

R. KOWALIK*

THE VOLTAMMETRIC ANALYSIS OF SELENIUM ELECTRODEPOSITION FROM H_2SeO_3 SOLUTION ON GOLD ELECTRODE**ANALIZA WOLTAMPEROMETRYCZNA PROCESU ELEKTROCHEMICZNEGO OSADZANIA SELENU NA ELEKTRODZIE ŻŁOTEJ**

The different voltammetry techniques were applied to understand the process of selenium deposition from sulfate solution on gold polycrystalline electrode. By applying the cycling voltammetry with different scan limits as well as the chronoamperometry combined with the cathodic and anodic linear stripping voltammetry, the different stages of the deposition of selenium were revealed. It was found that the process of reduction of selenous acid on gold surface exhibits a multistage character. The cyclic voltammetry results showed four cathodic peaks which are related to the surface limited phenomena and which coincide with the bulk deposition process. The fifth cathodic peak is related to the reduction of bulk deposited Se^0 to Se^{-2} ions. Furthermore, the connection of anodic peaks with cathodic ones confirmed the surface limited process of selenium deposition, bulk deposition and reduction to Se^{-2} . Additionally, the cathodic linear stripping voltammetry confirms the process of H_2SeO_3 adsorption on gold surface. The experiments confirmed that classical voltammetry technique proved to be a very powerful tool for analyzing the electrochemical processes related with interfacial phenomena and electrodeposition.

Keywords: Selenium, selenous acid, electrodeposition, adsorption, cyclic voltammetry, gold

Zastosowano różne techniki woltamperometryczne w celu pełnego zrozumienia procesu osadzania selenu metodą elektrochemiczną na elektrodzie złotej. Wykorzystano w tym celu cykliczną woltamperometrię, a także chronoamperometrię połączoną z katodową i anodową woltamperometrią inwersyjną. Wykazano, że proces osadzania selenu jest bardzo złożony i zachodzi w kilku etapach. Wyróżniono etap podpotencjałowego osadzania selenu, następnie zachodzi redukcja zaadsorbowanych cząsteczek kwasu selenowego(IV), po którym następuje nadpotencjałowe osadzanie selenu. W zakresie wysokich nadpotencjałów dochodzi do redukcji Se^0 do jonów Se^{2-} . Powyższe eksperymenty potwierdziły wysoką przydatność technik woltamperometrycznych jako metody badawczej w celu analizy mechanizmu osadzania powłok metodą elektrochemiczną.

1. Introduction

The importance of selenium and its wide range of applications were described in many papers [1-3]. The main industrial application of Se are related to its semiconducting properties and its application in materials engineering. It plays also significant role in biology, pharmacy and medicine. Therefore, a lot of attention has been focused on its physical and chemical properties. Among others, the electrochemistry of selenium is being thoroughly investigated and the papers concerned with this topic increasingly appeared in the literature [4] (and references therein). This is a consequence of the fact that the electrochemistry gives many possibilities of producing selenium [5], recover it from wastes [6], analyze its concentration in solutions [7] and carrying out synthesis of various materials containing this element e. g. semiconductors, nanoparticles and quantum dots based on polychalcogenides [2, 8-17]. Potential uses of such materials are highly desirable in technological applications related with optoelectronics, ad-

vanced thin film solar cells, IR detectors, solid state lasers, multipurpose sensors or thermoelectric materials [1, 3, 4].

It was found that the process of electrochemical deposition of selenium plays a key role in the synthesis of semiconductor thin films or nanostructures of selenium [2, 9-11, 13, 15, 17, 18]. Selenium induces the process of compounds synthesis and enables the co-deposition of metals at potentials more positive than their equilibrium potentials. Furthermore, the analysis of the surface-limited process of selenium electrodeposition has been extensively studied due to its possible application in Electrochemical Atomic Layer Deposition method [8]. There is a hope that the understanding of the mechanism of selenium electrodeposition and accompanying interfacial phenomena will enable to control the synthesis of semiconductor compounds at atomic level.

Many techniques were involved to analyze the process of Se deposition from aqueous solutions. Among others, the voltammetry as a classical method is most often applied for such a purpose. The very good reports by Andrews et al. [19], Stickney et al. [20-24], Alanyalioglu et al. [25] Machado et al.

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, DEPARTMENT OF PHYSICAL CHEMISTRY AND METALLURGY OF NON-FERROUS METALS, FACULTY OF NON-FERROUS METALS, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND

[26, 27] and Kowalik [28] provided extensive analysis of selenium electrodeposition on gold. Nonetheless, some aspects of the voltammetry results are still not clear. Consequently, the goal of this work is to analyze in details the process of reduction of H_2SeO_3 on gold electrode from sulfate solution, and to interpret properly the voltammetric results, in particular the origin of the cathodic and anodic peaks.

2. Experimental

All the electrochemical measurements were performed using a flow cell combined with solutions bottles, a distribution multivalve and potentiostat. The whole system was operated by the computer. An Autolab PGSTAT30 potentiostat equipped with EQCM UELKO M106 was used for the voltammetry measurements combined with microgravimetric study. The experiments were carried out in the closed Teflon® cell with three electrodes. The working electrode were slide glass covered of 300 nm thick gold film with the area of 0.38 cm^2 deposited by magnetron sputtering described in our previous paper [29]. A platinum spring was used as a counter electrode and an Ag/AgCl leakless electrode as a reference electrode. All the potentials below are given with respect to this electrode. The chemicals used in this work were of analytical grade. The pH of solutions was adjusted to 2.0 by sulfuric acid addition. The solution was deoxidized with argon, which was bubbled into the solution before measurements. All the experiments were conducted in room temperature. Before the experiments the electrodes were cleaned in the 0.1 M H_2SO_4 solutions by sweeping the potential in the range 1.4 to -0.4 V.

3. Results and discussion

Cyclic voltammetry

The electrochemical behavior of the gold electrode in selenous acid was analyzed by cyclic voltammetry (Figure 1). The onset potential of the voltammetric experiment was set at 0.5 V vs. Ag/AgCl electrode and was swept in the negative direction first, then reversed at -0.6 V. Subsequently, the potential was changed to the second reverse potential 1.1 V and the whole scan was finished at the initial potential 0.5 V. During the sweeping in the negative direction five reduction peaks A, B, C, D and E are observed. The nature of these peaks was analyzed in acidic environment by several groups and is described in the subsequent papers [19, 20, 22-28]. It should be noted that common feature for all these reports is gold substrate, but of different quality (single crystal or polycrystalline) and pretreatment procedures. Additionally, different scan rates were applied during voltammetric experiments by various authors. Consequently, small shifting and overlapping of peaks are noticeable as compared with those presented in Figure 1.

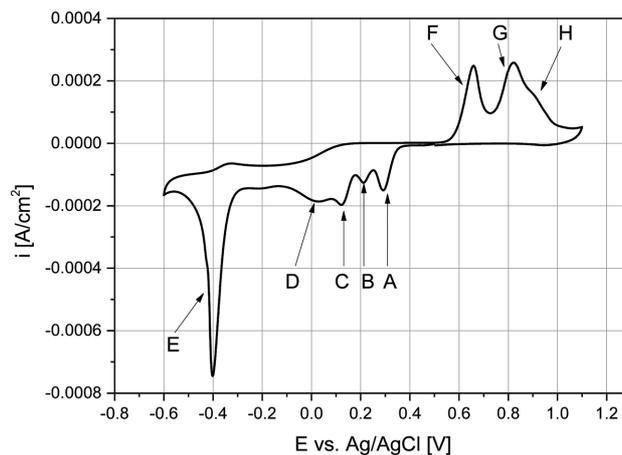


Fig. 1. Cyclic voltammogram on gold electrode in 0.001 M H_2SeO_3 , 0.1 M Na_2SO_4 pH=2, scan rate 50 mV/s

As a result of these studies, various interpretations of the voltammetry results were proposed. Stickney et al. [20, 22, 23] suggested that peaks A and B are related with surface limited deposition process and they are similar to the underpotential deposition process, in spite of the fact that the overpotential is applied. Peaks C and D are very confusing and also behave as effects of surface limited process, but more than one monolayer is deposited on the surface according to these authors. As the deposition of Se is continued at more negative potentials, the results indicate the real bulk deposition of Se.

Alanyalioglu et al. [25] assigned the first two peaks to a reduction of adsorbed selenate to selenite, and following third peak as a reduction of adsorbed selenite to selenium. The fourth peak is assigned as a bulk deposition of selenium and the fifth as a reduction of Se^0 to Se^{2-} ions.

Machado et al. [26, 27] analyzed the process of selenous acid behavior by voltammetry under similar conditions. The most important feature noticed by Machado et al. is the adsorption of H_2SeO_3 on the gold substrate. They suggest that peaks A and B, which overlapped in their experiment, are related to the reduction of adsorbed selenous acid on gold electrode, and are interpreted as underpotential deposition of selenium. Then, peaks C and D, which overlapped in their case too, are identified as the bulk deposition of Se. Finally, the peak E corresponds to the formation of H_2Se .

The three peaks are noticed when the scan is reversed to the positive direction, and according to the literature [20, 22-27] they are related with selenium oxidation. The peak F is related with the dissolution of bulk selenium and G with underpotentially deposited selenium. Then the peak H is explained as the oxidation of selenium which diffused into the gold electrode [19].

Variation of the scan limit

To better analyze the selenous acid behavior the different scan limits were applied during the voltammetric experiments (Figure 2a-d). Application of different first vertex potentials unveils the relation between cathodic and anodic peaks and enable us the analysis of electrode reactions taking place during Au electrode polarization. The onset potential of the voltammetric experiments was set at 0.5 V vs. Ag/AgCl electrode and it was swept in the negative direction first. The first ver-

text potential was applied and it was changed from 0,4 to -0,6 V. Subsequently, the potential was swept to the second vertex potential 1.2 V and finished at the initial potential 0.5 V. The first cathodic peak A appeared at potential 0.3 V and it is connected with anodic peak G at potential 0.8 V. The switching of the first vertex potential in more negative direction causes the increase of the anodic peak and it enables to distinguish the small cathodic peak B at potential 0.2 V. The next anodic peak F appeared when the potential 0.1 V is passed and the peak C starts to appear. Moreover, the small anodic peak H appeared at potential 1.0 V. By extending the voltammetric scan up to -0.3 V causes the increase of the peak F. When the first vertex potential crossed -0.4 V the high cathodic peak E appeared and a decrease of the peak F is observed, while the peaks G and H remained unchanged.

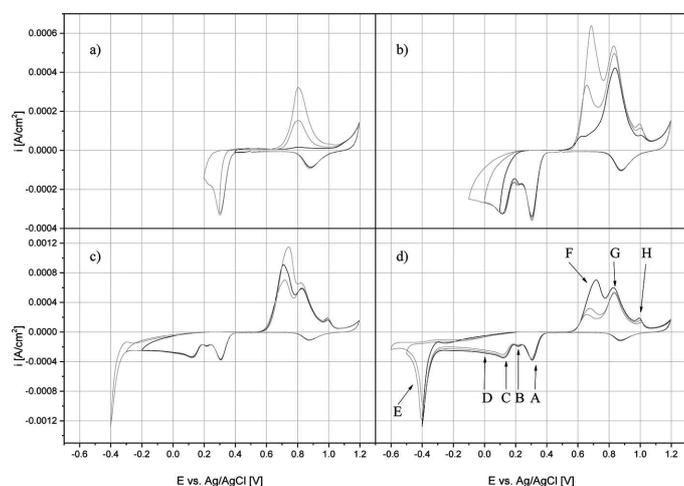


Fig. 2. Cyclic voltammograms on gold electrode in 0.001 M H₂SeO₃, 0.1 Na₂SO₄, pH=2, scan rate 50 mV/s in different ranges of potentials

The next voltammetry experiment consisted in switching the second vertex potential. The collection of cyclic voltammograms obtained on gold electrode in 0.001 M H₂SeO₃ solution

is presented in Figure 3e-f. The procedure was repeated three times in every case. It started at potential 0.5 V vs. Ag/AgCl and was changing in the negative direction first. Then it was reversed at -0.6 V. Subsequently, the potential was swept to the second reverse potential and stopped at the initial potential 0.5 V. The different second reverse potentials were applied and ranged from 0.6 to 1.1 V. When the second vertex potential was set at 0.6 V (Figure 3a), all peaks appeared during the sweeping from the initial potential to the -0.6 V during the first cycle. When the cycle was repeated second and then third time, the reduction peaks A, B, C and D did not appear. The shape of the last two cycles were the same. This fact indicates that the disappearing reduction peaks A, B, C and D are connected with the surface phenomena. When the scan was repeated second and third time, the cathodic current started to flow below potential 0.2 V. The current density was much smaller as compared to the current density registered during first cycle and it indicates the bulk deposition of selenium. It suggests that the beginning of the bulk deposition process coincides with the peaks C and D. The switching of the second vertex potential at 0.7 V revealed the anodic peak F (Figure 3b). Concurrently in the range of potentials from 0.2 to -0.2 V the cathodic current is higher in the second and third cycle, as compared with the related voltammograms in the Figure 3a. The appearing peaks C and D are distinguishable and it confirms their connection with peak F. The further change of the second vertex potential to the more positive direction reveals the anodic peak G and its relation with peaks A and B.

In turn the peak E appeared in every cycle, and only small decrease of its intensity was observed in subsequent cycles. According to the results depicted in Figure 2a-d, the peak E caused the diminishing of the peak F. It seems that peak E is an effect of the reduction of bulk deposited Se⁰ to Se⁻² according to the reaction:

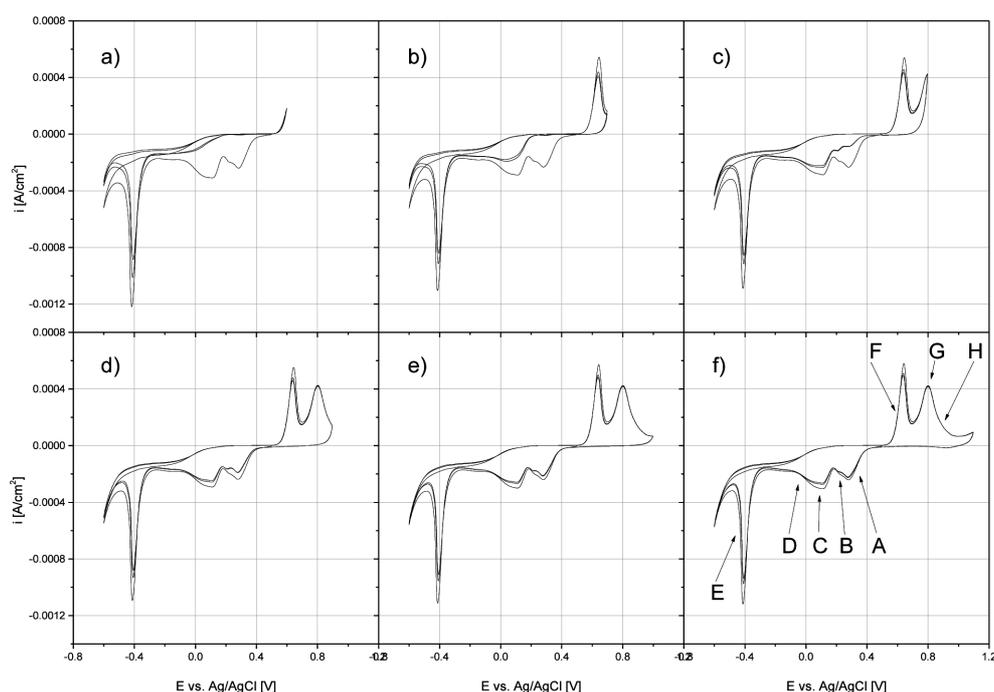


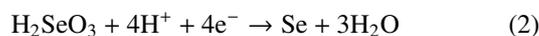
Fig. 3. Cyclic voltammograms on gold electrode in 0.001 M H₂SeO₃, 0.1 M Na₂SO₄ pH=2, scan rate 50 mV/s in different ranges of potentials

Anodic stripping linear voltammetry

The anodic stripping linear voltammetry experiments were carried out in the flow cell to avoid the possible oxidation of selenous acid, when the electrode is positively polarized. The voltammetric experiments were preceded by the process of selenium deposition at different potentials for 30, 60 and 120 s. Subsequently the electrolyte was exchanged for 0.1 M Na₂SO₄ with pH=2 and the stripping was carried out without the presence of H₂SeO₃. The shape of anodic peaks is presented in Figure 4a-d. The anodic peaks start to appear when the electrode is polarized at 0.4 V and correspond to the peak G in Figure 1. The series of linear anodic stripping voltammetry scans after deposition at different times is presented in Figure 5a-l and the total charge under the anodic peaks obtained after the deposition of selenium is shown in Figure 6. It is observed that when the time of polarization increased, the size of the peak slightly increased after deposition at potentials 0.4 and 0.3 V. Such a behavior indicates the surface limited process of deposition. When the potential 0.2 V was applied, the second anodic peak appeared and it corresponds to the peak F. The size of the peak F increased, but the size of the peak G remains unchanged. The effect of increasing of the peak F is observed when the electrode was polarized in the range of potentials from 0.2 to -0.1 V. According to the previous voltammetric results (Figure 3a-f) the process of selenium bulk deposition starts from potential 0.2V.

When the potentials -0.2 V and -0.3 V were applied, the shape of the anodic peaks were radically changed. It suggests the new form of deposited selenium. The shapes of the anodic peaks are very characteristic and appeared only when the potentials -0.2 and -0.3 V were applied. The shape of the linear voltammogram obtained after deposition at -0.2 V gives three peaks and after deposition at -0.3 V reveals even four peaks. The shape of the peaks changed when the time of deposition increased. The total charge under the group of anodic peaks

increased linearly when the potentials -0.2 and -0.3 V were applied and indicates the bulk deposition process. The convoluted shape of these peaks suggests the different structure of the deposited selenium. This effect can be explained by different mechanism of the deposition of selenium. Selenium can be deposited by the four electron process at more positive potentials:



However, some authors proposed different mechanism of selenium deposition connected with the direct six electron reduction of H₂SeO₃ to H₂Se (3), and followed by the process of synproportionation (4):

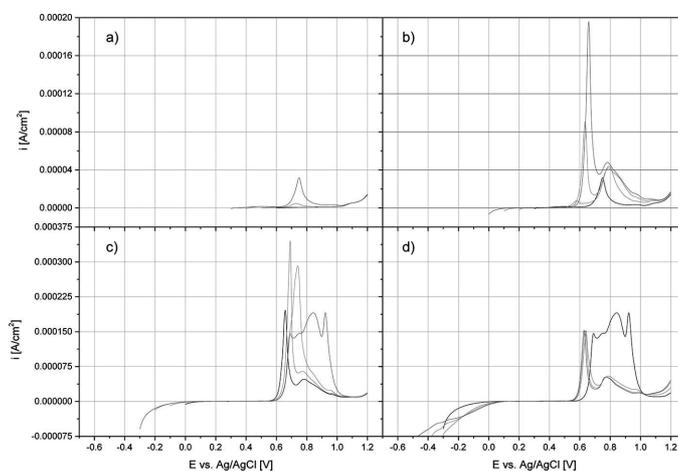
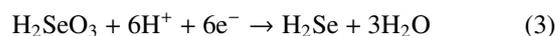
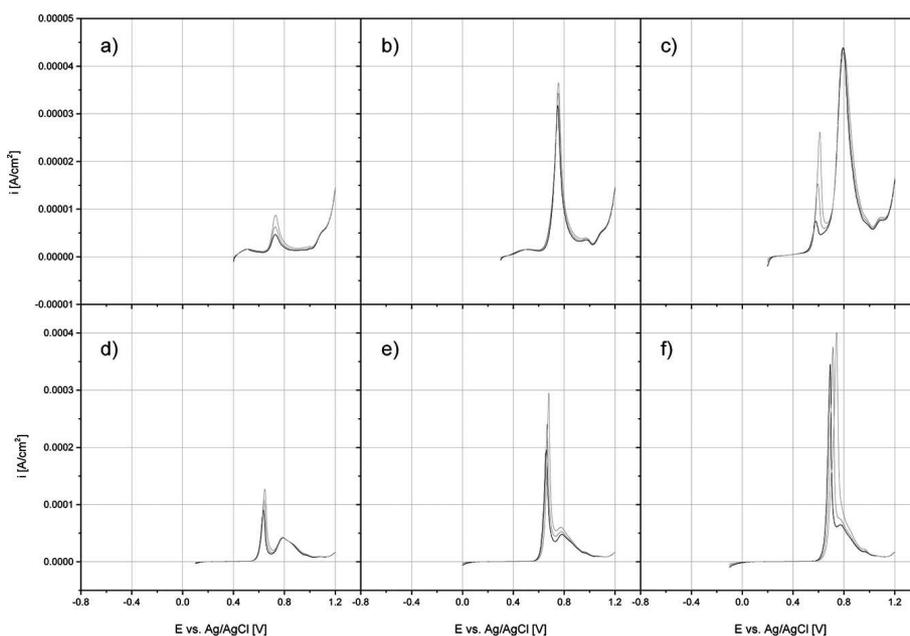


Fig. 4. Linear anodic stripping voltammetry scan in 0.1 M Na₂SO₄ pH=2 after 30 s of selenium deposition in 0.001 M H₂SeO₃ 0.1 M Na₂SO₄ pH=2, scan rate 10 mV/s



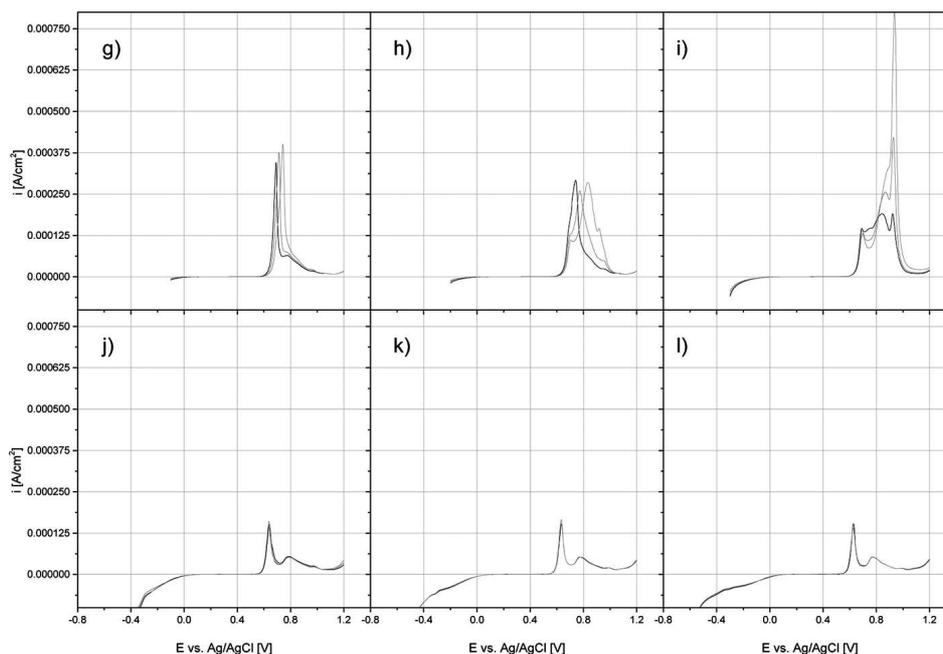


Fig. 5. The collection of linear anodic stripping voltammetry scans in 0.1 M Na_2SO_4 pH=2 after selenium deposition at different potentials for different times in 0.001 M H_2SeO_3 0.1 M Na_2SO_4 pH=2, scan rate 10 mV/s

According to the presented results it can be assumed that the reaction (3) is possible at the potential -0.2 V. As a result, two competing pathways of selenium deposition are open when the potential -0.2 V is crossed. The coexistence of different forms of deposited selenium, with diverse electrochemical properties, manifests itself by convoluted shape of anodic peaks overlapping each other.

When the potentials from -0.4 to -0.6 V were applied, the size of the peaks diminished in comparison with that obtained at -0.2 and -0.3 V. However, the shape of the anodic peaks is very similar and does not depend on the potential and time of deposition. This result indicates that the part of the deposit dissolved. It clearly confirms the reduction process of Se to Se^{2-} according to reaction (1).

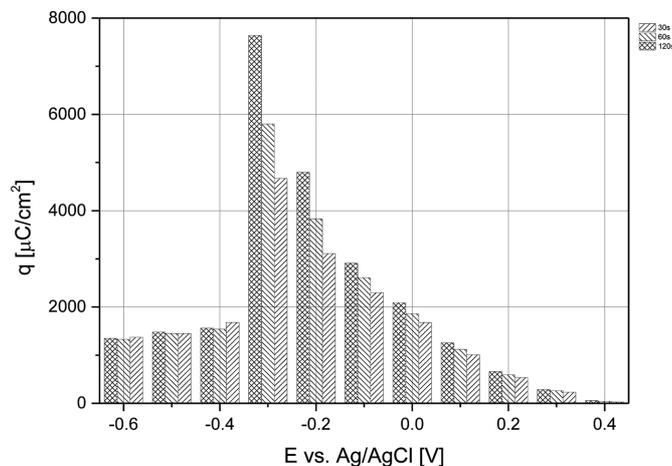


Fig. 6. The total charge under anodic peaks obtained during of linear anodic stripping voltammetry scans in 0.1 M Na_2SO_4 pH=2 after selenium deposition at different potentials for different times in 0.001 M H_2SeO_3 0.1 M Na_2SO_4 pH=2

Cathodic stripping linear voltammetry

The cathodic stripping linear voltammetry experiments were precluded by the process of selenium deposition. The deposition was carried out at different potentials from 0.4 to -0.3 V for 30, 60, 120 and 240 s. Subsequently, the electrolyte was exchanged for 0.1 M Na_2SO_4 , pH=2 and the stripping was carried out without the presence of H_2SeO_3 . At first, the cathodic linear stripping voltammetry was carried out starting from the potential of deposition to -0.6 V. Next, the electrolyte was changed again for the fresh 0.1 M Na_2SO_4 , pH=2 and the anodic linear stripping voltammetry were carried out from the potential -0.6 to 1.2 V. An example of cathodic scans is shown in Figure 7. Values of the charge under the peak E obtained after the experiments are compared in Figure 8.

The common features of the voltammograms obtained after the electrode was polarized at potential from 0.8 to 0.4 V were observed. The peaks A, C, D and E appeared at the cathodic linear stripping voltammetry curves (Figure 7). It seems that due to lower scan rate the peak B did not appeared. It has to be mentioned that according to the cyclic voltammetry and anodic linear stripping voltammetry the deposition of selenium starts at 0.4 V (see Figure 3a-f and Figure 4a-d). The peaks C, D and E increased with increasing time of deposition. Moreover, peak A does not depend on the time of deposition. It unambiguously indicates that the mentioned cathodic peaks are related with the reduction of adsorbed H_2SeO_3 species, and does not depend on the applied potential.

The additional experiments were carried out to confirm the process of adsorption of H_2SeO_3 species on gold surface. The stripping voltammetry experiments were carried out after keeping the electrode at open circuit potential (OCP) for different times in the selenous acid solution. The voltammetry results are identical with those obtained after polarization of the electrode at potentials 0.8 to 0.5 V. The peaks A, C, D and E appeared on the voltammograms. It confirms the process of

adsorption of H_2SeO_3 on the gold surface. In turn the presence of peak E indicates that some part of the deposited selenium undergoes further reduction according to reaction (1).

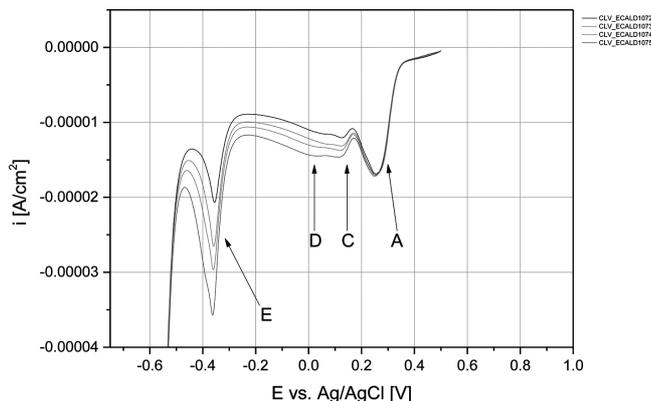


Fig. 7. Linear cathodic stripping voltammetry scan in 0.1 M Na_2SO_4 pH=2 after selenium deposition at -0.5 V in 0.001 H_2SeO_3 , 0.1 M Na_2SO_4 pH=2, scan rate 10 mV/s

The detailed analysis of the linear cathodic stripping voltammetric curves allows to explain this effect. The molecules of selenous acid adsorb on gold surface, but the amount of adsorbed species exceeds the required amount for the deposition of the first sub-monolayer of selenium. It is worth noting that when the time of the polarization of the electrode increased, the height of the peak A did not increase on the linear cathodic stripping voltammograms (Figure 7). It means that the peak A is related to the surface limited process of selenium deposition. Moreover, peaks C and D increased with time of deposition, and this indicates that they are related to the excess of adsorbed selenous acid molecules. The peak A is related to the reduction of the H_2SeO_3 molecules and the deposition of the first sub-monolayer of selenium on the gold surface. Next, the still existing molecules of selenous acid undergo the reduction and bulk selenium is formed on the gold electrode. Consequently, peaks C and D appeared on the curves. Finally, the peak E appeared as a result of bulk selenium reduction to Se^{2-} . Additionally, these features appeared at the voltammetry results when the electrode was kept at open circuit potential for different times.

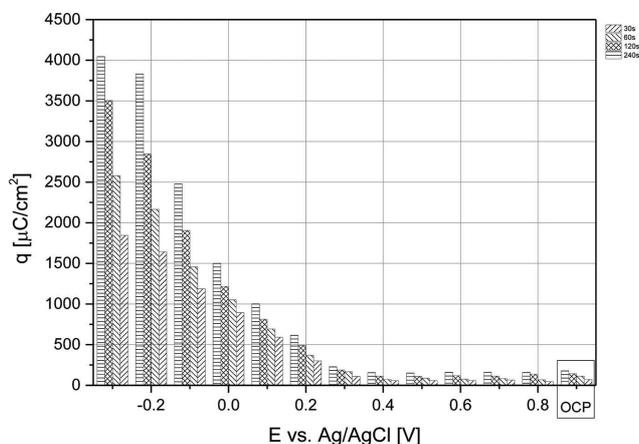


Fig. 8. The total charge under cathodic peak E obtained during of linear cathodic stripping voltammetry scans in 0.1 M Na_2SO_4 pH=2 after selenium deposition at different potentials for different times in 0.001 H_2SeO_3 , 0.1 M Na_2SO_4 pH=2

The increasing size of the peak E is evident when more negative potentials than 0.3 V were applied, in particular at potentials -0.2 and -0.3 V. It is in very good agreement with all previous results and confirmed beginning of the bulk deposition of selenium starting from the potential 0.2 V.

The following linear anodic stripping voltammetry experiments indicate that during cathodic stripping voltammetry all the bulk deposited selenium was dissolved. The peak G is evident after the deposition at potentials from 0.8 to -0.2 V, and also after keeping the electrode at open circuit potential (OCP). The charge under the anodic peak did not depend on the applied potential and time of deposition (Figure 9).

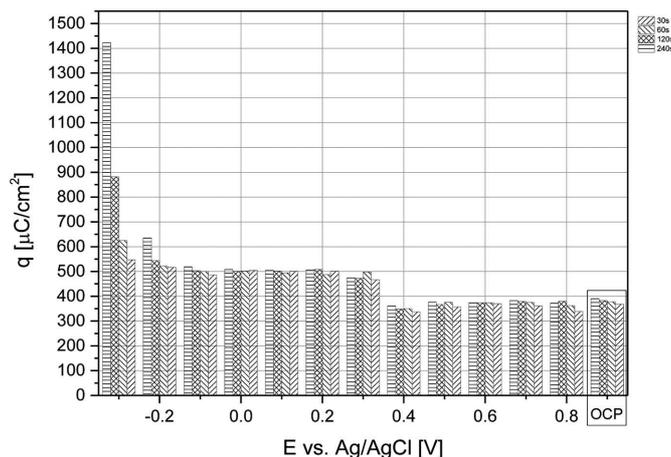


Fig. 9. The total charge under anodic peaks obtained during of linear anodic stripping voltammetry scans in 0.1 M Na_2SO_4 pH=2 after selenium deposition at different potentials for different times in 0.001 H_2SeO_3 , 0.1 M Na_2SO_4 pH=2

The linear cathodic stripping voltammetry was not sufficient to dissolve the whole bulk deposited selenium when the deposition was carried out for the time longer than 30 s at potential -0.3 V. More than one anodic peak appeared on the voltammograms, similarly to the results obtained after deposition at -0.3 V (Figure 4a-d). Thereby the total charge under the anodic peaks increased with time.

4. Conclusions

The process of the H_2SeO_3 reduction on the polycrystalline gold electrode from sulfate solution was thoroughly investigated. The process of the reduction is proceeded by adsorption of H_2SeO_3 species on gold surface. The voltammetric results unambiguously demonstrate that the first four cathodic peaks A, B, C and D (Figure 1) are related to the surface-limited phenomena. The first two peaks are related to the reduction of adsorbed H_2SeO_3 and deposition of first sub-monolayer of selenium. The amount of the adsorbed species exceed the amount required for the obtaining of first sub-monolayer of Se on gold surface. Therefore, the third and fourth peaks are results of the reduction of remaining adsorbed H_2SeO_3 which gives the bulk selenium. This process overlaps with the direct reduction of H_2SeO_3 from the solution and bulk deposition of Se. The stripping voltammetry methods confirmed the process of surface limited deposition of selenium above potential 0.2 V. The bulk deposition starts at 0.2 V

and is clearly detected by stripping voltammetry. The reduction of the Se^0 to Se^{2-} starts below -0.3 V. Moreover the oxidation of the deposited selenium manifests itself by few overlapping anodic peaks. They are due to the coexistence various forms of selenium deposited according to different mechanisms and additionally due to the interaction with the gold substrate. All Se forms are characterized by different electrochemical properties and therefore the convoluted shape of the anodic peaks appeared during voltammetric measurements.

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