



Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Determining the parameters governing the electrochemical stability of thiols and disulfides self-assembled monolayer on gold electrodes in physiological medium

Adam Kolodziej^a, Francisco Fernandez-Trillo^{a,b,c,*}, Paramaconi Rodriguez^{a,**}^a School of Chemistry, University of Birmingham, Edgbaston B15 2TT, UK^b School of Pharmacy, University of Birmingham, Edgbaston B15 2TT, UK^c Institute of Microbiology and Infection, University of Birmingham, Edgbaston B15 2TT, UK

ARTICLE INFO

Keywords:

Self-assembly monolayer of thiols
 Disulfides
 Electrochemistry
 Desorption
 Surface structure

ABSTRACT

Herein we study the electrochemical potential-dependent and time-dependent stability of thiols and disulfides as self-assembled monolayers on gold electrodes. The stability of four representative sulfur-containing compounds: 3-mercaptopropionic acid, 2-mercaptoethanol, 1,4-dithiothreitol and DL-thioctic acid, was assessed in simulated physiological conditions (i.e. phosphate buffer saline). The stability of these molecules was evaluated using cyclic voltammetry and step-potential chronoamperometry. Coordination of the thiols and disulfides significantly affects the stability of the self-assembled monolayer. In addition, studies performed using gold single crystal (100) and (111) electrodes show the superior binding strength of the SAM on the Au(100) surface structure.

1. Introduction

The functionalization of metal surfaces by self-assembled monolayers (SAMs) of alkanethiols and closely related compounds is a continuously expanding area with enormous impact on corrosion, lubrication, biomimetics, and sensing among others fields [1–7]. Recently, SAMs have also found relevant applications in drug/gene delivery and imaging [8,9]. The controlled release of drugs and related compounds, is highly relevant in medical applications, for instance to minimize negative side effects, as well as extend the circulation and half-life of these bioactive compounds [1,10–12].

Thiol-functionalized molecules have been widely studied by electrochemical means due to its importance in mentioned areas. Understanding the stability of these S-Au SAMs is of paramount importance to benchmark the reliability and reproducibility of the electrochemical devices fabricated with these materials [13–15]. For example, in the development of electrochemical sensors, a robust and stable monolayer would be desirable, in particular one that can operate in a wide potential window. However, SAMs are subject to oxidative and reductive desorption that compromises the integrity of the monolayer. Reductive desorption is more restrictive due to its occurrence at the potentials more likely to be analytically useful [16,17]. For these reasons, reductive desorption of thiols from gold surfaces have been

studied by a variety of electrochemical, probe microscopy and spectroelectrochemical techniques [13–15,18–34]. While electrochemical and spectroelectrochemical methods provide important information on the coverage, potential window stability and the charge number per molecule adsorbed; in situ probe microscopy gives information about the packing, unit cell and adsorption symmetry of thiols as a function of the potential.

Previous studies have been mostly conducted using cyclic voltammetry (CV) and chronoamperometry (CA) in alkaline media due to the high solubility of thiolates under these conditions. Important contributions to the understanding on thiols coverage and stability on model systems have been reported by Lipkowski group over the last two decades. Recently, Kunze et al. and Laredo et al. have reported the importance of the methodology implemented to determine the coverage of thiol monolayers on Au(111) single crystal electrodes. In these reports it is highlighted how reductive desorption methods present systematic errors due to the uncertainties associated with the charging current correction. These authors introduced a step potential chronocoulometry as a potentiostatic method to measure the charge density at the electrode at different potentials in 0.1 M NaF, 0.1 M HClO₄ and 0.1 M NaOH [13–15]. However, the understanding of the stability of adsorbed sulfur-containing molecules on gold electrodes at physiological conditions has enormous implications in sensing and the

* Corresponding author.

** Correspondence to: P. Rodriguez, School of Chemistry, University of Birmingham, Edgbaston, B15 2TT, UK.

E-mail addresses: f.fernandez-trillo@bham.ac.uk (F. Fernandez-Trillo), p.b.rodriguez@bham.ac.uk (P. Rodriguez).<http://dx.doi.org/10.1016/j.jelechem.2017.07.039>Received 17 April 2017; Received in revised form 19 June 2017; Accepted 19 July 2017
1572-6657/ © 2017 Published by Elsevier B.V.

controlled delivery of drugs in blood (pH = 7.2–7.6) [35–37].

Noteworthy, in addition to the pH, the reductive desorption of thiols is influenced by the surface structure of the metal substrate. Such structure-reactivity relationship is attributed to the different coordination of surface atoms [19] and a difference in binding energies to various basal planes [21,22,28,38–40]. In order to provide a rational understanding of the role of the surface structure on the stability of thiols in electrochemical media, spectroelectrochemical methods have been also used [18,29,30]. Recently, Bizzotto et al. have used fluorescence microscopy and thiols tagged with fluorescent probes to track the reductive desorption of thiols as a function of the surface structure of polyoriented bead-type gold electrodes [18,31]. The report by Bizzotto concludes that (111) is more amenable to desorption of thiol SAMs when compared to the other surface sites of the polycrystalline gold electrode.

The implementation of thiols SAM in controlled delivery of drugs and nanosensing requires an understanding of the parameters governing the desorption of thiols from polycrystalline surfaces that mimic monocrystalline surfaces and its behaviour in physiological media.

Aware of these needs, here we present a progressive step-potential approach that provides potential and time-dependence insights of the reductive desorption of adsorbed monolayers of thiols from polycrystalline gold electrodes in a physiological media containing phosphate and chloride ions. The protocol was evaluated over 4 representative sulfur-containing molecules: 3-mercaptopropionic acid (1), 2-mercaptoethanol (2), 1,4-dithiothreitol (3) and DL-thioctic acid (4) in a phosphate saline buffer solution (DPBS). The progressive step-potential experiments provide relevant information on the stability of the thiols as a function of their nature; at the same time these experiments provide relevant information on the kinetics of the reductive desorption process. We also evaluated the influence of the surface structure of the gold electrode for the desorption of two selected compounds: 3-mercaptopropionic acid (1) and DL-thioctic acid (4) in a phosphate saline buffer solution.

2. Experimental

An exhaustive cleaning procedure of the glassware was implemented to ensure reproducible experimental conditions [41]. On a daily basis, the glassware was soaked overnight in an acidic solution of KMnO_4 . The glassware was then removed from the KMnO_4 solution, and rinsed with a diluted solution of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ with a ratio of 1:3. The glassware was finally rinsed with boiling Milli-Q water (18.2 M Ω cm, 1 ppb total organic carbon) at least 5 times to ensure the absence of sulfate ions in the working solution. A three compartment electrochemical cell was employed with a high surface area gold flag counter electrode and a Hg/Hg₂SO₄ reference electrode. All the results were converted to RHE scale as presented in the manuscript. Measurements were performed on μ AutoLab III potentiostat. Prior to experiments, Argon (6N, BOC) was used to deoxygenate electrolytic media.

Gold disk electrodes were prepared from high purity (Sigma Aldrich, 99.999%) gold wire. Prior to each experiment, the gold disk electrode was mechanically polished with diamond slurry, rinsed with Milli-Q water, flame-annealed and cooled down under argon atmosphere.

Au(111) and Au(100) bead-type single-crystal electrodes (icryst) were flame annealed and cooled down in Ar atmosphere prior to each experiment. The blank voltammetry of the gold electrode was registered prior to each set of experiments to confirm the cleanness of the system (both electrode and electrolyte). Dulbecco's phosphate-buffered saline solution (DPBS pH = 7.4, Lonza) was used as the electrolyte throughout the manuscript. This electrolyte was selected to mimic physiological conditions (i.e. pH and osmolarity) and has been used in a range of scientific reports including examples in drug delivery [42] or cell culture [43]. All the experiments were performed at room

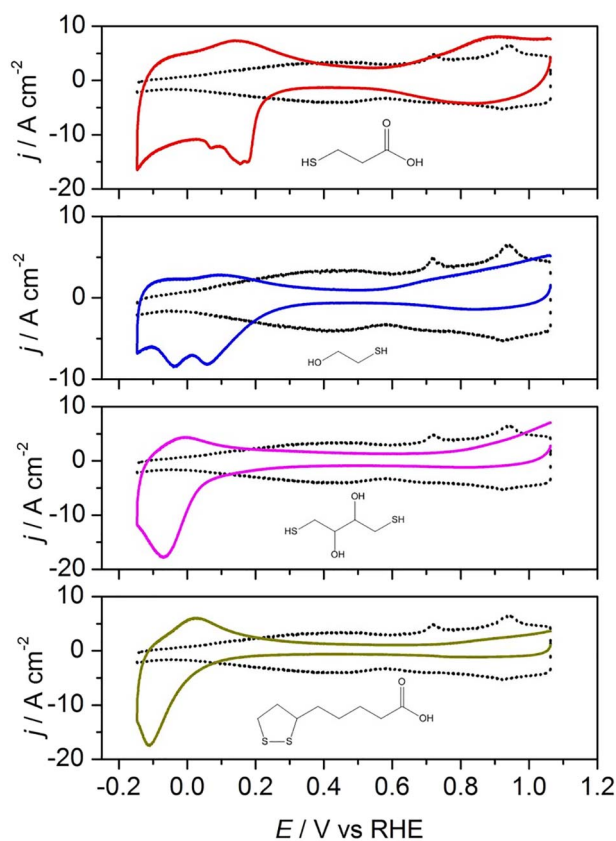


Fig. 1. Voltammetric profiles of polycrystalline gold electrodes modified with 3-mercaptopropionic acid (1), 2-mercaptoethanol (2), 1,4-dithiothreitol (3) and DL-thioctic acid (4) recorded in DPBS. Blank voltammeteries of the electrodes in absence of the adsorbed molecules are shown for comparison (dotted line). Scan rate $\nu = 50 \text{ mV s}^{-1}$.

temperature which fluctuates between 14 °C and 20 °C.

Gold electrodes were functionalised with self-assembled monolayers of the desired compound by immersing the clean gold electrode, following flame-annealing and rinsing with Milli-Q water, in a solution containing 10 mM of the desired compound. The gold electrode was immersed for 10 min at open circuit potential (OCP). Solutions were prepared as follows: 3-mercaptopropionic acid (1) (Sigma Aldrich, $\geq 99\%$) in 3:1 mixture of Milli-Q water and absolute ethanol; 2-mercaptoethanol (2) (Sigma Aldrich, $\geq 99\%$) and 1,4-dithiothreitol (3) (Sigma Aldrich, $\geq 98\%$) in Milli-Q water; and DL-thioctic acid (4) (Alfa Aesar, 98%) in absolute ethanol. The excess of physisorbed molecules was removed by rinsing with a copious amount of Milli-Q water.

3. Results and discussion

3.1. Assessment of the stability of 3-mercaptopropionic acid, 2-mercaptoethanol, 1,4-dithiothreitol and DL-thioctic acid on Au polycrystalline electrode in phosphate buffer solution

Fig. 1 shows the voltammetric profiles of the surface-modified Au electrodes with the four different compounds evaluated 1–4. The blank voltammetry of bare gold polycrystalline electrode is included for comparison. In all the cases, a decrease of the double-layer charging current can be observed while the features associated to the lifting of the reconstruction of Au and to the adsorption/desorption of phosphate anions disappear [44]. These changes in the voltammetric profile are a clear evidence of the presence of compounds 1–4 on the surface. Differences in the capacitive current for each molecule correspond to different surface defects formed by each monolayer [45].

In these voltammetric profiles, several features could be identified. At lower potentials (-0.15 to 0.25 V vs RHE) reduction peaks

Download English Version:

<https://daneshyari.com/en/article/6661697>

Download Persian Version:

<https://daneshyari.com/article/6661697>

[Daneshyari.com](https://daneshyari.com)