Pressure-Driven Bipolar Electrochemistry

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(7 pages)

<u>Chemicals, materials, fabrication procedures and instrumentation</u>

Au-coated glass slides (100 nm Au, EMF Corp., Ithaca, NY) were used to fabricate split BPE electrodes using previously reported photolithographic techniques (Mavré, F.; Chow, K-F.; Sheridan, E.; Chang, B-Y.; Crooks, J. A.; Crooks, R. M. *Anal. Chem.* **2009**, *81*, 6218-6225). For Type 2 BPE microdevices, Cr and Ag were deposited on the anodic end of the BPE by lift-off (Chow K-F.; Chang, B-Y.; Zaccheo B. A.; Mavré, F.; Richard M. Crooks *J. Am. Chem. Soc.* **2010**, *132*, 9228–9229).

Poly(dimethylsiloxane) (PDMS) (Sylgard 184, Dow Corning, Midland, MI) was used to construct the microchannels. PDMS microchannels were prepared by a replica micromolding method (Xia, Y.; Whitesides, G. M. *Angew. Chem. Int. Edit.* **1998**, *37*, 550-575). Two reservoirs (1.0 mm diameter) were punched at the ends of the channel to accommodate introduction of solution. The PDMS microchannel was configured perpendicularly to the Au electrodes, irreversibly sealed to the glass substrate (Duffy, D. C.; McDonald, J. C.; Schueller, O. J. A.; Whitesides, G. M. *Anal. Chem.* **1998**, *70*, 4974-4984), and connected to a syringe pump using Teflon tubing. The *p*-benzoquinone and hydroquinone were purchased from Acros Organics. Millipore DI H_2O (18.2 MΩ-cm) was used throughout.

A syringe pump (Model PHD Ultra, Harvard Apparatus, Holliston, MA) was used to flow solution through the

microchannel. Current passing through the split BPE was measured by connecting the two microbands via an ammeter (Model 6517B Electrometer, Keithley Instruments, Inc., Cleveland, OH). Current data were processed using LabView software (National Instruments, Austin, TX). The potential difference between the poles of the split BPE was measured using a voltmeter (Model 2700 electrometer, Keithley). Cyclic voltammograms (CVs) in the two-electrode cell were recorded using a computer-based potentiostat (Model CHI750B potentiostat, CH Instruments, Austin, TX). Micrographs were collected using an optical microscope (Nikon AZ 100, Nikon Co., Tokyo, Japan) equipped with a CCD camera (Cascade, Photometrics Ltd., Tucson, AZ). Optical micrographs were processed using V++ Precision Digital Imaging software S3 (Digital Optics, Auckland, New Zealand).
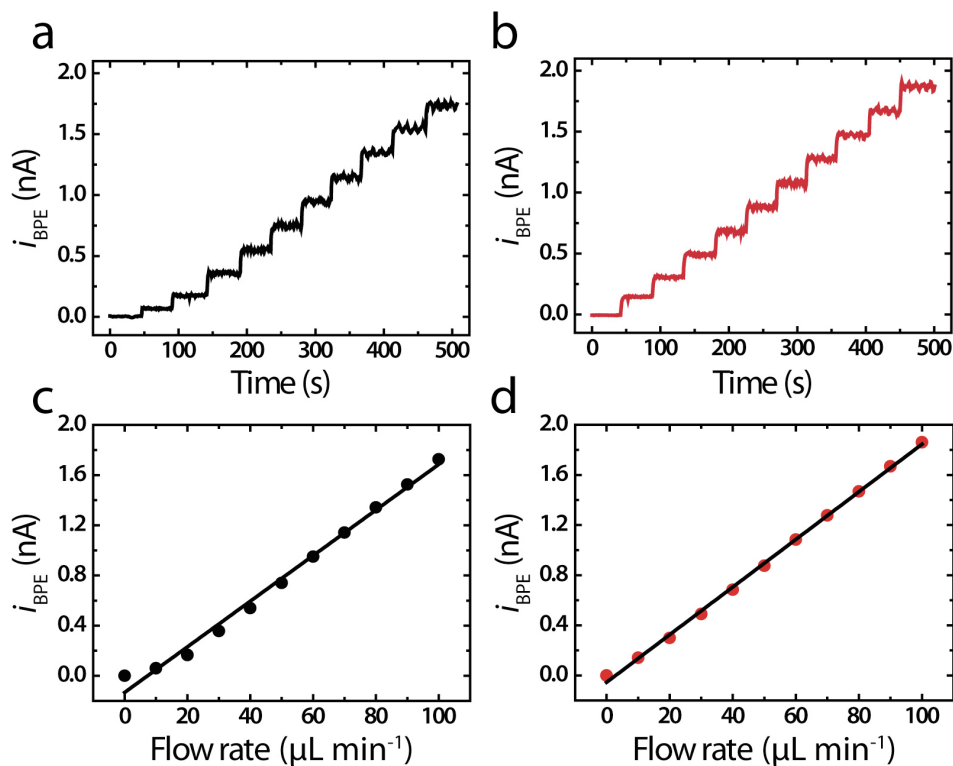
Figure S1

Plots of ΔE_{elec} vs. flow rate obtained using a Type 1 microdevice and either (a) DI H_2O, or (b) DI H_2O plus 1 mM BQ/HQ in the channel. The black lines represent the best linear fits. Linear regression equations are (a) $y = 0.081x$ and (b) $y = 0.007x$, with $R^2 = 0.99$ in both cases. The volumetric flow rates employed (10 to 100 µL min^{-1}) correspond to ΔP values of 0.65 kPa to 6.5 kPa, respectively (Hagen–Poiseuille equation).
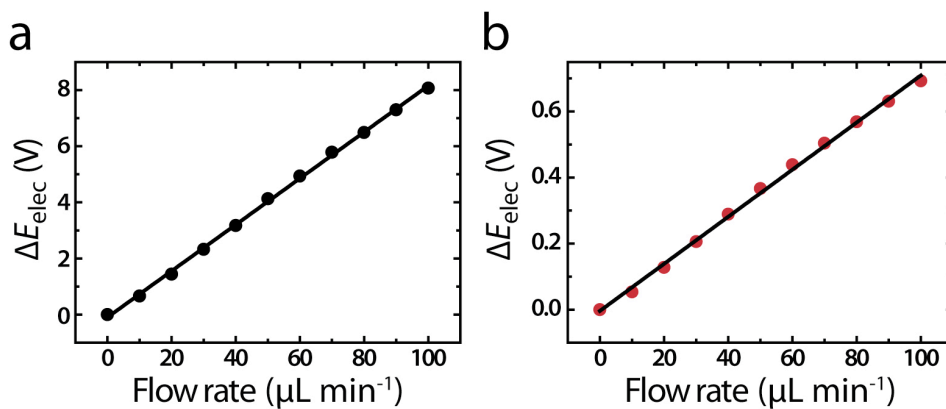
Figure S2

(a and b) Plots of i_{BPE} vs. time, measured while varying flow rate from 10 to 100 µL min^{-1} in increments of 10 µL min^{-1}. (c and d) Plots of i_{BPE} vs. flow rates. The microchannels contained: (a and c) DI H$_2$O, and (b and d) DI H$_2$O plus 1 mM BQ/HQ. All data were obtained using a Type 1 microdevice. The black lines in (c and d) represent the best linear fits. Linear regression equations are (c) $y = 0.016x$ and (d) $y = 0.018x$, with R^2 = 0.99 in both cases.

Linear regression equations for data in Figure 1e (main text) are $y = 0.201x$ for DI H$_2$O and $y = 2.573x$ for 1.0 mM BQ/HQ. R^2 was 0.99 in both cases.

Figure S3

Plot of i_{BPE} vs. time measured while recording the optical micrographs in Figure 2 (main text). The average current during the experiment (from the onset of flow at 70 s to 1470 s when flow was stopped) was 0.63 nA.
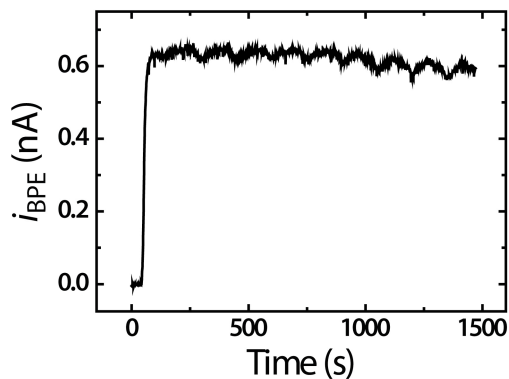
Note that in a separate, similar experiment i_{BPE} decreased to zero when flow was stopped. However, if flow is allowed to continue after the entire Ag BPE anode is oxidized, we observe that Ag continues to etch outside the microchannel, under the PDMS layer. This indicates that a small leak appears between the BPE anodic pole and the microchannel, due to the formation of Ag^+ at the interface between Ag and PDMS.

Figure S4

Optical micrographs of the BPE Ag anodic pole in a Type 2 microdevice before and after flowing DI H_2O plus 1 mM BQ through a microchannel for 1 h at a flow rate of 25 μL min^{-1}. The ends of the split BPE were not connected. Accordingly, current could not flow through the BPE and faradaic reactions could not occur. The micrographs indicate that anodic Ag dissolution can only occur if coupled to a cathodic reaction (compare to Figure 2 in the main text).