Electrochemical Investigation of the Deposition/Dissolution of Selenium in Choline Chloride with Urea or Ethylene Glycol Ionic Liquids

ANCA COJOCARU[1]*, MARIAN SIMA[2]*

[1]University Politehnica of Bucharest, Laboratory of Applied Physical Chemistry and Electrochemistry, 132 Calea Grivitei, 010737, Bucharest, Romania

[2]R&D Natl. Inst. for Materials Physics Magurele, Bucharest, Romania

The electrochemical behaviour of Se(IV) ion on Pt electrode in ionic liquids containing choline chloride – urea and choline chloride – ethylene glycol eutectics (1:2 mole ratio) was investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in open air conditions. Cyclic voltammograms showed a cathodic peak of selenium massive deposition preceeded by one or more waves corresponding to UPD processes. It is followed by another cathodic peak of Se(II) anion formation. It was found a diffusion control of reduction process and, therefore, the value of the diffusion coefficient of Se(IV) ion in ChCl-urea ionic liquid at 60^{0}C was calculated. EIS spectra as Nyquist and Bode plots confirm the potential range for bulk selenium deposition and formation of thin selenium films.

Keywords: selenium, electrodeposition, ionic liquids, choline chloride, urea, ethylene glycol

This study is part of a program concerning the electrodeposition of BiSeTe–type films used for new thermoelectric devices. As components of these films, selenium and tellurium belong to the same chemical family as oxygen, the VIB group elements, holding one more valence electron than Bi atoms. The phase diagram of Se-Te mixture shows a continuous solid solution without a maximum or minimum [1]. Bismuth–based chalcogenides are commonly used for thermoelectric devices such as thermoelectric generators and coolers [2-5]. The electrochemical preparation of selenides as Bi_2Se_3 [6] and especially telluroselenides $Bi_2(Se,Te)_3$ [7-16] has attracted considerable interest, being also ideally suited to various applications: solar cells, photoelectrochemical devices, micromechanical systems (MEMS), optical filters, optical recording materials, superionic materials and sensor and laser materials; thus they play an important role in a global sustainable energy solution.

Bi_2Se_3 and $Bi_2(Se,Te)_3$ thin films have been made by using a variety of experimental techniques such as metallurgical procedure, phase vapour deposition, sputtering and electrodeposition. Electrodeposition is a powerful method for growing thin films and/or nanostructures with potential thermoelectric properties, being the least costly procedure for the fabrication of nanostructured materials and miniaturized devices due to its easy operation with no vacuum demand, simple equipment, high deposition rate, and easy scalability. In most cases, the electrodeposition allows to produce films of controlled composition by adjusting the electrolyte composition and electrolysis conditions. The cathodic process implies the presence of all the elements (two or three dissolved precursors), but the weak solubility of Bi(III) and chalcogenide ions imposes an acidic aqueous electrolyte. In most papers concerning $Bi_2(Se,Te)_3$, nitric acid solution was used, even if sometimes other acid electrolytes (HCl, $HClO_4$ or H_2SO_4 solutions) were chosen.

In the last 10 years investigations to develop and promote alternative more environmentally friendly electrochemical media have been reported, including the class of the so-called "choline chloride based ionic liquids". Such ionic liquids have remarkable properties which make them adequate as metal electrodeposition electrolytes [17,18] Recently it has been shown the possibility of thermoelectric film deposition using ionic liquids consisted in eutectic mixtures of choline chloride (2-hydroxy-ethyl-trimethyl ammonium chloride) with urea [19] or malonic acid [20,21]. However, the electrodeposition of selenium in such ionic liquids was not reported, yet.

Selenium, regarded as a metalloid, is a relatively noble element, the polarographic and most voltammetric studies being interpreted in terms of a two-step Se(+IV)→ Se(0)→ Se(–II) scheme, where the reduction of Se(0) takes place at the more negative potentials [22]. Quadrivalent selenium cation (introduced usually as selenous acid) exhibits polarographic waves in a number of aqueous electrolytes including hydrochloric, sulfuric, nitric, and perchloric acids [23]. Literature shows that the interest in Se films is associated to their good semi-conducting properties and light sensitivity. Se electro-deposition has been extensively investigated in conventional aqueous solutions and the complexity of cathodic mechanism was recognized due to the fact that selenium appears in different solid phases. In [24] is described the deposition of thick amorphous Se deposits on various metal substrates using SeO_2 precursor dissolved in acidic or slightly alkaline (up to *p*H 8.0) baths in the temperature range of 20–40 ^{0}C. Cattarin et al. [25] studied the Se electrodeposition onto Ti electrodes from acidic selenite baths with different Se(IV) cation concentrations. Other studies were also performed in aqueous baths [26-32] showing that cathodic reduction of selenious acid is the best way to obtain Se films. Some metallic electrodes (e.g., Au) promote the undepotential deposition (UPD) of

* email: a_cojocaru@chim.upb.ro; msima@infim.ro

Se(0) via strong metal–Se interactions. The underpotential deposition (UPD) of selenium ad-atoms refers to the submonolayer amounts of selenium deposited on inert foreign metal substrate. This UPD process proceeds at the more positive potential than massive (bulk) selenium deposition.

Usually, the electrodeposition of selenium from aqueous solutions at room temperature leads to the formation of amorphous red selenium, which tends to passivate electrode surfaces.

The crystalline phases, namely the rhombohedral, α, β and γ monoclinic and trigonal (hexagonal) phases may also be deposited electrochemically; the gray hexagonal phase is the most dense and stable and useful for co-deposition with other elements for thermoelectric (as BiSeTe films) and solar cells (as InSe, CdSe or $CuInSe_2$) applications. The works of Endres and his group [33-35] suggested the utilization of ionic liquids for Se deposition due to their wide electrochemical window and extremely low vapour pressures. Thus, these authors prepared grayish films of hexagonal and rhombohedral Se phases at relatively higher temperatures (70–100^{0}C) using 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ionic liquid [33]. In their recent paper [35] the electrochemical behavior of H_2SeO_3 on gold and copper substrates was investigated in 1-butyl-1-methyl-pyrrolidinium trifluoromethylsulfonate ionic liquid – water mixtures and the influence of the deposition parameters such as time and bath temperature on the crystallinity of the film obtained from H_2SeO_3 powder precursor was examined. Also, the research performed recently by [36] focused on the influence of precursor chemical nature ($SeCl_4$ and SeO_2) on the electrochemical behaviour, as well as the phase, morphology and crystallinity of deposits prepared from 1-ethyl-3-methylimidazolium tetrafluoro-borate/chloride at temperatures higher than 100^{o}C.

In this paper, we present the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) preliminary results regarding the electrodeposition and dissolution of selenium films on Pt electrodes. Two ionic liquids consisted in eutectic mixtures of choline chloride (ChCl) with urea (denoted as ChCl-urea) and with ethylene glycol (ChCl-EG) were investigated as baths for Se electrodeposition at constant temperature (60^{0}C).

Experimental part

All the chemicals were analytical grade and used in the experiments as purchased, without being recrystallized or dried. The background electrolytes were prepared by mixing in 1:2 molar ratio the choline chloride (99%) with urea or ethylene glycol, respectively; all three reagents were from Aldrich. The appropriate binary mixtures were heated at above 90^{0}C for 30 min until a homogeneous colourless ionic liquid is formed. SeO_2 powder (purchased from Alfa Aesar) was then added as precursor for Se(IV) cations. The molarities of selenium ions were calculated using density values of 1.1940 gcm^{-3} and 1.0963 gcm^{-3} for ChCl-urea and ChCl-EG, respectively, at 60^{0}C working temperature, both determined in our laboratory.

The cyclic voltammetry and electrochemical impedance spectroscopy investigations were carried out in open air conditions, without stirring the electrolyte. In the standard three-electrode cell, the working electrode consisted either in a Pt foil (0.5cm^2) or in a Pt disk embedded in a Teflon rod (exposed surface area 0.07 cm^2); a large Pt plate and an Ag wire immersed in the same ionic liquid containing selenium ions were the auxiliary electrode and quasireference electrode, respectively. All measurements were performed at 60^{0}C constant temperature using a Zahner elektrik IM 6e potentiostat. The cyclic voltammograms were recorded with scan rates up to 100 mVs^{-1}. EIS characterization was carried out in a 10 mHz-100 kHz frequency range with an *ac* voltage amplitude of ±5 mV. Nyquist and Bode spectra were interpreted on the basis of an equivalent electrical circuit, as electrochemical model of the interface, using a specialized fitting software Zview Scribner Assoc. 2.90c.

Results and discussions

Regarding the relatively good solubility of selenium compounds in ChCl-urea or ChCl-EG ionic liquids in such amounts to have a significant electrochemical response for Se(IV) ions, an explanation may be the high value of temperature (60^{0}C) and also the presence of chloride anion Cl^- as ligand, which may form selenium complex species. The complexing process is usual in ChCl containing ionic liquid media. For instance, by dissolution of bismuth oxide precursor in the electrolyte we supposed the formation of $BiCl_4^-$ complex species, leading to a lower diffusive ionic species than simpler Bi(III) ion [19]. Also, the tellurite (TeO_2) was considered to be converted into tellurium chloride and incorporated in ionic liquid as $[TeCl_{4+x}]^{x-}$ species [20,21] with also lower diffusion coefficient than Te(IV) ion. Correspondingly, we consider in this work that it is possible for selenium ionic species to be in a complex form of $[SeCl_{4+x}]^{x-}$, most probable with x equals to 1 or 2. Certainly, during the cathodic process the complex ion decomposes firstly, yielding Se(IV) cations.

Results of applied CV technique in ChCl-urea and ChCl-EG ionic liquids containing Se ionic species

The analysis by cyclic voltammetry technique was carried out to determine the electrochemical reversibility of electrode process of Se(IV) cations and the appropriate potential ranges for electrodeposition / dissolution of semiconductor Se films. Typical cyclic voltammograms of the Se species recorded on Pt electrode in non-stirred ChCl-urea eutectic are presented in figures 1 (a,b). We selected the CV curves obtained by sweeping the potential from stationary potential in cathodic direction (until -1.0 V limit) and returning to anodic region (limit of +1.2 V) and back. It is important to mention that the CVs in ionic liquid without selenium species, recorded with enlarged potential range, -1.4V ÷ +1.4V (see references [19,37]), did not show any supplementary electrode process except the cathodic and anodic processes of background electrolyte.

As figures 1a and 1b show, the voltammograms display a cathodic peak at –0.3 ÷ -0.4 V (*vs.* Ag quasireference electrode) for the lowest scan rates, that corresponds to the reduction of Se(IV) species to elemental selenium. At more negative potential, the current increases continuously. The cathodic peak becomes prominent and moves gradually at higher scan rates, up to -0.7 V potential value (at 100mV/s). Correspondingly, CVs show on anodic branches a broad peak (actually, a shoulder or a wave) in the range of +0.8 ÷ +1V, that is assigned to dissolution of the selenium film. Thus, the corresponding peak separation, ΔE_p, recorded for various scan rates ranges in a larger potential interval, from 1.1 to 1.6 V.

However, it can be noticed that the shape of cathodic branch is more complicated, because the peak of selenium deposition is preceeded by one or more waves; according to literature, these correspond to undepotential deposition (UPD) of Se(0), processes that clearly appear by interaction of Se ad-atoms with foreign substrate, of platinum. This paper evidences for the first time the underpotential

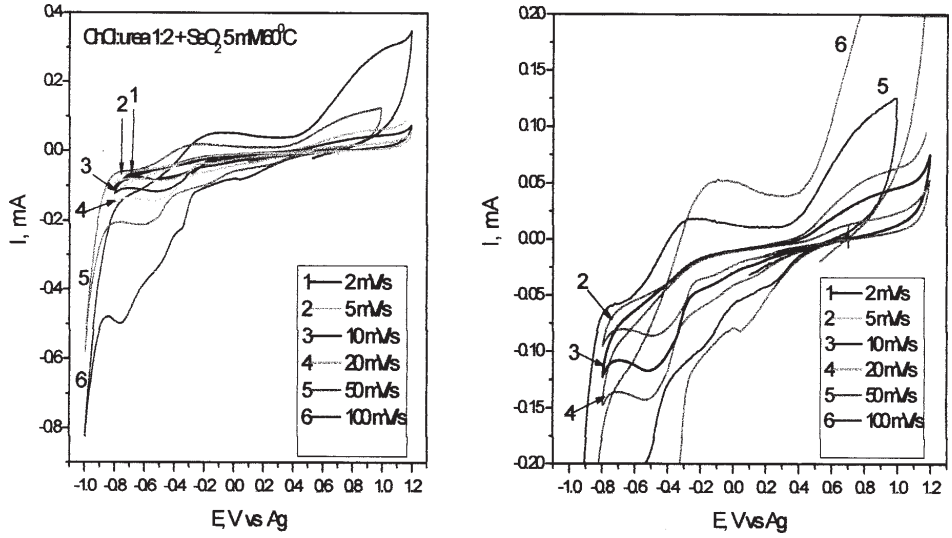

Fig. 1. Cyclic voltammograms of Pt electrode (0.07 cm^2) in ChCl-urea eutectic containing 5mM SeO_2 at 60°C: (a) CVs recorded for all studied scan rates; (b) a detail showing curves for selected low scan rates

deposition (UPD) of Se in choline chloride based ionic liquids. Supplementary, an additional anodic process is recorded in the potential region of -0.8 ÷ -0.2V, that can be attributed to the oxidation of a new species which appears by reduction process at very negative potentials.

Similar results can be also found in the CVs measured in Se ion containing ChCl-EG ionic liquid at 60°C temperature. In figure 2 a series of voltammograms recorded by extending the potential limits in both cathodic and anodic direction is shown. The CV curves in figures 2a-2c exhibit the same cathodic peak (denoted as C1) and the anodic peak (denoted as A1) located at potentials -0.25V and +0.95V *vs.* Ag quasi-reference electrode, respectively. For ChCl-EG system, the additional cathodic/anodic couple occurs in figures 2b and 2c, with peaks denoted as C2 and A2. This couple seems to be more reversible than C1/A1 couple, because the corresponding peak separation, ΔE_p, ranges in a more narrow potential interval, 0.50-0.55 V. According to figure 2d we notice that the CV in ChCl-EG ionic liquid without selenium species does not show significant electrode processes except the cathodic and anodic processes of background electrolyte with cathodic and anodic limits of -0.9V and +1V, respectively.

Some examples of CV curves obtained at various scan rates and SeO_2 concentrations are presented in figures 3-5. The existence of C1/A1 and C2/A2 electrochemical couples is clearly noticed in these Figures where all peaks are amplified in their peak currents with SeO_2 concentration and scan rate. It may be seen that with higher scan rates the peak separation (ΔE_p) for both couples increases gradually, especially by significant shifting of their cathodic peaks.

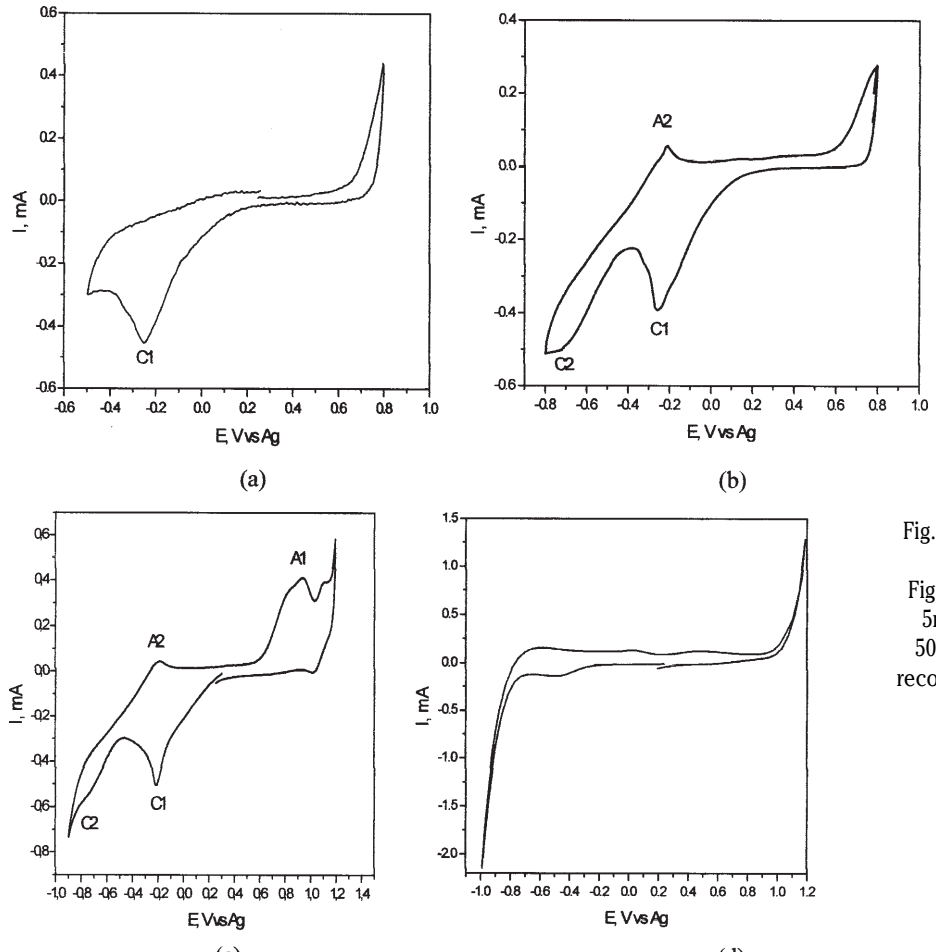

Fig. 2. Cyclic voltammograms of Pt electrode (0.5 cm^2) in ChCl-EG eutectic at 60°C. Figures (a-c): CVs for ionic liquid containing 5mM SeO_2 with scan rates of 100mV/s (a), 50mV/s (b) and 100mV/s (c). Figure (d): CV recorded for background electrolyte, 100mV/s.

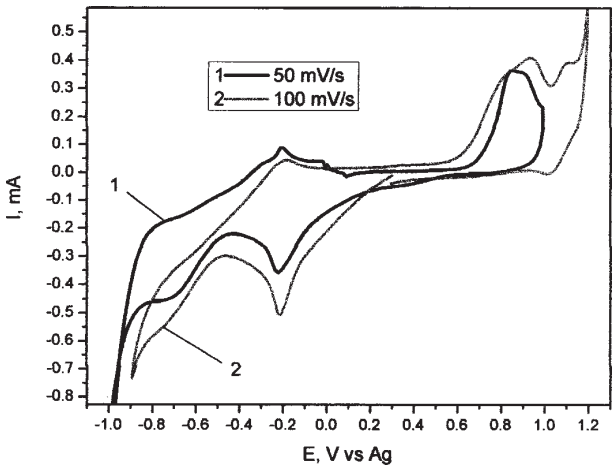

Fig. 3. CVs of Pt electrode (0.5cm^2) for ChCl-EG ionic liquid containing 5mM SeO_2 at 60^{0}C.

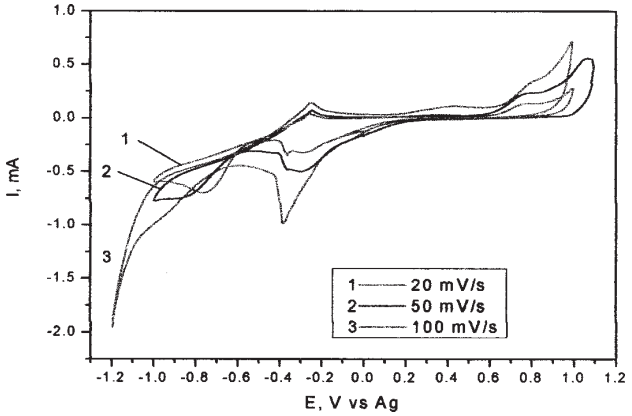

Fig. 4. CVs of Pt electrode (0.5cm^2) for ChCl-EG ionic liquid containing 10mM SeO_2 at 60^{0}C.

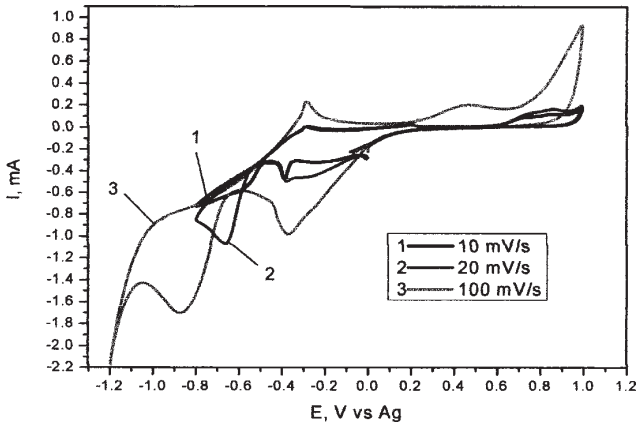

Fig. 5. CVs of Pt electrode (0.5cm^2) for ChCl-EG ionic liquid containing 20mM SeO_2 at 60^{0}C

In a tentative to interpret the obtained data for the main cathodic process:

$$Se(IV) + 4\,e \rightarrow Se(0)\,film \qquad (1)$$

this may be written as a simple discharge of complex anions $[SeCl_{4+x}]^{x-}$ with delivering corresponding number (4+x) of Cl^- anions. Gray selenium deposits and no obvious change of color were observed in the scanning process from open circuit potential to peak C1 on Pt electrode. The formation of gray selenium is probably favored by working temperature (60^{0}C) in both ionic liquids.

However, we must take into consideration, apart from Cl^- ions content, the existence in our ionic liquids of 3-5 wt.% water in the initial choline chloride, so the formation of H_2SeO_3 seleneous acid is possible to occur. Therefore, a direct discharge is expected in the cathodic process, according to the most used reaction shown in literature:

$$H_2SeO_3 + 4\,H^+ + 4e^- \rightarrow Se + 3\,H_2O \qquad (2)$$

It may be observed from reaction (2) that three water molecules are supplementary produced, thus enriching with water the ionic liquid medium. This fact is important in the Se electrodeposition using ionic liquids, thus favoring deposition of gray Se [35]. Also, the shape and the potential region for both cathodic and anodic peaks are different from those reported for Se ions in aqueous (nitrate or chloride) acid solutions [30]. The main reason for this disagreement could be the difference in chemical nature of electrolytes, aqueous or ionic liquid.

The second cathodic peak C2 can be related to a six-electron reduction of H_2SeO_3 to Se^{2-} species; this process was proposed by all authors in aqueous solutions and may be written according to eq. (3):

$$H_2SeO_3 + 6H^+ + 6e^- \rightarrow H_2Se + 3H_2O \qquad (3)$$

Eq. (3) may be justified if the electric charge for C2 process (the area under the peak C2) would be much higher than that involved in C1 process; although we did not determine this charge, the shape of voltammograms suggested this fact (see for instance fig. 5, CV for 100mV/s). As shown above, this couple C2/A2 is more reversible than C1/A1 couple.

The obvious differences in peak potential separation and peak shapes reveal that the reduction/oxidation processes of Se(IV) on Pt surface are all quite irreversible (from electrochemically point of view). However, we consider that these electrode processes are actually moderately irreversible with a percentage of peak separation, ΔE_p, due to a large non-compensated ohmic drop inside the ionic liquid.

In a quantitative analysis it can see that both cathodic peak currents (C1 and C2 currents) increase with scan rate and selenium ion concentration. Although the dependences with square root of scan rate of the peak currents in our experiments is not quite straightforward we determined approximately the diffusion coefficients of Se(IV) ion in both ionic liquids, assuming a diffusion-controlled deposition process of selenium. For this, we used the well-known Randles-Sevcik equation for a pure solid deposit [38]:

$$I_{pc} = 0.6401\,nFAc\sqrt{\frac{nF}{RT}\,v\,D} \qquad (4)$$

In eq.(4), n is the number of electrons changed in electrode process; F, R and T are the Faraday number, ideal gas constant and absolute temperature, respectively; A – the surface area of electrode; c – ion concentration; v –the scan rate; D – the diffusion coefficient of ionic species. From our data, and using in the above equation number of transferred electrons n=4 and peak currents for C1 process, we obtained a value of $4880\,\frac{A\,cm\,s^{1/2}}{mol\,V^{1/2}}$ for the ratio $\frac{I_{pc}}{A\,v^{1/2}\,c}$ in ChCl-urea ionic liquid, that corresponds to a value of 1.8×10^{-6} cm^2/s for the diffusion coefficient at 60^{0}C; this is a plausible value, with a conventional order of magnitude for diffusion coefficient. However, using the same procedure for ChCl-EG systems with three SeO_2 concentrations, non-satisfactory values (less than 10^{-7} cm^2/s) were obtained in all cases. The explanations may be

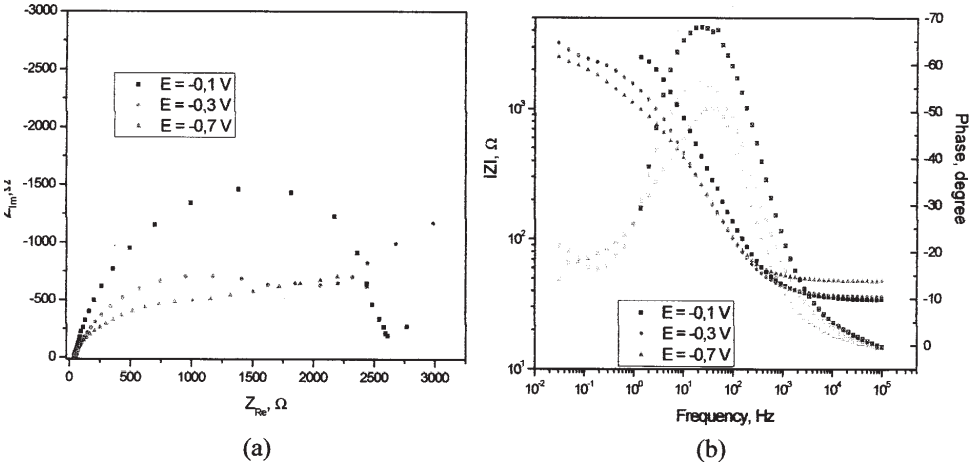

Fig. 6. Nyquist (a) and Bode (b) spectra obtained at various polarization potentials for Pt(0.07cm^2) / ChCl-urea eutectic with 5mM SeO_2 concentration; 60^{0}C

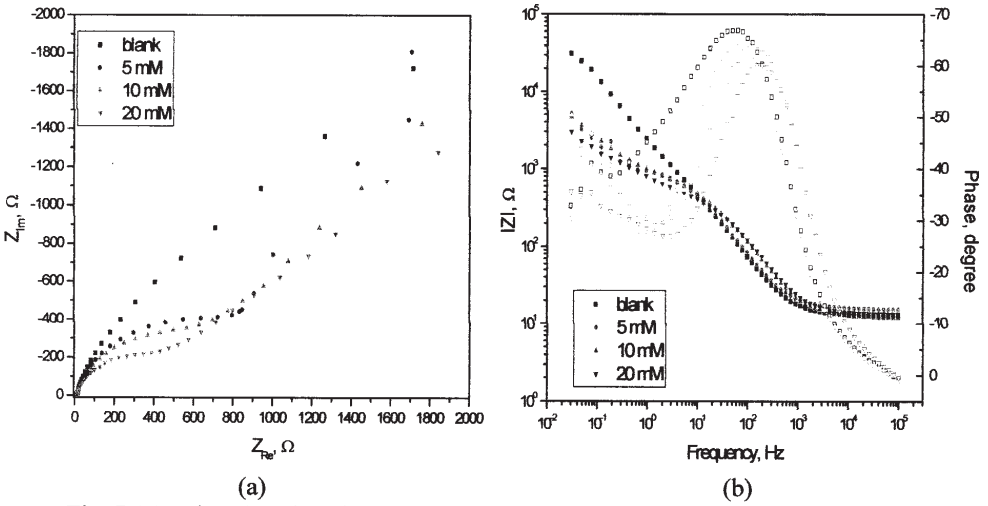

Fig. 7. Nyquist (a) and Bode (b) spectra obtained at -0.3V polarization potential for Pt(0.5cm^2) / ChCl-EG eutectic with various SeO_2 concentrations; 60^{0}C

related to the weaker solubility of SeO_2 in this system coupled with the more complex cathodic mechanism.

Results of applied EIS technique in ChCl-urea and ChCl-EG ionic liquids containing Se ionic species

The similar behaviour of selenium ion during cathodic deposition on Pt, in both cases of ChCl-urea and ChCl-EG ionic liquids used as electrolytes, is also revealed on the electrochemical impedance (EIS) spectra that can give us information about the rate of cathodic process and properties of films. We have obtained EIS diagrams by polarizing Pt electrode at various electrode potentials: first at potentials where the reduction process did not start (0÷-0.1V), then in the region of the reduction process with a significant cathodic current (-0.3÷-0.4V) and, finally, in the area of very negative values (-0.7V) where the massive metal deposition may interfer with cathodic reduction of blank electrolyte. Figures 6 show the recorded Nyquist and Bode (we have drawn both impedance modulus and phase angle *vs*. frequency dependences) diagrams in ChCl-urea ionic liquid.

The Nyquist spectrum recorded at -0.1V shows clearly a single capacitive semicircle for all frequencies, indicating a lack of any process except charging of double layer. The nondepressed shape of this semicircle demonstrates a good uniformity of platinum electrode surface used as cathode. A quite different shape is for Nyquist spectra at -0.3V and -0.7V polarizations where the capacitive semicircle in the region of high frequencies is followed by a linear dependence of imaginary part of impedance against the real part. This linear portion is shorter especially when the first nuclei of electrocrystallised metal occur forming a monolayer (at -0.3V). The semicircle diameter (that means the charge transfer resistance, R_{ct}) decreases gradually with polarization, demonstrating an increase of the rate (exchange current) of cathodic process. The large linear portion for more negatively polarized samples (-0.7V) is correlated with the thickening of film onto platinum electrode. Bode diagrams also prove the gradual decrease of the impedance modulus together with a decrease of phase angle from almost capacitive behaviour (almost -70^0) to quasi-diffusive behavior (-50^0).

Figures 7 demonstrate the Nyquist and Bode graphs for Pt/Se electrode in ChCl-EG system with various SeO_2 concentrations. A single polarization potential value (-0.3V) was selected to be published here, because all spectra recorded in ChCl-EG for other potentials (either more positive or more negative than -0.3V) show a very similar behaviour as cathodic processes in ChCl-urea ionic liquid. In Nyquist diagram, the gradually decrease of the semicircle diameter (diminution of the charge transfer resistance) with increasing SeO_2 concentration indicates the gradual increase of electrodeposition current. The large linear portions for lower frequencies are correlated with the thickening of stable selenium film onto platinum electrode, a process that is more significant in this system compared with ChCl-urea system.

The obtained Nyquist and Bode spectra were interpreted on the basis of an equivalent electrical circuit as electrochemical model of the interface, using a specialized fitting software Zview 2.90c. Figure 8 exhibits the proposed equivalent circuit used for fitting the experimental data. The resistances of this circuit are $\mathbf{R_s}$ -ohmic resistance of ionic liquid and charge transfer resistance, $\mathbf{R_{ct}}$, denoted in figure 8 as **R1**. The other components are **CPE1** - a constant phase element and **W1** – a Warburg diffusion impedance. **CPE1** impedance takes into account the deviation of

Table 1
VALUES OF THE CIRCUIT PARAMETERS FOR PT ELECTRODES (0.07 AND 0.5 cm^2) POLARIZED AT VARIOUS ELECTRODE POTENTIALS (E) IN ChCl-UREA AND ChCl-EG ELECTROLYTES WITH SeO_2 CONTENT; TEMPERATURE 60°C

Circuit element	ChCl-urea ionic liquid			ChCl-EG ionic liquid			
	Se 5mM E= -0.1V	Se 5mM E= -0.3 V	Se 5mM E= -0.7 V	Blank E= -0.3V	Se 5 mM E= -0.3 V	Se 10 mM E= -0.3 V	Se 20 mM E= -0.3 V
R_S, Ωcm^2	3	3	3	7	8	6	7
CPE1-T, μFcm^{-2}	305	1104	745	82	90	75	52
CPE1-P	0.87	0.77	0.84	0.90	0.88	0.90	0.89
R_{ct}, Ωcm^2	220	148	104	1604	587	488	350
W1-R, Ωcm^2	197	2393	208	11108	16074	17262	2840
W1-T, Hcm^2	0	125	1	1	5	67	16
W1-P	0.57	0.56	0.47	0.54	0.60	0.64	0.45

electrochemical double layer from pure capacitive behaviour and has the expression:

$$CPE1 = \frac{1}{T(j\omega)^P} \quad (5)$$

where T is the capacity element of CPE, ω – the angular frequency, j – the imaginary vector unit ($j=\sqrt{-1}$) and P – the CPE exponent. CPE acts as a pure capacitor when the exponent is unity, P = 1, and shows a pure diffusion behavior when P=0.5. The Warburg diffusion impedance has a similar expression with eq. (5), but with three components: W1-R (resistive part), W1-T (inductive part) and W1-P (the exponent).

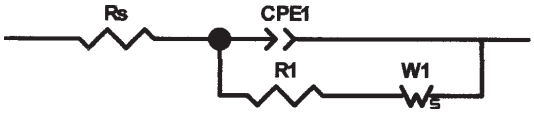

Fig. 8. Schematic representation of the electrical equivalent circuit diagram

Table 1 contains the values of equivalent circuit elements for the best fitting of experimental data obtained with Pt electrodes. As can be seen from this Table, the ohmic resistances of both ionic liquids have very low values, a fact that it is a characteristic feature for ionic liquids; however, the ChCl-urea system seems to be more conductive than ChCl-EG at the constant temperature (60°C). Values of the tents or hundreds microfarads per square centimeter were calculated for film/ionic liquid capacitances and values of P coefficient in a narrow range (P=0.8-0.9) show a low deviation from pure capacitor (P=1). We noticed that in both ionic liquids the charge transfer resistance decreases by shifting the electrode potential from stationary potential towards negative direction. At electrode potentials where the voltammetric peak is recorded, R_{ct} has a smaller value in ChCl-urea than in ChCl-EG; also, it decreases with SeO_2 concentration, proving an increase of the deposition current. Therefore, the EIS behaviour is in good agreement with behavior shown on CV curves. The values of Warburg components W1-R and W1-T did not allow any interpretation, but the values of W1-P exponent in the range 0.45-0.64 are very close to the theoretical ones for diffusion control of cathodic process (P=0.5).

Conclusions

The preliminary investigation by cyclic voltammetry and electrochemical impedance spectroscopy of selenium behavior showed that the cathodic process during the single deposition of Se films in ChCl-urea and ChCl-EG ionic liquids is a quasireversible process which is mainly controlled by diffusion. However, only for ChCl-urea system the voltammetric data at various scan rates allowed an estimation of the diffusion coefficients of plausible order of magnitude at 60°C temperature. The results of electrochemical impedance measurements showed that the cathodic process of selenium ions in ChCl-urea and ChCl-EG ionic liquids have almost similar characteristics.

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