Electrochemical Correlation Spectroscopy (ECS) in nanofluidic channels

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We recently introduced a new technique which we have called Electrochemical Correlation Spectroscopy (ECS). Much like its optical counterpart, Fluorescence Correlation Spectroscopy (FCS), ECS relies on measuring fluctuations in the signal in very tiny detection volumes. Contrary to other electrochemical techniques that usually measure current, in ECS we are more interested in fluctuations in current. An autocorrelation analysis of these fluctuations can yield new information about molecular processes, that couldn't be obtained any other way.

The tiny detection volume in the present case is a nanoscale channel of height ~ 50 nm bound on either side by two plane-parallel metal electrodes (Figure 1). These devices can be considered the nanoscopic equivalent of classical thin-layer cells.

![Figure 1](image)

The fabrication of these channels involves 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](image)

Redox active molecules can freely diffuse in and out of the channel and be reduced and oxidized at either one or the other suitably-biased electrodes, giving rise to a redox-cycling current.

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

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

Here \( i_p = \frac{neD}{z} \) is the current per molecule, \( z \) is the spacing between the two electrodes, \(-e\) the charge on an electron and \( D \) the diffusion constant. However, as molecules diffuse in and out of the channel, the number of molecules in the channel, \( N(t) \), fluctuates about a mean value, \( \langle N \rangle \), that is set by the bulk concentration of the redox-active molecules in the reservoir. This fluctuation in the number of molecules in the channel results in corresponding fluctuations in the redox-cycling current, \( I(t) \).

Figure 3 shows the power spectral densities (PSD) obtained from the current-time traces for 1.2 mM Fc(MeOH)\(_2\) in H\(_2\)O (red points) and 1.0 mM Fc in acetonitrile (blue points). An analytic expression for the PSD of these fluctuations was derived for the present geometry and is 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](image)

We extend these measurements to probe differences in adsorption behavior of ferrocene and methanol-substituted ferrocenes. We have also functionalized the electrode surfaces with self-assembled monolayers (SAMs) of various organo-thiol compounds to further study the adsorption dynamics of redox molecules on SAM surfaces. These studies are important especially in context of redox-cycling based sensor designs with surface modifications, where adsorption of the analyte molecule can severely compromise the sensor sensitivity.

These devices are also capable of detecting single molecules and we will discuss our recent results in this direction.