

## VOLTAMMETRIC AND IMPEDANCE STUDIES OF ELECTRODEPOSITION OF Te AND ITS BINARY COMPOUNDS WITH Bi AND Sb USING *CHOLINE CHLORIDE – UREA* BASED ELECTROLYTE

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Cyclic voltammetry and AC impedance techniques were used to investigate electrode processes of Te, Bi, and Sb ions (introduced as TeO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, SbCl<sub>3</sub> precursors) on Pt electrode in a ionic liquid consisting in choline chloride – urea (1:2 moles) eutectic as electrolyte. The concentrations (mM) of precursors in the experiments were: 10.91 TeO<sub>2</sub>, 5.42 Bi<sub>2</sub>O<sub>3</sub> + 5.45 TeO<sub>2</sub>, and 3.62 SbCl<sub>3</sub> + 7.27 TeO<sub>2</sub>, respectively. The working temperature was kept constant at 80°C. Cyclic voltammograms showed redox couples corresponding to cathodic deposition and anodic dissolution of Te, Bi-Te or Sb-Te. Their cathodic peak currents increase with square root of scan rate, thus proving a diffusive controlled electrode process for all systems. The processes of Te deposition, as well as BiTe and SbTe co-deposition, were also evidenced by electrochemical impedance spectroscopy (Nyquist and Bode diagrams) performed in the same conditions of concentration and temperature.

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### 1. Introduction

In the recent years, room temperature ionic liquids are increasingly applied for electrochemical purposes; thus, the electrodeposition of numerous metals and alloys has been demonstrated using a variety of ionic liquids with both discrete and complex anions [1,2]. The advantages of these novel baths include: electroplating of electronegative metals, *e.g.* Al, Ta, Nb, Mo, W and even of metals on water sensitive substrate materials such as Mg; significantly reduced hydrogen evolution as compared with the acidic aqueous baths conventionally employed, leading to avoidance of hydrogen embrittlement; easy to achieve alloy deposition; lower electrical energy consumption comparing with aqueous solutions. Ionic liquids show electric conductivity due to their complete ionic structure, are electrochemically robust with a large potential window and have an extremely low vapour pressure. The thermal stability of the ionic liquid is useful to obtain crystalline semiconductor films through direct electrodeposition at higher temperatures without subsequent annealing.

Thermoelectric materials convert thermal to electrical energy and *vice versa* with high efficiency, making them ideally suited to power generation in satellites and microcoolers for computers or electronic microdevices. The excellent features of devices are no moving parts, environmental benign, high reliability and long operation life. Bismuth telluride, Bi<sub>2</sub>Te<sub>3</sub> and its ternary compounds with antimony or selenium are the most widely used thermoelectric materials for room temperature applications [3]. Actually, antimony telluride acts as dopant in Bi<sub>2</sub>Te<sub>3</sub> to form p-type (Bi<sub>1-x</sub>Sb<sub>x</sub>)<sub>2</sub>Te<sub>3</sub> solid solution. Both Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> compounds can be synthesized

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as thermoelectric films by electrodeposition, providing an alternative process to classical methods (crystallisation, evaporation, metallurgical). We mention that the electrodeposition in aqueous electrolytes of  $\text{Bi}_2\text{Te}_3$  has mostly been carried out from nitric acid baths [4-7]; aqueous solutions containing hydrochloric acid [8], perchloric acid [9, 10] and alkaline (diphosphate) [11] electrolytes were also used recently.

Examples of the electrodeposition of tellurium, bismuth or antimony as pure metals or their compounds from ionic liquid media are relatively fewer, in spite of the possibility of a their nanoscale fabrication [12]. Historically, most of such electrochemical studies that were carried out in ionic liquids employed molten chloroaluminates [13] and imidazolium salts [14,15]. It has recently been shown that a ionic liquids can be formed as eutectic mixture of a quaternary ammonium salt (such as choline chloride, with formula: 2 hydroxy-ethyl-trimethyl-ammonium, **ChCl**) with a hydrogen bond donor species (such as a glycol, amide or carboxylic acid). Very promising is a ionic liquid consisting in choline chloride:urea (1:2 moles) eutectic, that can be used as electrolyte for various electrochemical processes.

We propose in the present work to report the film deposition of Te and its binary compounds with Bi and Te using the eutectic of choline chloride and urea as supporting electrolyte; we mention that such films were not reported in literature as cathodic deposits in ChCl containing media. The electrochemical procedure of metallic material deposition applied by us is an environmentally friendly method compared with the conventional methods of deposition using aqueous baths, because of replacement of many hazardous and toxic materials currently used in galvanic industry and the bath is air and moisture stable, biodegradable and economically viable to large-scale processes..

In spite of the lack of data of solubility of inorganic salts, it is expected for Te, Bi and Sb precursors to dissolve in a large amount in ChCl based ionic liquids. It was shown [15] that  $\text{TeCl}_4$  dissolve readily in 1-ethyl-3-methylimidazolium chloride/tetrafluoroborate (EMI-Cl- $\text{BF}_4$ ) in the range 80-140 $^\circ\text{C}$ , whereas a Bi compound in the form of  $\text{Bi}(\text{NO}_3)_3$  dissolves in ChCl [16]. Also, it was investigated a mixture of 1-butyl-1-methylimidazolium chloride ( $\text{C}_4\text{MIM}$ ]Cl) with  $\text{ZnCl}_2$  (45:55 molar ratio) as a ionic liquid electrolyte in which  $\text{SbCl}_3$  was dissolved and Sb film may be electrodeposited [17]. In the present study,  $\text{TeO}_2$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{SbCl}_3$  were dissolved in ChCl:urea (1:2 moles) eutectic and electrolysis experiments were performed. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were chosen as electrochemical techniques in order to evidence electrochemical couples of deposition/ dissolution of Te, Bi-Te, and Sb-Te, respectively.

## 2. Experimental details

The background electrolyte was prepared by mixing choline chloride (Aldrich 99%, used as purchased, without being recrystallized or dried) with urea (Aldrich 99%); by heating the two components in 1:2 molar proportions at above 80 $^\circ\text{C}$  for 30 min, a homogeneous colourless liquid is formed.  $\text{TeO}_2$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{SbCl}_3$  reagents (99%, Alfa Aesar) as precursors of  $\text{Te}^{4+}$ ,  $\text{Bi}^{3+}$  and  $\text{Sb}^{3+}$  ions were also used as received, being dissolved in the supporting electrolyte ChCl-urea. In order to calculate the solution molarities we used a density value of ChCl-urea of 1.13398  $\text{g cm}^{-3}$ , determined in our laboratory at 80 $^\circ\text{C}$  working temperature.

The electrochemical cell was connected to a Zahner elektrik IM 6e potentiostat driven by PC computer and provided with a frequency analyzer (FRA). A platinum sheet (0.5  $\text{cm}^2$ ) was used as working electrode, whereas the auxiliary electrode was a platinum mesh. A silver wire immersed in the working electrolyte constituted in ionic liquid containing tellurium and/or bismuth (or antimony) ions was the quasi-reference electrode [6]. The Pt working electrode was polished with alumina paste, rinsed and dried before every measurement. The cyclic voltammograms were recorded at various scan rates from 2 to 100  $\text{mVs}^{-1}$ . EIS characterization was carried out in 10 $^{-1}$  Hz  $\leq f \leq 10^5$  Hz frequency range with an *ac* voltage amplitude of  $\pm 5$  mV; the impedance of Pt cathode polarized gradually in the range of -0.25  $\div$  -0.75 V (vs. Ag quasi-reference electrode) was determined. 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.). Both voltammetric and EIS experiments were performed at 80°C constant temperature.

### 3. Results and discussion

#### 3.1 Cyclic voltammetry

A typical cyclic voltammogram of  $\text{Te}^{4+}$  ions in ChCl-urea (1:2) eutectic recorded on Pt electrode for a large domain of potentials (from +1.2 to -1.2 V and back) is shown in Figure 1. It may be determined a *potential window* of more than 2V for supporting electrolyte, which is about 2 times wider in comparison with similar parameter of aqueous solutions (1.23V).

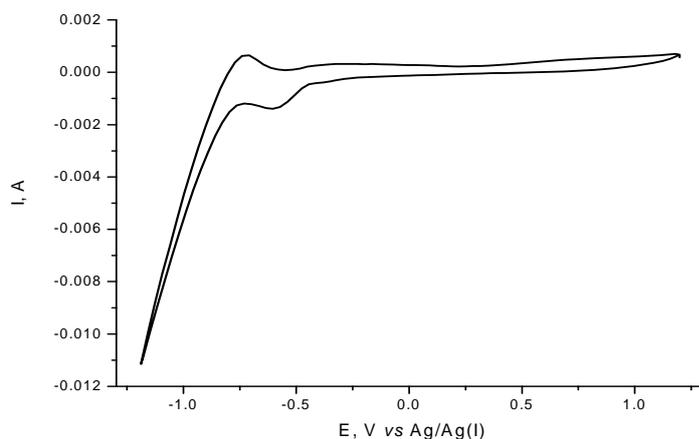


Fig. 1. Cyclic voltammograms within extended potential range on Pt ( $0.5 \text{ cm}^2$ ) for  $10.9 \text{ mM TeO}_2$  dissolved in ChCl-urea (1:2 moles) eutectic; scan rate  $50 \text{ mVs}^{-1}$ ; temperature  $80^\circ\text{C}$

Fig. 2 shows a series of voltammograms on Pt for the same ionic liquid containing  $10.9 \text{ mM TeO}_2$ , but in a limited (more narrow) potential domain. Only a single couple of reduction/oxidation peaks can be seen from both Figures 1 and 2, the electrochemical processes being assigned to deposition of Te film and its stripping from Pt electrode, respectively.

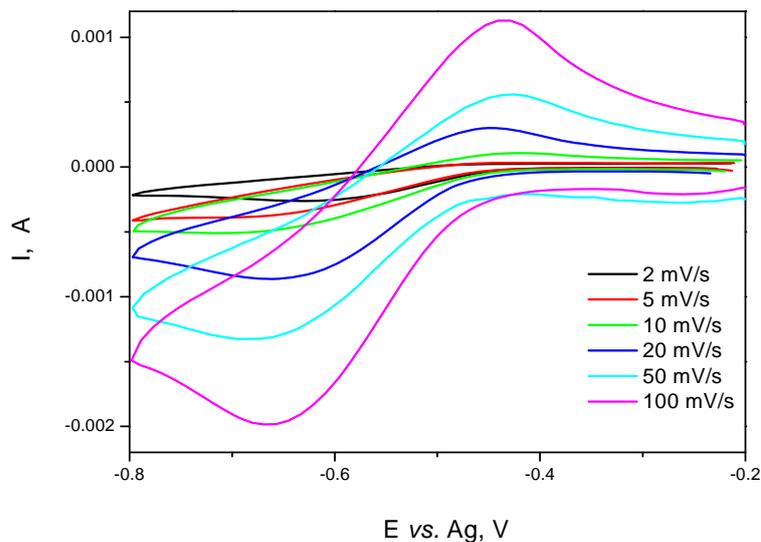


Fig. 2. Cyclic voltammograms on Pt ( $0.5 \text{ cm}^2$ ) for  $10.9 \text{ mM TeO}_2$  dissolved in ChCl-urea (1:2 moles) ionic liquid for various scan rates; temperature  $80^\circ\text{C}$

Note that in Fig. 1 a supplementary increase of current (a peak) in the beginning of returning anodic scan is evidenced before the main anodic peak of tellurium dissolution (in the potential region of  $-0.8 \div -0.6\text{V}$ ). This new anodic peak or wave is due to the electro-oxidation of products formed cathodically by polarizing the Pt electrode at high negative potentials; at this moment we cannot say anything about the chemical nature of these products, which are certainly related to the electrode processes of the large organic cations of chloride+urea complex, the existing components in ionic media together with  $\text{Cl}^-$  ions.

A comparison of the electrochemical behaviour of tellurium, bismuth, and antimony as singular ionic species present in ionic liquids, at identical working temperature ( $80^\circ\text{C}$ ) and scan rate ( $20\text{mVs}^{-1}$ ), is shown in Figure 3. According to the shapes of voltammograms it can be obviously seen that all electrode processes for single ions are quite similar. Thus, Figure 3 exhibits only one reduction peak -deposition of Te, Bi or Sb, as metallic films- and a single dissolution peak -the corresponding film stripping. Of course, although the onset of cathodic process for all ions seems to be at almost identical potential values (*cca*  $-0.45\text{V}$  vs. Ag quasi-reference electrode) the curves have different peak potentials and peak currents, depending on the chemical nature of ion; also, the order of potential values on the potential scale may be changed by scanning at other rates.

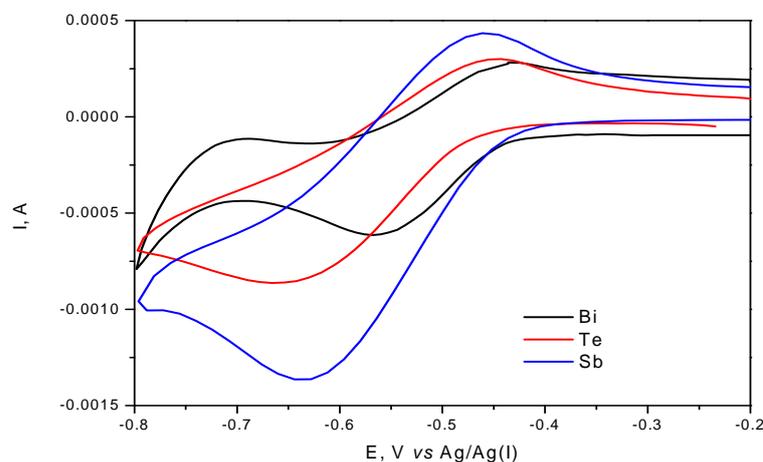


Fig. 3. Comparison of cyclic voltammograms on Pt ( $0.5\text{ cm}^2$ ) for  $10.9\text{ mM}$  concentration of single ions ( $\text{Te}^{4+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Sb}^{3+}$ ) dissolved in ChCl-urea (1:2 moles) ionic liquid; scan rate  $20\text{ mVs}^{-1}$ , temperature  $80^\circ\text{C}$

The cyclic voltammetric behaviour of  $5.4\text{ mM Bi}_2\text{O}_3 + 5.5\text{ mM TeO}_2$  and in  $3.6\text{ mM SbCl}_3 + 7.3\text{ mM TeO}_2$  solutions in ChCl-urea is described in Figures 4 and 5, respectively. In the range of the electrode potentials between  $-0.8$  and  $-0.2\text{V}$ , the voltammograms in these Figures were also exhibited a single pair of conjugated peaks. Each reduction peak may be associated with simultaneous deposition (co-deposition) of tellurium with bismuth or antimony, respectively, resulting deposits of Bi-Te or Sb-Te compounds. By scanning in the anodic direction, on each voltammogram in Figures 4 and 5 a single stripping peak is also observed, considered to be the result of the binary compound dissolution. Because any chemical analysis of the layers was not performed, we discuss here about  $\text{Bi}_{1-x}\text{Te}_x$  or  $\text{Sb}_{1-x}\text{Te}_x$  systems having a general stoichiometry and not about compounds  $\text{Bi}_2\text{Te}_3$  or  $\text{Sb}_2\text{Te}_3$  which are known to be useful in thermoelectricity.

Unfortunately, the co-deposition potentials in choline chloride+urea eutectic obtained experimentally for Bi-Te and Sb-Te, as well as deposition potentials of single metals, cannot be compared with literature; we already mentioned above that these data are not reported until now. Moreover, there are known the differences in standard potential scales that are specific on each ionic liquid used as support electrolyte.

Regarding the reversibility of electrochemical processes, Figures 2, 4 and 5 evidenced a shift of cathodic peak potential to more negative values if scan rate increases. Correspondingly, on

anodic branches a shift of anodic peak potential to more positive values is also recorded. This behaviour suggests rather a quasi-reversible deposition/dissolution response of Te, Bi or Sb ions, with a certain degree of irreversibility, more pronounced for electron transfer for Bi or Sb ionic species.

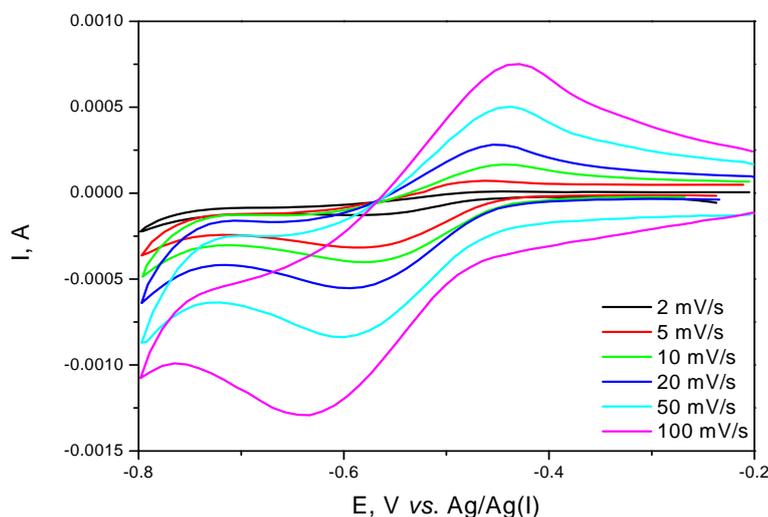


Fig. 4. Cyclic voltammograms on Pt ( $0.5 \text{ cm}^2$ ) for  $5.4 \text{ mM Bi}_2\text{O}_3$  and  $5.5 \text{ mM TeO}_2$  dissolved in ChCl-urea (1:2 moles) ionic liquid for various scan rates; temperature  $80 \text{ }^\circ\text{C}$

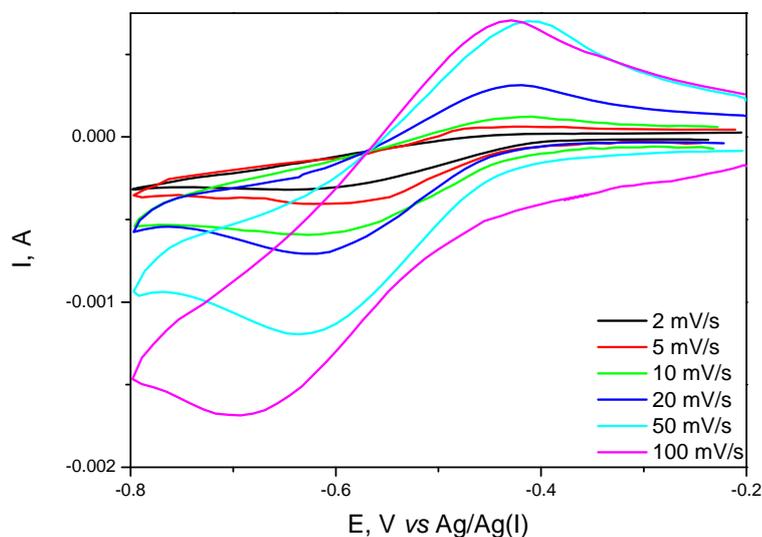


Fig. 5. Cyclic voltammograms on Pt ( $0.5 \text{ cm}^2$ ) for  $3.6 \text{ mM SbCl}_3$  and  $7.3 \text{ mM TeO}_2$  dissolved in ChCl-urea (1:2 moles) ionic liquid for various scan rates; temperature  $80 \text{ }^\circ\text{C}$

The values of peak parameters obtained by processing the voltammetric data are listed in Table 1, where peak potentials for cathodic and for anodic process ( $E_{pc}$ ,  $E_{pa}$ ) together with corresponding peak currents ( $I_{pc}$ ,  $I_{pa}$ ) for each scan rate ( $v$ ) are indicated.

Table 1. The determined peak parameters (current and electrode potential) from cathodic and anodic branches of voltammograms (Figs 2,4,5) recorded for Te, Bi-Te and Sb-Te deposition/stripping on Pt (0.5 cm<sup>2</sup>)

Film nature	Scan rate (mVs <sup>-1</sup> )	I <sub>pc</sub> × 10 <sup>3</sup> (A)	E <sub>pc</sub> (V)	I <sub>pa</sub> × 10 <sup>3</sup> (A)	E <sub>pa</sub> (V)
Te	2	0.260	-0.625	0.020	-0.449
	5	0.406	-0.715	0.030	-0.432
	10	0.585	-0.703	0.106	-0.424
	20	0.864	-0.660	0.295	-0.449
	50	1.336	-0.673	0.558	-0.428
	100	1.982	-0.665	1.137	-0.435
Bi-Te	2	0.148	-0.576	0.009	-0.453
	5	0.306	-0.577	0.066	-0.477
	10	0.402	-0.580	0.164	-0.449
	20	0.549	-0.594	0.277	-0.452
	50	0.837	-0.603	0.496	-0.442
	100	1.294	-0.640	0.747	-0.432
Sb-Te	2	0.296	-0.571	0.018	-0.481
	5	0.393	-0.594	0.058	-0.464
	10	0.508	-0.611	0.116	-0.431
	20	0.713	-0.622	0.310	-0.422
	50	1.217	-0.634	0.699	-0.406
	100	1.693	-0.694	0.706	-0.432

Another observed feature was an increase of cathodic peak current with scan rate on each voltammogram. We can verify if the kinetics of electrodeposition processes of both single Te and BiTe (or SbTe) films have a diffusion control, by plotting I<sub>pc</sub> - v<sup>1/2</sup> dependences.

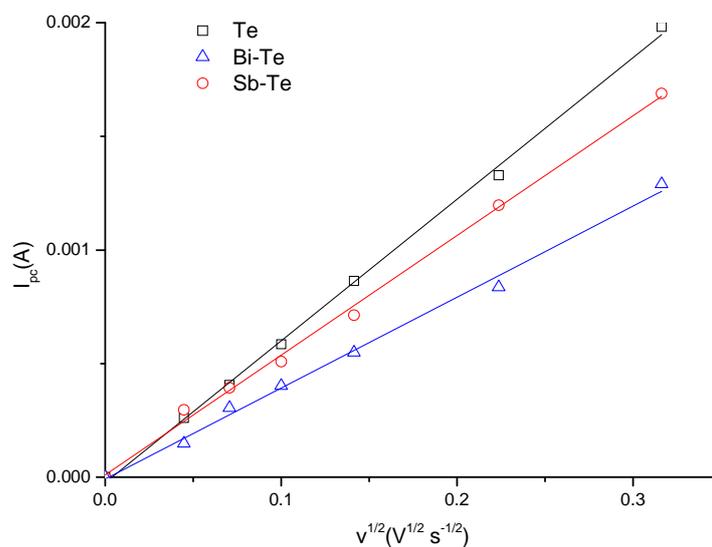


Fig. 6.  $i_p - v^{1/2}$  linear plots for cathodic deposition of Te, Bi-Te and Sb-Te films on Pt (0.5 cm<sup>2</sup>) using ChCl-urea eutectic as electrolyte; ion concentrations shown in captions of Figs 2, 4, and 5; temperature 80 °C

As Figure 6 shows, the straight lines are obtained in all three cases, proving a diffusion-controlled electrochemical process, in which the charge transfer step is always fast. This fact

allows us to calculate the diffusion coefficient of Te(IV) ionic species using the well-known Randles-Sevcik equation for a reversible metal deposition [18]:

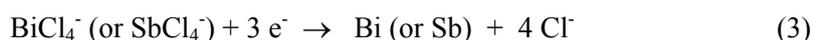
$$I_{pc} = 0.6104nFAc\sqrt{\frac{nF}{RT}}vD \quad (1)$$

where  $n$  – the number of electrons changed in electrochemical process,  $F$  and  $R$  are the Faraday number and ideal gas constant, respectively,  $A$  – the surface area of electrode ( $0.5 \text{ cm}^2$ ) and  $T$  – the absolute temperature ( $353.15 \text{ K}$ ).

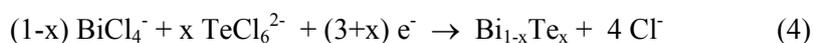
Values of  $6.19 \times 10^{-3} \text{ As}^{1/2}\text{V}^{-1/2}$  for the current function ( $I_{pc}/(A \times v^{1/2} \times c)$ ) and of diffusion coefficient  $D = 1.75 \times 10^{-7} \text{ cm}^2\text{s}^{-1}$  were computed for Te species, taking number of transferred electrons  $n=4$ . This order of magnitude for diffusion coefficient at  $353 \text{ K}$  is generally much lower than in aqueous solutions ( $D$  about  $10^{-5} \text{ cm}^2\text{s}^{-1}$ ), but it is expected for diffusion in such ChCl-urea ionic liquid that has higher viscosity and density as aqueous media. Also, the linear  $I_{pc} - v^{1/2}$  plots for BiTe and SbTe co-deposition processes demonstrate the similar diffusive control in the deposition mechanism, where a simultaneous diffusion of both Te and Bi species (or Te and Sb species) is certainly involved. By comparing with the slope for Te ion reduction, the obtained lower values of slopes in these last cases may be an indication of a less transferred electrons than  $n=4$ , a part of tetravalent Te ions being replaced with trivalent Bi (or Sb) ions.

Regarding the mechanism of cathodic processes, literature indicates that usually the metal ions are present in ionic liquid media as complex ions. For instance, Te(IV) species may exist as  $\text{TeCl}_6^{2-}$  anions in ionic liquids EMI-Cl- $\text{BF}_4$  [15]; in general, the formation of complex ions brings the reduction potentials of tellurium and bismuth (or antimony) ions close to each other, thus allowing co-deposition, in spite of differences in the standard electrode potentials.

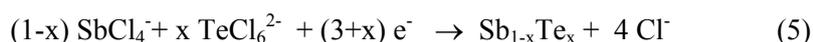
In our work with chloride-rich medium,  $[\text{TeCl}_6]^{2-}$ ,  $\text{BiCl}_4^-$  and  $\text{SbCl}_4^-$  complex species may be formed by dissolution of  $\text{TeO}_2$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{SbCl}_3$  precursors in ChCl+urea ionic liquid. Thus, it is a good reason to suppose for the Te, Bi and Sb ions to have the same behaviour as in chloride concentrated aqueous solutions. Therefore, the direct discharge of ions to elementary Te, Bi or Sb metals may be described as one of the following electron transfer processes:



We assume for the formation of Bi-Te compound a direct co-reduction of bismuth and tellurium ions:



Deposition of Sb-Te follows a similar co-reduction reaction:



By applying equations (4) and (5) for  $\text{Bi}_2\text{Te}_3$  and  $\text{Sb}_2\text{Te}_3$  synthesis a value of  $x=0.6$  is obtained, that means a number of transferred electrons in electrochemical process  $n=3.6$ . Taking into account that five metal ions participate in the electroreduction process to obtain  $\text{Bi}_2\text{Te}_3$  (or  $\text{Sb}_2\text{Te}_3$ ) thermoelectric compounds it results an overall 18 electrons in the synthesis, in good agreement with literature [6]. This possibility of direct co-reduction of tellurium ions with bismuth (or antimony) ions allowed also to perform a good control on Bi/Te or Sb/Te ratios in the electrodeposited binary compounds with Te varying content.

### Electrochemical impedance spectroscopy studies

Electrochemical impedance spectroscopy (EIS) has been regarded as a very powerful, non-destructive, and informative technique for investigating the characteristic features of electrode/electrolyte interface and distinguishing between different processes during metal deposition. The EIS spectra, presented in Figures 7-9, were obtained at different potentials of Pt electrode corresponding to the following domains: before metal deposition, the onset of deposition, massive deposition showing cathodic peak or diffusion limited current. Nyquist (imaginary part vs. real part of impedance) and Bode (phase angle vs. frequency, only) plots are shown in these Figures for Te, Bi-Te and Sb-Te systems.

From Fig. 7 it can be found comparatively that the plot recorded at a starting potential of -0.3V (more positive than the onset of Te ion reduction) shows only a capacitive semicircle behaviour, with the highest diameter of *ca.* 3000 $\Omega\text{cm}^2$  and the largest Bode phase angle, of  $-60^\circ$ . By polarizing the Pt electrode from -0.4V to -0.75V, in the range of the onset and massive deposition of metallic films, EIS spectra in Figures 7-9 for Te, Bi-Te, and Sb-Te are similar to each other in shape, with a semicircle appearing in the high frequency domain and a straight line (a tail or a part of second semicircle) in the low frequency region. From all three Figures, it can be noticed that the experimental values of ohmic resistance of solution remained practically the same, of the order 12-15  $\Omega\text{cm}^2$ .

The inset of Fig. 7 shows details of the high frequency semicircle for Te deposition; this becomes smaller in diameter, suggesting a more intensive reaction process, reaches a minimum (value of 100 $\Omega\text{cm}^2$  at -0.5V) and then at further polarization the semicircle enlarges (diameter of 140 $\Omega\text{cm}^2$  at -0.65V). The diffusive linear portion has a slope of 1, whereas the maximum Bode angles first diminish from  $-38^\circ$  (-0.4V) to  $-27^\circ$  (-0.5V) and then return to a higher value, of  $-32^\circ$  (-0.65V).

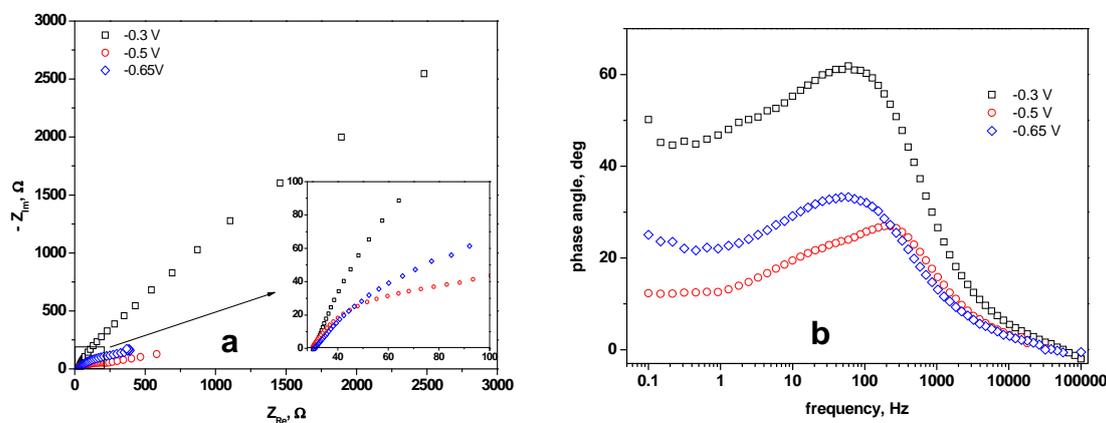


Fig. 7. Nyquist (a) and Bode (b) plots measured at different potentials on Pt ( $0.5\text{ cm}^2$ ) from ChCl-urea eutectic containing 10.9 mM  $\text{TeO}_2$ ; temperature  $80^\circ\text{C}$ .  
Inset: high frequency data on an enlarged scale.

Figures 8 and 9 display clearly two time constants which belong to consecutive steps. In order to interpret these impedance data we consider that by polarizing the Pt substrate, a tellurium (or a very rich in tellurium compound) film is first deposited and then a diffusion-controlled deposition of binary (Bi-Te, Sb-Te) compound is carried out. In Figures 8 and 9 the small diameters of semicircles ( $50\text{-}80\ \Omega\text{cm}^2$ ) at high frequencies suggest an increased rate of deposition of binary compound than of pure Te; also, the overall film seems to have a better electrical conductivity. Correspondingly, the maximum Bode angle increases from  $-22^\circ$  (in both cases at -0.5V) to  $-32^\circ$  (for Bi-Te at -0.7V) or  $-35^\circ$  (Sb-Te at -0.75V), this behaviour proving a diffusion control of the process.

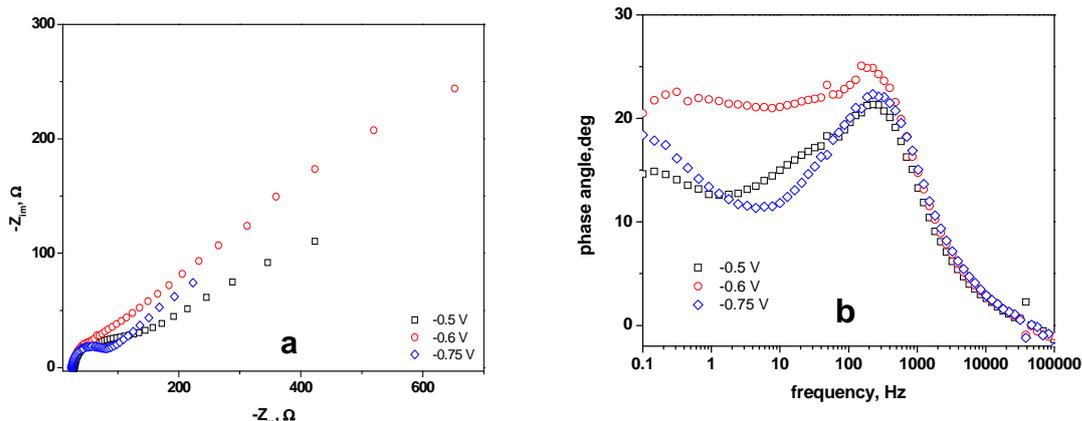


Fig. 8. Nyquist (a) and Bode (b) plots measured at different potentials on Pt ( $0.5 \text{ cm}^2$ ) from ChCl-urea eutectic containing  $5.4 \text{ mM Bi}_2\text{O}_3$  and  $5.5 \text{ mM TeO}_2$ ; temperature  $80^\circ\text{C}$

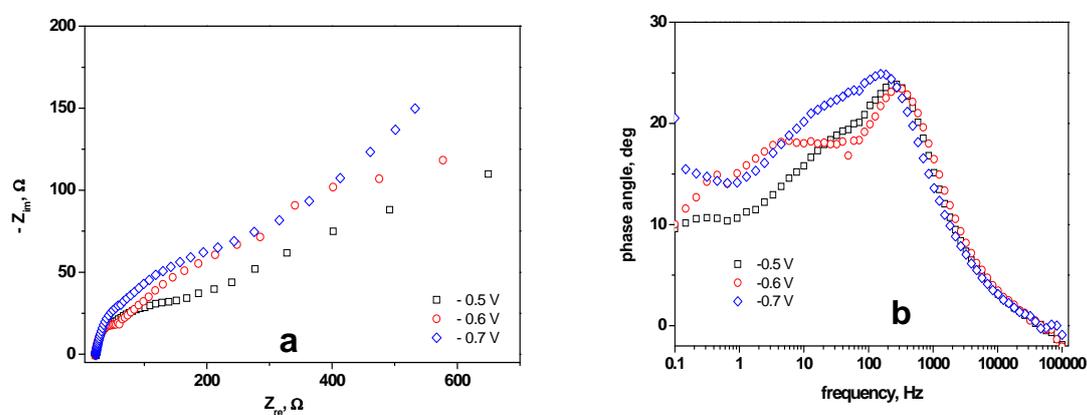


Fig. 9. Nyquist (a) and Bode (b) plots measured at different potentials on Pt ( $0.5 \text{ cm}^2$ ) from ChCl-urea eutectic containing  $3.6 \text{ mM SbCl}_3$  and  $7.3 \text{ mM TeO}_2$ ; temperature  $80^\circ\text{C}$

A physical model describing all the charge transfer and diffusional processes occurring at the interface has also been used to interpret the impedance spectra. An equivalent electric circuit shown in Figure 10 was used to fit the EIS experimental data. In this circuit,  $R_s$ , in a series connection, represents the invariable ohmic resistance of electrolyte, while a film capacitance ( $C_1$ ) is in a parallel combination with a film resistance ( $R_1$ ) and a second parallel combination consisted in a constant phase element ( $CPE_1$ ) and charge transfer resistance ( $R_2$ ). Table 2 contains the values of equivalent circuit elements for the best fitting of experimental data.

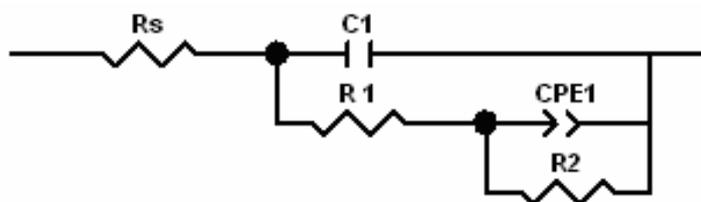


Fig. 10. Schematic representation of the electrical equivalent circuit:  $R_s$  – solution resistance;  $C_1$  and  $R_1$  – capacitance and ohmic resistance of the film, respectively;  $CPE_1$  – constant phase element describing the double layer capacitance;  $R_2$  - charge transfer resistance.

Table 2. Values of the fitted parameters of the equivalent circuit corresponding to EIS spectra for Pt electrode ( $0.5 \text{ cm}^2$ ) in *ChCl*-urea eutectic containing  $10.9 \text{ mM TeO}_2$ ,  $5.4 \text{ mM Bi}_2\text{O}_3 + 5.5 \text{ mM TeO}_2$ , and  $3.6 \text{ mM SbCl}_3 + 7.3 \text{ mM TeO}_2$ , respectively at a fixed potential of  $-0.5\text{V}$ ; temperature  $80^\circ\text{C}$

Circuit parameter	Te deposition	Bi-Te deposition	Sb-Te deposition
$R_s, \Omega$	30.7	29.1	28.9
$C1, \mu\text{F}$	10.09	16.41	16.94
$R1, \Omega$	12.09	23.11	26.83
CPE 1 -T ( $\mu\text{F}$ )	914	2660	1626
CPE 1 -P	0.437	0.433	0.512
$R2, \Omega$	289.5	600.4	638.3

It is seen that the fitted values of  $R_s$  correspond very well with EIS experiments, while  $C1$  and  $R1$  values are characteristic for conductive deposits on Pt substrate. Also, Table 2 exhibits an increased charge-transfer resistance ( $R2$ ) of the deposition processes in the order:

$$\text{Te} < \text{Bi-Te} < \text{Sb-Te},$$

this indicating the highest exchange current density (directly proportionally with reaction rate) for the Te deposition; this is two times higher than for Bi-Te deposition or for Sb-Te deposition.

The constant phase element CPE 1 takes into account the non-ideal capacitive behaviour of the electrochemical double layer due to the non-homogeneous processes on the changeable surface of the electrode. The impedance of this component is described by the equation (6) [19]:

$$Z(\text{CPE}) = \frac{1}{T (i\omega)^P} \quad (6)$$

where the parameter  $T$  is associated with a pure capacitor and the value of  $P$  exponent ranges between 0 (pure resistor) and 1 (pure capacitor). The symbols  $i$  and  $\omega$  have their usual meanings,  $i = \sqrt{-1}$  and  $\omega$  – the angular frequency,  $\omega = 2\pi f$  ( $f$  – frequency, Hz). It results from  $T$  values (few thousands of microfarads) a large deviation of real surface area of covered Pt electrode from geometrical one;  $P$  values are closed to 0.5, demonstrating the diffusion control of deposition process in all cases.

#### 4. Conclusions

Cyclic voltammograms at  $80^\circ\text{C}$  on Pt showed a single redox couple corresponding to cathodic deposition and anodic dissolution of Te, Bi-Te or Sb-Te films using a ionic liquid consisting in choline chloride – urea (1:2 moles) eutectic. The cathodic peaks are positioned within a narrow potential region, identical for all three processes, thus justifying the supposition that Te is first formed, followed by binary compound (Bi-Te, Sb-Te) co-deposition. Both cyclic voltammetry and electrochemical impedance data indicated a diffusion control of cathodic process. Also, all the results indicate that Te, Bi-Te and Sb-Te films could be deposited using ionic liquid electrolyte based on chloride choline + urea mixture (1:2) by choosing the appropriate operating conditions.

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