



# A study of the electron transfer inhibition on a charged self-assembled monolayer modified gold electrode by odd random phase multisine electrochemical impedance spectroscopy



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## ABSTRACT

The interest of self-assembled monolayers (SAM) comes from their wide range of very specific technological applications. The SAMs having a terminal charged group are of great importance as model surfaces for electron transfer studies. The electron transfer for highly charged electroactive ions at a SAM modified electrode involves an electrostatic interaction. The present work studies a negatively charged SAM of 2-mercaptobenzimidazole-5-sulfonate (MBIS). The adsorption of the molecule on polycrystalline gold is described by X-ray photoelectron spectroscopy (XPS) and the reductive desorption of MBIS. The behavior of the MBIS monolayer towards the electron transfer of the ferri/ferrocyanide reaction is investigated by cyclic voltammetry and odd random phase multisine electrochemical impedance spectroscopy (ORP-EIS). This technique ensures reliable experiments and enables a statistically founded modeling. The combined electrochemical and surface study allows the investigation of the characteristics and electrochemical properties of the MBIS monolayer formed on polycrystalline gold to provide a quantitative modeling, which is physically and statistically validated. The major contribution of this work is the use of ORP-EIS and XPS to understand how the interaction between a charged SAM and electroactive ions affects the electron transfer.

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## 1. Introduction

The construction of self-assembled monolayers (SAM) on material surfaces is of great interest for a wide range of technological applications in fields like molecular recognition, biosensors, corrosion inhibition or wetting control. The self-assembly of thin organic layers in solution has been widely studied because a well-ordered structure can be prepared in an easy and inexpensive manner. A lot of work has been focused on SAMs formed by adsorption of thiol compounds on gold.

SAMs with terminal charged groups are used as electrode modifiers in numerous applications. They are especially interesting as model surfaces for electrochemical studies on double-layer structure or electron transfer [1–6]. Their particularity relies on the electrostatic interaction that occurs for the electron transfer of highly charged electroactive ions at the SAM modified electrode.

The attraction or repulsion between the analyte ions and the charged head groups of the SAM alters the electron transfer.

The charge transfer on a SAM modified electrode is strongly influenced by the nature of the electrode surface and the structure of the double layer [7]. Impedance spectroscopy is a powerful technique to study these interfacial parameters. Odd random phase multisine electrochemical impedance spectroscopy (ORP-EIS) extracts information from the measurements to ensure reliable experimental data and a statistically founded impedance modeling [8–10].

The formation and properties of alkanethiols have been extensively studied, but in the last years interest has moved to small aromatic thiols [4,11–13]. These molecules allow a more reversible electron transfer than the alkanethiols [6]. However, with a charged terminal group, the molecule might be less efficient towards the electron transfer [13–15].

In this respect, the present work examines a negatively charged SAM of 2-mercaptobenzimidazole-5-sulfonate (MBIS) on polycrystalline gold. The sulfonic acid group is preferred to carboxylic acid because of its strong acid character, which ensures the presence of the charge regardless of the pH.

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Initially, the presence of a MBIS layer on the gold surface is verified by means of X-ray photoelectron spectroscopy (XPS) and the reductive desorption of MBIS from gold. The XPS study provides information about the chemical state of the elements of the MBIS molecule on gold. A description of the chemical structure of the SAM is achieved by angle-resolved analysis.

The reductive desorption of the MBIS molecule from polycrystalline gold is investigated. A thiol SAM is desorbed from the gold surface by a one-electron reduction process in an alkaline aqueous solution [16], where the chemical bond between the substrate atoms and sulfur atom of thiol is broken.

The behavior of the MBIS layer towards the electron transfer of the negatively charged  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  couple are examined by cyclic voltammetry and ORP-EIS. The latter technique brings a reliable analysis of the electrochemical properties of the modified electrode.

This paper aims a quantitative analysis of the influence of the anion-anion repulsion on the electron transfer of the redox probe at the charged-SAM modified electrode. Its major contribution is the combination of ORP-EIS and XPS to the electron transfer studies on ion-monolayer interactions.

## 2. Experimental

### 2.1. Chemicals and solutions

The following chemicals are used:  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (both Merck p.a.),  $\text{KClO}_4$  (Merck a.c.s.) and 2-mercaptobenzimidazole-5-sulfonic acid sodium salt (Sigma-Aldrich, 98%). The MBIS salt is purified by recrystallization in a mixture of absolute ethanol and water 9/1 (v/v). All solutions are prepared with Milli-Q water. The electrolyte for the electron transfer studies consists of a solution of 1 mM ferri/ferrocyanide (1:1) in 0.02 M  $\text{KClO}_4$ .

### 2.2. Pretreatment of the gold electrode

The gold electrode is a 6 mm diameter disk electrode, made by inserting a polycrystalline gold rod in an insulating mantle of polyvinylidene fluoride. It is especially designed for surface analysis techniques; the gold rod is inserted in a short casing (8 mm tall) that can be detached from the main casing. The gold electrode is first polished with alumina ( $0.30 \mu\text{m}$ ) water slurry on a polishing cloth (Struers), then rinsed with Milli-Q water. To ensure the cleanliness of the electrode, repeated cyclic voltammograms for the oxidation and reduction of the gold surface are performed [4,12]. The gold electrode is cycled in the supporting electrolyte solution between  $-0.50$  and  $1.25$  V (vs  $\text{Ag}/\text{AgCl}$ ) at  $50$  mV/s, until no change between successive voltammograms is observed. After the measurements on the MBIS modified electrode and before the electrode pretreatment, the monolayer is removed from the gold surface by reductive desorption of the thiol in  $0.1$  M KOH.

### 2.3. Formation of the SAM

A scheme of the MBIS molecule is shown in Fig. 1. It is a heterocycle thiol with a sulfonate group located at the extremity opposite to the thiol group, through which the anchoring to the gold occurs.

The self-assembled monolayers are formed by simple immersion of the gold electrode in an aqueous 1 mM MBIS solution. Different adsorption times are considered in this investigation. After the adsorption of the SAM, the electrode is thoroughly rinsed with Milli-Q water, dried with nitrogen and transferred to the electrochemical cell.

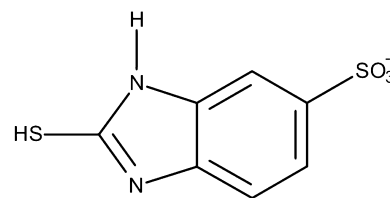


Fig. 1. Chemical structure of 2-mercaptobenzimidazole-5-sulfonate (MBIS).

### 2.4. XPS

XPS analysis are performed on the gold electrode by means of a Physical Electronics 5600 photoelectron spectrometer, using a monochromated  $\text{Al K}\alpha$  X-ray source and operating at 120 W. The survey and the high-resolution spectra are collected using a pass energy of 187.85 eV and 46.95 eV respectively. The analyzed area has a diameter of 1.1 mm.

An angle-resolved analysis of the monolayer on polycrystalline gold is carried out. The electrode is tilted at five take-off angles:  $15^\circ$ ,  $30^\circ$ ,  $45^\circ$ ,  $60^\circ$  and  $75^\circ$ . The XPS spectra are expressed in terms of binding energy (BE). The binding energies of the peak positions are calculated as the mean of the peak BE for each angle; the precision is expressed as the maximum absolute deviation of the peak binding energies. The integrated intensities of raw peaks are quantified for the analysis of the spectra. The fitting of the XPS peaks is done by CasaXPS software using a Shirley background subtraction and a mixed Gaussian-Lorentzian shape. The thickness of the monolayer is estimated by the Structure Analysis tool in MultiPak v9.0 software.

### 2.5. Voltammetry measurements

The electrochemical experiments are acquired using a three-electrode set-up. The counter electrode is a platinum grid. The reference electrode is  $\text{Ag}/\text{AgCl}$ . The working electrode is the gold electrode.

All measurements are performed in an amber glass cell with a water jacket connected to a thermostat (Lauda RE 304), at a temperature of  $25 \pm 0.5^\circ\text{C}$ . Before the experiments, the electrolyte is purged with nitrogen gas for 30 min. A nitrogen blanket is kept above the electrolyte during the experiments.

The cyclic voltammograms are measured using an Autolab potentiostat PGSTAT12, controlled by Nova 1.7 software. To study the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  reaction, the potential is swept from the equilibrium potential between  $-0.10$  and  $+0.50$  V vs  $\text{Ag}/\text{AgCl}$  for the reaction at the bare electrode, and between  $-0.40$  and  $+0.80$  V vs  $\text{Ag}/\text{AgCl}$  for the reaction at the MBIS modified electrode. The scan rate is 50 mV/s.

### 2.6. ORP-EIS measurements

The measuring set-up consists of a Wenking potentiostat POS 2 (Bank Elektronik) and a National Instruments PCI-4461 DAQ-card. The applied multisine signal is digitally composed with MATLAB R2010a software (MathWorks Inc). MATLAB is also used for processing the collected data and controlling the DAQ-card. The perturbation signal applied is a 5 mV rms variation around the equilibrium potential. The impedance spectrum is acquired in the frequency range 0.01 Hz - 10 kHz.

10 impedance measurements of the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  reaction are performed. The experiments are measured consecutively on the MBIS modified electrode, but when the reaction is studied on the bare gold, the electrode needs to be cleaned every 4 measurements (as described in Section 2.2). Otherwise, a high increase of the impedance magnitude is observed, due to surfaces processes

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