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ELECTRODEPOSITION OF BISMUTH, TELLURIUM AND ANTIMONY FROM IONIC LIQUIDS BASED ON CHOLINE CHLORIDE AND UREA AS THERMOELECTRIC FILMS

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ABSTRACT. The aim of this work was to study the electrodeposition of Bi, Sb and Te as singular components of thermoelectric films using an ionic liquid medium (choline chloride + urea; 1:2 molar mixture). Ionic complex species ($BiCl_4^-$, $SbCl_4^-$ and $TeCl_6^{2-}$) were supposed as participant species at the cathodic process, and were prepared by dissolving BiO_2, $SnCl_3$ and TeO_2 in 0.5 - 10 mM concentrations. Cyclic voltammograms on Pt exhibited a single couple of reduction/ oxidation peaks at all scan rates (2 – 200 mVs^{-1}) and temperatures (40 – 85 ^{0}C). Values of diffusion coefficients and activation energy for diffusion were also estimated. Nyquist and Bode spectra, obtained from electrochemical impedance measurements, proved the diffusion control. By fitting the experimental data with an equivalent electrical circuit of modified Randles type the differences in double layer capacitances and also in charge transfer resistances for the three cathodic processes of Bi, Sb or Te ions were evidenced.

Keywords: electrodeposition, bismuth, antimony, tellurium, cyclic voltammetry, electrochemical impedance spectroscopy

INTRODUCTION

Bi and Sb are elements of Vth group with relatively good electrical properties and a superposition of valence and conduction bands; tellurium is a semiconductor belonging to VIth group. All these elements are involved in preparation of binary or ternary thermoelectric materials. The increase of Sb content in BiSb solid solution leads to enlargement of band gap and to diminution of thermal conduction, thus improving its thermoelectric behavior. BiSb alloys are very attractive materials for thermoelectric refrigeration at low temperature (below 200K). Bismuth and antimony telluride-based materials are of great interest for thermoelectric applications in the temperature range of 200-400 K, whereas BiSbTe ternary compound (written sometimes as Bi_2Te_3-Sb_2Te_3 mixture) is the best for both thermoelectric refrigeration and thermoelectric power generation [1-3].

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In addition to bulk thermoelectric materials, which are processed by solidification methods or powder metallurgy, films varying from sub-micron to several microns thick have been studied, because of their potential applications in miniature thermoelectric devices and thermobatteries. In general, the thermoelectric films are fabricated by chemical or physical vapor deposition. Compared to these techniques, the electrodeposition may offer some advantages, including it cost-effectiveness, rapid deposition rates, and relative ease in controlling film thickness.

In last years ionic liquids were increasingly applied for electrochemical deposition of numerous metals on various substrates [4], replacing the traditional baths of aqueous solutions. An ionic liquid as solvent in the electrodeposition bath shows a good electric conductivity, a large potential window as well as a high thermal stability. From literature examination, we noticed that experiments with electrodeposition of tellurium, bismuth or antimony as pure metals or their compounds using ionic liquid media are relatively seldom reported. Historically, most of such electrochemical studies employed imidazolium salts [5,6] or molten chloroaluminates [7] as electrolytes.

Recently, we reported [8] results on film codeposition of Te with Bi and Sb (as binary compounds) using a bath consisting in the eutectic of choline chloride (**ChCl**) and urea as supporting electrolyte, with additions of Bi oxide or Sb chloride, respectively. To our best knowledge such processes in ChCl containing ionic liquids have not been yet reported. The choice of ChCl-urea system was related to the works of Abbott *et al*. who showed [8] that an ionic liquid can be formed by mixing choline chloride (2 hydroxy-ethyl-trimethyl-ammonium) with a hydrogen bond donor species such as an amide (urea).

The electrochemical procedure of thermoelectric material deposition reported here is environmentally friendly compared with the conventional methods of deposition using aqueous baths and also compared with other ionic liquids used as deposition baths. We found out that Bi, Sb and Te precursors (in our experiments BiO_2, $SbCl_3$, TeO_2, respectively) dissolve relatively easy in ChCl-urea eutectic and we performed electrolysis experiments at 40 - 85^0C using this electrolyte. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were chosen as electrochemical techniques in order to evidence processes of deposition/ dissolution of Bi, Sb and Te.

RESULTS AND DISCUSSION

Regarding the relatively high solubility of bismuth, antimony and tellurium compounds in ChCl-urea (1:2) ionic liquid in such amounts to have a significant electrochemical response for Bi(III), Sb(III) and Te(IV) ions, an explanation may be the presence of chloride anion Cl^- as ligand forming complexes. For instance, by dissolution of bismuth oxide and antimony chloride precursors in the electrolyte we suppose the formation of $BiCl_4^-$ and $SbCl_4^-$ complex ions in ChCl-urea eutectic, leading to a low diffusive ionic species [8]; correspondingly, tellurite TeO_2 should be converted in tellurium chloride and incorporated in ionic liquid as $[TeCl_{4+x}]^{x-}$ ions with low diffusion coefficients, too [6]. Similar situation was suggested for zinc chloride dissolved in quaternary ammonium halides [10] which forms complex chlorozincate anions, $ZnCl_3^-$, $Zn_2Cl_5^-$ and $Zn_3Cl_7^-$. The existence of $BiCl_4^-$ and $SbCl_4^-$ ions in very concentrated aqueous chloride electrolytes (6M HCl or 5M NaCl + 1M HCl solutions) was supposed in our previous work [11].

Cyclic voltammetry measurements were carried out, within 40 - 85^{0}C temperature range, in order to investigate the electrochemical reversibility of electrode process and the appropriate potential range for electrodeposition/ dissolution of single metal films. Typical cyclic voltammograms of the separately investigated ions recorded on Pt electrode in the absence of solution stirring are presented in Figures 1-3. We selected the CV curves at various scan rates which were obtained by sweeping the potential from stationary potential in cathodic direction (until -0.8 V limit) and returning to anodic region (a limit of maximum 0 V) and back. The CVs with enlarged potential range did not show any supplementary electrode process except the cathodic and anodic processes of background electrolyte.

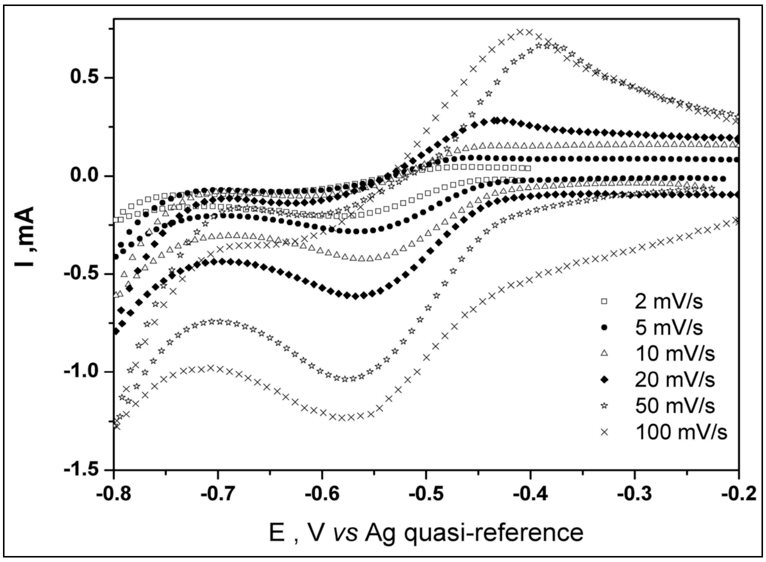

Figure 1. Cyclic voltammograms of Bi(III) ions on Pt electrode in ChCl – urea eutectic; Bi(III) concentration: 10 mM; temperature 80 ^{0}C.

During the examination of the electrochemical behavior of Bi ionic species (Fig. 1) only a couple of reduction/oxidation peaks can be observed at all scan rates. At lowest scan rate and 80^{0}C temperature the cathodic peak and the anodic peak are located at potentials -0.53 V and -0.43 V *vs.* Ag quasi-reference electrode, respectively. With higher scan rates the peak separation for this couple, ΔE_p, increases from 100 mV to *cca.* 200 mV. Similar results were also found in the CVs recorded in Sb(III) and Te(IV) containing solutions (Figs. 2 and 3). As Fig. 2 shows, for Sb(III) containing ionic liquid and 80 ^{0}C temperature the reduction/oxidation peaks are located at potentials -0.6 V and -0.53 V, respectively, and the corresponding peak separation, ΔE_p, recorded for various scan rates ranged in a larger potential interval, 70 - 300 mV. For either Bi ions or Sb ions the metallic film formation may take place as:

$$\underset{(SbCl_4^-)}{BiCl_4^-} + 3\,e^- \rightarrow \underset{(Sb^0)}{Bi^0} + 4\,Cl^- \qquad (1)$$

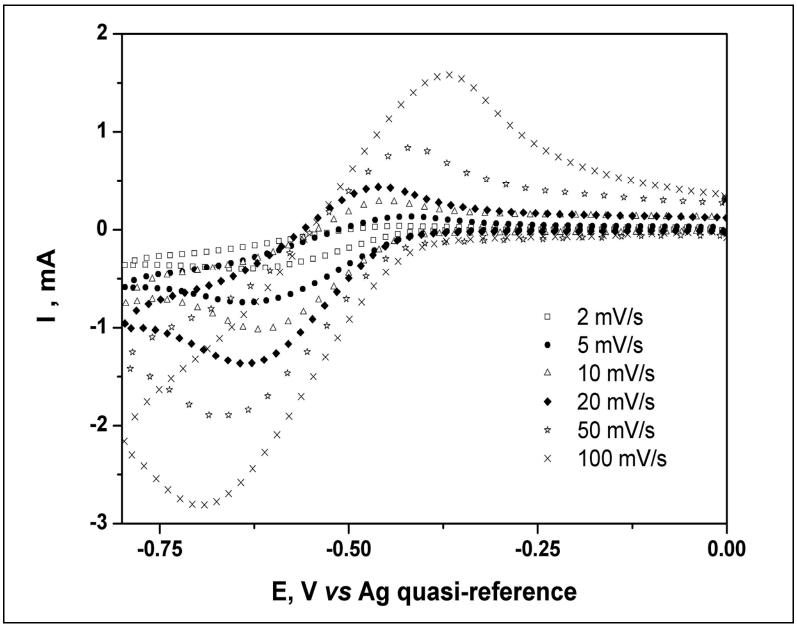

Figure 2. Cyclic voltammograms of Sb(III) ions on Pt electrode in ChCl – urea eutectic; Sb(III) concentration: 10 mM; temperature 80 ^{0}C.

In the example illustrated by Fig. 3, the voltammetric curves at 70 ^{0}C temperature for Te ion reduction on Pt show a single reduction peak (*e.g.* at potential about -0.6 V for 10 mVs^{-1} scan rate) attributed to deposition of tellurium film; also a single anodic peak (*e.g.* about -0.38 V for 10 mVs^{-1} scan rate), corresponding to the stripping of deposit, was recorded. So, a direct discharge of $[TeCl_{4+x}]^{x-}$ ions, written $TeCl_6^{2-}$ as the most probable anion [6], is expected in the cathodic process:

$$TeCl_6^{2-} + 4e^- \rightarrow Te + 6Cl^- \qquad (2)$$

The increase of scan rate gives rise to a peak separation values for Te(IV)/Te couple within 200 - 280mV potential interval.

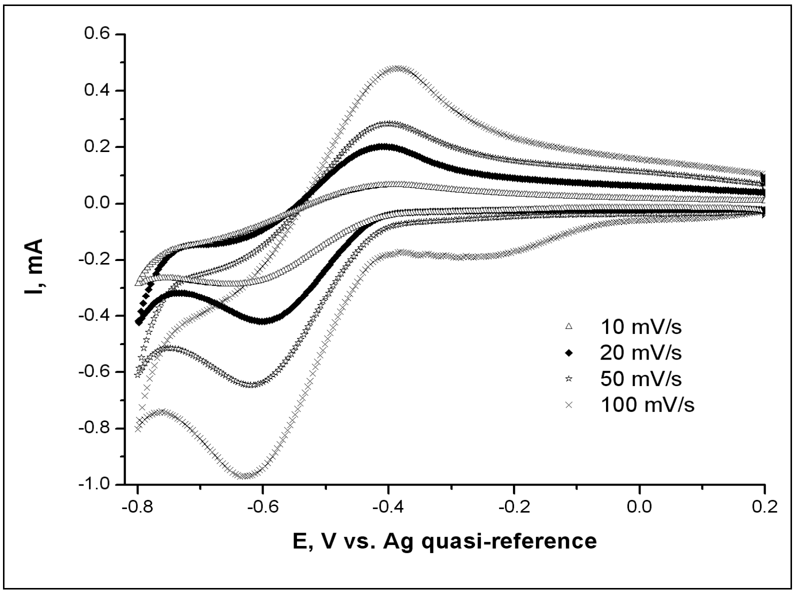

Figure 3. Cyclic voltammograms of Te(IV) ions on Pt electrode in ChCl – urea eutectic; Te(IV) concentration: 5.5 mM, temperature 70 ^{0}C

The above observations of CV shapes are valid at all investigated ion concentrations and working temperature. The cathodic peaks representing the formation of Bi^0, Sb^0 and Te^0 have a shape with a relatively large diffusion current if the applied potential was more negatively. The oxidation peaks on the anodic branches of voltammograms correspond to redissolution of freshly deposited metallic layer. The peak potential separation and peak shapes reveal that the reduction/oxidation processes of Bi(III), Sb(III) and Te(IV) on Pt surface are all quite irreversible (from electrochemically point of view). However, we consider that these electrode processes are actually moderately irreversible, due to a quite large contribution in the potential peak separation of a non-compensated ohmic drop inside the ionic liquid.

It may be observed from reactions (1) and (2) that four or six chloride ions are supplementary produced, thus enriching the ionic liquid medium with complexing agent. This fact is important in alloy electrodeposition, because complexation brings the reduction potentials of bismuth, antimony and tellurium ions close to each other, favouring their co-deposition. In the investigated ionic liquid the underpotential deposition (UPD) of Bi, Sb or Te was rarely noticed. Also, the shape and the potential region for both cathodic and anodic peaks are different from these reported for Bi, Sb and Te ions in aqueous (nitrate or chloride) acid solutions [11]. The main reason for this disagreement could be the difference in chemical nature of electrolytes, aqueous or ionic liquid.

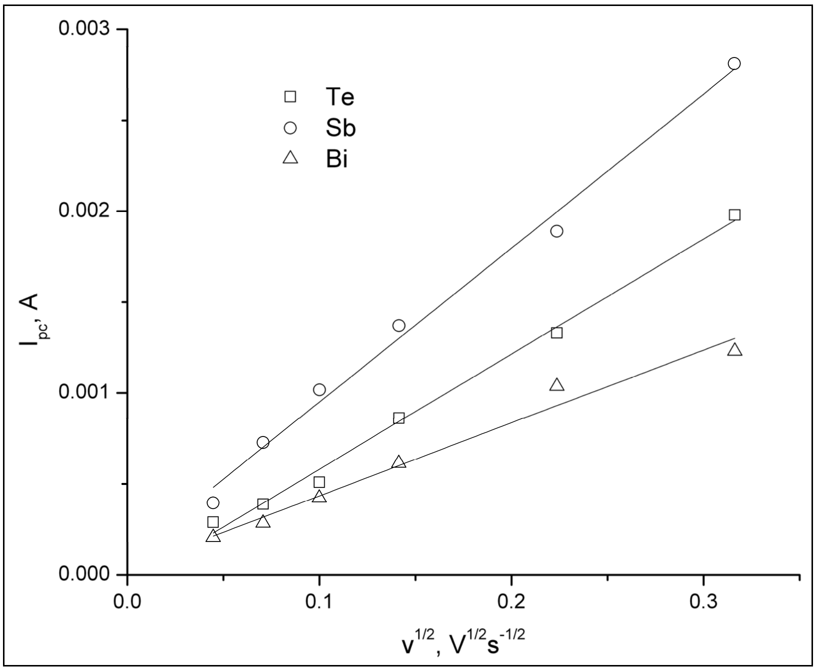

Figure 4. I_{PC} *vs.* $v^{1/2}$ dependence for Bi, Sb, Te electrodeposition on Pt in ChCl – urea eutectic at 80^0 C; the same 10 mM concentration for all three ions: Bi(III), Sb(III) and Te(IV) ions.

In a quantitative analysis of CVs, it can see that both cathodic and anodic peak currents increase with the potential scan rate and temperature. As Figure 4 shows, linearly dependences of cathodic current (I_{pc}) with square root of scan rate ($v^{1/2}$) are obtained in all three cases, proving a diffusion-controlled deposition process. This fact allowed calculation of the diffusion coefficients of Bi(III), Sb(III) or Te(IV) ionic species, using the well-known Randles-Sevcik equation for a metal deposition [14]:

$$I_{pc} = 0.6401\, n F A c \sqrt{\frac{nF}{RT} v D} \qquad (3)$$

In Eq.(3), 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; v – the scan rate; D – the diffusion coefficient of ionic species. Using the above equation reliable results for diffusion coefficient may be obtained by performing a series of CV experiments with various ion concentrations and scan rates under a severe control of temperature. From our preliminary investigations we obtained D values for Bi, Sb or Te ionic species of the order of 10^{-7} - 10^{-5} cm^2s^{-1}. For instance, we found at 353 K a diffusion coefficient D = 1.75×10^{-7} cm^2s^{-1} for Te(IV) species, taking number of transferred electrons n = 4 [8]; similarly, D values of the order of 10^{-6} cm^2s^{-1} were obtained for Bi(III) or Sb(IIII) species, with higher D values for antimony species. However, this order of magnitude for diffusion coefficient at 353 K is generally much lower than in aqueous solutions (D about 10^{-5} cm^2s^{-1}), a fact which is expected for diffusion in such ionic liquid media having higher viscosity and density than aqueous media.

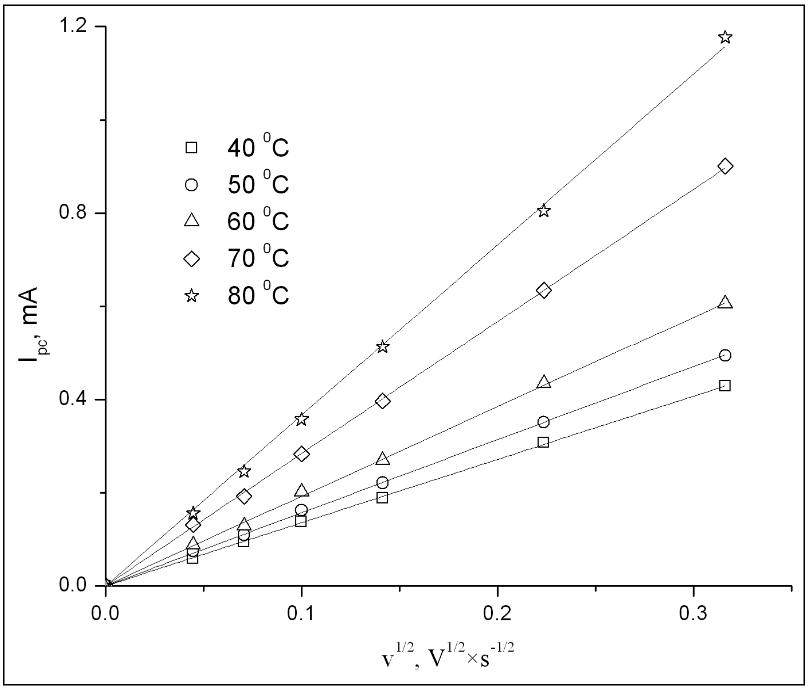

Figure 5. I_{PC} *vs.* $v^{1/2}$ for Sb deposition on Pt in ChCl – urea eutectic at various temperatures; Sb(III) concentration = 5 mM

Regarding the influence of temperature upon the diffusion coefficient an Arrhenius exponential dependence was found, from which the activation energy for diffusion was estimated. As examples, Figs. 5 and 6 present I_{PC} *vs*. $v^{1/2}$ straightlines as well as ln D *vs*. 1/T Arrhenius dependence for Sb deposition at various temperatures, using a constant Sb(III) ion concentration in ChCl-urea eutectic. Similar behavior was noticed for all three investigated ions in the same ionic liquid. In general, the obtained values of $E_{activation}$ ranged within 50 - 100 kJ/mole interval, with higher value for Te ions, this being probable due to the differences in ionic radius.

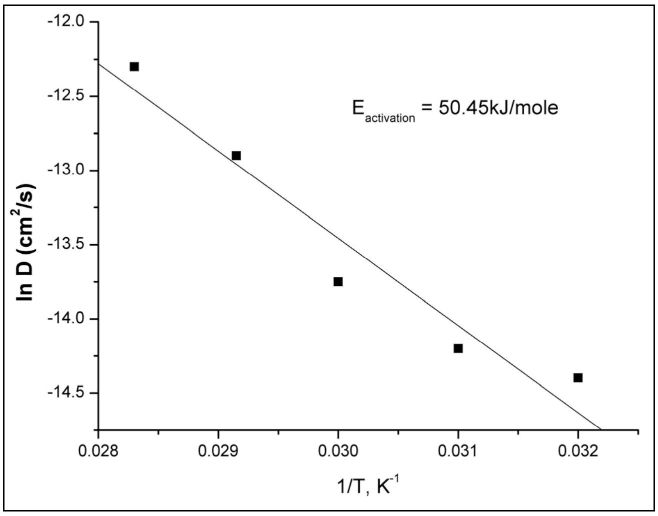

Figure 6. Arrhenius dependence of diffusion coefficient for Sb(III) ion, in *ln D vs. 1/T* coordinates; Sb(III) concentration = 5.5 mM

The differences in Bi, Sb and Te behavior during cathodic deposition on Pt using ChCl-urea ionic liquid are also revealed on the electrochemical impedance (EIS) spectra that can give us information about the cathodic process and properties of films. Figures 7 - 9 show Nyquist and Bode diagrams obtained at various electrode potentials, the temperature being 80 ^{0}C. During the experimental procedure, the potential of the cathode was consecutively maintained at increasingly negative values: first at potentials where the reduction process does not start (-0.3 ÷ -0.35 V), then in the region of beginning the process, reaching the maximum cathodic current (-0.4 ÷ -0.5 V) and, finally, in the area of massive metal deposition (-0.6 ÷ -0.7 V).

The Nyquist spectra show clearly capacitive semi-circles in the region of high frequencies, followed by a linear dependence of imaginary part of impedance against the real part. The shape of depressed semi-circles may be attributed to the non-uniformity of platinum electrode surface used as cathode, especially when the first nuclei of electrocrystallized metal occur forming a monolayer, which is then thickened. The large linear portions for more negatively polarized samples are correlated with the thickening of film onto platinum electrode. The gradually decrease of the semi-circle diameter (diminution of the charge transfer resistance), if the electrode potential is more negative, indicates the increase of electrodeposition current.

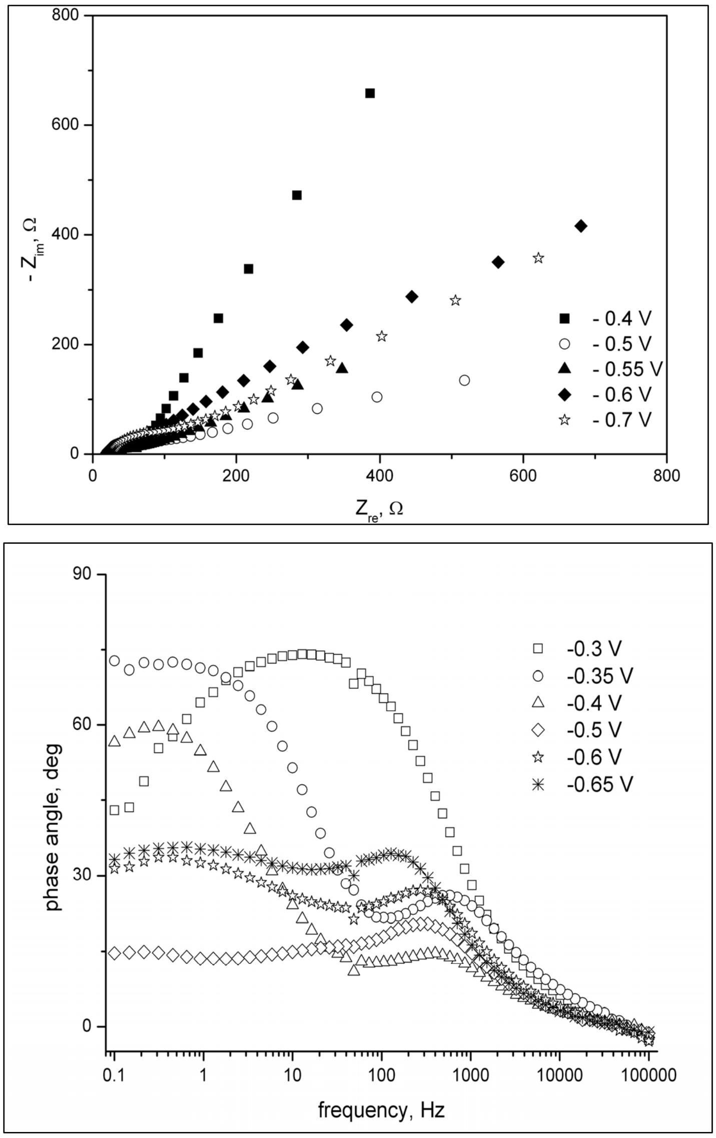

Figure 7. Nyquist and Bode spectra obtained at various potentials on Pt (0.5 cm^2) in ChCl-urea eutectic + 10 mM Bi_2O_3; 80 ^{0}C

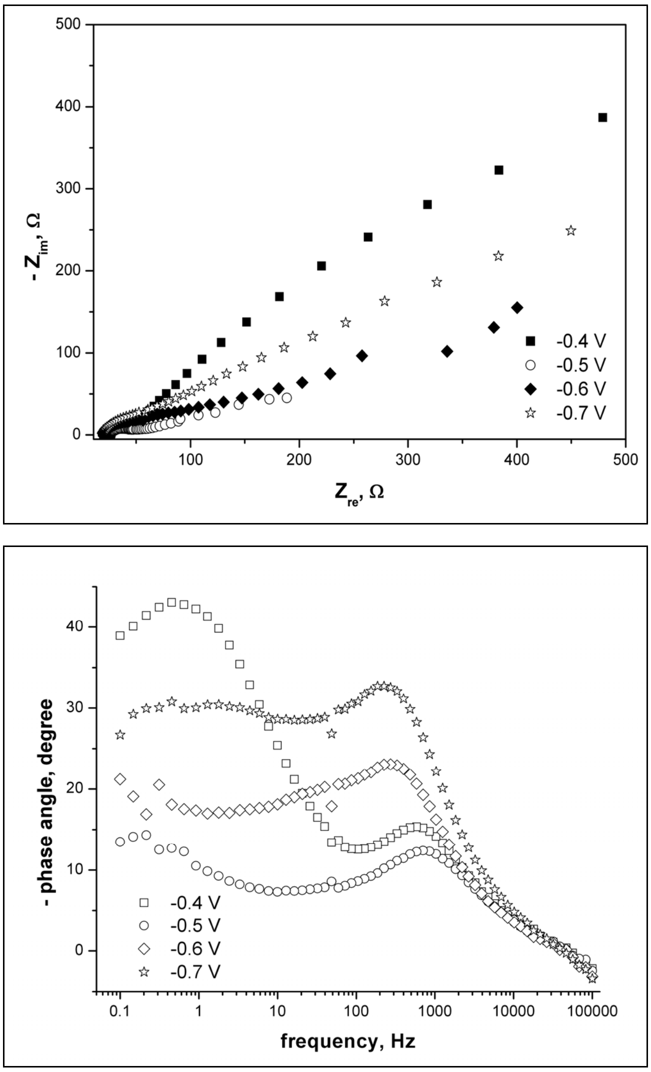

Figure 8. Nyquist and Bode spectra obtained at various potentials; Pt/ ChCl-urea eutectic + 10 mM $SbCl_3$; 80 ^{0}C

The same behavior by polarizing Pt electrode at various electrode potentials is evidenced in Bode diagrams (we selected the phase angle *vs.* frequency dependence, only). In Fig. 7 the phase angle at -0.3 V shows a single maximum around -75^0, meaning a significant capacitive behavior when Bi deposition does not start. For more negative potentials, this maximum shifts toward higher frequencies and diminishes drastically together with occurrence of a new maximum located at low frequencies that may be attributed to Bi film formation. Phase angle of -60^0 means an intermediate behavior between capacitive and diffusion response, whereas the values of -20^0 and less illustrate the massive deposition. Bode spectra for Sb and Te ions show the same characteristics; however, the variation of phase angle in Fig. 9 indicates a Te deposition already at -0.4 V and a less electrical conductive deposit.

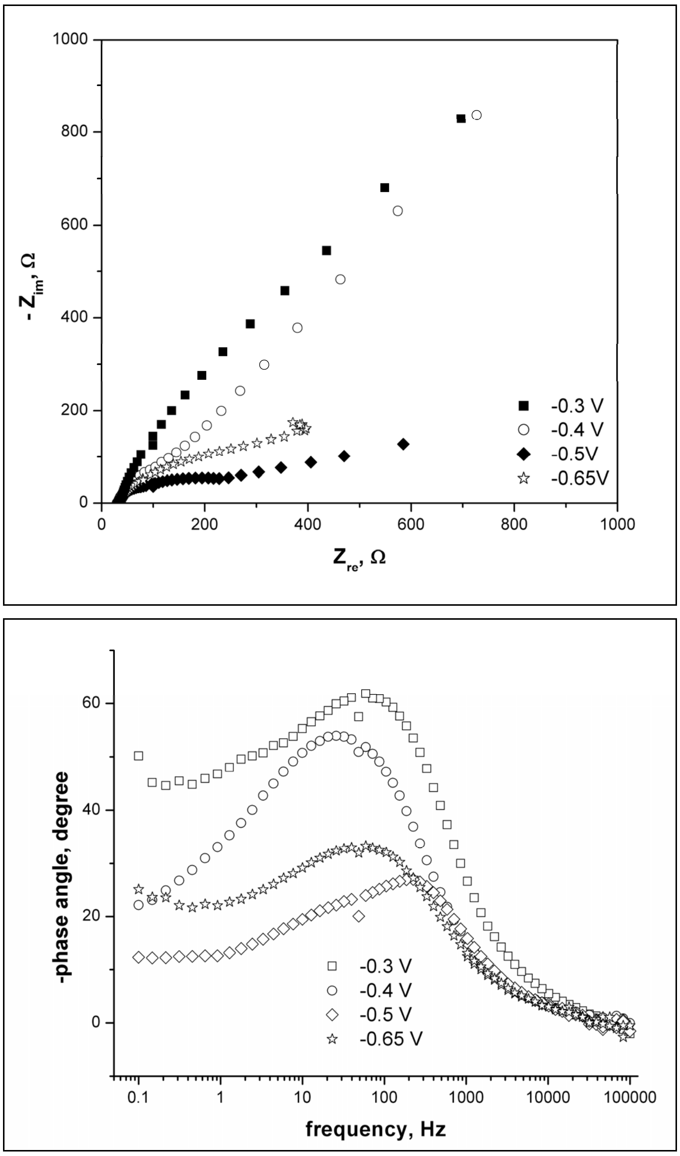

Figure 9. Nyquist and Bode spectra obtained at various potentials; Pt/ ChCl-urea eutectic + 10 mM TeO_2; 80 ^{0}C

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 (Scribner Assoc.).

Figure 10 exhibits the proposed equivalent circuit used for fitting the experimental data. The elements of this Randles modified circuit are: R_s -ohmic resistance of electrolyte solution; C_1 -film capacitance in a parallel combination with the film resistance (R_1) and a second parallel combination consisted in a constant phase element (CPE_2) and charge transfer resistance (R_2). The constant phase element CPE_2 takes into account the deviation of electrochemical double layer from pure capacitive behavior and has the expression:

$$CPE_2 = \frac{1}{T(j\omega)^P} \qquad (4)$$

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 behaviour when P=0.5.

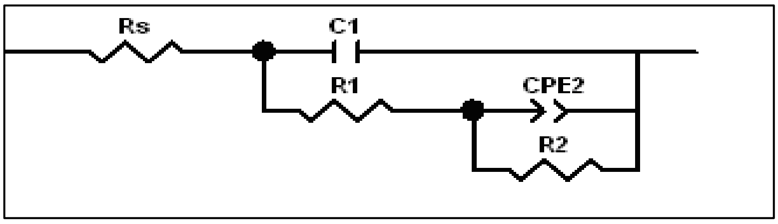

Figure 10. Schematic representation of the electrical equivalent circuit diagram; the used symbols are presented in text

Table 1 contains the values of the equivalent circuit elements for the best fitting of experimental data. As can be seen from this Table, the ohmic resistance of ionic liquid has, as expected, a constant value for a given temperature (80 ^{0}C). Values of the same order of magnitude were recorded for film/ionic liquid capacitances and film resistances in various polarization states. Values of P in a narrow range (P= 0.43 - 0.65) show the diffusion control of cathodic process. However, there are differences in behavior of electrochemical double layer of Bi, Sb or Te interfaces (CPE-T values), explained by different semiconductor properties after massive deposition of films. Also, it is obvious that in all three cases the charge transfer resistance (R_2) decreases by shifting the electrode potential towards negative direction until the voltammetric peak is recorded; the subsequent increase of R_2 occurs at potentials corresponding to the diffusion limiting current zone. Therefore, the EIS behavior is in good agreement with CV curves.

Table 1. Values of the circuit parameters for Pt electrode (0.5 cm^2) polarized at various electrode potentials (E); temperature 80 ^{0}C

Ion	Values of electrical circuit elements						
	E, V	**Rs,** Ω	**C1**, μF	**R1,** Ω	**CPE-T**, μF	**CPE-P**	**R2,** Ω
Bi	-0.3	14.9	9.34	8	50	0.79	23720
	-0.35	14.6	12.61	28	300	0.88	8760
	-0.4	30.8	14.96	30	820	0.80	6340
	-0.5	26.3	14.07	20	2800	0.43	570
	-0.6	19.3	16.86	27	1600	0.54	1960
	-0.65	23.8	18.65	40	1000	0.52	3950
Sb	-0.3	17.0	15.09	61	247	0.88	25530
	-0.4	23.7	13.11	18	1775	0.64	1600
	-0.5	26.9	12.73	16	6200	0.48	253
	-0.6	20.9	15.13	15	1980	0.38	57
	-0.7	14.5	16.34	16	1940	0.44	2280
Te	-0.3	15.8	10.65	4	100	0.66	26770
	-0.4	31.5	11.39	90	300	0.65	37960
	-0.65	34.5	12.42	62	500	0.51	554

CONCLUSIONS

The cyclic voltammograms and electrochemical impedance spectra showed that the cathodic process during the single deposition of Bi, Sb or Te films in an ionic liquid medium (choline chloride + urea, 1:2 molar mixture) is mainly controlled by diffusion. Only a couple of reduction/oxidation peaks was observed at all scan rates and temperatures, involving ionic complex species ($BiCl_4^-$, $SbCl_4^-$and $TeCl_6^{2-}$) as participants. The diffusion coefficients have values of 10^{-7}-10^{-5} cm^{2}s^{-1} and activation energies for diffusion are of the order of tens kJ/mole. The results of electrochemical impedance measurements showed that Bi, Sb or Te films have almost similar semiconductor characteristics with a faster process for Sb deposition.

EXPERIMENTAL SECTION

The preparation of choline chloride+urea ionic medium, cell and electrochemical procedures were described elsewhere [8,12,13]. The supporting electrolyte was prepared by mixing choline chloride (Aldrich) with urea (Aldrich) in 1:2 molar proportions at above 90^{0}C for 30 min. The working solutions were made by dissolution of bismuth oxide, antimony chloride and tellurium dioxide (all reagents purchased from Alfa Aesar) as precursors of Bi(III), Sb(III) or Te(IV) ionic species. Concentrations in molarities were found in 0.5 to 11 mM range by using density values for ChCl-urea eutectic of 1.131-1.134 gcm^{-3}, determined in our laboratory within working temperature range (40 – 85 ^{0}C). The working electrode was a Pt sheet (0.5 cm^2), the auxiliary electrode was a cylindrical gauze of Pt, whereas the quasi-reference electrode was a Ag wire immersed in the same electrolyte. Cyclic voltammetry and electrochemical impedance spectroscopy investigations were controlled by a Zahner Elektrik IM6e potentiostat provided with a frequency analyzer (FRA). The scan rates in recorded voltammograms were in 2 - 100 mVs^{-1} range and in the impedance study a.c. voltage has frequencies between 10^5 and 10^{-2} Hz with amplitude of ± 10 mV.

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