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MICROGRAVIMETRIC STUDIES OF SELENIUM ELECTRODEPOSITION ONTO DIFFERENT SUBSTRATES

MIKROGRAWIMETRYCZNA ANALIZA PROCESU ELEKTROCHEMICZNEGO PROCESU OSADZANIA SELENU NA RÓŻNYCH PODŁOŻACH

The mechanism of selenium electrodeposition from sulfuric acid solution on different substrates was studied with the electrochemical techniques. The cyclic voltammetry was combined with the quartz crystal microbalance technique to analyze selenium deposition process. The electrochemical reduction of selenous acid on gold, silver and copper electrodes was investigated. It was found that reduction of selenous acid is a very complex process and it strongly depends from the applied substrate. The voltammetric measurements indicate the range of potentials in which the process of reduction of selenous acids on the applied substrate is possible. Additionally, the microgravimetric data confirm the deposition of selenium and they reveal the mechanism of the deposition process.

Keywords: selenium, electrochemistry, electrodeposition, cyclic voltammetry, electrochemical quartz crystal microbalance

Przedstawione w niniejszej pracy wyniki badań opisują mechanizm elektrochemicznego osadzania selenu z roztworów siarczanowych na różnych podłożach. W celu dokładnej analizy zachodzących procesów elektrodowych w badaniach zastosowano technikę cyklicznej woltamperometrii połączoną z elektrochemiczną mikrowagą kwarcową. W pracy porównano procesy redukcji kwasu selenowego(IV) na elektrodach złotej, srebrnej i miedzianej. Dzięki zastosowanym technikom badawczym jednoznacznie określono zakres osadzania się selenu na wybranych podłożach oraz wskazano możliwy mechanizm przebiegających reakcji elektrodowych.

1. Introduction

Recently, the electrochemistry of selenium is under very deep investigation and the papers related with this topic increasingly appeared in the literature [1-4]. This is a consequence of the fact that selenium is widely used in the many branches of the industry from pharmacy to electronics [2,4-7]. Furthermore, the electrochemistry itself gives many possibilities of producing selenium [8], to recover it from wastes [9], to analyze its concentration in solutions [10,11] and to carry out synthesis of various materials containing this element. The electrochemical properties of the H_2SeO_3 – Se system are essential for understanding of the process of the electrodeposition of thin films or nanostructures of selenium [12-14]. They also play a key role in the synthesis of compound semiconductors like ZnSe or $CuInSe_2$ [3]. The selenium induce the process of synthesis of II-IV compounds and enables the co-deposition of metals at potentials more positive than its equilibrium potential [15]. It is also effectively applied as a seed layer for semiconductors deposition [16].

Electrochemical method is commonly used in the industry for the metal and alloys deposition [17-21], but it is not so popular for the deposition of semiconductor thin films [22-24].

Mostly, this is the effect of the very complicated mechanism of a deposition process of these materials. In case of selenium and its compounds, the complex nature of the deposition is related with many oxidation states (+6, + 4, -2) and its very high reactivity. Due to the latter, there is a serious problem of the interaction of selenium with the substrate during the process of deposition [25-27]. Some authors however use this feature for the synthesis of semiconductors by ECALE method [28-34]. Expect for mentioned reactivity with the substrate it is worth to mention its corrosion properties or overpotential of hydrogen evolution from aqueous solutions. The former one limits the potential window for electrochemical operation due to the process of the substrate dissolution, the latter one can promote H_2Se evolution and disturbs the process of either selenium or its compounds deposition [35].

The electrodeposition of selenium was examined mostly on gold [25,36-41,13], platinum [42] and glassy carbon electrodes [43]. They are commonly used due to their wide electrochemical window and a very weak reactivity. Recently, other metals and semiconductors joined the group of materials applied in this process as a substrate. In case of either selenium or its compounds electrodeposition, metals like silver [25,32], copper [44,35], nickel [45-47], titanium [48,49,45-47,50] and

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stainless steel [51] were applied. Additionally, the semiconducting materials like ITO [50,52] and silicon [53-55] are also used, particularly for the semiconductors electrodeposition.

In this paper the processes of electrodeposition of selenium on gold, silver and copper from sulfuric acid solution were compared. The effect of the applied substrates on the process of deposition was analyzed by cyclic voltammetry combined with electrochemical quartz crystal microbalance.

2. Experimental details

Autolab PGSTAT30 potentiostat equipped with EQCM UELKO M106 was used for the cyclic voltammetry measurements combined with microgravimetric study. The experiments were carried out in the closed Teflon® cell with three electrodes. The working electrodes for EQCM measurements were 10 MHz AT-cut quartz crystals with evaporated and unpolished gold, silver and copper thin film (OMIG S.A.) with electrochemically active areas of 0.23 cm^2. A platinum spring was used as a counter electrode and an Ag/AgCl 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 sulphuric acid addition. The solution was deareated with argon, which was bubbled into the solution before measurements. Before the experiments the electrodes were cleaned in the 0.1 M H$_2$SO$_4$ solutions by sweeping the potential in the range 1.4 to -0.6 V for the Au, -0.1 to -1.0 V for Ag and -0.3 to -1.0 V for Cu electrode. All cyclic voltammograms and microgravimetry scans were recorded at a rate of 20 mV s^{-1} and they were scanned first to the negative direction first.

3. Results and discussion

The general mechanism of the electrochemical deposition of selenium from H$_2$SeO$_3$ solution was depicted by a number of authors [25,26,36,42,43,52,56-62]. The common group of reactions is proposed, which are possible during the polarization of the electrode. The process of reduction of selenous acid are possible by 4 and 6 electron reduction:

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \qquad (1)$$

$$H_2SeO_3 + 6H^+ + 6e^- \rightarrow H_2Se + 3H_2O \qquad (2)$$
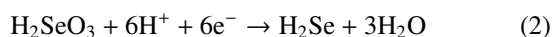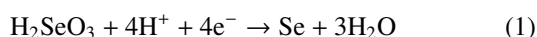
Moreover, the deposited selenium can be reduced to H$_2$Se according to the reaction:

$$Se + 2H^+ + 2e^- \rightarrow H_2Se \qquad (3)$$

Additionally, the presence of H$_2$Se enables the synproportionation reaction:

$$H_2SeO_3 + 2H_2Se \rightarrow 3Se + 3H_2O \qquad (4)$$

Different research methods are applied to analyse the electrodeposition processes. The very convenient approach is consists in connecting cyclic voltammetry with electrochemical quartz crystal microbalance [27,63-69]. The electrochemical

quartz microbalance will facilitate determination of potential ranges in which flow of charge is accompanied with the electrode mass change and it will confirm the character of electrode processes taking place (adsorption, underpotential deposition, overpotential deposition, etc).

The relation between the change of frequency (Δf) and the mass change is described by Sauerbrey's equation [70]:

$$\Delta f = -\frac{2f_0^2 \Delta m}{A \sqrt{\mu_i \rho_i}} = -K \Delta m \qquad (5)$$

where Δf is the quartz crystal frequency change, Hz; f_0 is the resonant frequency of the quartz crystal, Hz; Δm is the mass change, g; A is the piezoelectrically active crystal area, cm^2; μ_i is the shear modulus of quartz crystal, GPa; ρ_i is the density of quartz, g cm^{-3}.

3.1. Au electrode

The gold electrode is very convenient as a substrate for electrochemical experiments due to its "noble" properties. It permits to apply a wider range of potentials in comparison with silver and copper electrodes. The electrode potential is swept from 0.5 to -0.9 V, then to 1.0 and finally ends up at 0.5 V. The process of reduction of H$_2$SeO$_3$ starts at 0.35 V and concurrently the increase of the mass is observed (Fig. 1). The first two peaks A and B are related with the strong interaction between gold substrate and selenium. According to some authors this process is surface limited and suggests the underpotential deposition of selenium on gold, although the discussed peaks are below its equilibrium potential [13,37,38,62,61,71]. The presence of two peaks related to UPD phenomenon is either an effect of the phase transition or it corresponds to changes in packing density of the deposited element [62,72].

The third peak C appeared at potential 0.1 V with the following small shoulder D just after it. The increase of the mass of the electrode accompanies the observed peaks. The peak C is related to the surface limited process according to the reaction (1) [58,73,38], but the following shoulder suggests a new electrochemical reaction and the explanation of that part of the voltammogram is very complicated. The decreasing current after passing the maximum of the peak C with simultaneous decreasing of the rate of deposition of selenium are observed. Next, when the shoulder D appeared, further decrease of the rate of deposition is registered. Surprisingly, when the potential is swept to the more negative values and the cathodic current decreases, starting from the potential -0.2 V the rate of Se deposition increases again. It can be expected that another reaction is responsible for the acceleration of selenium deposition.

The next cathodic peak E appeared at the potential -0.4 V and it is associated with decreasing mass of the electrode, unambiguously indicating the reaction (3). The decreasing mass of the electrode is recorded only in the very short range of potentials. When the peak E reaches its maximum, the process of deposition starts again from the potential -0.45 V. The slope of the Δf-E curve in that range -0,45 to -0,6 V indicates a very high rate of the deposition. It can be suggested that two different mechanisms are responsible for the deposition of selenium, namely a combination of reactions (2) and (4), as well as (3) and (4). The process of deposition is slow at more

negative potentials due to the intensive reduction of hydrogen ions (6), which starts at -0,6 V.

$$2H^+ + 2e^- \rightarrow H_2 \uparrow \qquad (6)$$

When the scanning is reversed from the potential -0.8 V, the mass of the electrode is decreasing. Bearing in mind that the cathodic current is recorded in that range of potentials, it can be assumed that deposited selenium is dissolving according to reaction (3). The two anodic peaks which appeared above the potential 0.5 V and detected decrease of the mass indicate the reaction of selenium oxidation. The occurrence of more than one anodic peak related to the oxidation of selenium is an effect of many different forms of the deposit resulting from the interacting with the substrate [59]. According to the registered frequency of the resonator, the whole deposit is dissolved, and below the potential 0.8 V the oxidation of gold electrode can be observed [61,62].
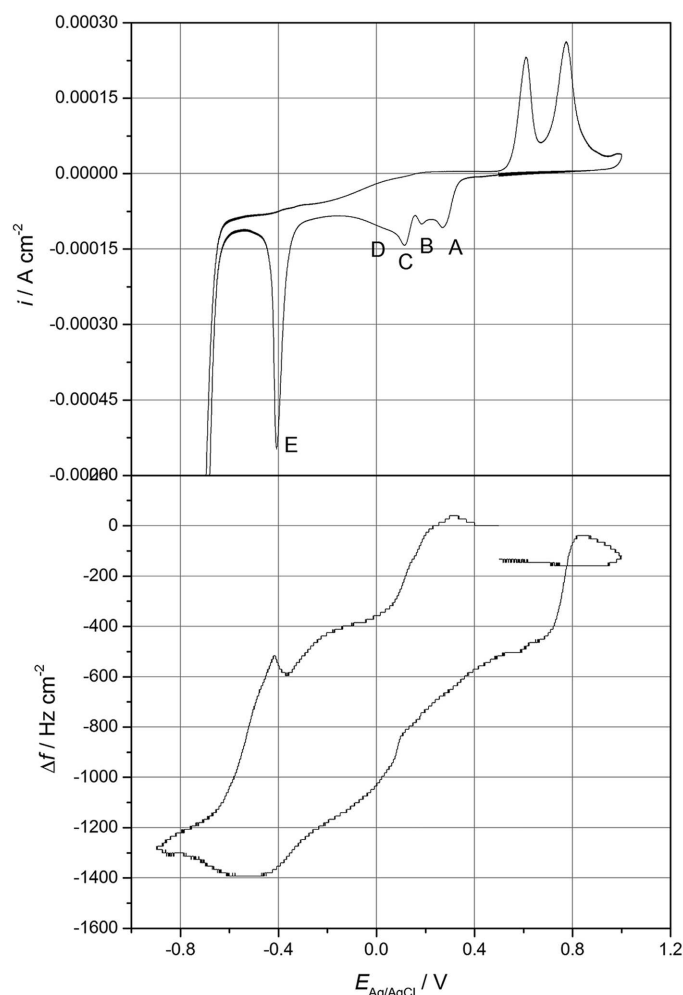

Fig. 1. Cyclic voltammogram and corresponding frequency curve measured on an Au surface in a solution containing 0.001 mol dm^{-3} H$_2$SeO$_3$, 0,1 mol dm^{-3} Na$_2$SO$_4$, pH=2

3.2. Ag electrode

The voltammetry experiment starts at the potential 0.1 V which is varied to the negative direction (Fig. 2). The potentials window is limited by the intensive hydrogen evolution at the negative potentials and a dissolution of silver at positive potentials. It can been seen that the reduction current starts to flow at the beginning of the experiment and slowly increases. The two small peaks A and B appeared next to each other on the I-E curve, at 0.05 V and -0.1 V respectively. They suggest that the two different processes can take place in the depicted range of potentials. The resonator response indicates the mass increase in the range of potentials, where both peaks appear.
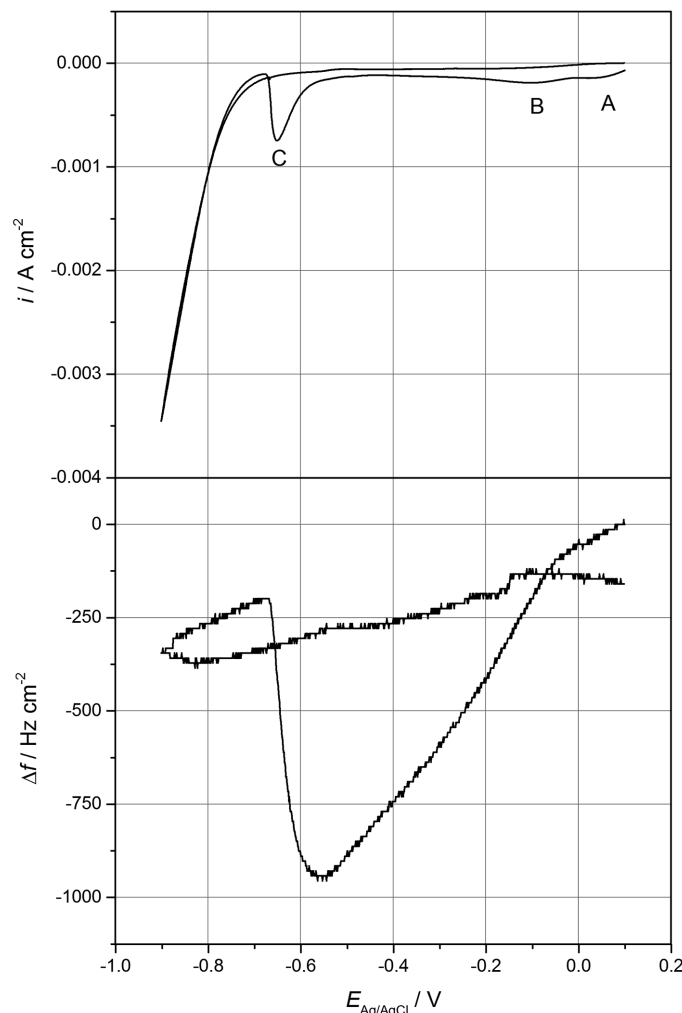

Fig. 2. Cyclic voltammogram and corresponding frequency curve measured on an Ag surface in a solution containing 0.001 mol dm^{-3} H$_2$SeO$_3$, 0.1 mol dm^{-3} Na$_2$SO$_4$, pH=2

It is very characteristic that the slope of the Δf-E dependence related to the first peak is milder as compared with the slope connected with the second one. It can be assumed that the first one is related to the surface phenomena and Ag$_2$Se formation and the second corresponds to the bulk deposition of selenium. The process of deposition is continued up to -0.55 V. Then, the frequency of the resonator starts increasing rapidly below the potential -0.55 V, where the very high reduction peak is recorded at the voltammogram. The deposited selenium is reduced to H$_2$Se according to the reaction (3). The process of the mass decrease is stopped when the deposit almost entirely is dissolved. Below the potential -0.65 V the resonator indicates the increase of the mass of the electrode. The interpretation of that part of the voltammogram is hindered by the intensive hydrogen ions reduction (6), which starts below potential -0,7 V. It can be assumed that selenium is deposited according

to the reaction (4). When the scanning was reversed at -0.9 V, the increase of the mass of the electrode had stopped and the dissolution of the deposit was observed again from potential -0.85 to -0.15 V. It means that selenium deposited by the reaction (4) dissolved. The very weak changes of the frequency of the resonator are recorded in the ranges of potentials from -0.15 to 0.1 V. They suggests the end of any deposition or dissolving processes.

3.3. Cu electrode

The voltammetric experiment starts on copper electrode at 0.0 V. Similarly to silver, the potentials window is limited by the intensive hydrogen evolution reaction from the negative potentials and also by the dissolution of the substrate from its positive side. When the scanning begins from potential 0.0 V, the reduction process starts immediately (Fig. 3). The trimmed peak A appeared at potential -0.05 V. Simultaneously, the mass of the electrode increases during sweeping the potential to the negative direction. The mass increase is stopped at the potential -0.6 V and short plateau is observed on the Δf-E graph between -0.6 and -0.7 V. Afterwards, the process of the reduction of Se^0 to Se^{-2} starts (3), and intensive decrease of the mass of the electrode is observed. The reaction (3) starts at the most negative potential compering with gold and silver electrodes and the mass increase is higher as compared to the experiment with the silver electrode. This effect is related to higher reactivity of copper and strong selenium – substrate interaction. Below potential -0.7 V the increase of current is recorded related to the the mass increases again, suggesting two possibilities: either reaction (1) or (4) takes place. The dissolution of the deposited selenium is observed again in the very narrow range of potentials from -0.85 to -0.9 V. Similarly to the results obtained on gold and silver electrodes this effect is difficult to analyse due to intensive hydrogen reduction reaction. The reaction (3) is responsible for the decreasing mass of the electrode at so negative potential. When the scanning is reversed to the positive direction, the mass of the electrode increases rapidly again. The part of the Δf-E curve from the potential -0.9 to 0.0 V can be divided into three ranges with different slopes separated by short plateaus: from -0.9 to -0.7 V, from -0.55 to -0.4 V and from -0.3 to 0.0 V. The shape of the Δf-E curve suggests that the different mechanisms are responsible for the deposition process during sweeping in the positive reaction. The deposition of selenium according to the reaction (4) is possible at more negative potentials, but that reaction has to be preceded by the reaction either (2) or (3). According to the equilibrium potentials, the combinations of reactions (3) and (4) is possible at more negative potentials, because of the more negative equilibrium potential of the reaction (3) than reaction (2). Consequently, the deposition of selenium above potential -0.3 V is proceeding according to reaction (1). The anodic peak during sweeping in the positive direction was not observed, similarly to the silver substrate. Moreover, the mass of the electrode increases during the sweeping in the positive direction on the contrary to the silver and gold electrodes, where almost all deposits were dissolved.

4. Conclusions

The electrochemical behaviour of selenium is a very complex process and it strongly depends on the nature of the substrate. The microgravimetric measurements combined with the cyclic voltammetry allow to distinguish the differences. The mechanism of the deposition of selenium occurs through the reaction (1) at most positive potentials on gold electrode, namely below 0,4 V.
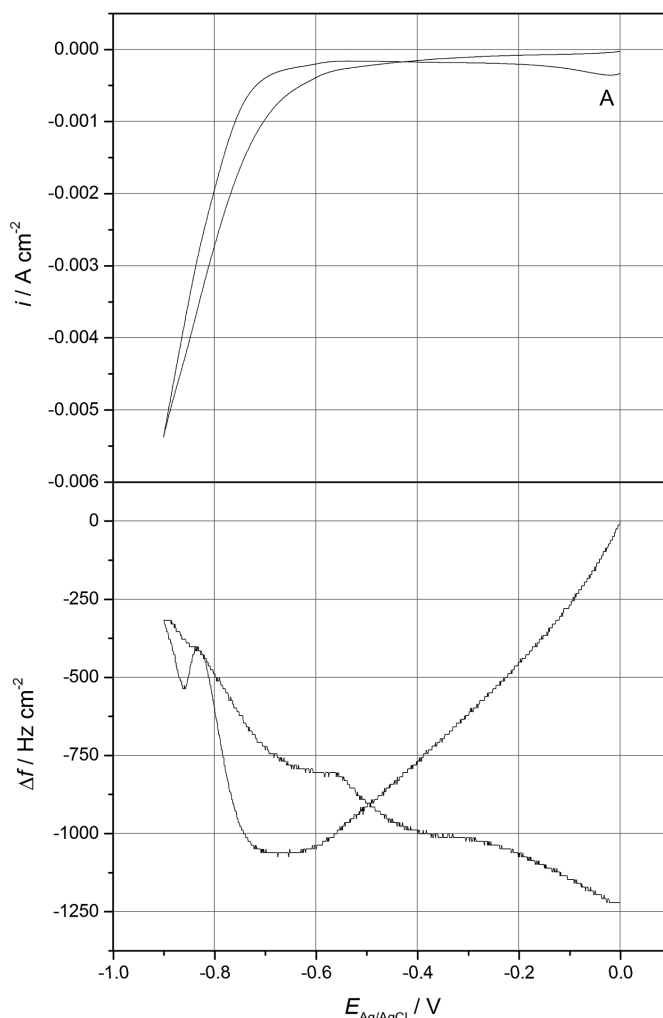
Fig. 3. Cyclic voltammogram and corresponding frequency curve measured on a Cu surface in a solution containing 0.001 mol dm^{-3} H$_2$SeO$_3$, 0.1 mol dm^{-3} Na$_2$SO$_4$, pH=2

When the potential 0.0 V is passed the deposition of selenium occurs through the reactions (2) and (4). This mechanism is not explicitly visible on the silver and copper substrates, when the potential is changed in the negative direction.

The deposition of selenium according to reaction (1) starts at potential 0,1 V on silver and at -0,1 V on copper electrode.

The reduction of Se(0) to Se(-2) starts at most positive potentials on gold, and the smallest weight loss due to reaction (3) is recorded. This effect is related with lower overpotential for hydrogen ions reduction on gold electrode compare to silver and copper ones. The deposition of selenium according to the combined reactions (3) and (4) starts immediately and

moreover, it is detected at the most positive potentials as compared to the other electrodes.

The total mass gain is the greatest on the gold electrode when the potential is changed in the negative direction. According to the Δf-E dependence the crucial reaction responsible for deposition of selenium on gold is reaction (4).

Contrary to the behaviour of the gold electrode, the very intensive dissolution of deposited selenium is registered on silver and copper due to the reaction (3) during sweeping in the negative direction. Probably this effect is related to the different states of deposited selenium and its strong interaction with the substrates.

Moreover, the characteristic behaviour is recorded on copper electrode, where deposition of selenium by different mechanisms is continued during the scanning in the positive direction. The process of deposition occurs intensively, opposite to the silver and gold electrodes. It is probably related with the higher reactivity of copper electrode as compared to gold and silver, and a possible diffusion of selenium into the substrate and the formation of copper selenides. When the values of ΔG^0 of selenides is compared, they suggest that the most stable are Cu_2Se phase (-103,94 kJ/mol) as compared to Ag_2Se (-82,93 kJ/mol) and AuSe (-36,39 kJ/mol) [74], which is compatible with reported results.

Summarizing, the present work showed that combining cyclic voltammetry and electrochemical quartz microbalance is a very useful way of the analysis of the electrodeposition of selenium. The obtained results will be very helpful for further investigations embracing chronoamperometric measurements combined with electrochemical quartz crystal microbalance and carried out on compound semiconductors deposition by pulsed methods [75].

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