The electrochemical reaction mechanism of arsenic on gold analyzed by anodic stripping Square-wave voltammetry

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A B S T R A C T

The reaction mechanism of the oxidative stripping of As(0) accumulated on a polycrystalline gold electrode is studied theoretical and experimentally by Square-wave voltammetry (SWV). A mathematical model was developed specifically to describe this reaction mechanism. A reaction scheme $E_{(ad)}C$ is considered in this model, where As(0) corresponds to the adsorbed reduced species. The electrochemical oxidation of As(0) produces a soluble species that undergoes a chemical reaction with pseudo-first order kinetics. Although the reduction of hydrogen at the electrode surface can contribute to the deposition of As(0), significant evolution of H_2 would compromise this process.

From the fits of experimental SW voltammograms, it is possible to estimate the value of the standard charge-transfer rate constant $k_s = (4 \pm 2)\,s^{-1}$, $\alpha = (0.20 \pm 0.01)$, the chemical reaction equilibrium constant $K = 3 \times 10^{-4}$, the adsorption constant $K_{ad} = 1 \times 10^{-2}$, the formal potential of the redox step $E°' = (0.055 \pm 0.002)$ V, and the surface concentration of accumulated As(0), $\Gamma_r^* = 3.3 \times 10^{-11}\,mol\,cm^{-2}$. The value of K corresponds to the ratio between the concentrations of the oxidized species and the product of the coupled chemical reaction Y. It was also found that the formation of Y involves a fast forward chemical reaction, since the kinetic constants of the chemical reaction can be estimated as $k_1 = 1 \times 10^5\,s^{-1}$ and $k_{-1} = 30\,s^{-1}$.

Finally, it was found that the electrochemical reaction involves 3 electrons and that the lost of the first electron of As(0) is the rate-determining step of this multiple-step multiple-electron electrochemical reaction.

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1. Introduction

Arsenic is considered toxic for humans and other living organisms [1–3]. The presence of this element in water sources is usually associated with natural events, although there are some pesticides that contain arsenic [2–4]. According to the US EPA, the maximum containment level of arsenic in drinking water is $0.010\,mg\,L^{-1}$. This regulation brought an urgent need for the development of arsenic sensors and the improvement of systems for water treatment [4]. Probably because of this, there are several analytical techniques available for the determination of arsenic species in water samples [1–4]. Although most of those techniques are well-established spectroscopies, such as atomic fluorescence spectroscopy, hydride generation atomic absorption spectroscopy, and inductively coupled plasma-mass spectrometry, they all require samples to be collected and transported to a centralized laboratory for analysis [1,2]. *In situ* measurements are thus highly desirable because they would minimize errors. Labor and cost associated with the spectroscopic methods make electrochemical techniques the most promising approach for developing *in situ* arsenic sensors [5–12]. In this regard, stripping voltammetric strategies not only have proven to give reliable results in laboratory conditions, but also they provide a relatively low-cost option that can be adapted to portable analytical devices [1–5].

To achieve detection limits of trace elements, arsenic species are usually reduced by a chemical reaction to As(III) and then accumulated at the electrode as As(0). Following the deposition step, the electrode potential is scanned to strip the accumulated As(0) from the electrode [1,2,4–13]. In the case of anodic stripping voltammetry (ASV), several researchers consider that the key to

the ASV detection of arsenic is related to the use of some kind of gold electrode material [1–3,14]. Diverse forms of gold electrodes have been studied including solid gold, gold film electrodes, and other electrode materials modified with gold nanoparticles [1,2,15].

Although solid gold would be the most robust surface, a strategy that ensures a long-term, reproducible, and programmable cleaning protocol is still required [1,4,5,15]. This is because metallic arsenic (As(0)) forms an amalgam with gold at the same time that it accumulates at the surface [5,15]. Cleaning protocols are therefore focused on releasing the As(0) that remains underneath the gold surface in order to restore its former conductivity [15]. Besides the complications associated with the diffusion of As(0), other mechanistic aspects related to the electrochemical reactions that take place during the deposition and stripping of arsenic accumulated on gold electrodes are also seldom studied [15–17]. In this regard, it should be considered that a suitable protocol for quantifying arsenic in water samples can be found once the diverse mechanistic aspects that complicate its reaction have been identified.

Square-wave voltammetry (SWV) has proved to be a powerful tool for analytical purposes as well as for the elucidation of reaction mechanisms [18–26]. The concentration gradients of reagents and products close to the surface are rebuilt several times due to the alternated application of the oxidation and reduction pulses of SWV [18,22–25]. The excitation waveform of SWV is characterized by the height of the base staircase (dE), the square-wave amplitude (E_{sw}), which corresponds to the half of the peak-to-peak amplitude of a symmetrical square-wave, and the square-wave frequency (f). The first pulse of the wave is a direct pulse, because it coincides with the advance of the stair, while the other is in opposite sense. The forward currents (Ψ_f) are collected at the end of the direct pulses, while the backward currents (Ψ_b) are saved at the end of the reverse pulses [18]. The differential peak current ($\Delta\Psi_p$) and the peak potential (E_p) are referred to the potential of the stair. From the analytical point of view, $\Delta\Psi_p$ and E_p are the most useful parameters of SWV. However, simulation of Ψ_f and Ψ_b is required to assign a reaction mechanism to an experimental system [22–25,27].

The electrochemical reaction mechanism of arsenic deposition has been studied on Au(111) because the charge-transfer process might vary for the different small domains of polycrystalline gold surfaces [15]. In that research work Tafel plots and a relatively simple reaction scheme were used to study the electrochemical process. It was concluded that the electrodeposition of arsenic is an irreversible electrode reaction and that the transfer of the first accepted electron is the rate-determining step (rds) [15].

In this opportunity, the electrochemical reaction of arsenic on a polycrystalline gold electrode is studied. Experimental results are analyzed and then simulated with a mathematical model where surface confined species of As(0) and a following homogeneous chemical reaction of As(III) have been considered.
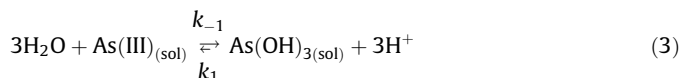
2. The model

The stripping step of arsenic can be described according to the following global reaction:

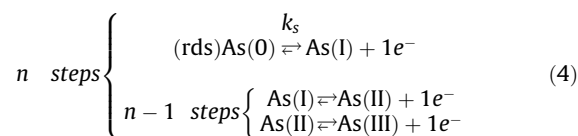$$3H_2O + As(0)_{(ad)} \rightleftarrows As(OH)_{3(sol)} + 3H^+ + 3e^- \tag{1}$$
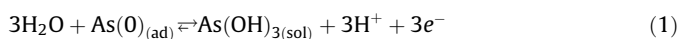
Eq. (1) has to be divided in simpler steps to find out a proper set of boundary conditions for this reaction. Incidentally, it has to be recognized that Eq. (1) merges chemical and electrochemical steps in the form of a global reaction. Thus, Eq. (1) can be splitted into the

following expressions:

$$As(0)_{(ad)} \overset{k_s}{\rightleftarrows} As(III)_{(sol)} + 3e^- \tag{2}$$

$$3H_2O + As(III)_{(sol)} \overset{k_{-1}}{\underset{k_1}{\rightleftarrows}} As(OH)_{3(sol)} + 3H^+ \tag{3}$$

For the sake of simplicity only the species arsenious acid has been considered. However, other species involving anions such as chloride should be present in appreciable amounts [17]. Since water and protons are in excess, k_1 and k_{-1} are pseudo-first order homogeneous rate constants of the chemical reaction, Eq. (3). The parameter k_s is the formal charge transfer rate constant of the global electron transfer reaction, Eq. (2). From the analysis of cathodic and anodic Tafel plots it was found that the transfer of the third electron is the rds of the reduction process, [15]. Accordingly, the global electron transfer reaction would involve the following successive transfer of individual electrons, [15]:

$$n \quad steps \begin{cases} (rds)As(0) \overset{k_s}{\rightleftarrows} As(I) + 1e^- \\ n-1 \quad steps \begin{cases} As(I) \rightleftarrows As(II) + 1e^- \\ As(II) \rightleftarrows As(III) + 1e^- \end{cases} \end{cases} \tag{4}$$

In the case of $n = 3$ and assuming that the charge transfer coefficient of the rds (β) is 0.5, the apparent charge transfer coefficient (α) of Eq. (4) should to be close to 0.2, since it is obtained from the ratio $\alpha = \beta/(3 - \beta)$, [15].

Eqs. (3) and (4) can be expressed in a more general form as:

$$R_{(sol)} \overset{K_{ad}}{\rightleftarrows} R_{(ad)} \overset{k_s}{\underset{ne^-}{\rightleftarrows}} O_{(sol)} \tag{5}$$

$$O_{(sol)} \overset{k_{-1}}{\underset{k_1}{\rightleftarrows}} Y_{(sol)} \tag{6}$$

Which is an EC reaction mechanism complicated by the adsorption of the reduced reagent. Since metallic arsenic can form amalgam with gold, soluble and adsorbed species of metallic arsenic have been considered [28]. The ratio $k_1 k_{-1}^{-1} = K$, which is the equilibrium constant that relates the concentrations of As(OH)$_3$ and the former species of As(III) that is released to the solution. In the case of As(III), it is expected that $k_1 << k_{-1}$ since the prevalent species is expected to be arsenious acid in aqueous solutions of low pH. The application of the second Fick's law to each of these species gives the following differential equations [18,29]:

$$\partial c_r/\partial t = D(\partial^2 c_r/\partial x^2) \tag{7}$$

$$\partial c_y/\partial t = D(\partial^2 c_y/\partial x^2) - k_1 [c_y - c_o K^{-1}] \tag{8}$$

$$\partial c_o/\partial t = D(\partial^2 c_o/\partial x^2) + k_1 [c_y - c_o K^{-1}] \tag{9}$$

where a common diffusion coefficient value, $D = 9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, was assumed. The following boundary conditions are considered:

$$t = 0, \ x \geq 0 : \quad c_r^{ini} K_{ad} = \Gamma_r^{ini}; \quad \Gamma_r^{ini} = t_{ac} k_s \exp[(1-\alpha)\varphi_{ac}]c_y^* \tag{10}$$