Towards Electrochemical Detection of Single Molecules: Redox Cycling in Nanofluidic Devices
Pradyumna S. Singh, Marcel A.G. Zevenbergen, Edgar D. Goluch and Serge G. Lemay
Kavli Institute of Nanoscience, Delft University of Technology
Lorentweg 1, 2628 CJ Delft,
The Netherlands

We report the fabrication of electrochemical devices consisting of twin plane-parallel electrodes separated by a nanofluidic channel (Figure 1). The devices can be considered the nanoscopic equivalent of classical thin-layer cells.

Figure 1. SEM image (top view) of a typical device.

The fabrication process involves a combination of lithographic patterning and electron-beam evaporation to form the electrodes and the nanocavity. The distance separating these plane-parallel electrodes (Au or Pt) can be tuned at will during the fabrication process; for the present experiments it was ca. 50 nm. Figure 2 shows an SEM image (top view) of a typical device.

Figure 2.

When operated in the redox-cycling mode (i.e., the two electrodes – top and bottom – are biased at the two extremities of the half-wave potential, \(E_{1/2}\), of a redox-active molecule), this molecule cycles between its reduced form on one electrode and the oxidized form on the other (Figure 1). The limiting current, \(i_{\text{lim}}\), so obtained is inversely proportional to the distance separating the two electrodes, \(z\),

\[ i_{\text{lim}} = \frac{nFADc}{z} \]

where \(F\) is the Faraday constant, \(A\) is the area of overlap between the two electrodes, \(D\) is the diffusion constant of the molecule and \(c\) is its concentration. According to the expression above, the limiting current scales linearly with concentration and this is experimentally verified in both aqueous and non-aqueous media (acetonitrile).

Because of the small channel height, mass transport is extremely rapid in the cavity. This allows us to measure very fast standard heterogeneous electron-transfer rate constants, \(k^* > 1\ \text{cm/s}\). We demonstrate this by measuring \(k^*\) for ferrocenedimethanol, \(\text{Fc(MeOH)}_2\), in aqueous solutions. Further, we find that \(k^*\) depends on the type and concentration of supporting electrolyte.

The redox-cycling current is a direct measure of the number of molecules in the cavity, \(N(t)\),

\[ i_p = \frac{neD}{z^2} N(t) \]

Here \(i_p = \frac{neD}{z^2}\) is the current per molecule. As molecules diffuse in and out of the channel, \(N(t)\) fluctuates about its mean value in the channel. This gives rise to corresponding fluctuations in the current as seen in the amperometric time traces. We find that the fluctuation amplitude of the current increases with increasing \(N\), an observation we attribute to diffusion noise which originates from the fluctuations of a small number of molecules inside the channel. Figure 3 shows the power spectral densities (PSD) obtained from the current-time traces for 1.2 mM \(\text{Fc(MeOH)}_2\) in \(\text{H}_2\text{O}\) (red points) and 1.0 mM \(\text{Fc}\) in acetonitrile (blue points). An analytic expression for the PSD of these fluctuations was derived for the present geometry and in good agreement with measurements as can be seen from the fits (green lines) in Figure 3. The PSD reveals a flat plateau at low frequencies and a \(f^{-3/2}\) power law decay at high frequencies. Contrary to expectations, we find that the shape of the spectrum depends upon the concentration. For low concentrations the corner frequency is shifted to lower values and there are deviations from expected behavior at higher frequencies. We explain these results by proposing the dynamic, non-specific adsorption of ferrocene in the channel.

Figure 3. Power Spectral Density (A Hz)

Because the signal (i.e., current) scales linearly with \(N\), and the fluctuations with \(N^2\), it is conceivable that in a device of a suitable height, \(z\), current due to electron-transfer events of a single or a few molecules is measurable. In a channel of \(z = 50\ \text{nm}\), for ferrocene in acetonitrile, the expected \(i_p \sim 160\ \mu\text{A}\) – a measurable current. We discuss our experiments in this direction, and report our recent observations of distinct step-like features in amperometric time traces which are suggestive of redox cycling of individual ferrocene molecules.