Adsorption of redox-active molecules on platinum and boron doped diamond electrodes in nanofluidic electrochemical sensors

Bachelorthesis Applied Physics

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Summary

Sensors are important to detect low concentrations or even single molecules of chemicals in a solution. One way to do such detection is by using an electrochemical sensor, especially in the nanofluidic regime. A nanofluidic electrochemical device used for these measurements, contains two electrodes separated by a few nanometers. The electrochemically active molecules undergo repeated oxidation and reduction (redox cycling) between the electrodes in the cell if the electrodes are applied with appropriate potentials. A limiting factor for the detection in these devices is the adsorption of molecules on the surface of the electrodes, because this reduces the faradaic current. In this project we investigate a way to minimize the adsorption in a nanofluidic electrochemical device. Boron doped diamond is a material on which little adsorption occurs macroscopically. Therefore the used devices contained two electrodes made of either platinum or diamond or a combination of diamond and platinum. The main goal is to compare two electrode materials i. e. boron doped diamond and platinum and to find which on which material the least adsorption occurs in nanofluidic electrochemical devices. To measure the adsorption we use electrochemical spectroscopic methods. Our main result is that the boron doped diamond electrodes adsorb less compared to the electrodes made of platinum.

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Introduction

Recently, there is a great scientific interest to detect low concentrations or even single molecules of various chemicals in a solution. An example of an application is the pharmaceutical or medical industry, where the detection of specific proteins or enzymes in blood samples can be used to determine an illness or disease.[1] Furthermore, there is a desire to create small detection devices that can be used to analyze very small amounts of a sample. The device would have to be selective and sensitive. Several methods to detect low concentrations are already available. Most of these techniques are optical techniques, such as fluorescence correlation spectroscopy (FCS).[2,3] A big disadvantage of optical techniques is that it is hard to implement them on small scales. Recently a comparable electrochemical system has been developed to accurately detect low concentrations on small scales[2]. Such chip like systems are known as nanogap devices or nanofluidic electrochemical sensors. They show a several fold amplification of an electrical signal resulting from an electrochemical reaction by using redox cycling. In redox cycling, two electrodes separated by a few nanometers, are biased at reducing and oxidizing potentials. Electrochemically active molecules diffusing through the nanochannel undergo repeated oxidation and reduction between these electrodes and therefore contribute many electrons to the current. This significantly increases the signal from a low concentration compared to a system in which ordinary redox cycling is used.

The small separation between electrodes leads to a large surface to volume ratio in these nanogap devices. As a result surface effects like adsorption are dominant in these devices. Adsorption is the binding of molecules to the electrode. Adsorption is different from absorption, which is the filling of pores in a solid. Since the molecules stick onto the electrode surface, they do not contribute to the electrochemical current and so adsorption decreases the redox cycling current.[1,4] This is a limiting factor in the detection of low concentrations in nanofluidic sensors. Minimalizing adsorption in nanogap devices is therefore very important to detect low concentrations of molecules. The amount of adsorption is dependent on the material of the used electrodes. One of the electrode materials of wide interest is boron doped diamond, due to its desirable electrochemical characteristics.[4,5,6] To the best of our knowledge no research on adsorption behaviour of boron doped diamond in nanofluidic regime is reported. The goal of this bachelor project is therefore to investigate the adsorption behaviour of boron doped diamond electrodes in nanogap devices. Because most of the nanogap devices currently used have platinum electrodes, a comparison will be made between the adsorption nature of platinum and diamond electrode materials. This leads to the following research question:

"Is the amount of adsorption of redox active molecules on boron doped diamond electrodes less than that on the platinum electrodes in nanofluidic electrochemical sensors?"

Our report is sectioned as follows: first a short overview of electrochemistry and electrochemical detection is given followed by methods to quantify adsorption in nanogap devices. After this the results are given along with an explanation and a discussion of the results. Finally our main conclusions are given.

Theoretical aspects

Electrochemistry

Electrochemistry is a branch of chemistry and physics that investigates and uses chemical and electrical reactions which take place in a solution, mainly at the interface of an electric conductor and an ionic conductor. These are respectively called the electrode and the electrolyte. These reactions involve transfer of electrons between the electrode and the electrolyte or compounds in the solution and are also known as redox reactions. Oxidation refers to a molecule losing one or multiple electrons, while reduction refers to a molecule gaining one or multiple electrons. This process is dependent on a certain energy (electric potential E_0) at which the electron transfer is likely to occur. These are characteristic for compounds and are given in standard potential tables under 'standard conditions'. By using the Nernst equation[7] it is possible to calculate the electric potential of a redox reaction in "non-standard" situations.

Electrochemical cells

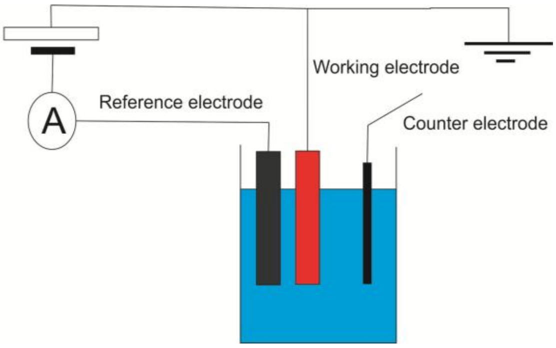

Figure 1: An electrochemical cell.

Cells where these redox reactions occur are called electrochemical cells and are usually made of at least two electrodes separated by one electrolyte, as depicted in figure 1. Typical electrode materials include solid metals, such as platinum, gold and silver, liquid metals such as mercury and carbon (graphite and doped diamond) and semiconductors such as silicon. Here charge is mainly carried by the transport of electrons or electron holes. In the electrolyte phase charge is carried by the movement of ions, usually in a solvent. For materials to be useful in electrochemical measurements, the resistance should be low in both the electrolyte and electrode.[8]

The overall reaction of an electrochemical redox reaction is in general made up of two independent half reactions that act at different electrodes to give an interfacial potential difference to the corresponding electrode. The electrode that is set to a standard fixed reference potential is the reference electrode. The other electrode at which the reaction of interest is carried out is called the working electrode (WE) and its potential is measured with respect to the reference electrode. The reference electrode is normally made up of phases (both solid and in the electrolyte) having essentially constant composition. The most used reference electrodes are the normal hydrogen electrode (NHE), the mercury electrode and the silver-silver chloride electrode (silver wire covered with silver chloride in a solution with potassium chloride, with a potential of 0.197V vs. NHE).[8] When the potential of the working electrode is more negative it is at reduction potential and when it is more positive it is at oxidizing potential. In traditional two electrode cells that consist of a working electrode and a reference electrode, current is necessarily forced to flow through the reference electrode whenever a measurement is performed. When this current is too high the measurement can be influenced, due to change in composition of the electrodes, so in cases of high current an additional auxiliary (or counter) electrode is used.[8,9]

Different electrochemistry measurements

When a potential is set over two electrodes in the oxidizing/reducing range of a redox-active couple a current (often called faradaic current) will flow due to the transfer of charge between the electrodes and the redox active couple. In electrochemistry, mostly this current is detected. These can give information on equilibrium potential, conductivity, transference number, diffusivity, adsorption and the rate of a reaction. The measurements are performed in different modes. The most used technique is ‘cyclic voltammetry’ (or potential sweep) and it is essentially a measurement of the current of a redox-active cell as a function of the applied (linear) potential. Amperometric measurements are made by setting the electrodes at a constant oxidizing or reducing potential, while the current is measured as a function of time.[10] Step measurements are performed by applying potential steps to the electrode, while measuring the current.

Current resulting from a redox reaction

In an electrochemical system, the faradaic current is proportional to the rate at which molecules are oxidized and reduced. Factors that determine this rate are mass transfer (migration, diffusion and convection), charge transfer kinetics, concentration and surface reactions like adsorption or desorption[8]. Migration is the transfer of the ions or the molecules in the electrolyte due to electric forces. This effect becomes more pronounced at low ionic concentration of the electrolyte. When ions are present in the electrolyte, a thin layer of oppositely charged ions will form around charged electrodes. This is called an electrical double layer and it effectively shields the electric field in the solution. The thickness of electric double layer is called Debye length.

When both convection and migration are minimized, diffusion is the main factor that limits the current. When a reaction of a redox-active species takes place, the concentration of that species near the electrode decreases and diffusion of ‘fresh’ species from the bulk to the electrode must take place. This requires some time and this time depends on the size of the electrode.

Electrode sizes

The redox-active molecules are gradually depleted in the region near the electrode by the ongoing redox activity. This leads to the formation of a concentration gradient in the solution. The existence of the gradient induces diffusion of electro-active material from regions of higher concentration (the bulk of the solution) to regions of lower concentration (near the electrode surface). For the large electrode diffusion is nearly completely linear in a direction perpendicular to the electrode surface, so the diffusion is mainly planar as seen in figure 2a. Because this is the case, the diffusion layer will exceed the distance a molecule can diffuse on the time scale of a typical experiment. This phenomenon makes that the cyclic voltammogram (CV) had peak shaped as shown in figure 4. However, when the voltage scanning rate is sufficiently low, the current reaches a steady state value. For large electrodes this time scale can be several minutes. A clear advantage of the macro electrodes is however that they can generally produce large currents in the order of several micro amperes.

Downscaling electrodes has several benefits. Because the radius is smaller, the steady state diffusive mass transport from the sides becomes relevant relative to the linear diffusion. For sufficiently small microelectrodes, this edge effect, or radial diffusion, becomes the dominant source of diffusion. This is depicted in figure 2b. Therefore the flux per unit time and area is greater. Thus smaller electrodes can be used to detect faster events. Apart from this effect smaller electrodes can be switched faster due to the very short RC time. This is because the capacitance scales with r^2 and the resistance scales with r^{-1}.[11] Thus the RC time will be proportional to r where r is the typical size of the electrode.

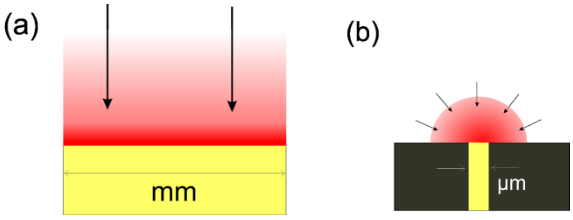

Figure 2: Diffusion behaviour for different electrode sizes. (a) macroscopic electrode with planar diffusion and (b) microelectrode with radial diffusion.

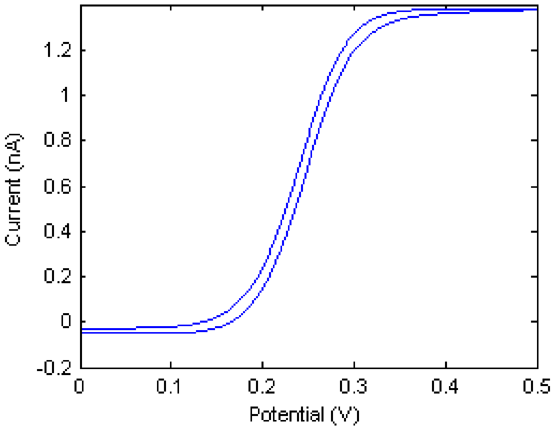

Figure 3: CV carbon UME in 1 mM ferrocenedimethanol at a scan rate of 20 mV/s.

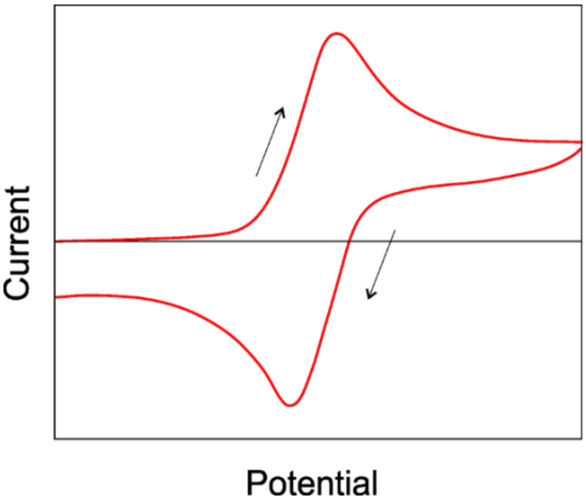

Figure 4: Sketch of a CV of a typical macroscopic electrode.

These small electrodes, which show this radial diffusion, usually have a surface area with diameters less than 25 µm and are called microelectrodes or ultra-micro electrodes (UME).[11,12] Because the diffusion of these electrodes is faster, steady state current can be achieved even at higher scan speeds unlike for the big electrode. Figure 3, shows the CV of a microelectrode. Using the same experimental conditions as for the macro electrode, a sigmoidal rather than a peak-shaped voltammogram was observed. The plateau in current at higher potentials is the diffusion limited steady state value. The diffusion limited current (hereafter referred to as the limiting current) is equal to:

$$i_L = nFAC_0m_0 \quad (1)$$[8,10]

With C_0 is the concentration of the redox active molecules in the bulk solution, $m_0 = D_0/\delta_0$ is the mass-transfer coefficient, F is Faraday constant, which is the number of coulombs per mole of electrons ($F = 9.648\,533\,99\text{x}10^4 \ \mathrm{C\,mol^{-1}}$), D_0 is diffusion constant, δ_0 is the Nernst diffusion layer, n is the number of electrons reduced/oxidized from a molecule and A is the overlapping surface area of the electrodes.

Important applications of these electrodes are in high speed voltammetry, electrochemistry in highly resistive solvents and in vivo voltammetry. The electrochemical behaviour of microelectrodes can therefore appear markedly different from that observed at conventionally sized electrodes. These electrodes typically produce currents in the pico ampère to nano ampère range, because there are less redox-active molecules present at the surface due to the smaller area. This can be a disadvantage although these current are sufficiently high to be measured with the proper equipment.

Redox cycling

A disadvantage of the aforementioned electrodes is that a relatively large concentration of redox-active molecules is required. Detection of low concentrations of even single molecules is therefore hard or even impossible. A solution to this problem can be redox cycling[2].

In redox cycling two electrodes are placed very close to each other, with a separation usually in the nanometer range. Therefore molecules primarily diffuse from one electrode to the other. One of the electrodes is biased at an oxidizing and the other at a reducing potential. Thus, while diffusing between the electrodes, molecules repeatedly get oxidized and reduced. During each redox-reaction an electron is transferred, so in redox cycling a single molecule contributes many electrons to the faradaic current. Redox cycling can increase the current about hundredfold[2] compared to ordinary redox reactions with the same concentration. This phenomenon was first reported by Bard et al.[13]

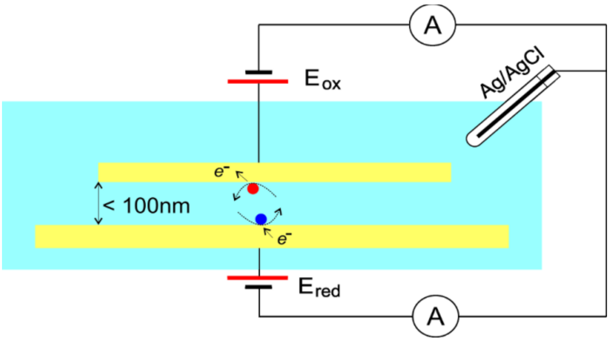

Figure 5: An illustration of a redox cyling nanogapdevice.

To make use of redox cycling, nanogap devices can be used. Nanogap devices are made of two parallel plate electrodes separated by a thin fluid layer. Figure 5 shows a nanogap device using redox cycling. The faradaic current is limited by the diffusion behaviour, with a limiting current of:[10]

$$i_{lim} = \frac{nFADc}{z} = nI_p \quad (2)$$

Here n is number of electrons delivered by the species, F is the Faraday constant, A is the area of overlap of the electrodes, D is the diffusion constant of redox molecule, c is concentration of species and z is the spacing between the electrodes.

Equation (2) implies that the electrodes do not need to be small (it is even useful to have a big surface area), but that the spacing between electrodes has to be small. A single molecule can contribute many electrons. The signal to noise ratio therefore increases. This is desirable in the detection of low concentrations of redox-active molecules. Figure 6 shows the voltammogram of ferrocinedimethanol under redox cycling conditions. Comparing figure 2 to figure 6, it is clear that the current increases significantly when redox cycling occurs. The shape of both curves is sigmoidal.

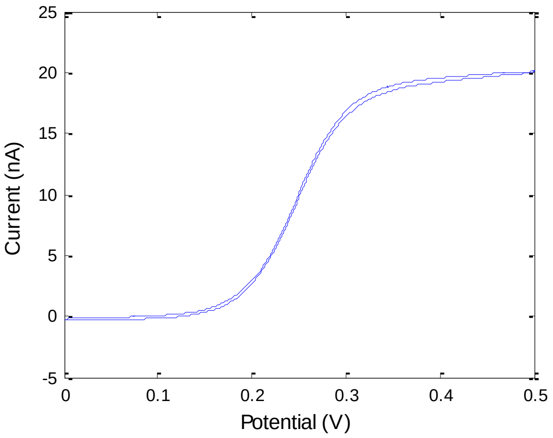

Figure 6: Typical CV of 1mM ferrocenedimethanol on a 10 µm device at a scan rate of 20mV/s.

Materials

As mentioned before, electrodes are essential in the concept of an electrochemical cell. But what characteristics are necessary or desirable for a working electrode? Most (micro)electrodes are made of carbon, gold or platinum due to inertness in chemical reactions and their practical usage[12]. Besides these characteristics, the potential window of a material is also important.[14] The potential window is the range at which the electrode itself does not participate in any redox reaction. Ideally the material is inert at all potentials, but such materials do not exist.[8] Redox reactions with the electrode material contribute to the faradaic current, so the behaviour of the analyte cannot be independently monitored. Therefore the electrode's potential window is a limitation in electrochemical measurements. So the choice for an electrode material depends on the oxidizing and reducing potentials of the analyte. Figure 7 illustrates the potential windows of a boron doped diamond and a platinum electrode.

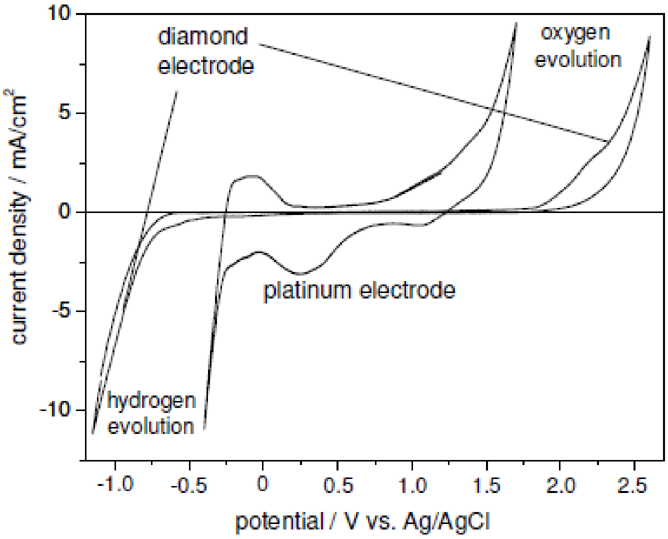

Figure 7: Cyclic voltammetry on platinum and diamond electrode in 0.2 M sulfuric acid at a scan rate of 100 mV/s. Courtesy: Condias[5].

Among the other before mentioned electrode materials, platinum is frequently used for having good (electro)chemical inertness and because it is relatively easy to fabricate. Usually the biggest disadvantage to the use of platinum, next to its high cost, is that platinum catalyses the reduction of water which takes place at fairly negative potentials. Also the formation of hydrogen gas from hydrogen ions (in acids) is catalyzed. This phenomenon is more expressed in platinum than in other materials. This reduction makes a measured faradaic current in a negative range unreliable. Another drawback of platinum is that the potential window is only in the range of -0.15 to 0.6 V.[15] A method for fabricating nanometer sized platinum electrodes is electrochemical etching of platinum in combination with cycle voltammetric/DC electrolysis deposition.

Gold electrodes behave comparable to platinum, but have limited usefulness in the positive potential range due to the oxidation of its surface. It can however be used for the preparation of modified surface structure electrodes, also known as self-assembled monolayers (SAMs).[12]

The main advantage of carbon electrodes is that that the potential window of carbon is large in both the negative and the positive range. The commonly used forms of carbon electrodes are glassy carbon and carbon paste (finely granulated carbon mixed with an oil substrate).[12] The first is relatively expensive and difficult to machine and the second is not very resistant to mechanical stresses, so these can be damaged easily. Another form of carbon can also be used as an electrode, namely doped diamond. Undoped diamond is electrically insulating because of its large bandgap, which is more than 5 eV, so in an undoped state it cannot be used as an electrode. Diamond can be made conducting by doping it with electron acceptors or donors (atoms from groups III and V in the periodic table of elements). For instance a p-type semiconductor can be made if diamond is doped with boron. Boron is most used because of its useful low charge carrier activation energy (0.37 eV).[4,16,17] These doped-diamond electrodes show good conductive behaviour and are good electrode materials with a large potential window (-1.2V to 2.5V) in aqueous solution and exhibit a low background current, which is desired in electrochemical measurements. Next to these useful features boron doped diamond exhibits high chemical and electrochemical stability. Boron doped diamond is mechanical robust and biocompatible which makes the material a suitable electrode material for various applications such as waste water treatment, water disinfection and of course (bio)electroanalytical applications. A disadvantage of this diamond lies in the high cost and the high pressures and temperatures (700°C) that are needed in the fabrication process. Diamond electrodes can be made by microwave plasma assisted chemical vapor deposition (CVD), but also by various other methods.[16]

Adsorption

A phenomenon that can influence the electrochemical signal is adsorption and desorption of the analyte, which is the binding and unbinding of the analyte to the electrode. The binding to the surface can be the result of a chemical bond (chemisorption) or because of a physical bond (physisorption). Chemisorption is the stronger of the two and mostly consists of ionic or covalent bonding of the molecules. The adsorption enthalpy is typically in the order of 40 - 800 kJ mol^{-1}. Physisorption is usually weak and reversible, with an adsorption enthalpy typically 5 - 40 kJ mol^{-1} (similar to heat of liquefaction).[7,18] So physisorption will mostly consist of 'weak' intermolecular forces like Vanderwaals forces and dipole-dipole interactions. Because all molecules have some interaction with each other, all molecule species can exhibit adsorption on a surface. The actual amount of molecules that is adsorbed depends on the molecule, the material of the surface, the temperature and the applied potential.[7,8] Increasing the temperature will in general decrease the adsorption of physisorbed molecules, because the thermal motion will be greater and thus makes adsorption less probable. This form of adsorption is normally very fast, usually faster than the speed at which measurements are performed.[19] This is due to the fact that there is almost no real extra activation energy needed (room temperature is enough). In the nanogap devices the adsorption of the redox species onto the channel and electrode surfaces is considerable, however undesirable as well. This is a direct consequence of the high surface to volume ratio of nanofluidic devices.[1]

Measuring adsorption

In this section four ways to characterize adsorption on the electrodes of the device are explained. These methods rely on time-current traces or the current response over time when the electrode potential is instantaneously changed (stepped). For the first two methods the fluctuations in the redox cycling current are used to calculate the adsorption from the root-mean square (rms) and from the power spectral density (PSD) of these fluctuations respectively. The two methods used on the potential step measurements involve the change in magnitude of current and the time the system takes to reach equilibrium (transient time) after a step.

Calculating adsorption from the root mean square of current traces

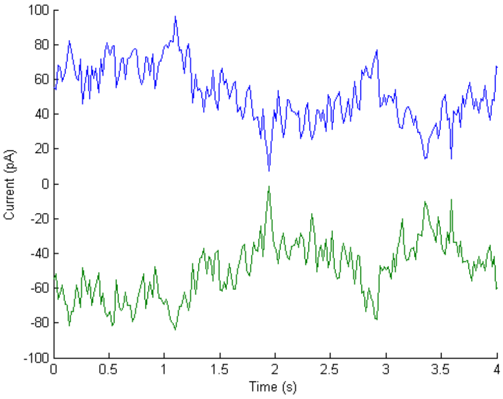

Figure 8: Typical current-time trace for the oxidizing (blue) and reducing (green) electrode, with the DC component modified to focus on the fluctuations.

When a reducing potential is applied to one of the electrodes and an oxidizing potential is applied to the other electrode redox cycling occurs. Because the active volume of the chip (i.e. the volume in between the overlapping areas of the top and bottom electrodes) is connected to a not redox-active channel and a bulk reservoir, molecules diffuse in and out of the active region due to Brownian motion.[20] This leads to a change in the concentration of redox active molecules in the active volume, so also to a change in the redox cycling current. A molecule that gets adsorbed does no longer contribute to the redox cycling current, which leads to a decrease in current. In the same manner desorption of a molecule leads to an increased current, so adsorption and desorption also cause fluctuations in the current.

A measurement of the cycling current over time is called a current trace. A few conditions must be met to be able to use the current traces to calculate the adsorption. The redox couple has the be stable. Furthermore, the current trace has to measured sufficiently fast and precise, so the current fluctuations are not averaged out. The average time molecules take to shuttle between the electrodes (shuttling time) is:[10] z^2/D. The average time a molecule stays in the active region (residence time) is:[10] L_e^2/D. L_e is the distance between the entrance hole and the active region of the device. The time between subsequent samples has to be lower than the shuttling and the residence time.

A plot of the measurement shows that the current has an average value and there is noise component around the average value as shown in figure 8. These small noise components can be attributed to diffusion and adsorption of molecules and of course to instrumental noise as long as the conditions above have been met.

First the average current will be described. The average current is a function of the average number of molecules in the active region and the current a single molecule contributes:

$$\langle I_F \rangle = i_p \langle N \rangle \tag{3}$$

With $\langle I_F \rangle$ the time averaged faradaic current, i_p the current a single molecule contributes and $\langle N \rangle$ the average number of molecules in the active volume.

For equation (3) to hold, the adsorption has to be reversible with kinetics quickly enough, so that the fluctuations are averaged over during the measurement.

To quantify the fluctuations in the current statistical physics is used. This tells us that probability distribution for the number of molecules in the active region is a Poisson distribution:

$$P_N = \frac{\langle N \rangle^N e^{-\langle N \rangle}}{N!} \tag{4}$$

The standard deviation σ (i.e. the square root of the variance) of the Poisson distribution is equal to:

$$\sigma = \sqrt{\langle N \rangle} \tag{5}$$

The standard deviation translates in the rms of the current trace:

$$I_{F,rms} = i_p \sqrt{\langle N \rangle} \tag{6}$$

Dividing the average current by the rms current and realizing that the average number of particles in the active region is the sum of the average number of particles in the solution $\langle N_{sol} \rangle$ and the average number of particles adsorbed on the electrodes $\langle N_{ads} \rangle$ gives:

$$\frac{\langle I_F \rangle^2}{{I_{F,rms}}^2} = \langle N \rangle = \langle N_{sol} \rangle + \langle N_{ads} \rangle \tag{7}$$

Equation (7) relates the adsorption to the rms current. In the case of no adsorption $\langle N \rangle$ is equal to number of molecules expected from the bulk concentration. When adsorption is present, $\langle N \rangle$ increases and because the time averages current is constant, the rms current decreases. That is the noise amplitude decreases with increasing adsorption.

It should be noted that noise from other sources than diffusion and adsorption, for example instrumental noise, contributes to the measured rms current and therefore leads to an underestimation of the adsorption. This problem can be solved by making use of a setup where the current is measured independently at both the top and the bottom electrodes versus the reference electrode. The noise caused by diffusion and adsorption is anti-correlated at the two electrodes when redox cycling takes place, but instrumental noise at the electrodes is uncorrelated. Therefore a cross correlation of the current measured at the top and bottom electrodes removes unwanted instrumental noise. A cross correlation leads to the following equations:

$$\begin{aligned} \langle I_{ox} I_{red} \rangle &= -\langle I_F \rangle^2 - {I_{F,rms}}^2 \\ \langle I_{ox} \rangle \langle I_{red} \rangle &= -\langle I_F \rangle^2 \end{aligned} \tag{8}$$

Combining equations (7) and (8) yields:

$$-\left(1 - \frac{\langle I_{ox} I_{red} \rangle}{\langle I_{ox} \rangle \langle I_{red} \rangle}\right)^{-1} = \langle N \rangle = \langle N_{sol} \rangle + \langle N_{ads} \rangle \tag{9}$$

Defining $ADS = \frac{\langle N_{ads} \rangle}{\langle N_{sol} \rangle} = \frac{\langle N \rangle}{\langle N_{sol} \rangle} - 1$, so the adsorption is expressed as a percentage relative to the average number of molecules in the solution, filling in $\langle N_{sol} \rangle = cVN_A$, as expected from the bulk solution and rewriting equation (9) gives:

$$ADS = -\left(1 - \frac{\langle I_{ox} I_{red} \rangle}{\langle I_{ox} \rangle \langle I_{red} \rangle}\right)^{-1} (cVN_A)^{-1} \tag{10}$$

With c the concentration of the redox active molecule, V the volume of the active region and N_A Avrogadro's constant.

Equation (10) describes the adsorption as a function of the measurable currents and known constants, so it can be used to calculate the adsorption on the electrodes from a current trace measurement.

Calculating adsorption from the power spectral density of current traces

Instead of using the time domain based approach for calculating the adsorption as described above, the method described below works in frequency domain.[3,10] In frequency domain the power spectral density (PSD) is used, which is the average power distribution as a function of the frequency. The PSD is calculated by taking the absolute value of the squared Fourier transform. In good approximation the relation between the PSD and the frequency is:

$$S(f) = \frac{S_0}{1 + \left(\frac{f}{f_0}\right)^{3/2}} \tag{11}$$

With S(f) the PSD of the current trace, S_0 and f_0 (the crossover frequency) constants.

At the crossover frequency f_0 the PSD starts to decline with a scaling of $f^{-3/2}$, which is typical for diffusion noise. The crossover frequency is given by:[3,10]

$$f_0 = \frac{D_{eff}}{\pi} \left(\frac{3}{{L_a}^2} (L_a + 6L_e)\right)^{2/3} \tag{12}$$

Here D_{eff} is the effective diffusion coefficient, L_a the length of the active region, L_e the distance between the entrance hole and the active region, as described before.

The effective diffusion coefficient decreases with increasing adsorption, because diffusion is temporarily stopped when a molecule is adsorbed. This phenomenon is called adsorption limited diffusion[1]. It is related to the number of molecules by:

$$\frac{D_{eff}}{D} = \frac{\langle N_{sol} \rangle}{\langle N \rangle} = \frac{\langle N_{sol} \rangle}{\langle N_{sol} \rangle + \langle N_{ads} \rangle} \tag{13}$$

With D the diffusion coefficient when adsorption is absent, hereafter referred to as the bulk diffusion coefficient.

This can be rewritten from the diffusion coefficients to the corresponding crossover frequencies given by equation (12) and expressed as $ADS = \frac{\langle N_{ads} \rangle}{\langle N_{sol} \rangle}$ just as in the rms approach.

$$ADS = \frac{\langle N_{ads} \rangle}{\langle N_{sol} \rangle} = \frac{f_0}{f_{0,eff}} - 1 \tag{14}$$

With f_0 the crossover frequency when adsorption is absent (expressed by equation (12)) and $f_{0,eff}$ the measured effective crossover frequency, which is shifted from f_0 because of adsorption.

The adsorption can be calculated by fitting equation (11) to the measured PSD to determine $f_{0,eff}$ and filling this in in equation (14).

Step measurements

In step measurements the current is measured over time, just as is the case in the current trace measurements. The potential at the electrodes is not kept constant over time. Usually one of the electrodes is kept at 0 V and the potential at the other electrode is stepped at certain intervals (but kept at a constant value in between steps). The potential step results in a current step, because the redox cycling current depends on the electrode potentials as discussed before. When the potential is stepped in the diffusion limited current range, no change is expected other than a short RC response.

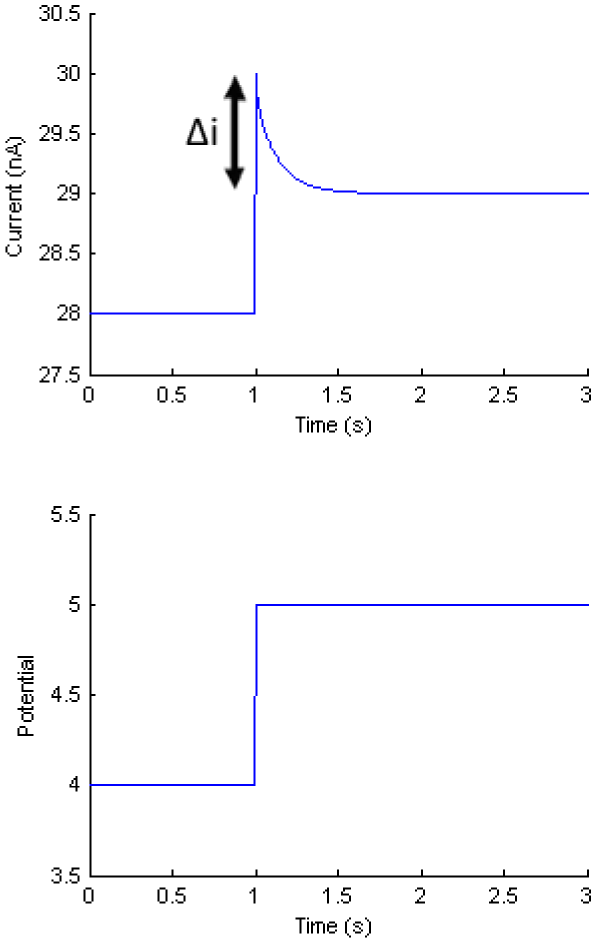

Figure 9: The current response (top) on a potential step (bottom).

Since the adsorption on the electrodes is dependent on applied electrode potential[3], molecules will instantaneously either adsorb on or desorb from the electrodes. This leads to a change in the concentration of redox active molecules in the active region, so this will also cause a decrease or an increase in the current, as illustrated in figure 9. Because this results in a concentration gradient in the channel, diffusion will eventually cause the concentration to return to the bulk concentration. Therefore the current will return to the value expected from cyclic voltammetry,[1] which is called the steady state current. The time scale associated with diffusion is considerably longer than the RC. Therefore the adsorption behaviour can be viewed independently of the capacitive behaviour.

The adsorption behaviour can be viewed from both the step height and the current transient of the current. These two methods will be explained below.

Step height and adsorption

As discussed above, a potential step leads to instantaneous increase or decrease in adsorption on the electrodes, resulting in a decrease or increase of the concentration in the active region. This means that an increase in adsorption results in an instantaneous decrease in the redox cycling current and a decrease in adsorption results in an instantaneous increase in the redox cycling current. As derived in the appendix the change in adsorption relates to the step height in the current as:

$$\Delta ADS = -\frac{\Delta i\, h}{eDN_A cA} \tag{15}$$

Where Δi is the step height in the current. It is the difference between the initial peak and the current after the concentration in the channel has returned to the bulk concentration.

Current transient and adsorption

As discussed above, after a potential step diffusion will cause the concentration in the active region to return to the bulk concentration. Because adsorption limits the diffusion, the diffusion coefficient of the fluid in the channel will decrease compared to the diffusion coefficient of the bulk solution[1]. This is due to the fact that molecules will also stay a characteristic time on the surface because of adsorption. If both diffusion coefficients are known, the adsorption can be calculated. Rewriting equation (13) to $ADS = \frac{\langle N_{ads} \rangle}{\langle N_{sol} \rangle}$ gives:

$$ADS = \frac{D}{D_{eff}} - 1 \tag{16}$$

The numerical solution of the diffusion equation $\frac{\partial c}{\partial t} = D_{eff} \frac{\partial^2 c}{\partial x^2}$ is well described by the following analytical expression:[1]

$$i(t) = i(0^+) + \left(i_{ss} - i(0^+)\right) \operatorname{erf}\left(2.97 \left(\frac{D_{eff} t}{L^2}\right)^{0.6}\right) \tag{17}$$

With $i(0^+)$ the current immediately after the potential step and i_{ss} the steady state current.

Equation (17) can be used to fit the data and determine the effective diffusion coefficient and now the adsorption can be calculated from the transient of the current after a potential step.

Experimental aspects

The earlier described methods (in the section 'Measuring adsorption') were used to measure the adsorption of redox active molecules on the electrodes of nanogap devices. First the general structure of the nanogap devices will be discussed, followed by the relevant details.

Devices

The bottom and top electrodes of the devices were made with either platinum or boron doped diamond. In some of the devices the bottom electrode was boron doped diamond while the top electrode was with platinum. We will refer to different types of devices by using the combination of the two materials. So devices with two platinum electrodes will be called 'platinum-platinum devices'. In this section we will discuss the used devices, the experimental setup and measurement methods.

The devices consist of three nanolayers on top of each other, of which the bottom and top one act as the bottom electrode and top electrode and the middle one as a sacrificial layer. The electrodes are connected to two contact pads per electrode on the side of chip. These connections are made of the same material as the electrode. In the case of diamond electrodes the connections have an extra layer of chromium to enhance the conductivity. The overlapping horizontal distance of the electrodes is called L_a. The sacrificial layer will later be removed to create a channel between the electrodes. Entrance holes are located at a distance L_e from the overlapping parts of the electrodes. Except for these entrance holes and the contact pads, the device is encapsulated by an insulating material, typically SiO_2. Figure 10 illustrates the dimensions of a nanogap device. Different types of devices are placed on one silicon wafer. And during measurements several different devices at various chips can be measured.

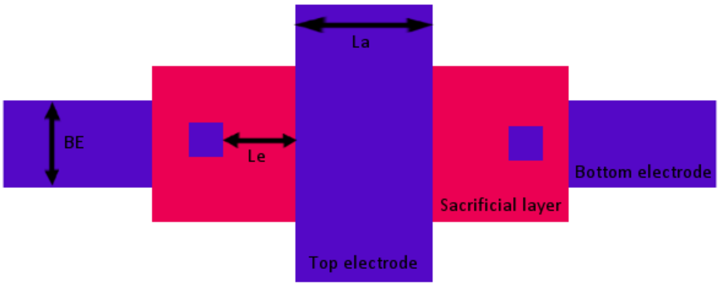

Figure 10: A top view of the nanogap devices' interior. The sacrificial layer is displayed in red, the bottom electrode and the top electrode and the entrance holes are depicted in purple.

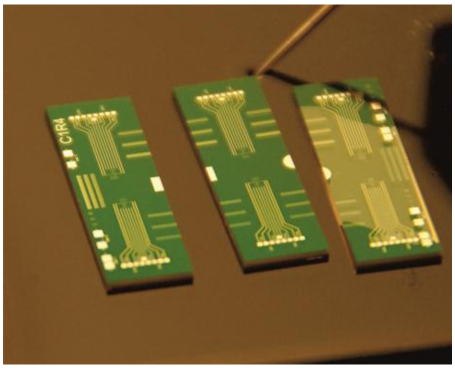

Figure 11: A picture of several chips each containing several platinum-platinum nanogap devices.

In the platinum-platinum devices, depicted in figure 11, and platinum-diamond devices the sacrificial layer is chromium and in the diamond-diamond devices the sacrificial layer is titanium, because of practical reasons in the fabrication of the devices. The height of the sacrificial layer, called h, was 50 nm in all the devices. The width of the electrodes is called BE and is 3 µm for all used electrodes. Table 1 shows the values of the dimension for the different devices used in the results.

Table 1: Dimension of the used devices			
	Platinum-platinum devices		
Device	**La (µm)**	**Le (µm)**	**BE (µm)**
ECS1	10	8	3
	Platinum-diamond and diamond-diamond devices devices		
Device	**La (µm)**	**Le (µm)**	**BE (µm)**
10-0.5B	10	0.5	3
10-1B	10	0.5	3
50-1B	50	0.5	3

Experimental setup

Before the device can be used for electrochemical measurements, the device has to be properly prepared. First the chip was cleaned with propanol and acetone. It was blown dry afterwards. During the experiments the channel is connected to an external reservoir. This is made of polydimethylsiloxane (PMDS) and is kept in place with a plastic clamp which can be moved using a lead screw XYZ stage. The PDMS plug has a small hole on the bottom which overlaps the two entrance holes. Metallic needles were placed on the contact pads to allow electrical measurements and application of a potential on the electrodes. These were placed at an angle, so the needles where less likely to damage the chip. A microscope was used to place the plug and the needles in the right positions.

To remove a possible corrosion layer on top of the chromium, the chip was placed in an oxygen plasma. To check for fabrication errors in the device, the needles were connected to the two contact pads of the same electrode. A small potential was applied, typically 50 mV, and the current was measured. If the connections are working, the current is reasonably large (in the order of 10^{-7} or 10^{-6} Ampère), because the electrode is short-circuited. In this way the top and bottom electrode are checked separately. Afterwards one of the needles was connected to a contact pad for the top electrode and the other was connected to a contact pad of the bottom electrode. A small potential was applied and a large current in the order of 10^{-7} to 10^{-6} Ampère was observed. In order to remove the sacrificial layer a chromium etch solution (CHF_3/O_2) is placed in the PDMS reservoir using a micro pipette. During the etching the current drops to the order of 10^{-11} to 10^{-10} Ampère, as illustrated in figure 12. When this current was reached, the etch was left in the channel for about fifteen minutes. After that, the etch was removed and the channel was flushed with Milli-Q water (18MΩ cm) a few times by putting it in the reservoir using a micropipette. The PDMS plug positioned on the chip is illustrated in figure 13a.

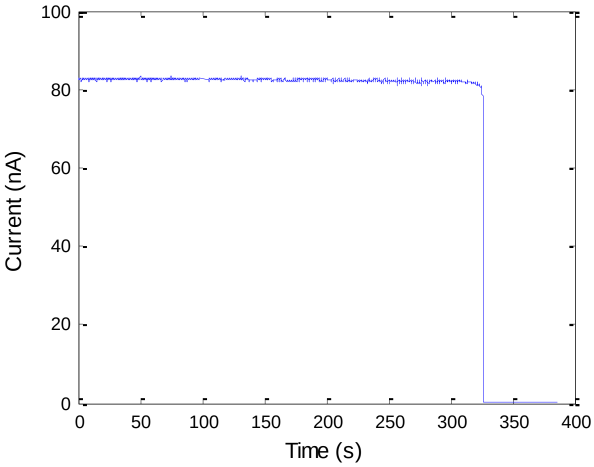

Figure 12: Current-time measurement during etching. The current drops from 85 nA to 0 nA.

The etching procedure was a bit different for the diamond-diamond devices, which had a titanium sacrificial layer. The etching of titanium was performed with sulfuric acid and hydrogenperoxide mixture in the ratio 10:2. This was heated for 4 hours on 120°C. It was therefore not possible to see the actual current drop of the etching, like is the case in the etching of the sacrificial layer in the platinum-platinum and the platinum-diamond devices. After this the chips were kept in water while not measuring.

Once the sacrificial layer is etched, all devices were treated with the following procedure. First all the devices are flushed with Milli-Q water, followed by placing sulfuric acid (200 mM) in the channel for about twenty minutes to clean the electrodes. Optionally the potential on one of the electrodes was scanned from -0.15 V to 1.2 V versus the reference electrode a few times while the other electrode was left floating. For this a AgCl/Cl reference electrode (type 3M BASi, US) was placed in contact with the fluid in the reservoir. This procedure was applied to both electrodes. During the scan the upper part of the platinum electrode gets oxidized and reduced to create a clean surface. In some cases the performance of the electrode decreased, so this procedure was usually applied after a few measurements. A LabView program was used to control two Keitley 6330 setups. During all the measurements an input cable from Keithley setups was connected to the mentioned reference electrode, which was in contact with the solution. The chip and the rest of the setup were placed on an air suspended table, to minimize vibrations, and in a grounded faraday cage to prevent background noise as illustrated in figure 13b. This is needed because the redox cycling currents are in the order of nano ampères.

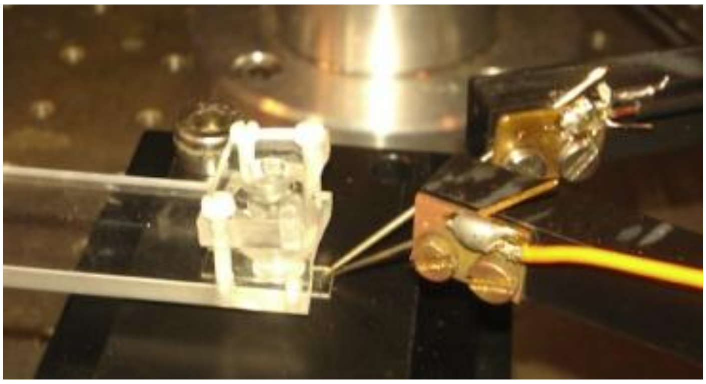

Figure 13a: The used setup: a PDMS plug and two contact needles placed on a chip.

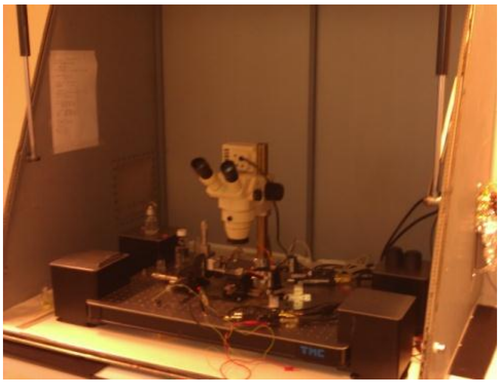

Figure 13b: An overview of the used setup: an overview

After cleaning with sulfuric acid the solution was removed from the device by using a micropipette. Some of the analytical solution was first used to flush this channel and was replaced by fresh solution. The majority of the solution was in the bulk reservoir and only a little was actually inside the channel. The total used amount was usually 100µL. The analytic solution consisted of 1mM ferrocenedimethanol, 1M potassiumchloride and 10µM sulfuric acid in Milli-Q water (18MΩ cm). The high amount of potassiumchloride was used to shield the electric field in the solution, for reasons explained in the theoretical aspects. The sulfuric acid was used, because it helps to remove any residual impurities from the electrode surfaces during the measurements. Ferrocenedimethanol ($Fe(C_5H_5CH_2OH)_2$ or $Fc(MeOH)_2$) (Sigma Aldrich), was the actual redox active molecule in the solution and its chemical structure is illustrated in figure 14. Ferrocenedimethanol is chosen because it transfers only one electron during a redox reaction and is well studied. The expected halfway potential of ferrocenedimethanol is 0.25V with respect to a silver-silverchloride reference electrode. This potential is well within the potential window of both platinum and diamond. The bulk diffusion constant of ferrocenedimethanol is $6.7*10^{-10}$ m^2 /s.[10]

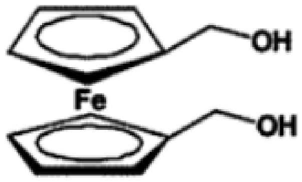

Figure 14: Chemical structure of ferrocenedimethanol (CAS:1291481)

Cyclic voltammetry (CV)

The cyclic voltammetry measurements were performed by applying a constant (typically zero) potential to one electrode, while scanning the potential on the other electrode from a reducing potential of 0 V to typically 0.5 V, which is within the oxidizing regime of ferrocenedimethanol. During the scan the redox cycling current is measured using the Keithley devices. All the potentials are applied versus the reference electrode. This measurement was repeated for the other electrode.

Cyclic voltammetry is used to characterize the device by comparing the measured CV to the expected CV as explained before. Deviations from the expected shape indicate problems for the device. The problems in the CV can be: the absence of a plateau at high potentials, a strong hysteresis loop indicating a large capacitance or adsorption and a low current response indicating that the redox cycling is not active. If the CV was as expected, the other measurements were performed. Otherwise the behaviour could improve after a few CV's or after scanning with sulfuric acid. If nothing helped, another device was prepared.

Current traces

In the current trace measurements the potential is held constant at the two electrodes. Typically one of the electrodes is kept at 0 V and the other is kept at 0.5 V. The current is then measured at a very high sampling frequency, typically 20ms, for 50 seconds. Traces were measured for both electrodes.

Potential step measurements

In the step measurements the potential of one of the electrodes is kept at 0 V while the other is stepped at regular intervals. The potential is raised in steps of 0.05 V at an adjustable interval, as shown in figure 15. The interval has to be long enough for the system to reach the steady state current before the potential is stepped again. This means a longer channel (the 50 µm channels for example) needs a longer measuring time.

On the diamond-platinum devices both the top and the bottom electrodes were measured so the differences between diamond and platinum electrodes can be seen.

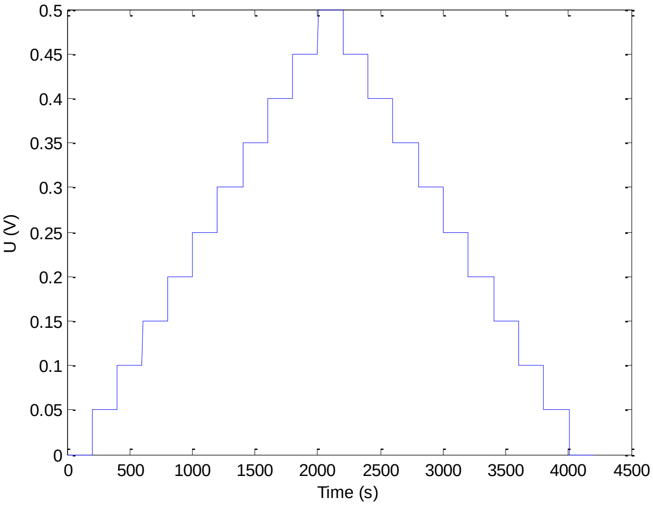

Figure 15: Potential step profile as a function of time.

Results

In this section the results of the measurements on the devices are presented. First some general aspects concerning the analysis of the measurements will be discussed. This will be followed by the error analysis. Then the results will be presented and discussed, starting with the cyclic voltammetry to check whether the device is working as expected. Next the traces and the PSD are discussed, followed by the results from the analysis of these measurements. Finally the step measurements are discussed and the resulting adsorption is presented.

General aspects

The CV curves are measured by sweeping the potential from 0 V to 0.5 V (the forward curve) and back (the backward curve). The current is measured at both electrodes versus the reference electrode. In the CVs shown the current at both electrodes are plotted in blue and green. Both the forward curve and the backward curve are shown. All the shown PSDs were calculated from the current traces by using segments of the measured traces. The traces where divided into 8 segments with 50% overlap. A PSD was calculated for each segment and the PSDs per segment are averaged.

The results of the traces of all the measurements are fitted with a low order polynomial. This removes current fluctuations on long time scales. The order of the polynomial should be as low as possible and not higher than 10. Higher order polynomials could also decrease the rms value by placing current peaks closer to the mean current.

The adsorption calculated from the rms of current traces is calculated by calculating the rms of the current fluctuation in Matlab (the scripts are included in the appendix). Then equation (10) is used to calculate the adsorption. The PSDs are fit to equation (11) to determine the crossover frequency of the PSD. This crossover frequency (f_0) is used to calculate the adsorption using equation (10). In the step measurements the effective diffusion is determined by fitting equation (17) to each step to obtain the effective diffusion coefficient. Equation (16) is then used to calculate the adsorption.
Equation (15) could be used to calculate the difference in the adsorption. This is not done quantitively, because we are not interested in the difference in adsorption. It is used qualitively though to determine whether adsorption or desorption occurs after a step.

Error analysis

Errors in the calculated adsorption come from errors in the measured current, the dimensions of the devices, the bulk diffusion coefficient and the analyte concentration. Statistical deviations in the results have to be considered too, as well as errors in the fits of the PSD and the fits to the step measurements. The experimental errors are all very small, because all the constants are known very precisely and the currents were measured very accurately by the Keithley devices. The concentration of the ferrocenedimethanol solution could change during the experiment, because water evaporates. However, this effect is negligible, because the experiments did not take long. The statistical deviations are much greater than the aforementioned errors. Therefore only statistical errors are considered for the calculations from the current traces. All errors in the adsorption calculated from the current traces are expressed by the standard deviation. For the step measurements the error is calculated by dividing the error in the effective diffusion coefficient, found from the fit, by the effective diffusion coefficient. The relative error in the effective diffusion coefficient is equal to the relative error in the adsorption. The relative error is multiplied by the adsorption to obtain the errors given in the results of the step measurements.

Platinum-platinum devices

In this section the results of the measurements on devices with two platinum electrodes are presented. First the cyclic voltammetry will be discussed to check whether the device is working as expected. Next the traces and the PSD are discussed, followed by the results from the analysis of these measurements. Finally the step measurement is discussed and the resulting adsorption is presented.

Figure (16) shows the CV curves of the platinum-platinum device ECS 1 for the top and the bottom electrodes. The figure shows that the current reaches a plateau as expected. The backwards curve almost overlaps the forward curve, indicating that the capacitance or adsorption or desorption of the electrodes is very small.

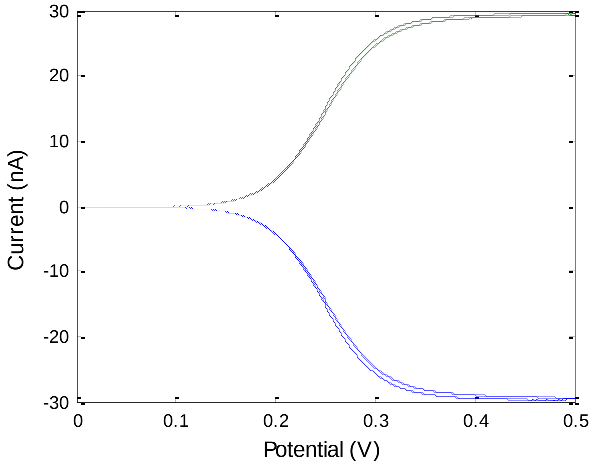

Figure 16a: Typical CV of ECS 1, scanning the top electrode at a scan rate of 20 mV/s. The green line is the current at the top electrode and the blue line is the current at the bottom electrode.

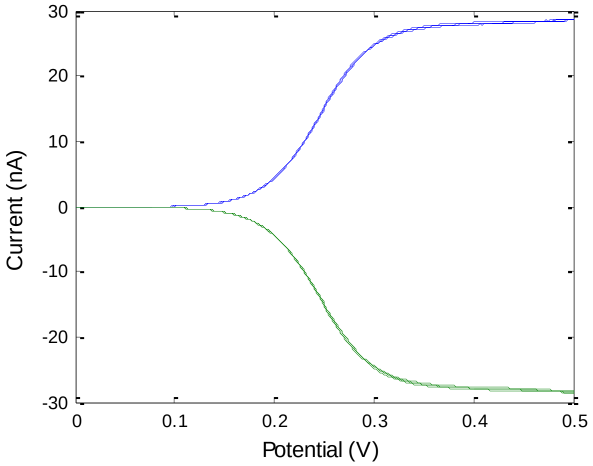

Figure 16b: Typical CV of ECS 1, scanning the bottom electrode at a scan rate of 20 mV/s. The green line is the current at the top electrode and the blue line is the current at the bottom electrode.

Figure 17 shows a typical trace measured on this device. The current increased slightly and linearly during the measurement, so the polynomial subtracted from the data is a linear curve. The current fluctuations are clearly anti-correlated and behave as expected, so these current traces are very suitable for analysis.

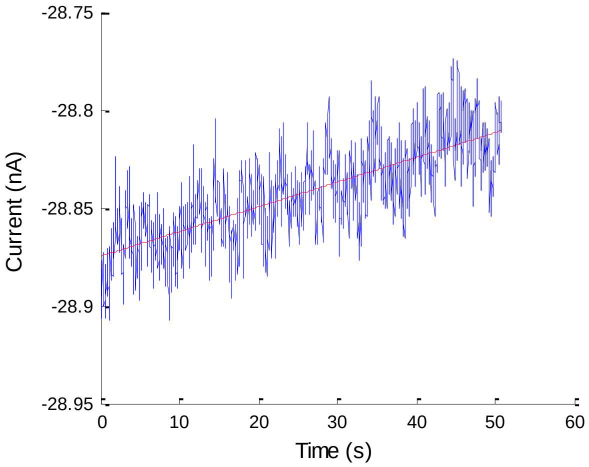

Figure 17a: Typical trace of bottom electrode of ECS 1 with the top electrode at 0.45 V and the bottom electrode at 0 V.

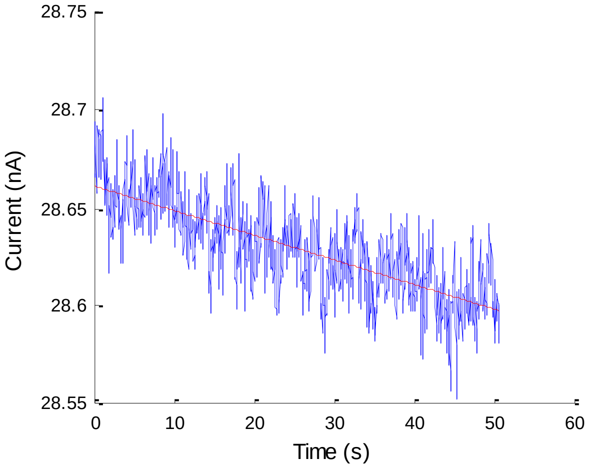

Figure 17b: Typical trace of the top electrode of ECS 1 with the top electrode at 0.45 V and the bottom electrode at 0 V.

Figure 18 shows a typical PSD of a trace on ECS 1 with the fit to equation (11) shown in black. The curve fits the measured PSD quite accurately, especially at higher frequencies, so the PSD decreases as $f^{-3/2}$ and the crossover frequency can be determined quite accurately.

Four current traces were taken with the bottom electrode at 0.45 V and six current traces were taken with the top electrode at 0.45 V. Table 2 shows the resulting average adsorption for both platinum electrodes using the rms and the PSD aproach, along with the standard deviation.

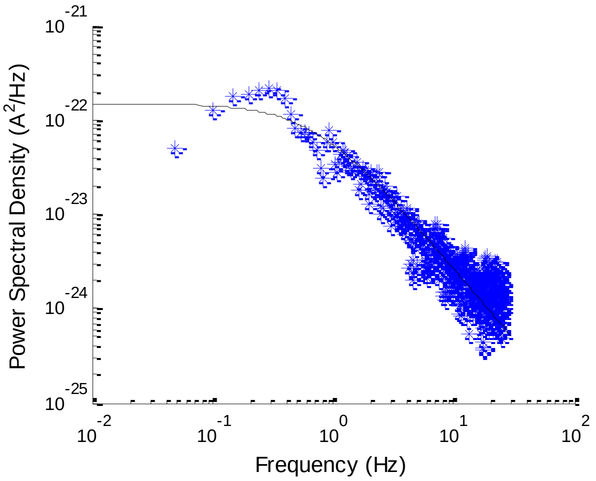

Figure 18: Typical PSD of ECS 1 with the top electrode at 0.45 V and the bottom electrode at 0 V.

Table 2: Adsorption on the electrodes of ECS 1 acquired from the rms and the PSD of current traces

	$\mathrm{ADS_{rms}}$	$\mathrm{ADS_{PSD}}$
Top electrode at 0.45 V	3.47 ± 0.65	2.18 ± 0.89
Bottom electrode at 0.45 V	2.12 ± 0.21	1.91 ± 0.76

Within the boundaries of the standard deviation the resulting adsorption is equal for the two different calculating methods. The bottom electrode shows a lower adsorption than the top electrode. This can be attributed to the fact that adsorption is very depended on the surface of the electrode and the conditions can differ a bit between the top and bottom electrode. Figure 19 shows the potential step measurement on the bottom electrode with the fits of each step to equation (17) shown in red. Equation (17) fits the measurement reasonably good, although the step from 0.35 V to 0.3 V does not clearly show any transient behaviour and a fit to equation (17) was not found. It is remarkable that the graph shows desorption behaviour on an increase in the potential and adsorption behaviour on a decrease of the potential, except for the step from 0.3 V to 0.35 V.

Table 3 shows the adsorption calculated from each step. The step from 0.3 V to 0.35 V could not be fitted using Matlab, so Origin was used for the fit. Because the error Origin finds from the fit differs significantly from the error Matlab find, the error for this measurement has been omitted.

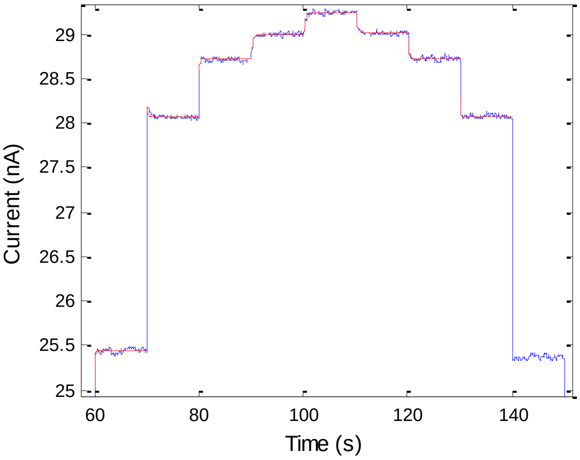

Figure 19: Potentential steps on bottom electrode of ECS 1. The steps shown are from 0.3 V to 0.5 V and back with steps of 0.05 V.

Table 3 shows that the adsorption is increasing with an increasing potential. The adsorption resulting from this measurement is very high for high potentials, which does not agree with the current trace measurements. A reason for the high adsorption could be that the RC response on a potential step influences the transient and therefore also the measured effective diffusion coefficient significantly.

Table 3: Adsorption on the bottom electrode of ECS 1acquired from the potential step measurement

From 0.25 V to 0.3 V	3,64 ± 0,60
From 0.3 V to 0.35 V	4,11
From 0.35 V to 0.4 V	5,75 ± 1,83
From 0.4 V to 0.45 V	34,00 ± 3,37
From 0.45 V to 0.5 V	27,50 ± 2,59
From 0.5 V to 0.45 V	21,50 ± 1,66
From 0.45 V to 0.4 V	15,50 ± 2,26
From 0.4 V to 0.35 V	8,09 ± 1,21

Platinum-diamond devices

On these devices the top electrode is made of platinum and the bottom electrode is made of boron doped diamond. Again cyclic voltammetry was performed to check the behaviour of the device, followed by current traces and potential step measurements. The benefit of platinum-diamond devices is that a comparison between adsorption on platinum and diamond electrodes can be made from measurements from a single device. Furthermore the measuring and device conditions are equal for the two electrodes. Over fourteen platinum-diamond chips have been measured but only tree four chips contained properly working devices. Three of these were 10 µm devices and one was a 50 µm device. Properly working devices were recognized by sigmoidal CV curves and current traces without unexpected peaks.

Representative CV's for 10 µm devices are shown in figure 20. Figure 20b shows the CV on the platinum top electrode. The current saturates at around 30 nA, indicating redox cycling is occurring. The current in cyclic voltammetry of the diamond bottom electrode, as shown in figure 20a, does not completely saturate. However current at 0.5 V is approximately equal to the expected limiting current of 30 nA for a 10 µm device. In all measured platinum-diamond devices the current does not saturate for the diamond electrodes. This seems to be either characteristic for diamond electrodes or results from anomalies in the devices. Thus there might have been a problem in the fabrication of the chips. In both CVs the halfway potential or steepest point in the curve seems to be around 2.5V, which is a value that is expected when using ferrocenedimethanol as an analyte and a silver-silver chloride reference electrode.

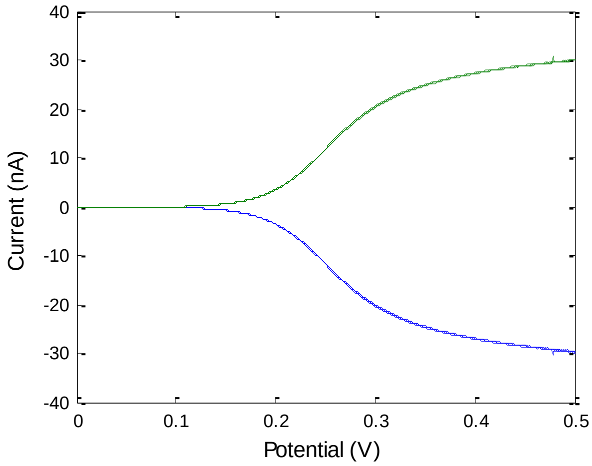

Figure 20a: Typical CV of 10-0.5B, scanning the bottom electrode at a scan rate of 20 mV/s. The green line is the current at the bottom electrode and the blue line is the current at the top electrode.

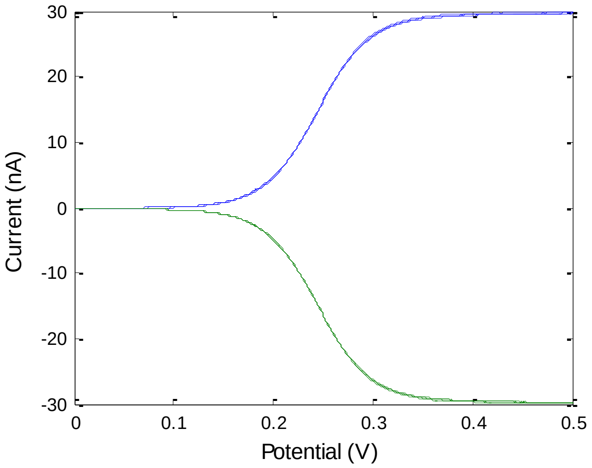

Figure 20b: Typical CV of 10-0.5B, scanning the top electrode at a scan rate of 20 mV/s. The green line is the current at the bottom electrode and the blue line is the current at the top electrode.

When the CV's of the two electrodes of a certain device were fine, current traces were made. A representative trace couple is shown in figure (21) for a 10-0.5B device with the diamond electrode at 0.45V and the platinum electrode at 0V. These traces are anti-correlated and during the measurement the current decreases linearly, so this can be easily corrected by subtracting a linear curve from the data. These kinds of traces are very suitable for analysis.

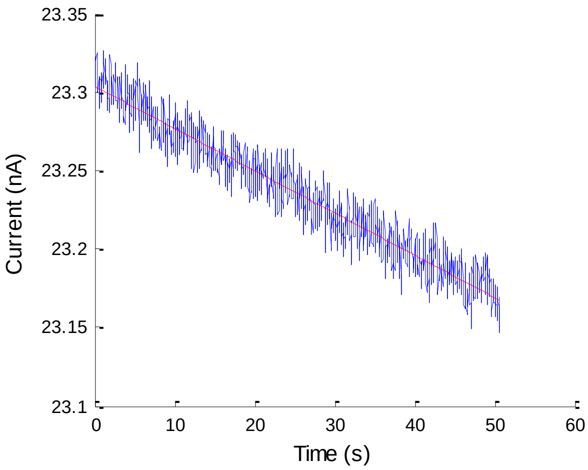

Figure 21a: Typical trace of bottom electrode of 10-0.5B with the bottom electrode at 0.45 V and the top electrode at 0 V.

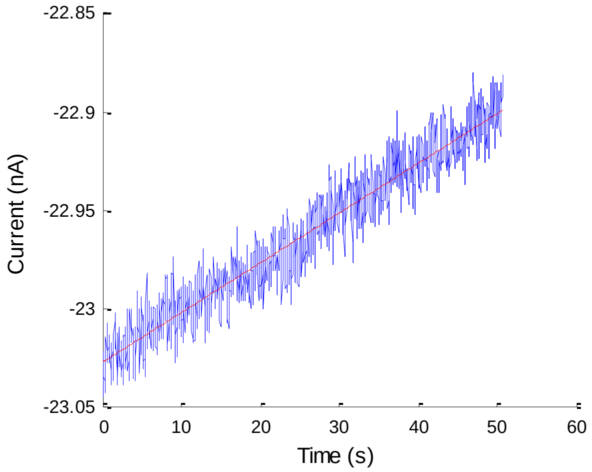

Figure 21b: Typical trace of top electrode of ECS 1 with the bottom electrode at 0.45 V and the top electrode at 0 V.

Figure 22 shows typical PSDs acquired from the current traces for the diamond and the platinum electrodes. From figures 22a and 22b it can be directly seen that the crossover frequency for platinum is lower than for platinum. This indicates that the adsorption on diamond is less than on platinum.

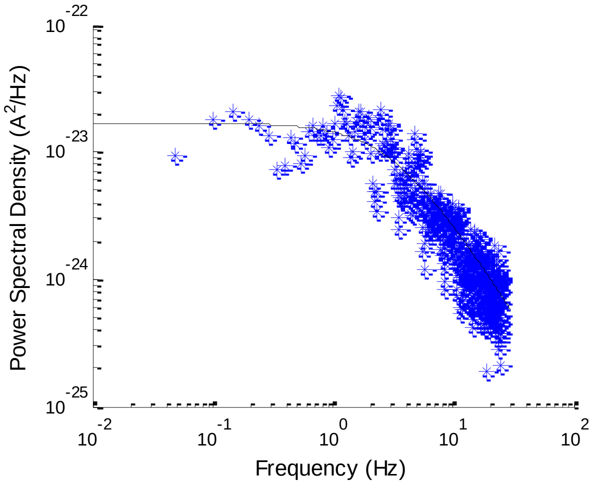

Figure 22a: Typical PSD of 10-0.5B with the bottom electrode at 0.45 V and the bottom electrode at 0 V.

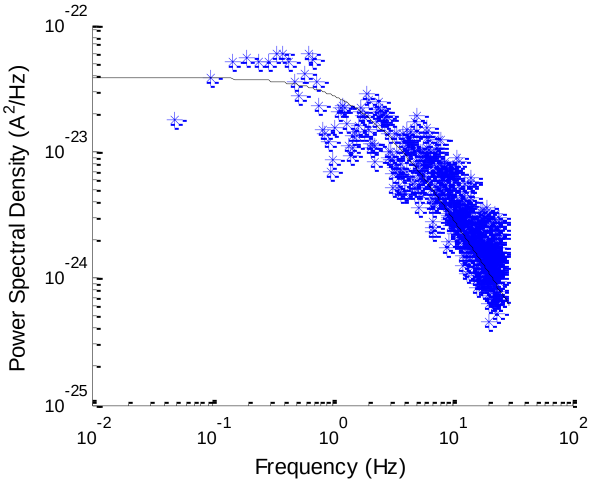

Figure 22b: Typical PSD of 10-0.5B with the top electrode at 0.45 V and the bottom electrode at 0 V.

Unfortunately not all the made traces and thus also the PSD showed behaviour as depicted in figures 21 and 22. Some current traces were not properly anti-correlated or showed large peaks, which were not expected from redox cycling. Steps in the current which could not be properly corrected were also observed. This kind of behaviour was more frequent in devices with longer electrodes. For these reasons traces with large peaks or steps were not used for the results.

The average adsorption and the error expressed as the standard deviation from the average the adsorption is shown in table 4 for two different measured devices (i.e. 10-0.5B and 10-1B). The errors were calculated with the same method used for the platinum-platinum devices.

Table 4: Adsorption on the electrodes platinum-diamond devices acquired from the rms and the PSD of current traces

Device: 10-0.5B	**ADS$_{rms}$**	**ADS$_{PSD}$**
Top electrode (platinum) at 0.45 V	5.21 ± 0.60	0.50 ± 0.40
Bottom electrode at (diamond) 0.45 V	0.23 ± 0.48	-0.6259 ± 0.11
Device: 10-1B	**ADS$_{rms}$**	**ADS$_{PSD}$**
Top electrode (platinum) at 0.45 V	1.58 ± 0.44	6.50 ± 1.91
Bottom electrode at (diamond) 0.45 V	-0.12 ± 0.15	5.21 ± 2.13

Table 4 shows that the adsorption calculated from the rms of the current fluctuations differs significantly from the adsorption calculated using the PSD. This difference could be a result from errors in the constants used in the calculations, such as the bulk diffusion coefficient. Although exact value of the adsorption cannot be determined because of the difference between the rms and the PSD results, the difference between the adsorption on the top and bottom electrodes can be analyzed for both calculation methods separately. Only for the PSD measurements on 10-1B the values for the two electrodes overlap within the error boundaries, so it cannot be stated with certainty that the adsorption is less on the diamond electrode than on the platinum electrode. It should be noted however that not all the PSD's had a 'perfect' fit. The other results do indicate that there is less adsorption on the diamond electrode than on the platinum electrode.

Current traces were also measured for different electrode potentials in the range from 0.325 V to 0.4 V on a different 10-0.5B device. No higher potentials were used, because this device showed high peaks in the trace, which were not expected from redox cycling. On platinum this occurred sooner than on diamond. The adsorption determined from tree or four traces on the same potential by use of the rms method and was averaged, the standard deviation was also determined. The results are displayed in figure 23.

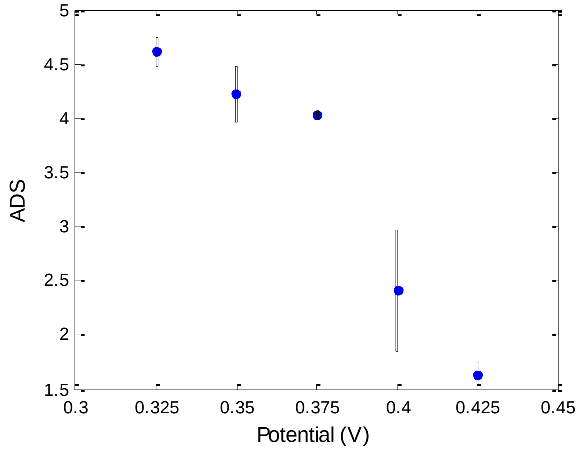

Figure 23a: Adsorption on the diamond electrode of 10-0.5B as a function of the potential on the diamond electrode.

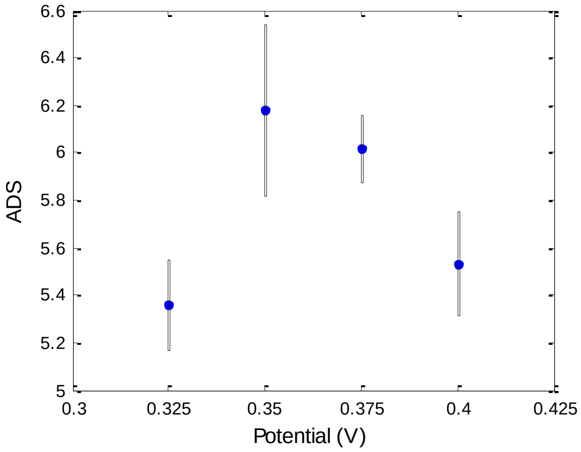

Figure 23b: Adsorption on the platinum electrode of 10-0.5B as a function of the potential on the platinum electrode.

Figure 23 shows that the adsorption is clearly dependent on the applied potential. The diamond electrode shows a different potential dependence than the platinum electrode. On the diamond electrodes the adsorption decreases on increasing the potential. For the platinum electrode the dependence cannot be determined. Comparing figure 23a and 23b reveals that on all potentials the adsorption on the diamond electrodes is lower than on the platinum electrodes. It should be noted however that figures 23a and 23b are the result of analysis on a single device. Therefore this behaviour should be reproduced, before any real conclusions can be made.

Next to the cyclic voltammetry and current trace measurements, step measurements are performed as well to determine the adsorption using a different method. The effective diffusion was determined by fitting formula (17) to a current transient resulting from a potential step. The adsorption is then calculated with formula (16). Step measurements were only taken if the CV of the device had a clear sigmoidal shape according to the expectation for ferrocenedimethanol in a redox-active device.
A representative step measurement on the top electrode of a ten micron device (10-1B) is shown in figure 24.

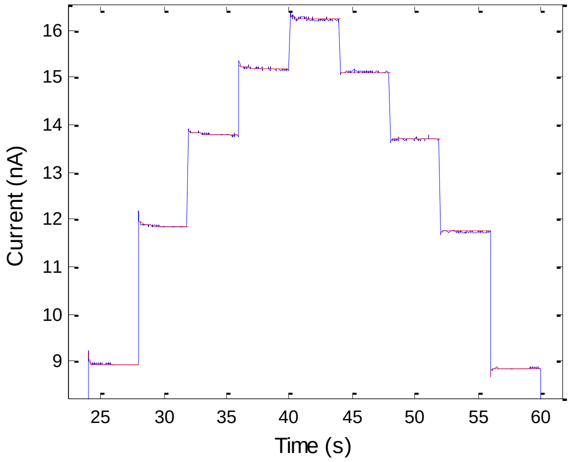

Figure 24a: Step measurement on the diamond electrode of a 10-1B device. The steps shown are from 0.3 V to 0.5 V and back with steps of 0.05 V.

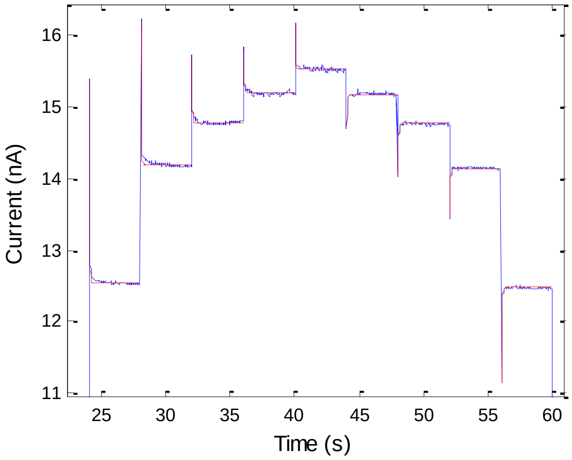

Figure 24b: Step measurement on the platinum electrode of a 10-1B device. The steps shown are from 0.3 V to 0.5 V and back with steps of 0.05 V.

Figure 24 shows desorption behaviour instead of the expected adsorption behaviour on an increase in the potential and the other way around. For the diamond electrode this agrees to figure (23a). For platinum electrodes the relation between adsorption and the applied electrode potential is not determined in our earlier presented measurement. An increase in potential seems to cause molecules to desorb from the electrode, causing an increase in current. For the diamond electrode the difference between the peak height and the steady state current is smaller than for the platinum electrode. This could suggest that difference in adsorption between different potentials is larger for the platinum electrode. On the other hand the peak height could be influenced by the RC response on a potential step. On the diamond electrode the current keeps increasing significantly on an increase of the potential, because the current does not saturate in cyclic voltammetry of diamond electrodes.

The adsorption is calculated from the step measurements by finding the effective diffusion coefficient from a fit of equation (17) to the current transient. Then the adsorption is calculated from the effective diffusion coefficient with equation (16). Step measurements were taken for the 50 µm long 50-1 device and for the 10-1B and 10-0.5B devices. In some cases the fit to equation (17) was not successful. Those results are omitted. Tables 5, 6 an 7 show the adsorption calculated from each step.

Table 5: Adsorption on 50-1 acquired from the potential step measurements

	ADS on diamond electrode	ADS on diamond electrode	ADS on platinum electrode
From 0.25 V to 0.3 V	2.10 ± 0.02	13.21 ± 0.23	2.36 ± 0.01
From 0.3 V to 0.35 V	2.20 ± 0.02	9.42 ± 0.13	2.37 ± 0.02
From 0.35 V to 0.4 V	2.30 ± 0.02	9.47 ± 0.17	2.24 ± 0.02
From 0.4 V to 0.45 V	2.63 ± 0.03	16.07 ± 0.64	1.97 ± 0.02
From 0.45 V to 0.5 V	3.76 ± 0.08		1.76 ± 0.02
From 0.5 V to 0.45 V	1.45 ± 0.05		0.90 ± 0.03
From 0.45 V to 0.4 V	1.55 ± 0.02	6.18 ± 0.66	0.69 ± 0.05
From 0.4 V to 0.35 V	1.81 ± 0.01	7.87 ± 0.19	0.93 ± 0.04
From 0.35 V to 0.3 V	1.88 ± 0.01	12.51 ± 0.29	1.72 ± 0.02

Table 6: Adsorption on 10-1B acquired from the potential step measurements

	ADS on diamond electrode	ADS on platinum electrode
From 0.25 V to 0.3 V	3.49 ± 0.24	2.60 ± 0.06
From 0.3 V to 0.35 V	39.75 ± 4.09	2.66 ± 0.09
From 0.35 V to 0.4 V	96.97 ± 15.14	2.02 ± 0.12
From 0.4 V to 0.45 V	112.11 ± 32.60	4.56 ± 0.26
From 0.45 V to 0.5 V	52.81 ± 12.79	2.62 ± 0.19
From 0.5 V to 0.45 V	12.91 ± 4.72	4.41 ± 0.26
From 0.45 V to 0.4 V	11.26 ± 2.78	2.40 ± 0.09
From 0.4 V to 0.35 V	3.74 ± 1.15	3.26 ± 0.11
From 0.35 V to 0.3 V	4.11 ± 0.47	2.88 ± 0.05

Table 7: Adsorption on 10-0.5B acquired from the potential step measurements

	ADS on diamond electrode	ADS on platinum electrode
From 0.25 V to 0.3 V	1.54 ± 0.05	1.09 ± 0.12
From 0.3 V to 0.35 V	1.55 ± 0.09	12.74 ± 1.14
From 0.35 V to 0.4 V	2.33 ± 0.32	15.08 ± 1.33
From 0.4 V to 0.45 V		14.48 ± 2.10
From 0.45 V to 0.5 V		20.89 ± 3.12
From 0.5 V to 0.45 V	15.89 ± 25.61	39.14 ± 6.30
From 0.45 V to 0.4 V	1.41 ± 0.55	22.63 ± 3.56
From 0.4 V to 0.35 V	1.99 ± 0.36	
From 0.35 V to 0.3 V	1.78 ± 0.09	

The adsorption calculated from the potential step measurements differs very much for different potentials and does not seem to have an obvious relation to the potential. The results from some measurements indicate unrealistically high adsorption, such as 112.11. Some errors are also very high, because the measured current was sometimes very noisy. A comparison between diamond and platinum gives different results for each device, so a conclusion concerning the difference in adsorption on platinum and diamond electrodes cannot be drawn from these step measurements.

Diamond – diamond devices

Figure 25 shows typical voltammograms of the top and bottom electrodes of diamond-diamond devices. Just as the diamond electrodes of the platinum-diamond electrodes the current does not saturate, but the halfway potential is at around 2.5 V, as expected. Furthermore the current at 0.5 V is in the order of the expected limiting current. The backwards curve in the voltammograms almost overlaps the forwards curve, so the capacitance is low. Again only devices with CV curves as shown in figure 25 were used to calculate the adsorption.

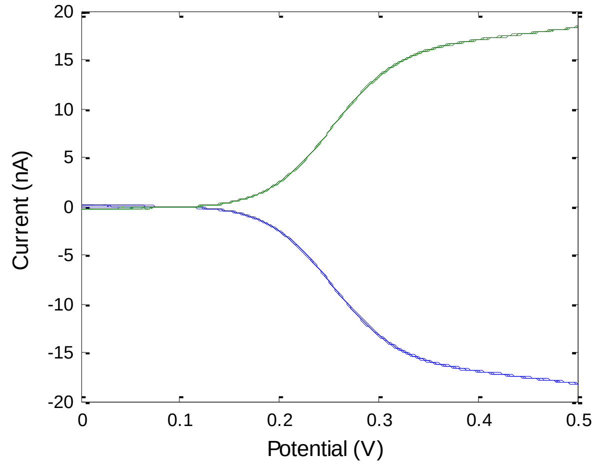

Figure 25a: CV of 10-1B, scanning the bottom electrode at a scan rate of 20 mV/s. The green line is the current at the bottom electrode and the blue line is the current at the top electrode.

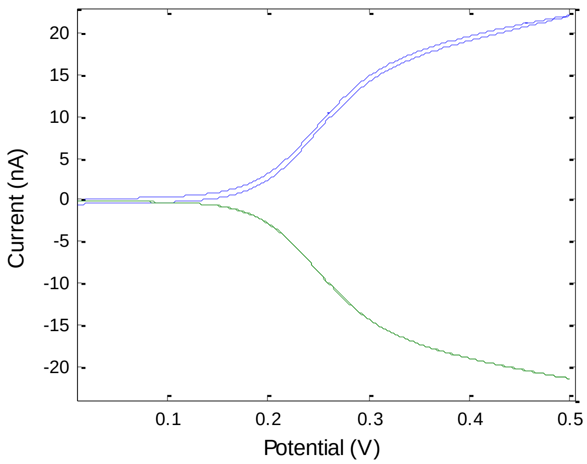

Figure 25b: CV of 10-1B, scanning the top electrode at a scan rate of 20 mV/s. The green line is the current at the bottom electrode and the blue line is the current at the top electrode.

Figure 26 shows typical current traces taken on diamond-diamond devices. They are anti-correlated and show no expected peaks. The current changes smoothly during the measurement, so a polynomial can be subtracted from the traces to correct for the changing current. A lot of traces had large peaks or steps in the current as described before. Eventually proper traces were acquired from three devices.

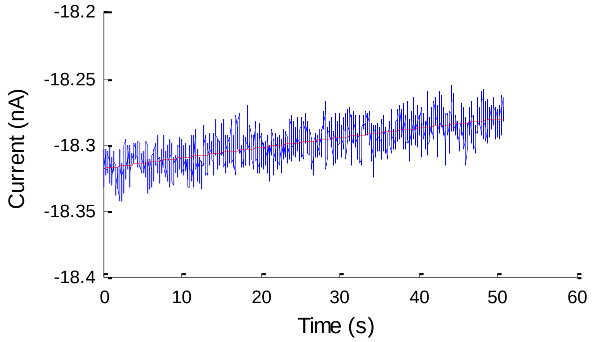

Figure 26a: Typical trace of bottom electrode of 10-1B with the top electrode at 0.5 V and the bottom electrode at 0 V.

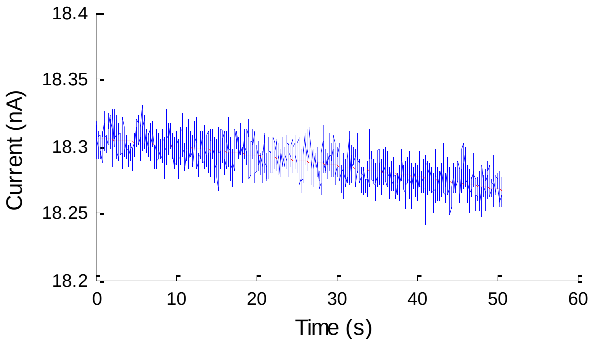

Figure 26b: Typical trace of top electrode of 10-1B with the top electrode at 0.5 V and the bottom electrode at 0 V.

Typical averaged PSDs for the bottom and top electrodes are shown in figure 27. The fits to equation (11), shown as a black line, fits PSDs good. Therefore these kinds of PSDs are suitable to determine the crossover frequency.

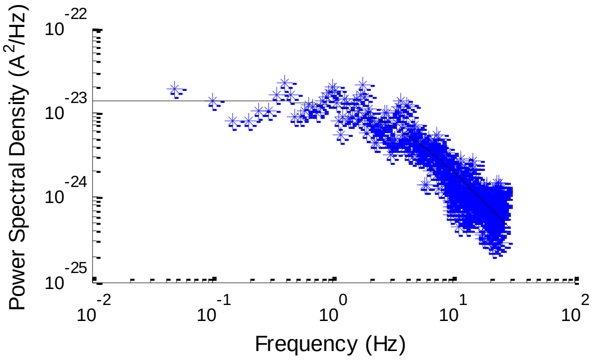

Figure 27a: Typical PSD of 10-1B with the bottom electrode at 0.45 V and the top electrode at 0 V.

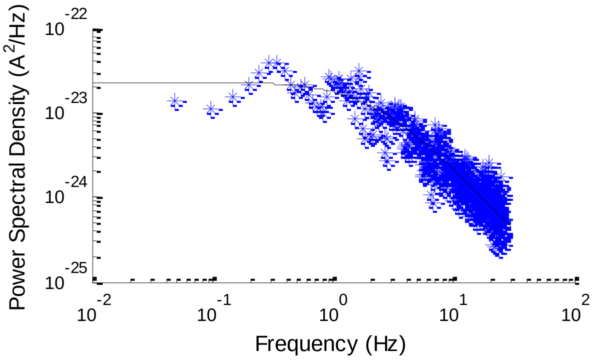

Figure 27b: Typical PSD of 10-1B with the top electrode at 0.45 V and the bottom electrode at 0 V.

Table 8 shows the calculated adsorption for the diamond-diamond devices.

Table 8:
Adsorption on the electrodes of diamond-diamond acquired from the rms and the PSD of current traces

Device: 10-1B (1)	**ADS_{rms}**	**ADS_{PSD}**
Top electrode at 0.5 V	1.33± 0.17	2.03±0.49
Bottom electrode at 0.5 V	-0.15± 0.1	4.73±0.40
Device: 10-1B (2)	**ADS_{rms}**	**ADS_{PSD}**
Top electrode at 0.5 V	4.90±1.11	0.59± 0.20
Bottom electrode at 0. 5 V	4.52±0.22	0.67±0.50
Device: 10-0.5B	**ADS_{rms}**	**ADS_{PSD}**
Top electrode at 0.5 V	3.93±0.09	3.80± 0.32
Bottom electrode at 0.5 V	1.43±0.18	8.48± 1.51

Table 8 shows that the adsorption calculated by the rms and PSD approaches can differ a lot. The adsorption of the two electrodes of single device calculated with the same method also differs significantly for two of the three traces. A reason could be that there is some mechanical noise in some measurements of the current traces. Because none of the CVs show a saturated current, the device does not behave exactly as expected. The reason for this is unknown, but this could influence the redox cycling current in some unexpected way, leading to incorrect calculations of the adsorption.

The potential step measurements are shown in figures 28 for a 10 µm long device (10-1B) and figure 29 shows a 50 µm device (50-1). In figure 28 the measured current fluctuates quite a lot, so the error in the effective diffusion coefficient is quite large. Figure 29 shows longer transient times, because the length of the device is longer. Some steps could not be fit, so no result for the adsorption could be calculated.

Table 9 and 10 shows the results of the step measurements. The transients resulting from a potential step were fitted by equation (17) to determine the effective diffusion coefficient. Then the adsorption is calculated using equation (16).

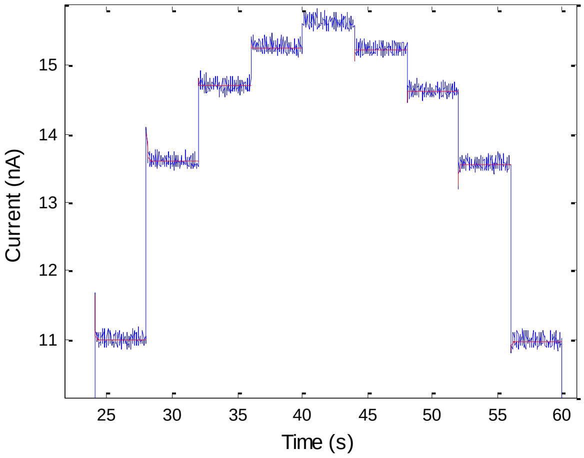

Figure 28a: Potential step of the bottom electrode of 10-1B device.

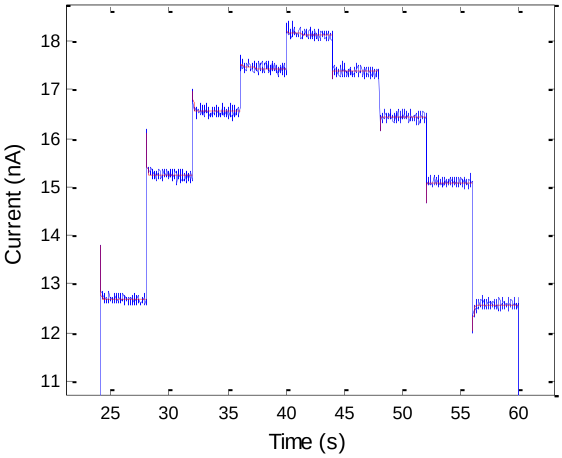

Figure 28b: Potential step of the top electrode of 10-1B device.

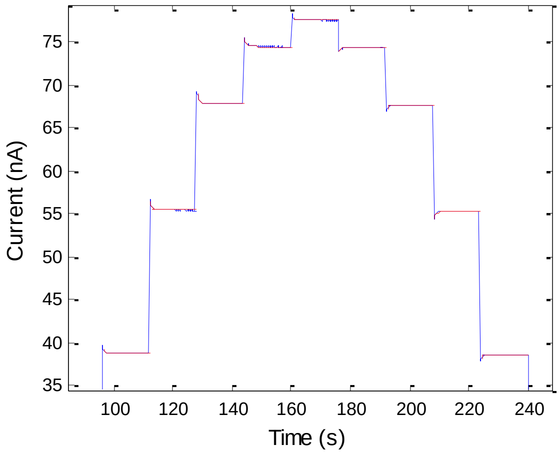

Figure (29): Potential step of the bottom electrode of 50-1B device.

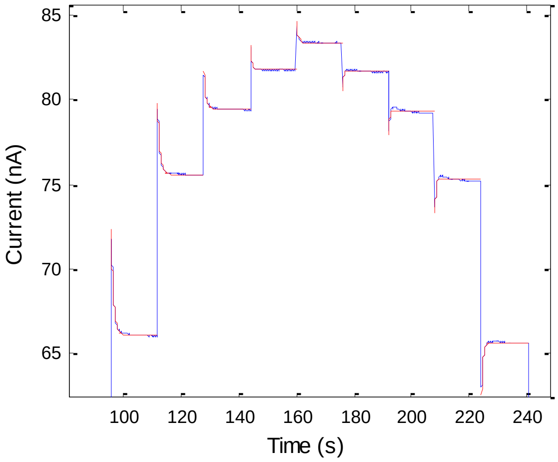

Figure (29): Potential step of the top electrode of 50-1B device.

Table 9: Adsorption on D-D 10-1B device acquired from the potential step measurements

	ADS on bottom electrode	**ADS on top electrode**
From 0.25 V to 0.3 V	2,10 ± 25,3%	3,90 ± 10,2%
From 0.3 V to 0.35 V	5,56 ± 24,5%	4,00 ± 14,9%
From 0.35 V to 0.4 V	0,05 ± ∞ %	4,89 ± 26,2%
From 0.4 V to 0.45 V	0,03 ± ∞ %	45,64 ± 46,9%
From 0.45 V to 0.5 V		151,49 ± 120,8%
From 0.5 V to 0.45 V	2,14 ± 81,5%	0,00 ± ∞ %
From 0.45 V to 0.4 V	1,96 ± 84,3%	3,78 ± 39,1%
From 0.4 V to 0.35 V	2,25 ± 47,2%	2,16 ± 35,4%
From 0.35 V to 0.3 V	6,35 ± 73,7%	5,53 ± 19,4%

Table 10: Adsorption on D-D 50-1B device acquired from the potential step measurements

	ADS on bottom electrode	**ADS on top electrode**
From 0.25 V to 0.3 V	2,10 ± 0,9%	2,36 ± 0,5%
From 0.3 V to 0.35 V	2,20 ± 0,8%	2,37 ± 0,7%
From 0.35 V to 0.4 V	2,30 ± 0,9%	2,24 ± 0,8%
From 0.4 V to 0.45 V	2,63 ± 1,2%	1,97 ± 0,9%
From 0.45 V to 0.5 V	3,76 ± 2,2%	1,76 ± 1,1%
From 0.5 V to 0.45 V	1,45 ± 3,6%	0,90 ± 3,8%
From 0.45 V to 0.4 V	1,55 ± 1,4%	0,69 ± 7,0%
From 0.4 V to 0.35 V	1,81 ± 0,6%	0,93 ± 4,3%
From 0.35 V to 0.3 V	1,88 ± 0,7%	1,72 ± 0,9%

Table 9 shows quite varying adsorption, both between the bottom and top electrode and for different potentials. At high potentials around 0.35 V the adsorption increases to unrealistically high values for the top electrode and the fit is not at all successful for the bottom electrode. The errors in the fit are also very high. The step measurements on this chip are therefore not very useful.

The adsorption found from the 50 µm device, as shown in table 10, is much more precise. It indicates an increasing adsorption with an increasing potential. On a decrease in potential from 0.5 V to 0.45 V the adsorption suddenly drops to increase again when the potential is lowered further. Low adsorption at high potentials was also measured on platinum-diamond devices. Thus minimal adsorption on diamond electrodes seems to occur at a high potential.

Discussion

In this section the results of the previous section will be discussed in general.

The CVs in the results were quite good for almost all of the platinum electrodes. They had a plateau at the expected current of 30nA and a halfway potential around 0.25 V measured with respect to the reference electrode. None of the diamond electrodes reached such a flat plateau. Instead the current kept increasing on higher potentials. This could possibly be a characteristic of the diamond electrode, but it could also be caused by electrochemical reactions from impurities. These impurities could be on the electrode surface or in the solutions used. They could have been cause by a problem in the etching procedure or in the fabrication of the devices.

In the adsorption calculations from the rms of the current traces, all current fluctuations were assumed to be caused by fluctuations in the number of redox-active molecules in the active region. External or instrumental noise, such as 50 Hz noise or vibrations, can therefore influence the measurements. 50 Hz noise should be cancelled by the grounded Faraday cage, but vibrations cannot be resolved completely. The used cross-correlation only removes instrumental noise that is different at both electrodes. Usually unexpected peaks in the redox cycling current from for example impurities cannot be corrected. These kinds of noise cause additional current fluctuations and thus lead to an underestimation of the calculated adsorption.

Ideally the value for the adsorption calculated by the rms method should give the same value as PSD calculated adsorption. Unfortunately this is not the case for most of the measurements. This difference might be caused by errors in the constants used in the calculations for both methods, such as the devices' dimensions, the concentration of ferrocenedimethanol in the solution or the bulk diffusion coefficient. However, these constants are known with negligible errors compared to statistical errors. The problem probably is in the fits to the PSDs. Those were sometimes quite inaccurate. This can be due to the fact that noise components from other sources than redox cycling distort the form of the PSD. In the rms calculations on the other hand instrumental noise is cancelled by the cross-correlation. The adsorption calculated from the rms of the current traces is therefore considered more accurate.

The fact that the diamond electrodes, especially those on the diamond-diamond devices, sometimes showed an adsorption comparable to the adsorption on the platinum electrodes could be explained by an problem in the fabrication of the structures. The diamond electrodes should be sp^3 hybridized. It is possible that a part of the carbon atoms are in non-diamond sp^2 hybridization state. This could lead to a lower chemical inertness and thus to more adsorption.[6] Another reason could be that the temperature during the measurements was room temperature, which might have been slightly different for different measurements. However, this effect should be minor.

From the results of the step measurements it is clear that the adsorption calculated from the current transient, was often not very realistic and inaccurate. This is mainly because not all the fits followed the curves perfectly. Especially in the ten micron devices a proper fit was not always possible. This is due to the very short transient times. The transient times are so short, because to the length of the active region and the distance between the active region and the entrance holes is very short. To measure transients of short duration more accurately, a higher sampling frequency can be used. The 50 µm devices show longer transient times, so these are more suitable for potential step measurements. Unfortunately most of the 50 µm electrodes measured, especially with the Pt-D devices, showed large peaks in the current traces. Therefore measurements were focused on the 10 µm devices.

Conclusion

Having analyzed the results, now the research question can be answered:

"Is the amount of adsorption of redox active molecules on boron doped diamond electrodes less than that on the platinum electrodes in nanofluidic electrochemical sensors?"

The adsorption calculations from the rms and the crossover frequency in the PSD on the two platinum-diamond devices (table 4) indicate that the amount of adsorption on boron doped diamond electrodes is less than on platinum electrodes. A comparison of the potential step measurement on the 10 µm platinum-platinum device (table 1) with the potential step measurements on the 50 µm diamond-diamond device (table 10) also shows that the adsorption on diamond is lower than on platinum. However, these measurements were taken on devices with different dimensions, so the cannot be firmly stated. The potential step measurements on the platinum-diamond devices are ambiguous. Some potential step measurements indicate approximately equal adsorption on diamond and platinum (table 5). Another measurement (table 6) seems to indicate the opposite. However, many step measurements give unrealistically high values of adsorption at potentials around 0.4 V – 0.5 V and have large errors. Therefore potential step measurements are less suitable to determine the adsorption than the rms and PSD calculations, especially on the short 10 µm devices.

Overall the results seem to indicate that the amount of adsorption on diamond is lower than on platinum electrodes, especially on high potentials around 0.5 V. However, this conclusion is supported by only a small number of devices. Therefore it would be good to repeat the experiment on more devices to confirm this conclusion. It has been observed that the adsorption on the electrodes of different devices of the same type can differ significantly. A larger number of measurements makes it possible to calculate an average adsorption for a certain device. Therefore a large amount of measurements would be beneficial to support the conclusion. Further research can be focused on measuring the adsorption on other electrode materials, under different conditions, such as acidic or basic conditions or at different temperatures. On the diamond electrodes adsorption at higher potentials than 0.5 V could also be researched.

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Appendix

Derivation of equation (15)

Using equation (2), the current response can be expressed as:

$$\Delta i = \frac{\Delta N_{sol} e D}{h^2} \tag{18}$$

If the number of molecules in the solution is called N_{sol} and the change the number of adsorbed molecules after the potential step is called ΔN_{ads}, the change in adsorption after the potential step can be expressed as:

$$\Delta ADS = \frac{\Delta N_{ads}}{N_{sol}} \tag{19}$$

Because of number of particles in the active region is conserved during the step, the change in the number of molecules in the solution is equal and opposite to the change of the number of molecules that get adsorbed on the electrodes: $\Delta\langle N_{ads}\rangle = -\Delta\langle N_{sol}\rangle$. This means the change in adsorption is:

$$\Delta ADS = -\frac{\Delta N_{sol}}{N_{sol}} \tag{20}$$

Filling in equation (18) and assuming the number of molecules before the potential step is the value expected from the bulk concentration ($\langle N_{sol}\rangle$= $cAhN_A$), equation (20) becomes:

$$\Delta ADS = -\frac{\Delta i\, h^2}{eD}\frac{1}{N_A cAh} = -\frac{\Delta i\, h}{eDN_A cA} \tag{21}$$

Matlab script for the calculation of the adsorption from current traces

The script loads a current trace from an external file. A polynomial is fitted to the current and substracted. Then the rms of the current fluctuations is calculated, followed by the calculation of the adsorption. From the same current trace the PSD is calculated. The PSD is fitted to equation (11) to determine the crossover frequency. Then the adsorption is calculated from the crossover frequency. Finally the current traces are plotted with the fitted polynomial and the PSD and its fit are plotted.

```
FIT_P=10;       %Polynomial fit parameter

FileName='06_DPt_10um1B_fc(MeOH)2_Btm0.45_btm0.ct';
DIR='C:\Users\User\Documents\Bacheloropdracht\Metingen\2012-06-08\10-
0.5B\10-05B\';
data = load(strcat(DIR,FileName,'.txt'));
fid1=fopen(strcat(DIR,'Analysis\','PSD_', FileName,'.txt'),'w');    %to
write the results
fid2=fopen(strcat(DIR,'Analysis\','Result_', FileName,'.txt'),'w'); %to
write the results
fid3=fopen(strcat(DIR,'Analysis\','avgPSD_', FileName,'.txt'),'w'); %to
write the results

%===================

%=== Constants ===
BE=3e-6; %width of the bottom electrode
Le=0.5e-6;%separation between the TE and the access hole
La=10e-6; %length of the top electrode (channel)
H=50e-9;%channel height
A=La*BE;% area in m^2
cB=1e-3; %mM concentration

NA=6.023e23;
e=1.6e-19;
nv=1;%valency

N_sol=NA*cB*H*A*1e3; % 1L=1e-3 m^3

%----I_limiting----------
D=6.7e-10;
i_lim=NA*e*A*D*cB*1e3/H
%=====================
%=====================

t = data(1:end,1);
y1 = data(1:end,2);
y2 = data(1:end,4);


  meanTopEl = mean(y1);
    meanBotEl = mean(y2);

    AdjTopEl = y1;
    AdjBotEl = y2;

    %Fit a nth order polynomial to the currents of Top and Bottom electrode
    TopElFit = polyfit(t,AdjTopEl,FIT_P);
    BotElFit = polyfit(t,AdjBotEl,FIT_P);
```

```
    %values of the above polynomial for all time t
    yTop = polyval(TopElFit,t);
    yBot = polyval(BotElFit,t);
    %----------------------------------
    figure ('Units','Centimeters','Position',[1 15 8.5 6.5]);
        hold on
        plot(t,y1*1E9,'-');
        plot(t,yTop*1E9,'r')
        xlabel('Time (s)','FontSize',8);
        ylabel('Current (nA)','FontSize',8);
        set(gca,'FontSize',7)
    figure ('Units','Centimeters','Position',[10 15 8.5 6.5]);
        hold on
        plot(t,y2*1E9);
        plot(t,yBot*1E9,'r')
        xlabel('Time (s)','FontSize',8);
        ylabel('Current (nA)','FontSize',8);
        set(gca,'FontSize',7)
    %-----------------------------------
    %Subtract the polynomial fit from the raw data and offset with the mean
    yTopNew = (AdjTopEl-yTop);
    yBotNew = (AdjBotEl-yBot) ;

    %------NOISE---------------

    I_rms = sqrt(mean(-(yTopNew.*yBotNew)))
    I_av_1 = mean(y1);
    N_amp = (I_av_1/I_rms)^2;
    ADS=(N_amp/N_sol)-1



%---------------PSD------------
% N=3000;
     TSampl=(t(size(t,1))-t(1)); % Length of the signal
    dTSampl=TSampl/size(t,1);
    Fs = 1/(dTSampl);
    N=length(t);

%%%--------------------------------------
n=1000;
m = n/2; % number of distinct frequency bins
Y = fft(yTopNew,n); % FFT of length 1024
Pyx = Y.*conj(Y) / n; % PSD = |Y|^2
f = (Fs/2) * [0:m]/m ; % the frequency bins (513).
Pyx(m+2:n) = [ ] ; % sneaky MATLAB trick for shortening a vector
Pyx(2:m+1) = 2*Pyx(2:m+1); % compensate for missing negative frequencies
Pyx=Pyx/(1*Fs);
%%%----------------------------------------
     [Pxx,Fx] = psd(yTopNew,N,Fs,hanning(N));
     Pxx(2:end-1) = Pxx(2:end-1)*2;
     Pxx = Pxx/Fs;

%%%--------------------
% yNew=abs(sqrt((-(yTopNew.*yBotNew))));
yNew=yTopNew;
%%%-------------------

 %%%[Pxx,f] = pwelch(x,window,noverlap,nfft,fs)
 [Pyy,Fy] = pwelch(yNew,gausswin(N),0, N, Fs);
```

```
 [Pxx,w]=pwelch(yNew); %%% averages over 8 segments with 50% overlap
 Fx_avg=w*(Fs/(2*pi));
 Pxx_avg=Pxx/(Fs/(2*pi));

 %=====================Fitting: Calculate f0 ======================
 fun=@(c,f)(c(1)./(1+(f./c(2)).^(3/2)));
 c1guess=Pxx_avg(1);
 [Pc2guess,ic2guess]=min(abs(Pxx_avg-c1guess/2));
 c0 = [Pxx_avg(1); Fx(ic2guess)];
 c=nlinfit(Fx_avg,Pxx_avg*1E22,fun,c0);
 c(1)=c(1)*1E-22;
 f0_m=c(2);
 fplot=1E-2:0.01:30;
 Pfit=fun(c,fplot);

 %================= Plotting PSD, PSG_avg & PSD fit ================
 figure ('Units','Centimeters','Position',[20 15 8.5 6.5]); hold on
 loglog(Fx_avg,Pxx_avg,'b*')
 loglog(fplot,Pfit,'k')
 xlabel('Frequency (Hz)','fontsize',8);
 ylabel('Power Spectral Density (A^2/Hz)','fontsize',8);
 set(gca,'XScale','log','YScale','log','FontSize',7)


for i=1:1:size(Pyy,1)
    fprintf(fid1,'%5.8f\t',Fy(i));
    fprintf(fid1,'%5.15e\n',Pyy(i));
%
end
for i=1:1:size(Pxx,1) %%% Averaged PSD from one trace
    fprintf(fid3,'%5.8f\t',w(i)*(Fs/(2*pi)));
    fprintf(fid3,'%5.15e\n',Pxx(i)/(Fs/(2*pi)));
%
end

%====================CALCULATE ADS FROM f0 ======================
Nsol=NA*H*A*cB*1e3;

f0=(D/pi)*(3/(La*La*(La+6*Le)))^(2/3)
f0_m

D_eff=(f0_m)*3.14*(3/(La^2*(La+6*Le)))^(-2/3);

N_freq=Nsol*(f0/f0_m);
ADSf=(f0/f0_m)-1

%
% ===Saving to File======================
 fprintf(fid2,'dTSampl %5.5f\v',dTSampl);
 fprintf(fid2,'FIT_P %5.1f\v',FIT_P);
 fprintf(fid2,'I_rms %5.10e\v',I_rms);
 fprintf(fid2,'I_av %5.10e\v',I_av_1);
 fprintf(fid2,'ADS_m %5.4f\v',ADS);
 fprintf(fid2,'f0 %5.4f\v',f0);
 fprintf(fid2,'f0_m %5.4f\v',f0_m);
 fprintf(fid2,'ADS_f0 %5.4f\v',ADSf);

 ADS
 ADSf
```

Matlab script for the calculation of the adsorption from potential step measurements

The selected steps are fit to equation (17) to determine the effective diffusion coefficient and the error in the fit. Then the adsorption is calculated from the effective diffusion coefficient.

```
FileName='26_ecs1_fcmeoh2_Btm_STEP';
DIR='C:\Users\User\Documents\Bacheloropdracht\Metingen\2012-05-01\';
data = load(strcat(DIR,FileName,'.txt'));
L=10E-6;                            %Length channel
tpoint=0.05;                        %Seconds per point
D=6.7E-10;                          %Theoretical diffusion
sfit=6:14;                          %Steps to fit

U=data(:,1);
t=data(:,2);
I1=data(:,3);   % In nA
I2=data(:,4);   % In nA

tplot=t.*tpoint;

%Look for increases U
steps=[];
Ustep=[];
for n=1:length(U)-1
    if U(n+1)-U(n)~=0               %Not equal
        steps=[steps n];
        Ustep=[Ustep U(n+1)];
    end
end
Nsteps=length(steps);               %Number of steps

%Analyze all steps using for loop
creg=zeros(Nsteps,3);               %Introduce coefficient matrix
dcreg=zeros(Nsteps,3);              %Introduce error matrix
for s=sfit
    clear c
    I=I1(steps(s)+1:steps(s+1));
    t2=t(steps(s)+1:steps(s+1)).*tpoint;
    t0=t2(1);

    %Fitting
        %Constants
        I0=I(1);
        stepheight=I(length(I))-I(1);

        %Solve I0+stepheight/2=I0+stepheight*erf(2.97*(D*thalf/L^2)^0.6)
        for D
        %1) Find thalf
        [dI ihalf]=min(abs(I-(I0+0.5*stepheight)));
        thalf=t2(ihalf)-t2(1);
        Dguess=fzero(@(D)(erf(2.97.*(D*thalf./L.^2).^0.6)-0.5),[1E-13 1E-
        7])
        c0=[I0 stepheight Dguess];  %[offset stepheight diffusion]

    fun=@(c,t)(c(1)+c(2).*erf(2.97.*(c(3).*(t2-t0)./L.^2).^(0.6)));
    try
    [c r J sigma]=nlinfit(t2-t0,I,fun,c0);      %[c r] are coeficients and
                                                residuals
    dc = sqrt(diag(sigma));
    catch
```

```
        continue
    end
    creg(s,:)=c;
    dcreg(s,:)=dc;
    U(s)
    Deff=c(3)

    Iguess=fun(c0,t2-t0);
    Ifit=fun(c,t2-t0);

end

%Plot everything
figure ('Units','Centimeters','Position',[10 15 8.5 6.5]);
plot(tplot,I1*1E9);
for s=1:Nsteps
    creg(s,1);
    if creg(s,1) > 0
        t2=t(steps(s)+1:steps(s+1)).*tpoint;
        t0=t2(1);
        Ifit=fun(creg(s,:),t2-t0);
        hold on; plot(t2,Ifit*1E9,'r')
    end
end
xlabel('Time (s)','FontSize',8);
ylabel('Current (nA)','FontSize',8);
set(gca,'FontSize',7)

%Place results in matrix
ADS=D./creg(:,3);
dADS=dcreg(:,3)./creg(:,3)*100; % in %
res=[Ustep' creg(:,1) dcreg(:,1) creg(:,2) dcreg(:,2) creg(:,3) dcreg(:,3)
ADS dADS];
%    U      I0        dI0        stepheigth dstepheigth Deff    dDeff ADS
fid1=strcat(DIR,'Analysis\','StepResults_', FileName,'.txt'); %to write the
results
```