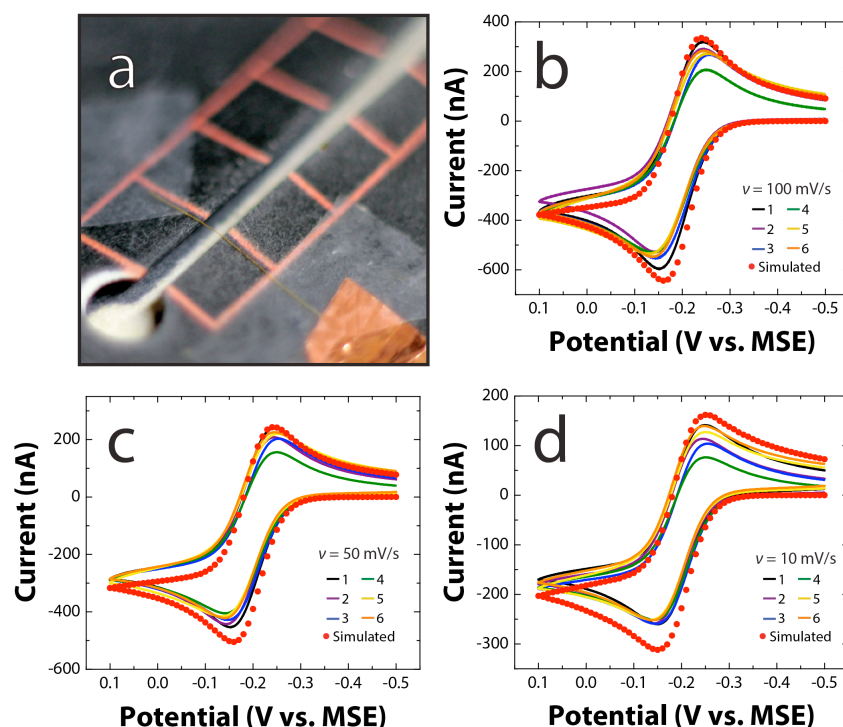


Figure S6. Results illustrating the reproducibility of the electrochemical response of independently fabricated hollow channel oPADs. (a) Photograph of a hollow channel oPAD having a $51.3\ \mu\text{m}$ Au wire working electrode placed on the top of Layer 3. The photograph was obtained after the device had been used to obtain the data in Frames b-d. The hemichannel (white paper channel) on Layer 4 is visible at the bottom of the inlet. The pink lines are alignment features for folding and wire placement. The reference (MSE) and counter electrodes (Pt wire) were placed in the outlet reservoir. (b-d) CVs as a function of scan rate obtained using six independently fabricated devices like the one shown in (a). The colored lines show the response of each device and the red circles show the results of finite element simulations.

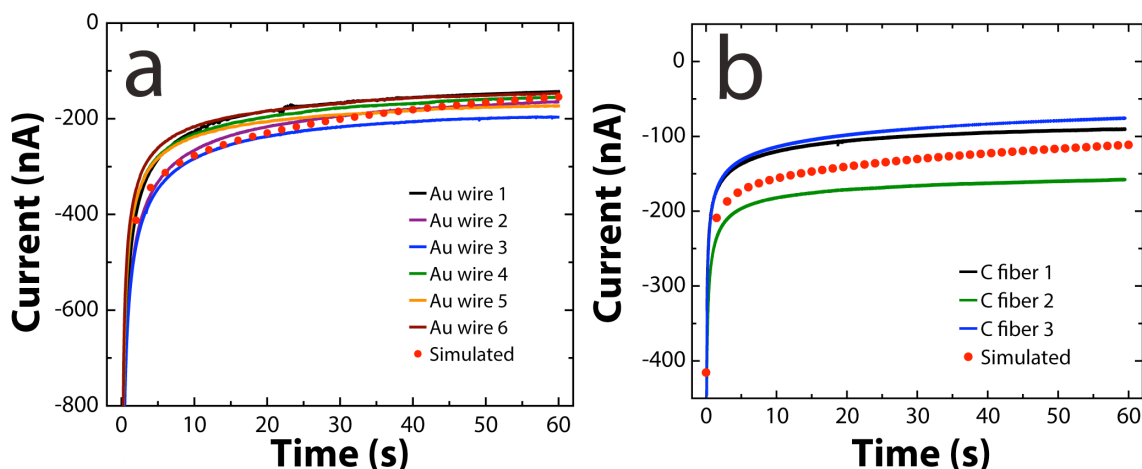


Figure S7. (a) Chronoamperometry collected using 6 individually fabricated hollow channel oPADs having a 51.3 μm Au wire working electrode. The experimental results (colored lines) can be compared directly to the simulated results (red circles). The average quasi-steady-state current (i_{qss}) at $t = 15$ s was -220 ± 20 nA, at $t = 30$ s i_{qss} was -186 ± 19 nA, and at $t = 60$ s i_{qss} was -163 ± 20 nA, indicating $\sim \pm 11\%$ variation for the 6 independently fabricated devices. The simulated values of i_{qss} at these times are -250, -201, and -155 nA, respectively. The differences between the average experimental values and the simulated results are 12%, 8%, and 6%, respectively. (b) Chronoamperometry collected from 3 individually fabricated hollow channel oPADs having a 10.0 μm C fiber working electrode. The experimental results (colored lines) can be compared directly to simulated results (red circles). The average quasi-steady state current (i_{qss}) at $t = 15$ s was -130 ± 40 nA, at $t = 30$ s i_{qss} was -120 ± 40 nA, and at $t = 60$ s i_{qss} was -110 ± 40 nA, indicating $\sim \pm 33\%$ variation between the 3 devices. The simulated values of i_{qss} at these times are -147, -130, and -111 nA, respectively. The differences between these average values and the simulated results are 11%, 9%, and 3%, respectively. In all cases, the electrolyte solution contained 1.0 mM FcMeOH and 0.10 M KNO_3 , the

reference electrode (MSE) and the counter electrode (Pt wire) were placed in the outlet reservoir, and the potential of the working electrode was stepped from -0.50 V vs. MSE to 0.10 V vs. MSE for 60 s.

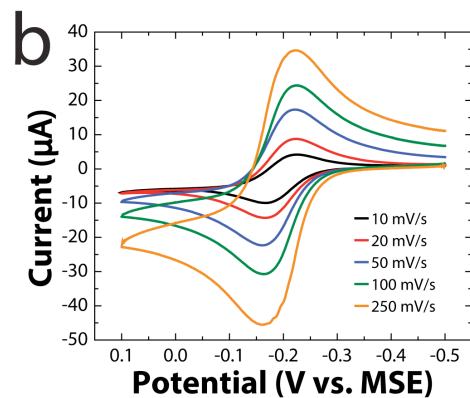
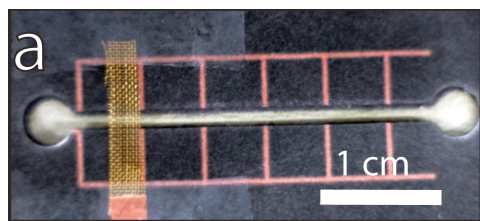


Figure S8. (a) Photograph of a HC-oPAD employing a Au mesh working electrode (100 mesh, 2 mm long and spanning the full width (1.3 mm) of the hollow channel). (b) CVs collected at different scan rates using the Au mesh electrode. The solution contained 1.0 mM FcMeOH and 0.10 M KNO₃. The resistance of the electrochemical cell was compensated at a level of 7.2 kΩ. The reference electrode (MSE) and the counter electrode (Pt mesh) were placed in the outlet reservoir.