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ELECTROCHEMICAL AND ELECTROGRAVIMETRICAL INVESTIGATION OF ZnS THIN FILM ELECTRODEPOSITION

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ABSTRACT. Electrodeposition mechanism of ZnS thin film from acidic thiosulphate solutions was studied by cyclic voltammetry and electrochemical quartz crystal microbalance. For that, investigation of thiosulphate ions reduction was performed both in presence and in the absence of zinc ions. The formation of the electrodeposited film was confirmed and composition was evaluated by electrogravimetry.

INTRODUCTION

Materials in which charge carrier motion is restricted by physical size, such as quantum dots, quantum wells and multiple quantum wells, possess interesting optical, electronic and transport properties, that have broad technological applications as well as being of fundamental interest. Devices based on these nanomaterials require obtaining of thin films, usually by the means of vacuum deposition techniques (such as molecular beam epitaxy, vapor phase epitaxy or metal-organic chemical vapor deposition). Increasingly, however, electrochemical depositions are attractive alternatives to the vacuum-based methods mainly due to their cost and ability of working at ambient temperature and pressure.

Electrodeposition of semiconductor films is a field which has been driven, to a large extent, by the need for large-area thin films for photovoltaic and photoelectrochemical solar cells [1]. Although not commonly used, ZnS has the advantage of the low toxicity of its components, replacing other toxic compounds as those containing As, Sb, Se, Te or Cd.

The electrochemical quartz crystal microbalace (EQCM) is a powerful, versatile electroanalytical tool which has been used in the study of many semiconductor compounds electrodeposition such as CdSe [2], CdTe [3,4], PbSe [5], PbTe [6], CuSe [7,8] and $CuInS_2$ [9]. The operation of the EQCM is based on the converse piezoelectric effect which means that an oscillating electric field causes a mechanical oscillation in the quartz crystal. The resonant frequency of the mechanical oscillation depends on the mass of the crystal, which allows its use in the determination of very small mass changes. If the deposit is rigid, the change in the resonant frequency, Δf, is proportional to the change in mass of the deposit on the crystal according, Δm, to the Sauerbrey equation (Eq. 2, see below) [10].

For characterizing the electrochemical processes at the electrode surface, the primary Δf vs. potential (E) EQCM data can be treated in different ways. In this paper a straight-to-forward method, based on ΔQ - Δm correlation, was used. Using Faraday's law it is possible to calculate the parametre $\Delta M/n$:

$$\Delta M / n = -F\ \Delta m / \Delta Q \tag{1}$$

where ΔM is the stoechiometric molecular (or atomic) mass variation of the solid phase species involved in reaction, n the number of exchanged electrons, ΔQ the charge consumed by the reaction and F the Faraday constant (96,485.31 C mol^{-1}). The minus sign is a result of used current convention (negative current indicates a cathodic process).

Usually, the ΔM/n parametre is specific for a given reaction. The theoretical values are listed in the text after each redox reaction. By comparing these values with the experimental found ones, it is possible to identify the reactions taking place at the electrode.

There are more alternatives to electrodeposit ZnS films [11-13]. Beside the codeposition of metallic zinc and elementary sulphur, followed by generation of ZnS by a solid-state chemical reaction, in this paper another alternative is investigated. It involves the precipitation of zinc ions with sulphide (ions or acid) electrogenerated by reduction of thiosulphate. If the experimental conditions ensure total reduction of thiosulphate without reduction of zinc ions to metal, it is possible to obtain a film with an ideal Zn:S stoechiometric ratio.

The elementary equilibriums involved in this procedure of ZnS formation are as follow:

- sequential reduction of thiosulphate ions, at first to elementary sulphur: [3]

$$S_2O_3^{2-} + 6H^+ + 4e^- \Leftrightarrow 2S_{(s)} + 3H_2O \qquad E^o_{S_2O_3^{2-},H^+/S} = +0.47\ V$$

$$\Delta M / n = 16.03\ g\ mol^{-1} \tag{R1}$$

and secondly (at low pH value) to hydrogen sulphide:

$$S_{(s)} + 2H^+ + 2e^- \Leftrightarrow H_2S \qquad E^o_{S,H^+/H_2S} = +0.14\ V$$

$$\Delta M / n = -16.03\ g\ mol^{-1} \tag{R2}$$

or globally:

$$S_2O_3^{2-} + 10H^+ + 8e^- \Leftrightarrow 2H_2S + 3H_2O \qquad E^o_{S_2O_3^{2-},H^+/H_2S} = +0.305\ V$$

$$\Delta M / n = 0\ g\ mol^{-1} \tag{R3}$$

It should be mentioned that the electrochemical sulphur formation step (R1) is potentially in competition with a homogenous chemical step, i.e. the decomposition of thiosulphidric acid generated in acidic media:

$$S_2O_3^{2-} + 2H^+ \Leftrightarrow H_2S_2O_3 \Rightarrow S_{(s)} + SO_2 + H_2O \tag{R4}$$

- formation of the ZnS film by precipitation:

$$H_2S + Zn^{2+} \Leftrightarrow ZnS_{(s)} + 2H^+ \qquad P_{s\ ZnS\ (\alpha)} = 1.6\ 10^{-24} \tag{R5}$$

leading to the global reaction:

$$S_2O_3^{2-} + 6H^+ + 2Zn^{2+} + 8e^- \Leftrightarrow 2ZnS_{(s)} + 3H_2O$$

$$E^o_{S_2O_3^{2-},H^+,Zn^{2+}/ZnS} = +0.362V\ ,\ \Delta M / n = 24.36\ g\ mol^{-1} \tag{R6}$$

The presence of the zinc ion can lead also to an undesired reduction to metallic zinc, as follows:

$$Zn^{2+} + 2e^- \Leftrightarrow Zn_{(s)} \qquad E^o_{Zn^{2+}/Zn} = -0.763\ V$$
$$\Delta M / n = 32.69\ g\ mol^{-1} \qquad (R7)$$

In order to stimulate the total reduction of thiosulphate, it must take place on experimental conditions (i.e. concentrations, pH) where the redox potential of (R1) is more positive than this of (R3). As indicated by the values of standard redox potentials, listed after each reaction [14], in standard conditions the total reduction is thermodynamically favoured by a margin of app. 0.17 V. Clearly, high concentration of thiosulphate and low pH value will favor (R1) in the competition with (R3). But these requirements cannot be simultaneously accomplished due to the homogenous reaction (R4), which leads to the obtaining of colloidal (mainly electrochemical inactive) sulphur. Although the presence of zinc ions impede on sulfur formation, a too high concentration would favor its reduction on metallic zinc as well.

In this study were examined some aspects of the ZnS thin film electrodeposition mechanism. Identification of the slow steps of the process and the reaction pathway were among the aims. For that, cyclic voltammetry and electrochemical quartz crystal microbalance were used in order to obtain qualitative and semi-quantitative information.

EXPERIMENTAL

The voltammetric measurements were performed using a Computer controlled (via an AT-MIO-16F-5, National Instruments, USA, data acquisition board) analogical potentiostat (PS3, Meinsberg, Germany). A data acquisition software package (developed in LabVIEW^{TM}, National Instruments, USA) ensures multi-channel input, including the frequency measurement via a high-speed digital timer/counter.

A standard three-electrode configuration was employed for the measurements. The reference electrode was a double-junction saturated calomel electrode and the counter electrode was a spiraled Pt wire.

Voltammetric measurements were performed using a Al (refined, 99.5% purity) disk electrode (A=0.032 cm^2), polished prior to use with a 1200 grade emery paper.

Planar AT-cut quartz crystals, with an Au film (A=0.503 cm^2) on a Cr adhesion layer, were used as a working electrode for EQCM measurements. The unpolished crystals were mounted vertically on a Teflon® holder, being operated at the fundamental mode (10 MHz). This EQCM cell (type EQCM-1, made at Department of Physical Chemistry, Eötvös Univesity, Budapest, Hungary) was a gift of Professor G. Inzelt.

All electrochemical measurements were performed at 20 ± 2 ^{o}C.

The electrolyte used in this study contained 10 mM $Na_2S_2O_3$, desired pH value of 3.2 being adjusted using dilute H_2SO_4 (p.a., Panreac, Spain). When present, the $ZnSO_4$ concentration was 0.15 or 0.5 mM. 0.2 M Na_2SO_4 (p.a. Riedel-de Haen) was used as supporting electrolyte. All the solutions were prepared using bidistillated water.

High purity, with metallic impurities of 10^{-5} % m/m or less, $Na_2S_2O_3$ and $ZnSO_4$ were used as received from Dr. E. -J. Popovici ("Raluca Ripan" Institute of Chemistry, Cluj-Napoca).

The EQCM allows simultaneous measurement of the electrode potential dependence of current and frequency oscillation change, Δf, of the quartz crystal. While integration of the electric current gives the charge consumed, ΔQ, during an electrode process, the quartz oscillation frequency change, Δf, can be correlated with the electrode mass modification, Δm, using Sauerbrey equation:

$$\Delta f = -2\,\Delta m\, f_o^2 / \sqrt{\mu\rho} = -C_S\,\Delta m \qquad (2)$$

where f_o is the fundamental frequency of the crystal, μ the shear modulus (2,947 10^{11} g $cm^{-1}s^{-2}$) and ρ the density (2,648 g/cm^3) of quartz. All the constants of the equation can be included into a single constant (Sauerbrey constant, C_S) which was determined experimentally by copper electrodeposition, from a suplhate acidic bath, assuming ideal faradaic efficiency. A C_S value of 649.7±0.7 Hz μg^{-1} was obtained, in good agreement with the theoretical value of 653.7 Hz μg^{-1}, calculated with Eq. 2. This corresponds to a remarkable sensibility of 1.54 μg Hz^{-1}. As indicated, a mass increase causes a decrease in the resonant frequency and a mass decrease results in a higher frequency.

RESULTS AND DISCUSSION

At the beginning, the case of ZnS electrodeposition on the Al electrode is considered. In order to obtain information about the occurring mechanism, electrodeposition was considered under sweeping potential conditions, cyclic voltammetry being the chosen technique.

Fig. 1 shows the cyclic voltammograms in a solution containing 10 mM $Na_2S_2O_3$ and Na_2SO_4 0.2 M at pH 3.2 recorded with the Al electrode. Since no relevant electrode processes are occurring at higher potentials, the starting potential used here is –1.0 V vs. SCE.

The most important feature of this voltammogram is the presence of a single chemical irreversible reduction peak. This is consistent with the reduction of thiosuplhate ions, leading to formation of sulphur as an intermediate species, only if the sulphur reduction step (R2) occurs easier than its generation (R1). At least thermodynamically, this is in good agreement with the presented standard potentials.

Another experimental evidence of the sulphur formation is the important evolution of the voltammogram shape and parametres during successive scanning. This occurs only if at the electrode interface are taking place important changes, like those generated by the obtaining of sulphur, either as adsorbed or as distinct solid-phase. It can be mentioned that, during successive scanning, the peak definition increases on initial cycles. After several cycles, however, the definition gradually decreases. For a better illustration of the different effects on the voltamograms, both first and second cycles will be taken into account.

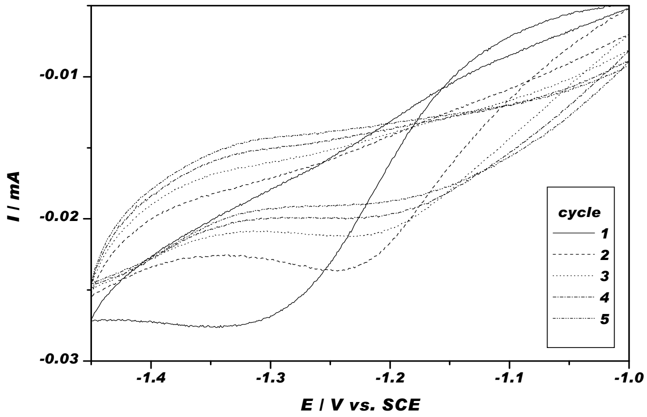
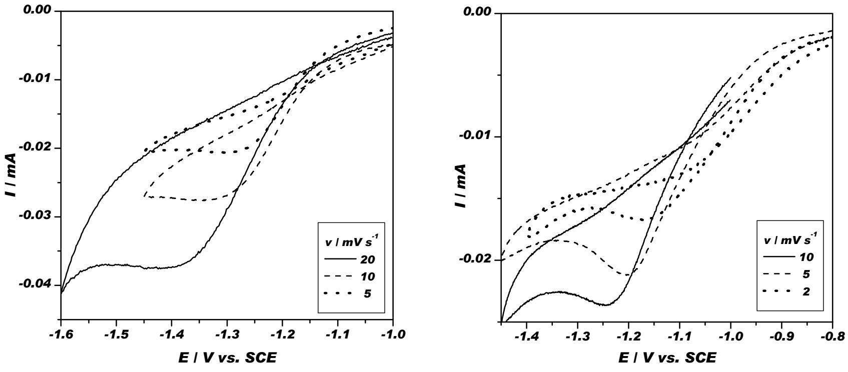


Fig. 1. *Multiple scan cyclic voltammograms recorded during reduction of 10 mM $Na_2S_2O_3$ and 0.2 M Na_2SO_4 at pH 3.2. Al electrode (A=0.032 cm^2). Scan rate: 10 mV s^{-1}.*

The scan rate influence on the voltammetric response can provide further information about investigated process, being presented in Fig. 2. The shift towards negative values of the peak potential, specific for an electrochemical irreversible system, reveals a slow charge transfer. Moreover, since it is indicated that the peak current is roughly proportional with the square root of the scan rate, specific for the systems with soluble reacting species, this peak can be related either to (R1) or (R3), totally excluding (R2).

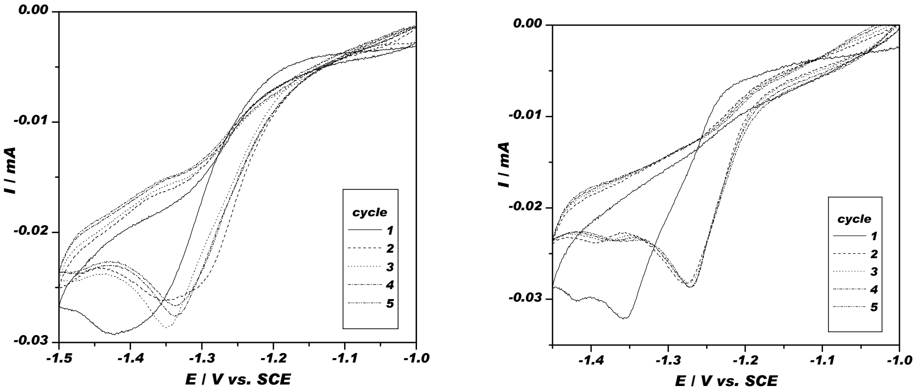


(a) **(b)**

Fig. 2. *Influence of scan rate on the voltammograms obtained during the first (a) or the second (b) scan. Conditions as in Fig. 1.*

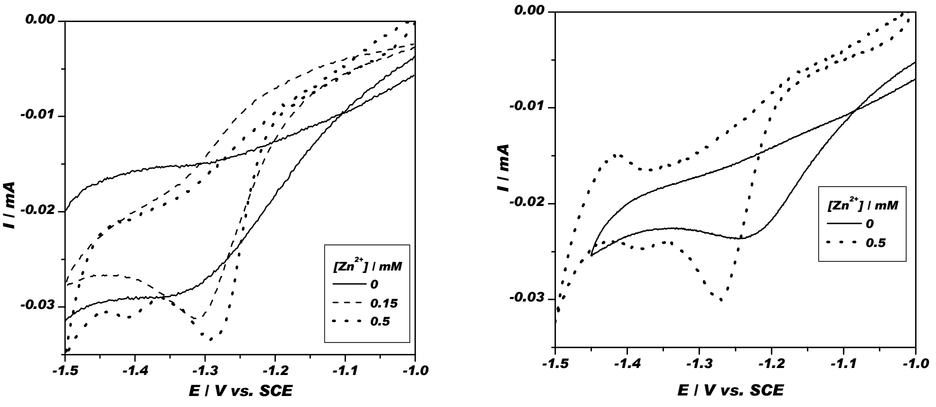
Unfortunately, the chemical irreversible nature of occurring peak prevents the obtaining of further thermodynamic or kinetic information. Commonly, the influence of pH on the peak potential (or, better, on the formal standard potential) allows the evaluation of the stoechiometric ratio between the number of exchanged protons and electrons, see for instance [15]. But all three possible reactions have close values of the mentioned stoechiometric ratio, i.e. 1.5, 1 and 1.33, which together with the inaccessibility of the formal standard potential values prevents the identification of the electrode process based on pH influence.

The addition of zinc ions into the electrolyte solution allows not only the obtaining of ZnS films, but also provides supplementary information on the thiosulphate reduction. The common shape of the voltammograms in presence of zinc ions is depicted on Fig. 3.



(a) **(b)**

Fig. 3. *Multiple scan cyclic voltammograms recorded during reduction of 10 mM $Na_2S_2O_3$ and 0.2 M Na_2SO_4 at pH 3.2, after 0.15 mM, in (a), or 0.5 mM, in (b), addition of $ZnSO_4$. Al electrode (A=0.032 cm^2). Scan rate: 10 mV s^{-1}.*



(a) **(b)**

Fig. 4. *Influence of the $ZnSO_4$ concentration on the voltammograms obtained during the second scan. Scan rate 10 mV s^{-1}, in (a), or 20 mV s^{-1}, in (b). Other conditions, as in Fig. 1.*

The most important feature is the presence of a new reduction peak (at ≈ -1.4 V vs. SCE), with the current roughly proportional to the zinc ions concentration. For this reason it was attributed to reaction (R7) leading to metallic zinc. This is in agreement to the calculated equilibrium potential (of ≈ -1.1 V vs. SCE). Furthermore, the enhancement of hydrogen evolution, on very negative potentials, proves also the metallic zinc formation, since on zinc the hydrogen evolution occur slower than on aluminum (e.g., compare Fig. 1 with Fig. 3b) [14]. Another feature is a faster stabilization of the voltammogram during successive scanning. This can be related to the obtaining of an electrochemical inactive (at least for the used potential window) film with both composition and thickness homogeneity.

But, more important, is the effect of zinc ions concentration on the reduction peak of thiosulphate, as presented in Fig. 4. Regardless of scan rate, it can be evidenced an increase of peak intensity and a decrease of peak width while the peak area remains, roughly, constant. Starting from peak current (I_p) and width at half-height (W_p) relations, for an electrochemical irreversible system: [16]

$$I_p = 2.99\,10^5 n(n_a\alpha)^{1/2} AC^* D^{1/2} v^{1/2} \tag{3}$$

$$W_p = \frac{152}{n_a\alpha} \quad [\mathrm{mV}] \tag{4}$$

some correlation can be established between the electrochemical response and the process chemistry. Here, n is the (total) number of exchanged electrons, n_a the number of electrons involved in the rate determining step, α the transfer coefficient, A the surface, v the scan rate, C^* the concentration and D the diffusion coefficient of the reacting species.

The above mentioned effects of the zinc ions addition can be explained by the increasing of the $n_a\alpha$ term. Very likely, during addition of zinc ions, the increasing of n_a parametre is the direct result of the activation of the slow electron transfer step. In this way, increasing the rate of the slower step up to the rate of other relatively slow elementary steps, the presence of zinc ions enhances the overall process. Since it does not involve additional reactions, the number of exchanged electrons remaining constant, the peak area (quantifying the electric charge involved) must be invariant, as experimentally evidenced. Because zinc ions presence influences only the sulphur reduction (R2), by shifting the equilibrium potential towards positive values caused by the precipitation process (R5), it can be assumed that the slow step is, or is contained by, reaction (R2). This is consistent to discussed single-peak exhibited by the voltammograms, only if kinetics of sulphur formation overcomes the thermodynamical limitations.

Fig. 5 reveals the influence of the scan rate on the voltammogram. Once again, both occurred peaks are electrochemically irreversible, due to the shift of the peak potential. Also, due to the dependence on the peak current it seems that are diffusion controlled as well.

Another parametre with potential relevance to the behaviour of the system is the starting potential. Fig. 6 shows this dependence. If a more positive starting potential was used (i.e. -0.8 V vs. SCE) an additional oxidation peak occurs at ≈ -0.95 V vs. SCE. Since this peak is not present in the absence of the zinc ions (corresponding voltammogram not presented here), it can be attributed to the oxidation of metallic zinc. Also the complex shape of this peak is common to a metal dissolution process, see for instance [17]. Even if present, the oxidation of ZnS (in fact of the sulphide at some soluble products) is unimportant, since the charge used for reduction largely exceeds that used for oxidation.

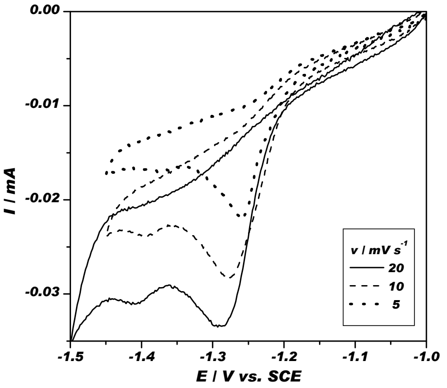
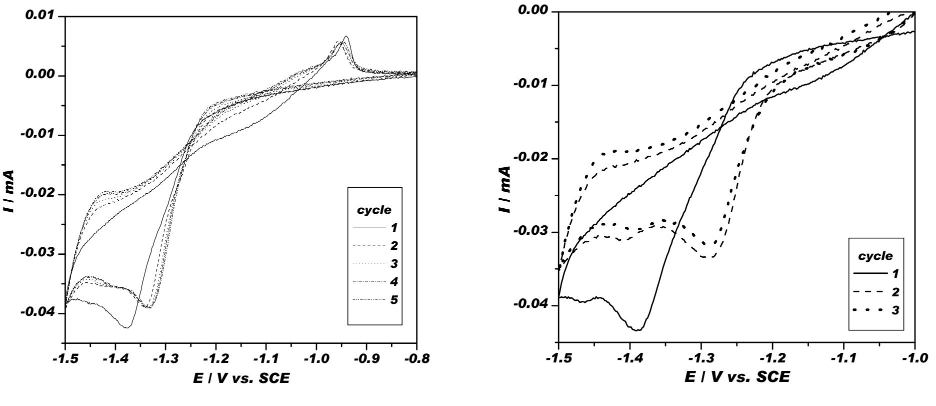


Fig. 5. *Influence of the scan rate on the voltammograms obtained during the second scan. Conditions as in Fig. 3 (b).*



(a) **(b)**

Fig. 6. *Influence of initial potential on the voltammograms obtained during multiple scan. Scan rate: 20 mV s^{-1}. Other conditions, as in Fig. 3 (b).*

Concluding the voltammetric investigation, it was revealed that, for the Al electrode, is possible to electrodeposit ZnS by zinc ions precipitation with sulphide electrochemically-generated from reduction of thiosulphate. Using a potential value in between -1.2 and -1.3 V vs. SCE (for investigated electrolyte solution), the formation of metallic zinc can be avoided. The only difficulty is the generation of sulphur, which potentially can be obtained not only as intermediate in the ZnS formation, but also as the reduction product. Unfortunately, for the investigated system, no evidence about the presence or absence of sulphur incorporation into the film was possible using cyclic voltammetry. Since it involves important mass changes at the electrode interface, EQCM measurements are much more appropriate for this kind of experiments.

EQCM measurements consist in simultaneous recording of current and mass deposited (via the resonance frequency of the quartz crystal) on the electrode during the potential shift. Thus, the results consist in a couple of representations: the current vs. potential (voltammogram) and mass vs. potential (often called voltamassogram) representations. Although the use of Au instead of Al for the electrode substrate changes somehow the reduction processes, the novel information provided surpasses this inconvenient.

Fig. 7 presents the EQCM measurements of thiosulphate reduction. Some difference can be noted: a small pre-peak wave is present (at ≈ -0.4 V vs. SCE) and the main peak is shifted towards positive potentials. Attempting the identification of occurred processes, the scanned range was divided into several potential windows. For each of these characteristic zones, the used charge (ΔQ) was calculated by integration of current intensity. Aiming the calculation of the ΔM/n parametre, the deposited mass (Δm) was determined using the voltamassogram. All these electrogravimetric parametres are presented in Tab. 1.

It was found that, during the initial cathodic scan (zone **Ia**), the reduction to sulphur (R1) prevails, since the determined ΔM/n parametre is close to the theoretic value of 16.03 g mol^{-1}. The lower founded value seems to indicate a slow sulphur desorption, leading to colloidal sulphur formation. At more negative potentials (zone **Ib**), the main reduction takes place. The -0.9 g mol^{-1} value indicates that the main process is the total reduction (R3), with a small contribution of sulphur reduction (R2) or desorption. At lowest potentials (zone **Ic**), in addition to (R3) a mass increasing process is present; it may well be the inclusion of hydrogen into the already deposited sulphur. During the anodic scan, the reduction process (R3) still prevails. Only at the highest potentials (zone **Ie**) the mass decreases; the slow release of the incorporated hydrogen can well be the explanation. After a complete cycle, little changes of the electrode surface can be evidenced.

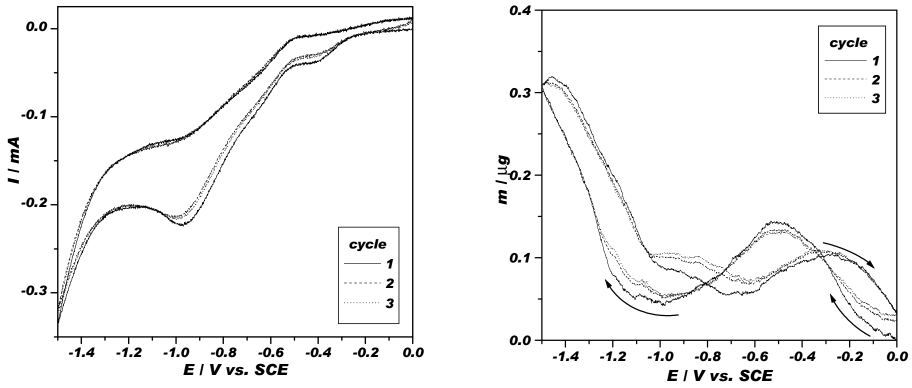


Fig. 7. *EQCM measurements of thiosulphate reduction. Electrolyte: 10 mM $Na_2S_2O_3$ and 0.2 M Na_2SO_4 at pH 3.2. Au electrode (A=0.503 cm^2). Scan rate: 10 mV s^{-1}.*

Table 1

Electrogravimetric parametres for thiosulphate reduction

Zone	Potential window	ΔQ / mC	Δm / µg	ΔM/n / g mol^{-1}
Ia	0 to -0.5 V	-0.91	0.14	15.2
Ib	-0.5 to -1.12 V	-10.33	-0.09	-0.9
Ic	-1.12 to -1.5 V	-9.77	0.26	2.6
Id	-1.5 to -0.5 V	-13.86	-0.25	-1.7
Ie	-0.5 to 0 V	-0.36	-0.03	-8.1

Overall, the total reduction to hydrogen sulphide is the predominant process. This explains the nature of chemical irreversibility of the voltammetric peak. Since the solubility of hydrogen sulphide in acidic media is limited, too small amount are available towards oxidation during anodic scan.

A similar procedure was used for the electrodeposition of ZnS, as it can be seen in Fig. 8 and Tab. 2. While the presence of the zinc ions causes little effects on the voltammograms, a striking difference is evidenced for voltamassograms. Not only that a tenfold mass change is exhibited, but after a complete cycle, the electrode mass has an important increase.

Once more, reduction to sulphur (R1) prevails on initial cathodic scan (zone **IIa**). But the charge used here is small enough (≈ 5%) to conclude that suplhur incorporation into the film cannot exceed 10% (in molar units). Compared to the cited Zn:S stoechiometric ratios, that usually are close to 1:2 [18,19], the described procedure of one-step electrodeposition of ZnS films gives much better results.

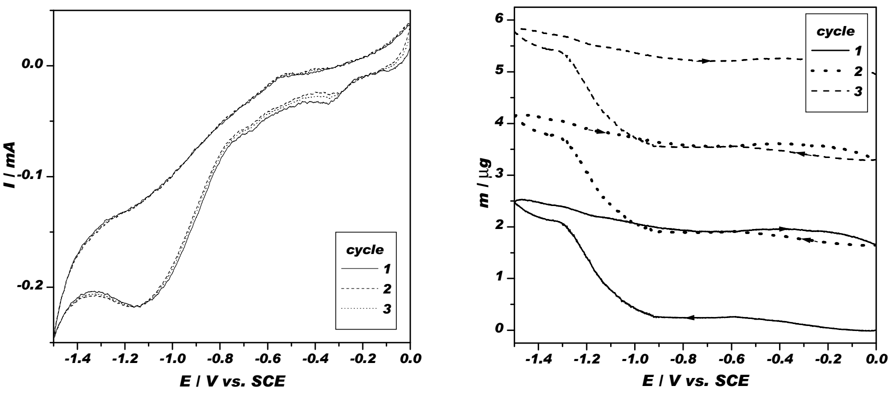


Fig. 8. *EQCM measurements of ZnS electrodeposition. Electrolyte: 10 mM $Na_2S_2O_3$, 0.5 mM $ZnSO_4$ and 0.2 M Na_2SO_4 at pH 3.2. Au electrode (A=0.503 cm^2).Scan rate: 10 mV s^{-1}.*

Table 2

Electrogravimetric parametres for ZnS electrodeposition

Zone	Potential window	ΔQ / mC	Δm / µg	$\Delta M/n$ / g mol^{-1}
IIa	0 to -0.6 V	-1.43	0.26	17.2
IIb	-0.6 to -0.9 V	-2.63	0	0
IIc	-0.9 to -1.3 V	-8.73	1.81	18.2
IId	-1.3 to -1.4 V	-2.29	0.47	15.7
IIe	-1.4 to -0.5 V	-15.07	-0.58	-3.7

After a depositless zone **IIb**, where the charge is unimportant, the main electrodeposition process takes place in zone **IIc** and **IId**. The obtained values of determined $\Delta M/n$ parametre and the absence of a zinc reduction peak indicate that here the ZnS formation (R6) is the main process. The absence of an oxidation voltammetric peak, accompanied with a mass decrease, also argues the metallic zinc deposition (R7). Zone **IIe** corresponds to a dissolution reduction; this can be explained either by sulphur reduction (R2) or by erosion of the ZnS film.

CONCLUSIONS

One-step electrodeposition of ZnS films from an acidified thiosulphate solution was investigated. The film formation is based on precipitation of zinc ions with sulphide electrogenerated by thiosulphate reduction. In this way, the film can be obtained with a close to ideal Zn:S stoechiometric ratio, which is extremely difficult to obtain with a co-deposition technique.

Cyclic voltammetry and electrochemical quartz crystal microbalance were used in order to obtain information about the electrodeposition mechanism. It was found that, under the investigated experimental conditions, the slow charge transfer step of thiosulphate reduction is, or is contained in, the sulphur reduction. Since sulphur is produced mostly at low overpotentials, a much different transfer coefficient favours the consumption (R2) in comparison to the production (R1) of sulphur.

Based on the unique gravimetric ability of EQCM, an evaluation of film composition is possible. While no evidence of metallic zinc was observed, only limited amounts of sulphur incorporated into the film was detected. A better than 1:1.1 value of Zn:S stoechiometric ratio was therefore estimated.

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