

# Studies on the electrochemical behavior of a cystine self-assembled monolayer modified electrode using ferrocyanide as a probe

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## Abstract

The preparation and electrochemical characterization of a cystine self-assembled monolayer (cys-SAM) onto a gold electrode is reported. The electron transfer of the  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple at the modified electrode surface was studied at different pH values by using cyclic voltammetry and electrochemical impedance spectroscopy. A reversible voltammogram for the redox couple was observed at the cys-SAM surface, indicating that the electron transfer is not restrained. Electrochemical impedance spectroscopy was used to evaluate the electron transfer dependence on the protonation of acidic/basic groups of the adsorbed thiol and an increase of the resistance was observed at higher pH solution values because of the repulsion between negatively charged groups. Calculated values of charge transfer resistance increased with the solution pH from 600 to 1700  $\Omega \text{ cm}^2$  in the pH range comprising 4.9 and 8.0. Quartz Crystal Microbalance experiments were performed for characterizing the cystine coverage and results showed a 58  $\text{ng cm}^{-2}$  mass increase during immersion of a gold electrode in a  $1 \times 10^{-3} \text{ mol L}^{-1}$  cystine solution, corresponding to  $1.4 \times 10^{14}$  molecules/ $\text{cm}^2$  ( $\Gamma = 2.3 \times 10^{-10} \text{ mol cm}^{-2}$ ). The influence of cystine concentration on the rate of adsorption was also investigated by cyclic voltammetry experiments.

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## 1. Introduction

The formation of self-assembled monolayer (SAM) by spontaneous adsorption of molecules from solution onto suitable substrates has been shown to be a versatile technique for surface modification with a number of applications, especially in the fabrication of electrochemical sensors [1–3]. The advantages of SAM-modified electrodes include the possibility of introducing different chemical functionalities with high level of order at a molecular dimension [4,5]. This ability allows the development of electrochemical active surfaces with specific functions, which can be used for selective interactions or to catalyze electron transfer reactions [6,7]. Furthermore, by deliberate control and manipulation of electrode surface properties a variety of attractive effects can be achieved, such as

improvement of selectivity, sensitivity and reproducibility [8,9].

Although a wide variety of substrates and functional groups are known to form SAM, thiol/disulfide monolayers on Au have received considerable attention in recent years [10–13]. The electron transfer at a thiol modified gold electrode can be influenced by many factors, such as alkyl chain length, active terminal groups and solution pH. Alkanethiols with terminal functionalized groups self-assembled on gold can block electron transfer between the electrode and electroactive species dissolved in the electrolyte solution. Several groups have investigated the relationship between the structure of the adsorbed molecule and electron transfer kinetics properties [14–17] as an attempt to enhance the use of these devices as practical sensors.

The electron transfer at these electrode surfaces has been mainly investigated by cyclic voltammetry [18,19] and electrochemical impedance spectroscopy [20,21], the most

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common electrochemical techniques used to study redox processes at covered monolayers. Mendes et al. [22] examined thiols with different alkyl chain lengths containing COOH terminal groups self-assembled on gold electrodes. The electron transfer of the  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple at the electrode was studied at different pH values by using cyclic voltammetry and electrochemical impedance spectroscopy. Changes in solution pH resulted in charge variation of the self-assembled monolayer terminal group and, consequently, the electrostatic interaction of the SAM with the electroactive species in the solution depended on the medium acidity. Raj and Behera [23] reported the electrochemical characteristics of 6-mercaptopyridine-2-thione (MNA) on a gold electrode. The SAM was investigated by cyclic voltammetric and impedance techniques and it was observed that the electron transfer for the redox reactions of different molecules at the monolayer was controlled by electrostatic and hydrophobic effects.

The kinetics of the formation of SAM surface coverage has been studied by reductive adsorption or desorption of alkanethiolate monolayers at gold surfaces [22,24–26]. However, there have been few studies on the kinetics of adsorption of SAM. For instance, El-Deab and Ohsaka [24] showed the time-dependent growth of a monolayer by reductive desorption of cysteine formed on a polycrystalline gold electrode. A 95% surface coverage of cysteine was attained after 300 s. Hager and Brolo [25] reported the desorption behavior of the thiol/disulfide redox couple, cysteine/cystine, monitored at a Au(111) single crystal electrode. The authors examined the formation of each peak in the adsorption reaction of cystine on the gold electrode by cyclic voltammetry and chronocoulometry in order to determine the monolayer surface coverage. Hong and Park [26] reported studies on the adsorption kinetics for the formation of redox active SAM on a gold electrode by using cyclic voltammetry to investigate the effects of concentration and time deposition. Dong [27] used an electrochemical quartz crystal microbalance (EQCM) to study the deposition of some thiol compounds on gold surfaces and the results showed that frequency shifts are more sensitive than electrochemical methods to evaluate the extent of coverage.

Cystine is a disulfide species that binds strongly to gold surfaces, hence it can be used to form SAM. As this organic molecule possesses amino and carboxyl groups attached to the  $(\text{SCH}_2\text{CHNH}_2\text{COOH})_2$  moiety, the surface charge density may be adequately controlled by changing the solution pH. This ability is especially desired to anchor enzymes in the fabrication of biosensors. Accordingly, in the present work we report our results on the evaluation of the interfacial properties resulting from the deposition of cystine on gold electrodes. The electron transfer kinetics of a redox probe at the modified surface was investigated by cyclic voltammetry and the results were compared with those obtained by electrochemical impedance spectroscopy. The cystine adsorption at the gold surface was characterized by EQCM studies.

## 2. Experimental

### 2.1. Chemicals

Cystine (Aldrich 99%), sulphuric acid (Aldrich 99%), potassium ferrocyanide ( $\text{K}_4\text{Fe}(\text{CN})_6$ ) (Aldrich 99%) and phosphoric acid (Aldrich 99%) were of analytical grade and the solutions were prepared by dissolving the compounds or concentrated solutions in deionized water processed through a water purification system (Nanopure Infinity, Barnstead). Cystine (cys) was prepared as 100% ethanolic solution.

### 2.2. Apparatus

The electrochemical cell was constituted of a gold disc electrode (geometric area =  $10 \text{ mm}^2$ ) as working electrode, a platinum wire and Ag/AgCl ( $3.0 \text{ mol L}^{-1}$  KCl solution) as auxiliary and reference electrodes, respectively. Cyclic voltammetric experiments were carried out using a 273 EG&G PARC instrument. Electrochemical impedance spectroscopy (EIS) experiments were carried out using an AUTOLAB potentiostat (EcoChemie), controlled by the FRA Software<sup>®</sup>. The impedance spectra were fitted to a Randles equivalent electrical circuit, which includes solution resistance ( $R_s$ ), double layer capacitance ( $C_{dl}$ ) and charge transfer resistance ( $R_{ct}$ ). The impedance at the formal potential of the redox couple was measured in the frequency range of 10 mHz to 50 kHz.

QCM measurements were performed in a conventional three-electrode electrochemical cell. The solution volume was 20 mL and the design of the electrochemical cell was described elsewhere [28]. The working electrode was a 6 MHz AT-cut piezoelectric quartz crystal with diameter of 25 mm and a piezo active electrode area of  $0.31 \text{ cm}^2$ . The electrochemical behavior of cystine is very similar at both quartz crystal and gold electrodes, therefore qualitative comparisons between results obtained with these electrodes is possible. Both electrode sides were previously evaporated with gold onto a chromium layer in order to improve adherence of gold onto the quartz substrate. Frequency resonance shift was transformed to mass change using the Sauerbrey equation [29] ( $\Delta f = -K\Delta m$ ) and the integral sensitivity constant,  $K$  ( $6.5 \times 10^7 \text{ g cm}^{-2} \text{ Hz}^{-1}$ ), was determined by silver electrodeposition [30]. Electrochemical experiments were carried out with a model PG 3901 Omnimeta potentio/galvanostat. Frequency shifts during the potential scan were measured by using a Standford Research Systems Instrument, model SR 620, connected to an oscillating circuitry (serial mode) and to a microcomputer for data acquisition.

### 2.3. Electrode preparation and electrochemical studies

The Au electrode surface was polished with  $1 \mu\text{m}$  alumina powder before chemical modification. After the polishing treatment, the electrode was abundantly rinsed

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