GIANT AMPLIFICATION OF REDOX CURRENT IN A NANOFLUIDIC CHANNEL

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Abstract

We have developed a nanofluidic device consisting of a 300 nm high, water-filled cavity bounded by two parallel electrodes which amplifies the electrochemical signal from redox molecules inside the cavity by a factor of ~400 through redox cycling.

Keywords: Electrochemical sensing, redox cycling, nanofabrication

1. Introduction

The ability to electrically detect and manipulate single molecules in solution with high time resolution represents an ongoing experimental challenge in micro- and nanofluidics, analytical chemistry and lab-on-a-chip applications. Electrochemically active molecules are particularly suited for electrical detection through Faraday currents at appropriately biased electrodes. Few electrons per molecule are involved in these reactions, rendering direct detection virtually impossible. This difficulty can be overcome by fabricating two planar electrodes in close proximity to each other: a single molecule undergoing a random walk in the region between the electrodes reversibly serves as reactant and product, thereby shuttling multiple electrons between the electrodes. This so-called redox cycling process [1] is illustrated in Figure 1.
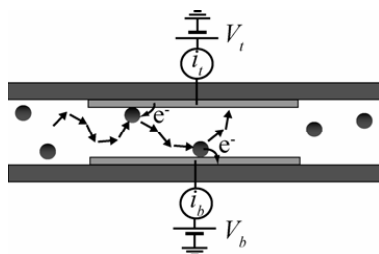

Figure 1. Illustration of the device concept. Electrochemically active molecules undergo a random walk between the two electrodes, thereby shuttling multiple electrons. V_t and V_b are the applied potential to the top and bottom electrode, while i_t and i_b are the corresponding measured currents.

2. Device Fabrication

We have developed a nanofluidic device consisting of a solution- filled cavity bounded by two parallel platinum electrodes separated by 300 nm. In brief, two planar electrodes separated by a silicon sacrificial layer were embedded in sputtered SiO_2. In the final step, the silicon layer was removed using a newly developed plasma etch process. This process uses a high-density, inductively-coupled SF_6 plasma with no added O_2, rendering the etching isotropic (Figure 2a).
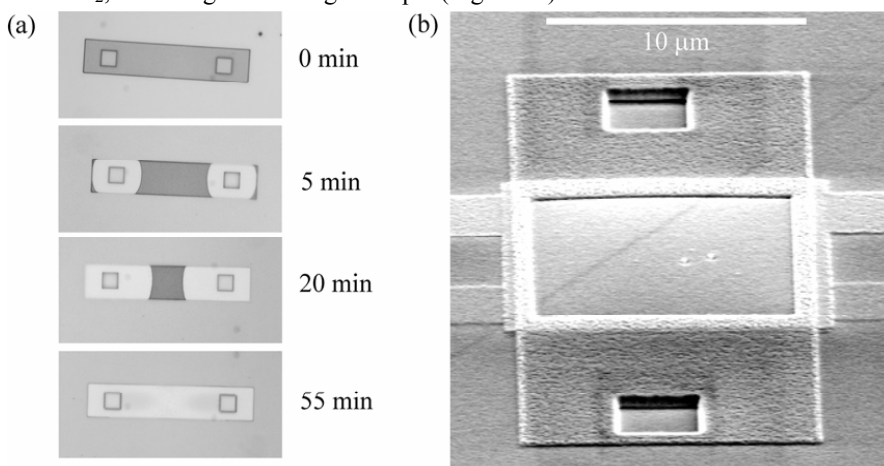

Figure 2. (a) Sacrificial etch of a 10 x 50 µm, 120 nm high Si test structure covered with 500 nm sputtered SiO_2. The plasma enters the cavity via two 5 x 5 µm access holes (squares). The etch proceeds gradually and after 55 min a channel is formed. (b) SEM image of a finished device. Fluid enters the 100 µm² area bounded by the parallel electrodes via two square entrance holes. Contacting wires can be seen on both sides.

3. Amplification of the electrochemical signal

The device achieves highly efficient redox cycling, resulting in the amplification of the electrochemical signal from redox molecules inside the cavity by a factor of ~400. This is demonstrated in Figure 3a. Because of the high concentration of inert salt (250 mM KCl), transport of the redox species (1mM ferrocenedimethanol) is entirely due to diffusion and the transport-limited steady-state current i_{ss} becomes

$$i_{ss} = eDAA_v c_0 z^{-1} \tag{1}$$

where $-e$ is the electron charge, D the diffusion constant (4.7 x 10^{-6} cm²/s), A the area of overlap between the electrodes (100 µm²), A_v Avogadro's number, c_0 the bulk concentration of redox-active molecules and z the distance between the electrodes. From the measured linear dependence of i_{ss} on the bulk concentration c_0, the height of the cavity was determined to be 282 nm (Figure 3b), consistent with expectations.

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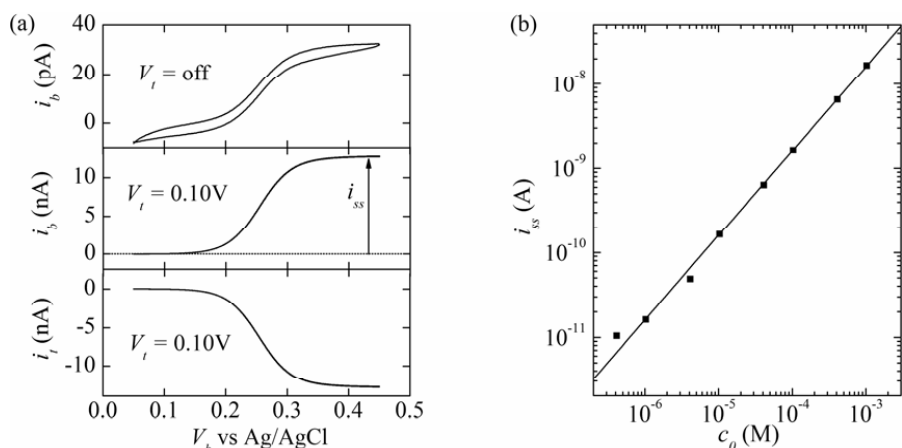*November 5-9, 2006, Tokyo, Japan*

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Figure 3. (a) Cyclic voltammetry (scan rate 1 mV/s) performed with the bottom electrode while the top electrode was electrically disconnected (top curve) and with V_t = 0.10V (middle curve). The steady-state current i_{ss} is amplified approximately 400 times in the second case. The bottom curve represents the current through the top electrode obtained simultaneously with the middle curve. It is a mirror image of the current through the bottom electrode, indicating that nearly 100% of the generated product is cycled. (b) Transport-limited current i_{ss} versus concentration. The solid line is a fit to Eq. (1).

4. Mesoscopic fluctuations in the number of redox molecules in the cavity

Since the electrochemical current is proportional to the number of particles in the cavity, fluctuations in this current probe fluctuations of the number of particles in the cavity [2]. At the smallest concentrations investigated (0.4 μM), we observed excess current noise of 67 fA rms, corresponding to fluctuations of as few as 70 molecules inside the cavity.

5. Conclusion

We have developed a nanofluidic device consisting of two planar electrodes separated by 300 nm. Redox cycling amplifies the electrochemical current by a factor ~400. Noise in the measured electrochemical current indicates sensitivity to fluctuations of as few as 70 molecules, and we expect that further downscaling will yield devices capable of detecting single redox molecules.

References

1. For a comprehensive review see C. Amatore in *Physical Electrochemistry* edited by I. Rubinstein (Marcel Dekker, New York, 1995).
2. M.A.G. Zevenbergen *et al.*, submitted.

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