Electrochemical behaviour of H₂SeO₃ at polycrystalline Pt electrode in sulphuric acid medium

Dijana Šimkūnaitė, Emilija Ivaškevič, Vitalija Jasulaitienė and Antanas Steponavičius

Institute of Chemistry, A. Goštauto 9, LT-2600 Vilnius, Lithuania The electrochemical behaviour of H_2SeO_3 at a polycrystalline Pt substrate was studied in 0.5 M H_2SO_4 medium using cyclic voltammetry and XPS technique. The dependence of the current-potential curve shape on such factors as the upper limit of the potential sweeps, the concentration of H_2SeO_3 and the application of continuous cycling was investigated and compared with those presented elsewhere. No indications for the formation of soluble selenide were found. In all instances the surface of Pt(poly) was found to be non-oxidized. The selenium coverages were evaluated depending on the potential scan rate and H_2SeO_3 concentration.

Key words: Selenious acid, reduction, polycrystalline platinum, acidic medium, cyclic voltammetry, XPS

INTRODUCTION

Selenium and its compounds are of great importance in various fields of electrochemistry and electrochemical engineering. H₂SeO₃ and selenite have been found to accelerate Cu²⁺ discharge in acidic CuSO₄ solutions [1–3]. Se(IV) compounds are widely used for preparing thin layers of binary or ternary selenides as semiconducting materials, including, in particular, copper selenides [4–14], cadmium selenides [16–20], zinc selenides [17, 21–23], silver selenides [24, 25], indium selenides [12, 26], etc, onto different substrates.

Much attention up to the present has been paid to electrocatalysis caused by the deposition of foreign adatoms onto electrodes the coverage of which is less than unity. In relation to this problem, a number of papers have demonstrated the advantage of the use of irreversibly adsorbed selenium adatoms in various redox reactions [27–36].

A Cu/CuSe microelectrode has been recently proposed for the selective detection of Nernstian response of cupric ions in biological media [37].

Bearing the mechanism of the electrochemical formation of copper selenides in mind, several studies concerning underpotential deposition (UPD) of copper onto a selenium-covered polycrystalline platinum electrode [38, 39] and also short-time overpotential deposition (OPD) of this metal onto Secovered Pt(poly) [39, 40] or onto Secovered Au(poly) [41] electrodes have been made in the last few years.

It has been found that when Se is added to Pb–Sn alloys, selenium suppresses the corrosion rate of alloys caused by either an introduction of Na_2SO_4 to H_2SO_4 solutions or a decrease in Sn content in the alloys below a certain limit [42].

In this context, it is obvious that the electrochemical behaviour of selenium species as the only electroactive species adsorbed at the surface of a substrate or present in the bulk solution is of fundamental importance. Among such selenium substances, Se(IV) ones as H₂SeO₃ are most widely used when the effect of selenium has to be studied.

Considerable work has already been done to investigate the mechanism and kinetics of the H₂SeO₃ reduction/oxidation process using different electrodes and solutions of various compositions [4, 6, 24, 26, 41, 43–52]. From the previous studies one can see that, first of all, such an investigation was rather complicated due to several factors including, among others, the sensitivity of Se(IV) electrochemistry to the substrate surface and to the occurrence of coupled chemical reactions. Such a feature of Se(IV) electrochemical behaviour has been pointed out in several papers, e. g., in [45, 51].

Next, as to the Se(IV) electrochemical behaviour in acidic media at a platinum substrate (a platinum electrode and an acidic medium have been chosen in the context of our previous investigations on the copper UPD and OPD processes in the presence of H₂SeO₃ [38–40]), several mechanisms have been proposed for the reduction of H₂SeO₃ [45, 49]. For example, a single reduction wave has been observed

with a Pt rotating disc electrode in 1.0 M $\rm H_2SO_4$ + 5 mM $\rm H_2SeO_3$ solution before the current increases rapidly with $\rm H_2$ evolution [45]. With each successive full potential scan cycle the limiting current has been found to decrease due to the formation of a passivating selenium film on the electrode surface. The following sequence has been proposed for the reduction of $\rm H_2SeO_3$ at a platinum substrate in sulphuric acid solution [45]:

$$H_{2}SeO_{3} + 6H^{+} + 6e \rightarrow H_{2}Se + 3H_{2}O$$
 (1)

followed by the chemical reaction

$$2H_{2}Se + H_{2}SeO_{3} \rightarrow 3 Se + 3H_{2}O.$$
 (2)

The rate of the chemical reaction (2) has been shown to depend on the H₂SeO₃ concentration [45]. As a consequence, at high H₂SeO₃ concentrations reaction (2) becomes fast and the overall process taking place at the Pt RDE surface appears to be

$$H_{2}SeO_{3} + 4H^{+} + 4e \rightarrow Se + H_{2}O.$$
 (3)

Later, it has been shown that the electrochemical behaviour of Se(IV) and the crystallographic structure of a selenium overlayer deposited onto a Pt substrate also strongly depend on the presence of surface platinum oxide [49]. In particular, the following mechanism has been proposed for the cathodic current peak at +0.29 V (SCE) (the first peak of the two observed during a cathodic-going sweep starting with +1.15 V (SCE) in 0.1 M NaClO₄ + $5 \cdot 10^{-4}$ M SeO₂ solution):

$$HSeO_{3}^{-} + 6H^{+} + 6e \rightarrow HSe^{-} + 3H_{2}O,$$
 (4)

$$HSe^- + PtO + H^+ \rightarrow PtSe + H_2O.$$
 (5)

So, the formation of PtSe as a surface compound has been thought to be possible. If the cathodicgoing sweep has started with a less positive potential, $e.\ g.,\ +0.75\ V$ (SCE), this current peak has not been observed.

The reactions (4) and (5) have also been used to describe the cathodic peak at about +0.20 V (SCE) observed with a Pt substrate in 0.1 M H_2SO_4 $+2.4 \cdot 10^{-4} \text{ M H}_2\text{SeO}_3$ solution [6]. In the same report it has also been noted that, with increasing the amount of surface platinum oxide, *e. g.*, by a positive shift of the potential anodic limit, height of this current peak increases correspondingly.

Because of the increasing interest to the effect of selenium on the peculiarities of copper UPD and on the first stages of copper nucleation and growth onto a foreign substrate in the presence of selenite [38–41], two aspects appear to be needed to underline here additionally. Firstly, the specificity of a platinum electrode used for the electrochemical measurements should be determined more fully. Secondly, the anodic $(E_{\rm s,a})$ and cathodic $(E_{\rm s,c})$ limits of the potential range applied should be restricted with respect to the copper UPD and OPD zones.

This paper deals with the electrochemical behaviour of H₂SeO₃ at polycrystalline platinum (Pt(poly)) in 0.5 M H₂SO₄ solution under potentiodynamic conditions of electrolysis. Results will also be discussed with the help of *ex situ* X-ray photoelectron spectroscopy (XPS) measurements.

EXPERIMENTAL

The working solution was 0.5 M $H_2SO_4 + \times mM$ H_2SeO_3 prepared from doubly distilled water, highest purity sulphuric acid H_2SO_4 (Russia) and selenious acid H_2SeO_3 (99.999% purity, Aldrich). Prior to each experiment, the solution was deaerated with Ar gas for 0.5 h.

All experiments were carried out at 20 ± 0.1 °C with a conventional three-electrode cell. The working electrode was a vertical disc 10.5 mm in diameter made from polycrystalline Pt foil (99.99% purity, Russia). The counter electrode was a Pt sheet ca. 4 cm² in area, and the reference electrode was an Ag/AgCl/KCl(sat.) electrode. In the text, all potentials were recalculated with respect to the standard hydrogen electrode (SHE), unless otherwise stated.

The real surface area of the working Pt(poly) electrode was determined from a hydrogen adsorption current-potential profile recorded at 50 mV s⁻¹ in 0.5 M $\rm H_2SO_4$ solution, taking a specific charge of 210 $\mu \rm C$ cm⁻² for the complete coverage of Pt(poly) by adsorbed hydrogen, as reported in [53]. The roughness factor (f) was found to be 2.05 \pm 0.05. Currents in the text are presented with respect to the visible surface area of the working electrode.

The pretreatment of the working Pt(poly) electrode prior to electrochemical or structural measurements was as follows: (a) prior to the first use, the Pt(poly) electrode was polished mechanically using diamond pastes down to 0.1 μ m to mirror-like finish; after polishing and degreasing with acetone, the electrode was immersed in H₂SO₄ + CrO₃ solution at ambient temperature for 24 h, rinsed with doubly distilled water and then activated electrochemically in 0.5 M H₂SO₄ by successive sweep cycles between +0.05 and +1.50 V with a scan rate (ν) of 50 mV s⁻¹ for about 6 h; (b) before each experiment, the cycling was repeated over the same region for about 1 h; after this electrochemical activation the electrode was transferred without rinsing to

another cell for the electrochemical measurements or the preparation of a sample to be investigated by X-ray photoelectron spectroscopy (XPS).

The electrochemical investigations were carried out using cyclic voltammetry (CV). The working Pt(poly) electrode was first allowed to stand at the starting potential ($E_{\rm start}$) for 2 min. The potential sweep was started with $E_{\rm start}$ = +0.85 V, at first toward more negative potentials. Cyclic voltammograms (CVs) were recorded using a PI 50–1 potentiostat (Belarus) interfaced through a home-made analogue to digital converter with a PC (Siemens) and a PR-8 programmer (Belarus) The experimen-

energies ($\rm E_b$) used for the determination of the composition of the specimen surface are shown in Table 1. The following elemental sensitivity factors were used to determine the contents (in at.%) of elements: Pt $4f_{7/2}$ 4.4, O 1s 0.66 and Se $3d_{5/2}$ 0.67 [58]. An argon beam was used to sputter-etch the specimen surface (100 μ A, ca. 30 nm min $^{-1}$, 2 min).

After such experiments, the potential was cycled between $E_{\rm s,a} = +1.5 \, {\rm V}$ and $E_{\rm s,c} = +0.05 \, {\rm V}$ in 0.5 M ${\rm H_2SO_4}$ solution at 50 mV s⁻¹ to dissolve selenium oxidatively. For each experiment a freshly prepared Pt electrode was used.

Table 1. Electron-binding energies (E _b) for elements and their compounds used as the standard values of E _b								
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Element	Oxidation state	Compound	Pt 4f _{7/2}	O 1s	Se 3d _{5/2}	Refs.		
Pt	0	Pt metal	71.0			[54]		
	2	PtO	72.2			[55]		
	4	Pt(OH),	72.4			[54]		
	4	PtO,	74.4			[54]		
	4	$Pt(SO_4)_2 \cdot zH_2O$	74.4			[54]		
	1	Oxide I*	73.6			[54]		
O**								
Se	0	Se elemental			55.0	[57]		
	4	SeO_2			ca. 60.9	[57]		

^{*} The assignment of oxide I has been made in reference to the intermediate surface oxidation state after completion of PtOH monolayer structure [54].

tal data acquisition was in numerical form with a time resolution of 4 or 50 ms per point.

XPS analysis was carried out for the following specimens: (i) freshly electrochemically activated Pt(poly); (ii) as in (i) followed by treating in 0.5 M $\rm H_2SO_4$ + 0.05 mM $\rm H_2SeO_3$ solution for 2 min at either +0.80 V or +0.35 V. After such a preparation, the specimens were immediately stored in the analysis chamber, the exposure time to room atmosphere being no more than 2 min. The Pt $4f_{7/2}$, O 1s and Se $3d_{5/2}$ XPS spectra were ex situ recorded on a VG ESCALAB MKII spectrometer with MgK $_{\alpha}$ radiation source (1253.6 eV) operated at 300 W (15 kV, 20 mA), a pass energy of 20 eV. For narrow scans, a step width of 0.1 eV was used. The standard values of binding

RESULTS AND DISCUSSION

Voltammetric measurements. Calculations showed that for the pH range (0.5 M H_2SO_4) pertinent to our work the stable selenious acid species corresponds to H_2SeO_3 . Hence, the electrochemical reactions (1) ($E_o = +0.360 \text{ V } [59]$) and (3) ($E_o = +0.740 \text{ V } [60]$) occurring simultaneously with the conproportionation reaction (2) as long as the Se(IV) species are present in the solution might mainly be taken into account within the working potential range, from +1.50 to +0.05 V.

A series of eight quasi-steady voltammetric I/E profiles (the 20th cycle) for the Pt(poly) electrode in 0.5 M $\rm H_2SO_4$ solution taken from the same cathodic limit $E_{\rm s.c} = +0.05$ successively to different ano-

[&]quot;It is common knowledge that in the general case the O *1s* spectra can be considered under an assumption of some distinct oxygen species at Pt surface, *i. e.* in terms of O *1s* signals of Pt-OH, Pt-OH₂ (adsorbed species of hydroxyl and water), Pt-O-Pt (oxygen in Me-oxygen-Me bond) and also of adsorbed molecular oxygen. Unfortunately, no plausible data on the O *1s* spectra characteristics for the platinum-oxygen systems were found. Nevertheless, mention may be made of the assignment of the main peak at about 532 eV to oxygen in Me-OH and Me-OH₂ bonds, where Me corresponded to rhodium [55], and also of the O *1s* signal at 531.8 eV to chemisorbed oxygen (PtO_{ads}) [56].

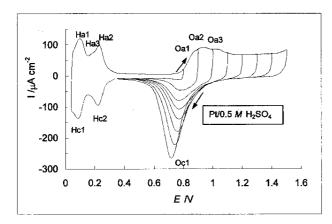


Fig. 1. Quasi-steady cyclic voltamograms (20th cycle) of polycrystalline Pt electrode in 0.5 M H₂SO₄ recorded at 50 mV s⁻¹ depending on a positive limit of potential sweeps [38]

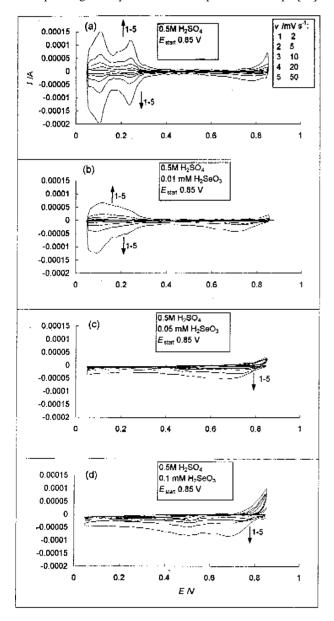


Fig. 2. Cyclic voltammograms (1st cycle) of Pt(poly) in 0.5 M $H_2SO_4 + H_2SeO_3$ solution depending on the concentration of H_2SeO_3 and the potential scan rate ν

dic limits $E_{\rm s,a}$ up to +1.50 V in 0.1 V increment are shown in Fig. 1.The general run of these CVs is quite close to that presented elsewhere [61]. The CVs recorded in the blank 0.5 M $\rm H_2SO_4$ solution for the Pt(poly) electrode are displayed here for comparison.

Figure 2 shows the CVs (the 1st cycle) in 0.5 M H₂SO₄ solution in the absence (a) or in the presence (b-d) of H₂SeO₃ at various potential scan rates (v) in the potential range from +0.85 to +0.05 V. A single but rather broad cathodic peak at about +0.70 V is observed at lower concentrations (c) of H₂SeO₃. This reduction wave becomes definitely better defined with increasing c of H_2SeO_3 and v. At higher c of H_2SeO_3 , two cathodic peaks at ca. +0.70 and +0.45 V can be revealed (Fig. 2d). It is quite clear from these results that, under conditions of our experiments, the reduction waves of H₂SeO₃ at platinum in an acidic medium are observed at much more positive potentials as compared to the earlier work [45]. The observed differences may be due to both the medium and the pretreatment of the wor-

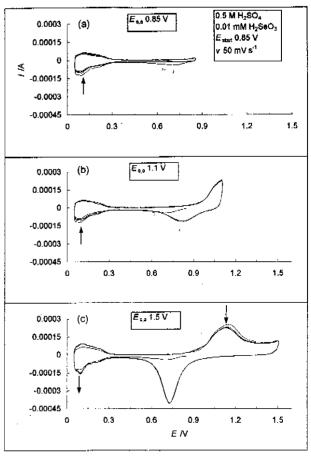


Fig. 3 Successive cyclic voltammograms of Pt(poly) in 0.5 M $\rm H_2SO_4 + 0.01~mM~H_2SeO_3$ solution at 50 mV s⁻¹ and different anodic reversal potentials $E_{\rm s,a}$. Arrows show the direction of change in the current with increasing the number of sweeps

king Pt electrode used in our study. The second cathodic peak at +0.45 V occurring on the negative scan (Fig. 2d) is rather similar to that defined as the 1st cathodic peak in [6].

As may be inferred from Figs. 3 and 4, the voltammetric profile for Pt(poly) in 0.5 M H₂SO₄ solution containing H₂SeO₃ is sensitive to the value of $E_{\rm sa}$. In particular, the height of the cathodic peak at ca. +0.70 V was found to increase with the positive shift of E_{sa} relative to the cathodic peak potential corresponding to the platinum oxide reduction [61] (peak Oc1 in Fig. 1). The second cathodic peak at a less positive potential (ca. +0.45 V) is also suppressed with each successive full cycle (Fig. 4). In this case, such a suppression of the cathodic wave can be seen even though $E_{\rm s,a}$ is markedly more negative than Oc1 (Fig. 4b). This fact suggests that the formation of a passivating layer supposedly consisting of red selenium [45] can also take place in the absence of platinum oxide. A similar picture is also observed at lower v, e. g., at 2 mV s⁻¹ (Fig. 5). So, the interrelation between the reduction of surface platinum oxide taking place in the blank H₂SO₄ solution at platinum ([61] and Fig. 1) and the peak height recorded with the working Pt(poly) electrode in the presence of H₂SeO₃ (Figs. 2-5) appears to be confirmed in specific cases, in good agreement with the previous considerations on the influence of surface platinum oxide on the Se(IV) reduction process [6, 49]. On the other hand, the evidences for the formation of a passivating film on the Pt(poly) surface without participation of surface platinum oxi-

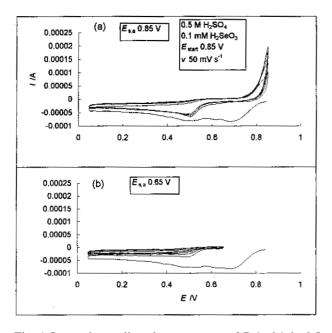


Fig. 4 Successive cyclic voltammograms of Pt(poly) in 0.5 M $\rm H_2SO_4+0.1~mM~H_2SeO_3$ solution at 50 mV $\rm s^{-1}$ and different $E_{\rm s,a}$

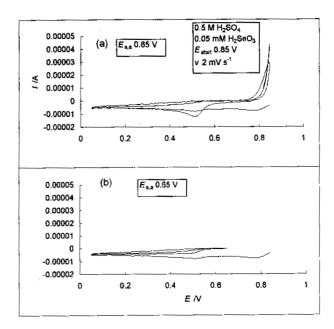


Fig. 5 The same as in Fig. 4 but with 0.05 mM $\rm H_2SeO_3$ and at 2 mV $\rm s^{-1}$

de were obtained as well. Suppression of the Se(IV) reduction process becomes well visible with applying the successive sweeps (Figs. 3–5), in agreement with the data reported in [45]. No indications of a further conversion of zero-valence selenium to soluble selenide were obtained, at least by the voltammetric measurements carried out in this work.

Surface analysis. The results of the XPS analysis are collected in Table 2. Typical Se $3d_{5/2}$ spectra recorded from the samples 3 and 4 are presented in Fig. 6.

The experimental Pt $4f_{7/2}$ peak at 70.9 eV (samples 1–4 in Table 2) is in good agreement with the literature standard value of E_b for metallic Pt (Pt°) and is markedly lower than any E_b for oxygenated Pt compounds (Table 1). Therefore, it can be concluded that the top layer of the Pt(poly) substrate in pure H_2SO_4 medium (sample 1) is non-oxidized as Pt°. Such a conclusion appears to be substantiated additionally by the fact that after sputtering the position of the Pt $4f_{7/2}$ signal remains unchanged (sample 2).

Relating the O Is spectrum characteristics obtained from sample 1, the following points need to be noted. The experimental value of E_b somewhat differs from the values of E_b that have been taken to describe chemisorbed oxygen at Pt [56] or maybe bound hydroxyl or water molecules at a surface of noble metals (Table 2). Nevertheless, there is a sufficient reason to suppose that the experimental data reflect the chemisorbed oxygen species.

As regards Pt(poly) treated in the presence of H_2SeO_3 (samples 3 and 4), one can see that no detectable difference in the experimental value of

Table 2.	XPS ((Pt $4f_{7/2}$,	0	1s and	Se 3	$d_{5/2}$) dat	a on t	he surface	of	polycrystalline	Pt	after	treatment	in	either	0.5 N	1
H,SO, o	r 0.5	M H,SO), H	- 0.05	mM	H,SeO,	solutio	ons									

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No.	Sample preparation	Elements	Binding energies, eV	Contents*, at.%	Plausible compounds
1	Pt(poly) after cycling in pure	Pt	70.9	86.9	Pt°
	0.5 M H ₂ SO ₄ solution between	O	531.2	13.1	oxygen(ads) (?)
	+0.05 and +1.50 V at				
	50 mV s ⁻¹ for 1.0 h				
2	As for sample 1, after	Pt	70.9	100	Pt°
	sputtering (at a depth of	O		_	
	ca. 60 nm)				
3	As for sample 1, followed	Pt	70.9	86.4	Pt°
	by treating in 0.5 M H_2SO_4 +	O	532.1	10.9	Se° (?)
	+ 0.05 mM H ₂ SeO ₃ solution	Se	54.3	2.7	oxygen(ads) (?)
	for 2 min at +0.80 V				
4	The same as for sample 3,	Pt	70.9	90.3	Pt°
	but at +0.35 V	O	532.1	3.7	Se° (?)
		Se	54.3	6.0	oxygen(ads) (?)

^{*} Contents of individual elements are given as rounded numbers.

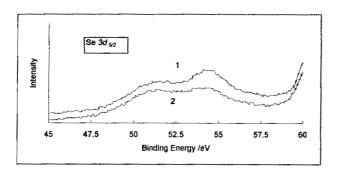


Fig. 6 Se $3d_{5/2}$ X-ray photoelectron spectra recorded from Pt(poly) after treatment in 0.5 M $H_2SO_4 + 0.05$ mM H_2SO_3 solution for 2 min at +0.35 V (1) and +0.80 V (2)

 E_b for the Pt $4f_{7/2}$ line is observed, no matter what value of potential was applied (Table 2). Such a fact, in our opinion, suggests the presence of non-oxidized Pt surface as in the previous case. Consequently, no evidences for the existence of the surface PtSe compound [6] (see reaction (5)) were found by the XPS measurements carried out under conditions of our experiments. Such a conclusion quite apparently calls for further investigation.

Although it is clear from the XPS results (Table 2, Fig. 6) that a certain amount of selenium is present at the Pt(poly) surface as a consequence of immersion in the acidic H_2SeO_3 solution, the question about the oxidation state of selenium seems to be not rigorously solved. The negative shift of E_b for the Se $3d_{5/2}$ peak relative to bulk Se cannot be attributed to the existence of any oxygenated Se(IV) compounds [57]. Then, such a feature of the selenium behaviour might be thought to be associated either with the pre-

sence of Se(-II) species or with the formation of a zero-valence selenium (Se $^{\circ}$) adlayer in amounts much less than a monolayer, analogously as it has been suggested for the Cu $2p_{3/2}$ peak from a copper adlayer deposited underpotentially [62]. The first case seems to be rather unlikely, as followed, in a general way, from the Se(IV) electrochemistry [4, 5, 7, 45] or, particularly, from the voltammetric data presented above. So, there are grounds to believe that selenium exists presumably as Se $_{ads}^{\circ}$ species in amounts less than a monolayer.

The O *Is* peak at 532.1 eV can be attributed to chemisorbed oxygen and/or to oxygen in the Pt-OH₂ bond. The former case appears to be more reasonable because of the exposure of the Pt(poly) substrate to the atmosphere before XPS investigations.

On the electrochemical behaviour of H_2SeO_3 at a platinum(poly) substrate. From the above, the following main points should be emphasized:

- (i) within the potential range +0.85 to +0.05 V, H₂SeO₃ undergoes irreversible reduction, most likely to zero-valence selenium Se°; in this regard, such a feature is in good agreement with the earlier work [6, 45, 49]; no indications for its further conversion to Se(-II) were found by either voltammetric measurements or the XPS technique;
- (ii) H₂SeO₃ reduction waves at Pt(poly) are observed in our work at more positive potentials as compared to the study [45]; this fact suggests that H₂SeO₃ reduction is sensitive not only to the chemical nature of the substrate, as pointed out in [45], but also to the state of the substrate surface after pretreatment;

(iii) on the whole, suppression of H_2SeO_3 reduction waves by the formation of a passivating selenium film during continuous cycling was confirmed; this suppression was found to occur in the potential range markedly more negative than the potential attributed to the surface Pt oxide reduction peak [61]; therefore, the presence of the latter oxide appears to be not the only factor favourable for H_2SeO_3 reduction to Se(0).

As regards the mechanism of the H_2SeO_3 reduction at Pt(poly) in the 0.5 M H_2SO_4 medium within the potential range +0.85 to +0.05 V, it seems reasonable to adopt to date the mechanism described by reactions (1) and (2), *i. e.* the six electron electrochemical reaction to form zero-valence selenium.

From the voltammetric profiles it is possible to measure the electric charges involved in the $\rm H_2SeO_3$ reduction process in the potential range +0.85 to +0.05 V. All these charges were corrected from the double layer contribution. This correction was made assuming that the differential capacity is constant in the whole potential range and equal to that measured at +0.40 V in each voltammogram.

Assuming that six-electron reduction reaction is the case, the selenium coverage (θ_{Se}) can be evaluated with the following equation:

$$\theta_{\text{Se}} = (1/6f) \cdot (Q_{\text{Se,corr}}/210),$$
 (6)

where $Q_{\mathrm{Se,corr}}$ is the corrected electric charge involved in the $\mathrm{H_2SeO_3}$ surface reduction process, f is the surface roughness factor, and 210 is the charge suggested to correspond to a process in which every Pt(poly) surface atom adsorbs a species that exchanges an electron upon adsorption. The calculations showed that at lower v, e. g., at 10 mV s⁻¹, θ_{s_0} is close to 0.27 provided that one Se adatom formed occupies 2.5 Pt surface atoms [63]. At higher values of v, θ_{s_e} becomes smaller, e. g., at 50 mV s⁻¹ in the presence of 0.05 or 0.1 mM H₂SeO₃ the calculated θ_{Se} is equal to about 0.07 or 0.15, respectively. So, the calculated value of θ_{se} is lower than the expected value of 0.4. In some instances, mostly in the case of the lowest v applied in our experiments, the calculated θ_{Se} was found to approach the expected value.

CONCLUSIONS

The main conclusions that can be drawn from the results presented in our work are as follows:

(i) selenious acid H_2SeO_3 was confirmed to be irreversibly reduced at the Pt(poly) substrate in a sulphuric acid solution within the potential range +0.85 to +0.05 V, i. e. between the potential corresponding to a surface platinum oxide reduction

and that close to the hydrogen evolution. This reduction corresponds to the six electron reaction and leads to the formation of the passivating selenium film:

- (ii) the voltammetric behaviour of H₂SeO₃ at Pt(poly) strongly depends on the upper potential limit of the sweeps and on the application of the successive sweeps, in agreement with the previous investigations. It was also shown that the presence of surface platinum oxide is not the only factor favourable for the H₂SeO₃ reduction. The kind of the pretreatment of Pt(poly) was established to be directly related to the position of the reduction waves;
- (iii) no indications for the formation of soluble selenide species were found by neither the voltammetric measurements nor the XPS investigations. In all instances the surface of Pt(poly) is non-oxidized;
- (*iv*) the selenium coverages (θ_{se}) were evaluated. This quantity was shown to be dependent on the potential scan rate and the concentration of H_2SeO_3 .

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D. Šimkūnaitė, E. Ivaškevič, V. Jasulaitienė,A. Steponavičius

H,SeO₃ ELEKTROCHEMINĖ ELGSENA ANT POLIKRISTALINIO Pt ELEKTRODO SIEROS RŪGŠTIES TERPĖJE

Santrauka

Ciklinės voltamperometrijos ir rentgenofotoelektroninės spektroskopijos metodais buvo tiriama H_2SeO_3 elektrocheminė elgsena ant polikristalinio Pt elektrodo 0,5 M H_2SO_4 tirpale. Voltamperinių kreivių pobūdis buvo nustatytas priklausomai nuo potencialo skleidimo viršutinės ribos, H_2SeO_3 koncentracijos bei nuo nepertraukiamo potencialo skleidimo taikymo. Gauti rezultatai buvo palyginti su anksčiau skelbtais duomenimis. Nei voltamperometriniu, nei RFES metodais negauta duomenų apie tirpių selenidų galimą susidarymą. Manoma, kad visais ištirtais atvejais polikristalinės platinos paviršius išlieka neoksiduotas. Įvertintas platinos elektrodo paviršiaus padengimas selenu ir jo priklausomybė nuo potencialo skleidimo greičio ir nuo H_2SeO_3 koncentracijos.