



# Study of selenium electrodeposition at gold electrode by voltammetric and rotating disc electrode techniques



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## ABSTRACT

The electrodeposition process of selenium has been studied by voltammetry (CV) in connection with a rotating disc electrode (RDE) technique. The paper discusses the mechanism and the rate-determining step of Se deposition. It has been determined that the rate of the Se monolayer-forming process observed at ca. 0.6 V vs. NHE is diffusion controlled, not surface activation barrier-dependent. It is proposed that this process is an overpotential deposition process (OPD) and not an underpotential deposition process (UPD). The diffusion coefficient for the reacting species was determined as  $2.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . The reacting species are proposed to be identified with  $\text{HSeO}_3^-$  ions. The transfer coefficient,  $\alpha$ , for this process was calculated as 0.3, exchange current density,  $j_0$ , as  $1.1 \times 10^{-6} \text{ A cm}^{-2}$ , and the rate constant,  $k$ , as  $9.1 \times 10^{-7} \text{ cm s}^{-1}$ , respectively.

Analysis of RDE data recorded for the Se bulk deposition process taking place at ca.  $-0.1 \text{ V}$  vs. NHE and fitting them with either the Levich or the Koutecký–Levich equation indicates that this process is a diffusion-dependent one. The calculated diffusion coefficient was determined as  $1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . These data, together with experimental condition (pH) allow one to propose  $\text{H}_2\text{SeO}_3$  molecules as those being reduced during the formation of the Se bulk deposited layer. The transfer coefficient,  $\alpha$ , for this process was calculated as 0.1, exchange-current density,  $j_0$ , as  $7.7 \times 10^{-6} \text{ A cm}^{-2}$ , and the rate constant,  $k$ , as  $1.6 \times 10^{-4} \text{ cm s}^{-1}$ , respectively. The comparison of kinetic parameters for six-electron and four-electron processes proves that the reaction responsible for building up the Se film is six-electron reaction.

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## 1. Introduction

Selenium is an element present in almost all environmental and biological materials. Nowadays, interest in selenium has increased considerably due to its inherent presence in modern electronic and optoelectronic devices, photovoltaics alloys, the possibility of its application in assembling of new-generation sensors, its detected presence in selenoproteins, and its possible application in a construction of an artificial eye [1–4]. Demand for production of such high quality selenium has increased a big interest in a possible electrochemical way of the production of this element. Electrochemical methods of electrodeposition are relatively inexpensive and simple to realize. Among a variety of techniques, the electrochemical ones are the only techniques which can be used for deposition of films on large and irregular surfaces. An electrodeposition offers strict control of an oxidation state of the

deposit, because the deposition occurs to be closer to an equilibrium state, and because the process is electrical in nature, it might be precisely controlled under electrochemical conditions.

Attempts to examine electrodeposition of selenium started in 1829 with Magnus [5] and ever since have been continued by others [5–14]. Several reviews have been published on the electrochemistry of selenium and its properties [15–17]. Since the nineties of the last century, the number of articles on selenium electrodeposition has been growing. The availability of new microscopic and spectroscopic techniques applied to electrochemical studies permits deeper insight into the process of selenium electrodeposition. However, the electrochemistry of selenium is still unclear because of the complexity of selenium electrochemistry, which is due to several interrelating factors, such as electrode surface passivation, deposition of Se in several allotropic forms, and different electroactivity towards different substrates. At a glassy carbon electrode a poorly defined voltammetry is observed [18] whereas well defined current waves are observed at gold [19]. For gold electrodes, underpotential deposition (UPD) [6] and formation of intermetallic compounds were proposed [20]. Deposited Se layers often exhibit a lack of electroactivity [21]

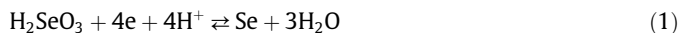
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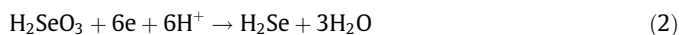
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Furthermore, bulk deposition of selenium is often accompanied by gas evolution of hydrogen and selenium hydride [11,22] These factors make the study and interpretation of results complicated.

Considerable work has already been done on the kinetics and mechanism of the reduction of tetravalent selenium. In early studies, a Se deposition on noble metals was proposed as follows [13]:



which is a net four-electron process involving two superimposed reactions. The first one is a six-electron reduction of Se(IV) to Se(-II):



Then, generated hydrogen selenide reacts with selenous ions in a comproportionation reaction:



However, the real mechanism of Se electrochemical deposition is much more complicated due to its several oxidation states. Depending on the experimental conditions, several reduction peaks (from two to five) on current–potential (CV) curves have been observed [12,22–25] These peaks have been attributed to UPD, the formation of inter-metallic compounds, the reduction of  $\text{HSeO}_3^-$  and  $\text{SeO}_3^{2-}$  ions, bulk Se electrodeposition, and gas-evolution processes. Such a situation, simultaneous occurrence of three reactions [1,2,5] leading to deposition and simultaneous gas evolution, makes for an exceptionally complicated determination of kinetics parameters and of the mechanism of the deposition process, as well as determination of the best conditions for the deposition of selenium. An additional difficulty is the wide scatter of experimental data, which is often observed.

Definition of the rate-determining step is the key to the description of bulk selenium deposition. There are two different views regarding this process. One of them is prompting a concerted six-electron process, [13,26,27] and the other one is encouraging a multistep reaction involving a surface process [12,28]. Phenomenologically, the occurrence of concerted six-electron process is unlikely because the time scale of the electron-transfer event is much shorter, ca.  $10^{-16}$  s, than that of the fastest chemical reorganization (associated with metal-ion ligand vibrational frequency), ca.  $10^{-14}$  s, so the probability of simultaneous six-electron transfer in a single step is low. However, in the case of low reorganization energy involved in the electron exchange between the electrode and a species in the solution, the process may sometimes appear as a “simultaneous-consecutive overall  $n$ -electron process”. This is because the reactant, the intermediate and the product, respectively, are chemically more alike than the reactant and product are [29].

An application of cyclic voltammetry (CV), in connection with the rotating disc electrode (RDE) technique, might give some information on the mechanism of the discussed processes and might lead to distinguishing either the reagent transport or the activation energy, which determines the process of interest. One could expect that a concerted six-electron process would be a diffusion-dependent one, i.e. it should obey pure Levich dependence, whereas in the multiprocess case, it should follow the Levich–Koutecký expression [30,31] because of surface processes. In this paper we report on the application of CV and RDE techniques to distinguish among surface processes determined by the energy of activation from the transport-limited processes determined by diffusion. To attain the presumed intention, RDE studies were done for a wide potential scan rate, which ranged from 5 to  $100 \text{ mV s}^{-1}$ , and for a wide range of rotation speed from 120 to 1600 rpm.

## 2. Materials and methods

### 2.1. Solutions

All solutions were prepared from Millipore-Q water. A supporting electrolyte solution, 0.1 M  $\text{HClO}_4$ , was prepared from concentrated reagent-grade perchloric acid. The  $\text{SeO}_2$  was obtained from Aldrich. The  $\text{SeO}_2$  concentration in the bulk of solution was  $1 \times 10^{-4}$  M. As a test of the experimental procedure the cadmium ion diffusion coefficient was measured. For those experiments, solutions contained 0.1 M  $\text{H}_2\text{SO}_4$  and  $1 \times 10^{-3}$  M  $\text{CdSO}_4 \cdot \text{CdSO}_4$  was obtained from Aldrich.

### 2.2. Electrodes

A gold rotating disc electrode of 5 mm diameter was used as a working electrode in these experiments. This electrode was polished with diamond powder down to  $0.05 \mu\text{m}$  and was cleaned in an ultrasonic bath to get rid of all polishing residues. The average surface area differed between electrodes by ca.  $\pm 5\%$  which was determined by the charge due to desorption of the adsorbed oxygen.

After each experiment the electrode was washed with 1:2 (v/v)  $\text{H}_2\text{O}_2$ : $\text{H}_2\text{SO}_4$  for selenium dissolution and then was rinsed with acetone and Millipore-Q water between experiments.

Counter electrodes were made of Pt/Pt gauze and electrode potentials were measured against either saturated calomel electrode (SCE), or Ag/AgCl electrode. All reported potentials are recalculated to a normal hydrogen (NHE) scale.

All experiments were carried out at  $22 \pm 2 \text{ }^\circ\text{C}$ .

### 2.3. Equipment

A three-electrode cell was used in all experiments. The current–voltage behavior was monitored with a programmed potentiostat (Metrohm Autolab PGSTAT128N), modulated step rotator (Pine) with an attached rotating disc electrode (RDE) was used. The Se deposition currents were measured for a sweep rate ranging from 2 to  $100 \text{ mV s}^{-1}$  and for electrode rotation speeds in the range from 120 to 1600 rpm.

### 2.4. Determination of reaction mechanism

To define the process which determines reaction rate, current data were fitted either with equation based on Randles–Ševčík equation but transferred to non equilibrium conditions, with Levich, or with Koutecký–Levich expressions [30–32].

Assuming the irreversibility of the studied process, the following equation might be used for the calculation of diffusion coefficients,

$$j_p = 2.99 \times 10^5 \times n^{3/2} \times \alpha^{1/2} \times D^{1/2} \times c \times V^{1/2} \quad (4)$$

where  $j_p$  is the peak current density,  $n$  is the number of exchanged electrons per molecule,  $D$  is the diffusion coefficient,  $c$  is the reagent concentration, and  $V$  is the potential sweep rate. The factor 2.99 comes from the inclusion of the physical constants and a temperature magnitude, and  $\alpha$  is the transfer coefficient.

RDE current density determined by mass transport is described by the Levich model and is given by the equation,

$$j_{\text{lim}} = 0.62 nFD^{2/3} \omega^{1/2} \nu^{-1/6} \quad (5)$$

where  $j$  is the measured limiting current density,  $F$  is the Faraday constant,  $\omega$  is the electrode angular rotation rate of an electrode, and  $\nu$  is a solution kinematic viscosity taken as  $1 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  [33].

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