ELECTRODEPOSITION BEHAVIOUR OF CADMIUM TELLURIDE FROM CHOLINE CHLORIDE-UREA IONIC LIQUIDS

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This paper reports the electrodeposition of Cd and CdTe films on Pt using ionic liquids based on choline chloride: urea eutectic mixture (ChCl-urea, 1:2 moles) in the 25-60^{0}C temperature range. TeO_2 and $CdCl_2$ were dissolved in ChCl:urea ionic liquid at concentrations in the range of 0.1-0.5mM and 50-100mM, respectively. The mechanism of Cd and CdTe electrodeposition was investigated by cyclic voltammetry and electrochemical impedance spectroscopy. In the case of simultaneous presence of Cd^{2+} and Te^{4+} ions in ChCl-urea ionic liquid as supporting electrolyte the recorded cyclic voltammograms had more complex shapes. On the cathodic scan the massive deposition of CdTe took place. On the anodic branch of this voltammogram two oxidation peaks occur evidently, the first one being certainly due to the dissolution of CdTe compound deposit. The second anodic peak is probably dissolution of a CdTe compound riched in Te or even a dissolution of pure tellurium firstly deposited. In a series of experiments we studied the electric conductive properties of CdTe films freshly prepared.The electrolyses for films deposition were also carried out using platinum sheets in ionic liquid without stirring.

1. Introduction

Electrodeposition of cadmium have widely used in the production of electronic materials for conductive devices that require corrosion resistance, solderability, ductility, anti-galling, anti-static, and anti-fungal characteristics [1-3]. Electrodeposition of semiconducting materials represents a new challenge, not only from the academic point of view, but also from the economic point of view, since this method presents interesting characteristics for large area, low cost and generally low temperature and soft processing of materials [4].

Cadmium telluride having its bandgap of 1.45 eV is a material of great technological importance for application in photovoltaic cells. This compound is one of few II–VI binary materials which can be in both n- and p- conductivity types [5]. Furthermore, the direct optical transition results in a large absorption coefficient that makes it a very attractive material, not only for photovoltaic conversion, but also for gamma-ray and infrared detectors, as well as electronic and opto-electronic devices [6].

The electrodeposition of CdTe semiconductor thin films is effected usually from aqueous acidic solutions [7–11]. The main shortcoming of acidic electrolytes is the occurrence of corrosion processes and co-electrodeposition of elementary Te together with CdTe deposit. To prevent the accumulation of Te in CdTe films, the concentration of Te(IV) ions in acidic electrolytes is usually recommended to be in a Cd(II)/Te(IV) ionic ratio of 10^4 at 363 K [12]. Lincot and co-workers [13] have investigated the reaction mechanism for CdTe deposition on the CdS electrode from acidic aqueous electrolytes. The mechanism of the formation of CdTe compound in ammonia electrolytes was discussed in the papers of Murase at al. [14,15].

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Pandey et al. [16-19] have demonstrated the advantage of ethylene glycol based baths over aqueous baths. They have electrodeposited CdTe film on different substrates at various temperatures (80, 120 and 140^0C) from $CdCl_2$, KI and $TeCl_4$ in ethylene glycol. Non-aqueous baths for semiconductor electrodeposition are interesting since they have attractive features and do not suffer from hydrogen evolution. Lade et al. [20] have prepared polycrystalline CdTe thin films with hexagonal crystal structure by galvanostatic electrodeposition method using ethylene glycol bath onto different substrates at deposition temperature of 80 ^{0}C. Surface morphology of CdTe revealed that the surface is compact, uniform and crack free.

Recently, it has been proved that ionic liquid media with interesting perspectives in metal electrodeposition are mixtures based on choline chloride, being very attractive in the field of metals, alloys or semiconductor electrodeposition [21,22]. The advantages of these novel baths include: electroplating of very electronegative metals (that are not possible to be deposited in aqueous media); significantly reduced hydrogen evolution at cathode; lower electrical energy consumption comparing with aqueous baths (including cost-effectiveness), precise control of composition and thickness of materials. Ionic liquids show good electrical conductivity due to their complete ionic structure, are electrochemically robust with a large potential window and have an extremely low vapor pressure. The thermal stability of the ionic liquid is useful to obtain crystalline semiconductor films through direct electrodeposition at higher temperatures without subsequent annealing.

Unfortunately, the studies of semiconductor electrodeposition are still rare in ionic liquids. The electrodeposition of cadmium and cadmium telluride was investigated at glassy carbon, polycrystalline tungsten and platinum electrodes in a basic 1-ethyl-3-methylimidazolium chloride:tetrafluoroborate room temperature molten salt [23,24].

It has recently been shown that an ionic liquid can be formed as eutectic mixture of choline chloride (2 hydroxy-ethyl-trimethyl-ammonium, ChCl) with a hydrogen bond donor species such as a glycol, amide or carboxylic acid [25].

We report in the present work the deposition of Cd and CdTe films using the eutectic of choline chloride and urea (1:2 moles) as supporting electrolyte; we mention that such semiconductor films were not reported in literature as cathodic deposits in ChCl containing media. The procedure of electrodeposition 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. Moreover, such ionic liquid bath is air and moisture stable, biodegradable and economically viable to large-scale processes.

Previously we have shown [26-28] that TeO_2 dissolve in ChCl-malonic acid and ChCl-urea eutectics. In the present study, $CdCl_2$ and TeO_2 were dissolved in ChCl: urea (1:2 moles) ionic liquid. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were chosen as electrochemical techniques in order to evidence electrochemical couples of deposition/ dissolution of Cd and CdTe, respectively.

2. Experimental details

The supporting electrolyte was prepared by mixing choline chloride (ChCl, Aldrich 99%, used as purchased, without recrystallization or drying) with urea (Aldrich 99%); by heating the two components in 1:2 molar proportions at above 80^0C for 30 min, a homogeneous colorless liquid is formed. $CdCl_2$ (Merck) and TeO_2 (99%, Alfa Aesar) reagents as precursors of Cd^{2+} and Te^{4+} ions were also used as received, being dissolved in the supporting electrolyte ChCl-urea. In order to calculate the solution molarities we used the density values of ChCl-urea determined in our laboratory.

An AUTOLAB PGSTAT 12 Ecochemie potentiostat provided with a frequency response analyzer was used for cyclic voltammetry and electrochemical impedance spectroscopy. A platinum sheet (0.5 cm^2) was used as working electrode, whereas the auxiliary electrode was a platinum mesh. A platinum wire immersed in the working electrolyte (*i.e.* ionic liquid containing cadmium and/or tellurium ions) was the quasireference electrode [26]. 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 mVs^{-1}. Electrodeposition processes were made on platinum electrode at different polarization potentials (versus Pt quasireference electrode), different temperatures or time durations. EIS characterization was carried out in 100 kHz $\geq$ f $\geq$ 0.1 Hz frequency range with an *ac* voltage amplitude of ±10 mV; the impedances were represented as Nyquist and Bode spectra.

3. Results and discussion

Typical cyclic voltammograms of ChCl- urea (1:2 moles) supporting electrolyte recorded on the Pt electrode are shown in Figure 1. It was noticed the large domain of potentials (from -1V to +2 V) representing the *potential window* of more than 3V for selected ionic liquid, which is about 2 times wider in comparison with similar parameter of aqueous solutions (1.23V).
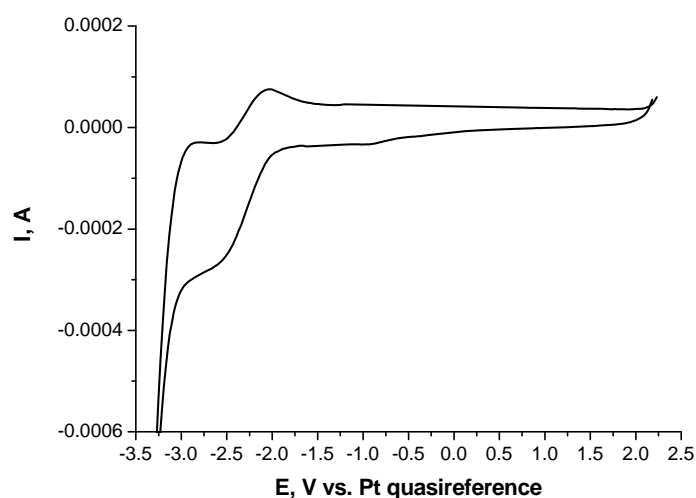
Fig. 1. Cyclic voltammogram within extended potential range on Pt (0.5 cm^2) for
ChCl-urea (1:2 moles) eutectic; scan rate 20 mVs^{-1}; temperature 40 ^{0}C

Electrodeposition of cadmium films

Figures 2-4 show the experimental results of application of cyclic voltammetry technique for Pt electrode in ChCl-urea eutectic. As Figure 2a illustrates, for 100 mM Cd^{2+} concentration the metallic Cd started to deposit at –0.95V, and displayed an increasing current during the negative going scan, with a cathodic peak at $-1\div$ -1.2V. The electrode process may be described by the simple reduction of lead ions:

$$Cd^{2+} + 2\,e^- \rightarrow Cd \tag{1}$$

Both peak current and limiting current increase with scan rate, suggesting diffusion control of this quite reversible process. A new increase of current at more negative potentials was attributed to the cathodic process of ionic liquid.

Only a single couple of reduction/oxidation peaks can be seen from Figure 2a, the electrochemical processes being assigned to deposition of Cd film and it's stripping from Pt electrode, respectively.

Figure 2b shows voltammograms recorded for the same Cd^{2+} ion concentration but at lower temperature (25^{0}C) comparing to Figure 2a (40^{0}C). In these conditions, the cathodic and anodic peaks corresponding to Cd^{2+}/Cd couple increase with scan rate. From a comparison of cathodic peak currents and limiting currents at 25^{0}C and 45^{0}C, it can be seen that their values increases with temperature.
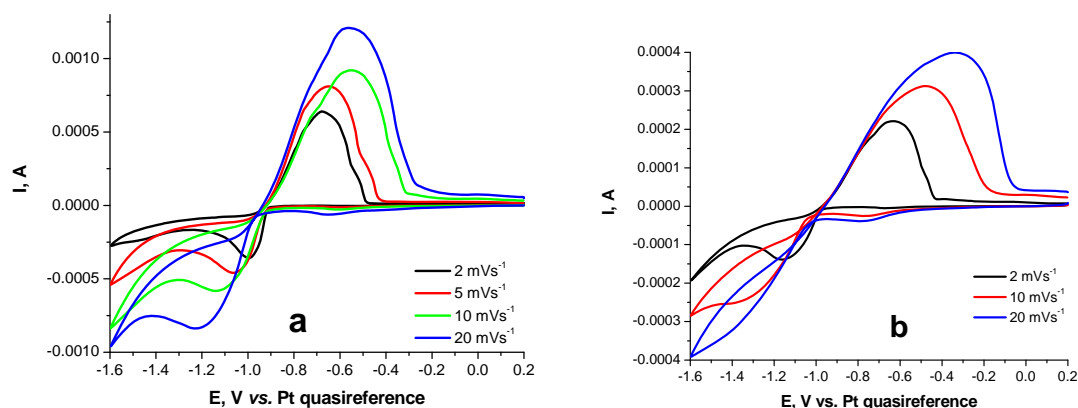
Fig. 2. Cyclic voltammograms on Pt electrode for 100 mM $CdCl_2$ dissolved in ChCl-urea (1:2 moles) ionic liquid at different scan rates; temperature: (a) 40^0C; (b) 25^0C

Regarding the reversibility of electrochemical processes, Figures 2 - 3 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 Cd ions, with a certain degree of irreversibility.

Decreasing the Cd^{2+} concentration in the electrolyte led to a significant decrease of amplitude of both cathodic and anodic peaks. Figure 3 illustrates the influence of scan rate for 50 mM Cd^{2+} at 40^0C constant temperature.

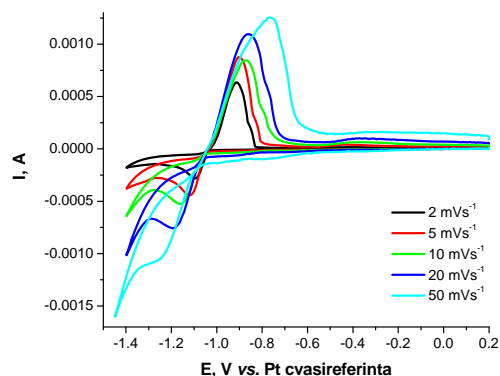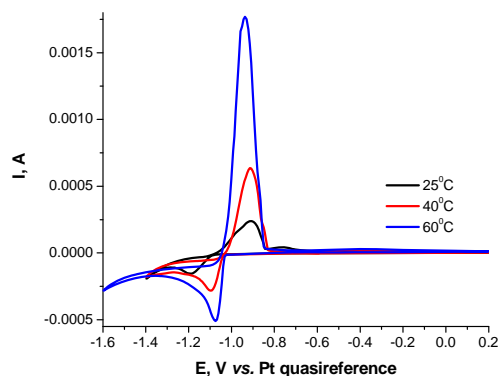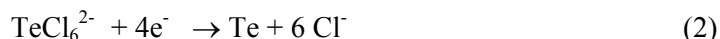*Fig. 3. Cyclic voltammograms for 50 mM $CdCl_2$ dissolved in ChCl-urea (1:2 moles) eutectic at different scan rates; temperature 40^0C*

Fig. 4. Cyclic voltammograms showing the influence of temperature for 50 mM $CdCl_2$ dissolved in ChCl-urea (1:2 moles) eutectic at constant scan rate of 2 mVs^{-1}

Figure 4 presents comparatively the voltammograms at constant scan rate of 20mVs^{-1} for the same Cd^{2+} ion concentration at different temperatures. The shapes of cathodic branches are very similar, with increasing currents with temperature. In the anodic scan, the current of anodic peak decrease with the increase of temperature.

Electrodeposition of cadmium telluride films

Previously, we reported the results of electrodeposition studies of tellurium as component in BiTe, SbTe and BiSbTe compounds using as electrolytes choline chloride eutectics with urea [26] and malonic acid [27]. However, in our case this mechanism does not certainly take place, due to the lack of water. In chloride-rich media as all eutectic containing choline chloride, we suppose that tellurium species may exist in solution as Te_x^{4-x} complex ionic species, most probable

as $TeCl_6^{2-}$ anion. In the absence of water a direct discharge to elementary Te is expected to be carried out on Pt electrode:

$$TeCl_6^{2-} + 4e^- \rightarrow Te + 6\,Cl^- \tag{2}$$

In the case of simultaneous presence of Cd^{2+} and Te^{4+} ions in ChCl-urea ionic liquid as supporting electrolyte the recorded cyclic voltammograms had more complex shapes. An example is given in Figure 6 where a comparison of the system Pt/ 50mM $CdCl_2$ + 0.5mM TeO_2 dissolved in ChCl-urea (1:2 moles) at different scan rates is presented.

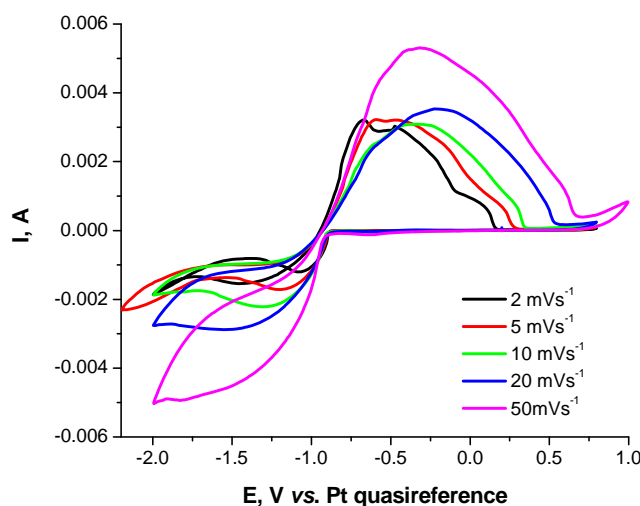Fig. 6. *Cyclic voltammograms on Pt for 50mM $CdCl_2$ and 0.5mM TeO_2 dissolved in ChCl-urea (1:2 moles) eutectic at different scan rates; Pt electrode (0.5 cm^2), temperature 40^0C*
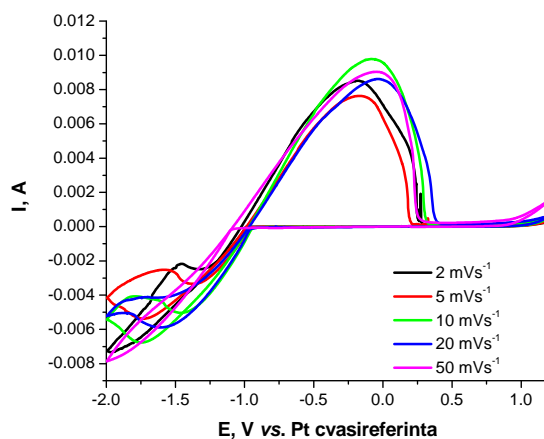

Fig. 7 .*Cyclic voltammograms for 50 mM $CdCl_2$ and 0.1 mM TeO_2 dissolved in ChCl-urea (1:2 moles) eutectic at different scan rates; Pt electrode (0.5 cm^2), temperature 40^0C.*

On the cathodic scan the massive deposition of CdTe took place exhibiting a peak at -1V. On the anodic branch of this voltammogram two oxidation peaks occur evidently, the first one being certainly due to the dissolution of CdTe compound deposit. The second anodic peak is probably dissolution of a CdTe compound riched in Te or even a dissolution of pure tellurium firstly deposited.

The mechanism of obtained CdTe compound may consist in a first deposition of a telurrium layer on Pt and the subsequently cadmium telluride deposition according to the process:

$$Cd^{2+} + 2\,e^- + Te \rightarrow CdTe \tag{3}$$

Cyclic voltammograms for systems with both precursors jointly dissolved but having lower Te concentration are presented in Figure 7. For this ionic liquid less riched in Te ions (0.1mM TeO_2) the voltammograms have higher peak current. Correspondingly, the same tendency is for anodic peaks, where the higher oxidation current was recorded for system with 0.1 mM TeO_2.

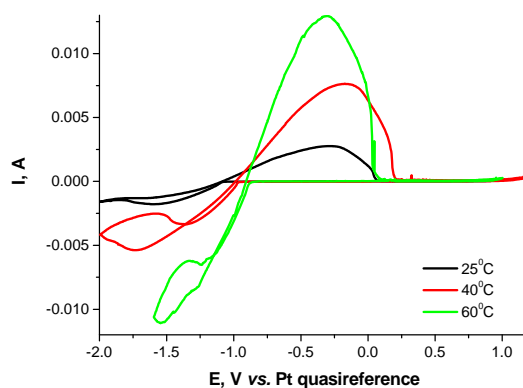Fig. 8. Cyclic voltammograms showing the influence of temperature for 50 mM $CdCl_2$+0.1 mM TeO_2 dissolved in ChCl-urea (1:2 moles) eutectic at constant scan rate of 5 mVs^{-1}

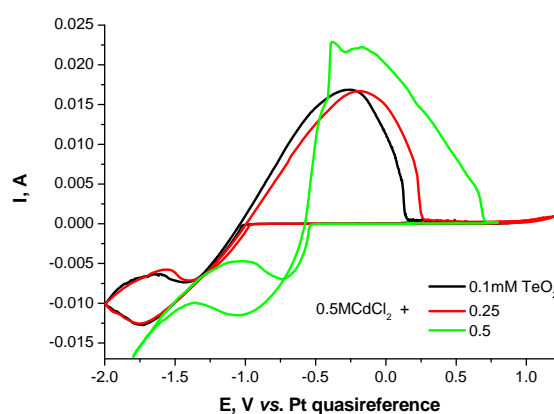
Fig. 9. Cyclic voltammograms showing the influence of Te ions concentrations for 50 mM $CdCl_2$+ x mM TeO_2 dissolved in ChCl-urea (1:2 moles) eutectic at constant scan rate of 10mVs^{-1}, temperature 60^{0}C

Figure 8 presents comparatively the voltammograms at constant scan rate of 5mVs^{-1} for the same Cd^{2+} and Te^{2+} ions concentrations at different temperatures. The shapes of cathodic and anodic branches are very similar, with increasing currents with temperature. A current crossover is observed on the cathodic branches in the -1.15 ÷ -1.45 V potential region at scan rate 5 mV/s, indicating a typical nucleation process. It is also found in voltammograms from previous Figures that nucleation overpotential is increased by scan rate. This phenomenon of nucleation overpotential occurs also at the more noble potentials with an increase in Te^{4+} concentration, as Figure 9 shows.

Figure 10 illustrates the same behavior of systems, of increase the peak current for more concentrated solutions in Cd^{2+} ions. This Figure shows that in electrolytes very concentrated in cadmium ions, do not exhibit a pronounced cathodic peak and a shift of peak potentials for both cathodic and anodic processes towards positive direction when the system is gradual riched in Cd ionic species. The interpretation of overall shifting of voltammograms in either positive or negative direction should be related to the deviation from 1:1 stoichiometry of CdTe compound, but the explanation of this phenomenon requires more experiments to be performed.

Unfortunately, the co-deposition potentials in choline chloride+urea eutectic obtained experimentally for CdTe, 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.
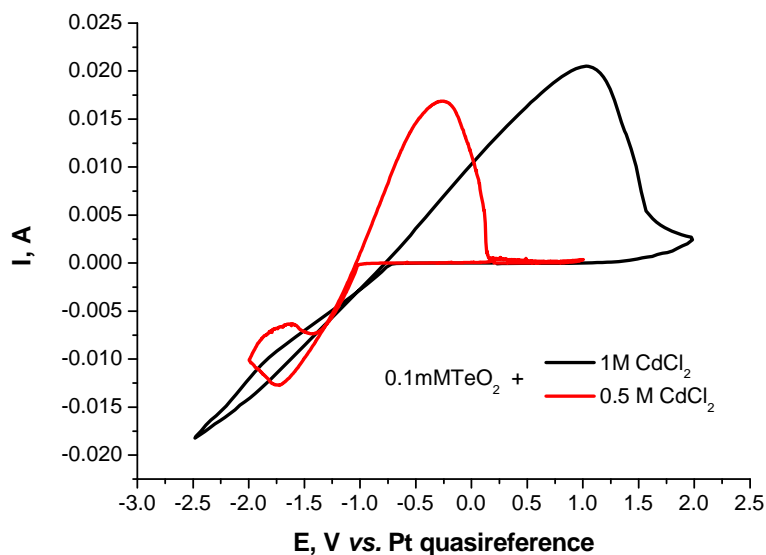

Fig.10. Cyclic voltammograms showing the influence of Cd concentration for 0.1 mM TeO$_2$ + x mM CdCl$_2$ dissolved in ChCl-urea (1:2 moles) eutectic at constant scan rate of 10 mVs^{-1}, temperature 60^{0}C

In a series of experiments we studied the electric conductive properties of CdTe films freshly prepared.The electrolyses for films deposition were also carried out using platinum sheets in ionic liquid without stirring. The cathode with an exposed area of 0.5 cm2 was located vertically and parallel Pt sheets were anodes. Figures 11-13 give some examples of experimental results by applying the electrochemical impedance spectroscopy.

In Figure 11 are presented the EIS results obtained at open circuit potential for three CdTe films electrodeposited on platinum with the same area (0.5 cm^2). The electrochemical deposition was made at 40^0 C during 30 minutes, at different polarization potentials from ChCl-urea (1:2 moles) ionic liquid containing 0.5M CdCl$_2$ and 0.5mMTeO$_2$ as precursors for Cd^{2+} and Te^{2+} ions. From Nyquist diagrams (Fig. 11a) it can be noticed that the experimental values of ohmic resistance of electrolyte remained practically the same, of the order 44-48 Ωcm^2.

It can be found for the sample deposited at -1V (which represents the starting cathodic potential on CV curves) only a capacitive semicircle behaviour in Nyquist diagram, with the highest diameter of *ca.* 150 Ωcm^2 and the largest Bode phase angle, of -22^0. For sample obtained by polarizing the Pt electrode at -1.1V, in the range of the onset and massive deposition of CdTe films, we can observe that a second semicircle appears in the low frequency region. The third EIS spectrum in Figure 11 was recorded for the sample prepared by electrodeposition at the -1.2V; it also shows two semicircles but having the smallest diameters. Both decrease of diameters and the maximum phase angle (from Bode spectra) reaching the minimum value at -5^0 demonstrate a supplemetary deposition of metallic cadmium onto the semiconductor CdTe compound.
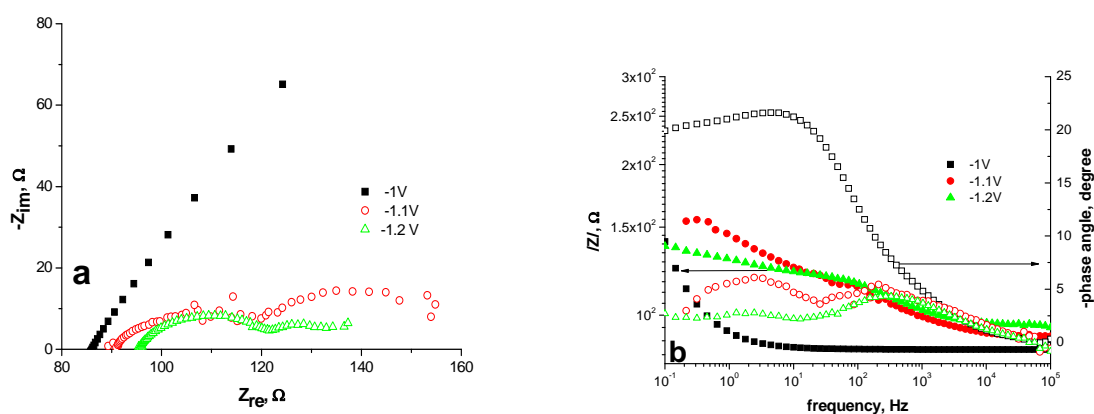
Fig. 11. Nyquist (a) and Bode (b) diagrams recorded at OCP (40^0C) for samples obtained by electrolysis at 40^0C, 30minutes, at different polarizations potentials of Pt electrode in ChCl-urea (1:2 moles) eutectic containing 50 mM $CdCl_2$ and 0.5mM TeO_2.

In support of these statements we have recorded the EIS diagrams presented in Figure 12. The polarization of -1.3V leads to CdTe deposits covered with thicker cadmium film. Arising the temperature produces a lower ohmic resistance of electrolyte, too.
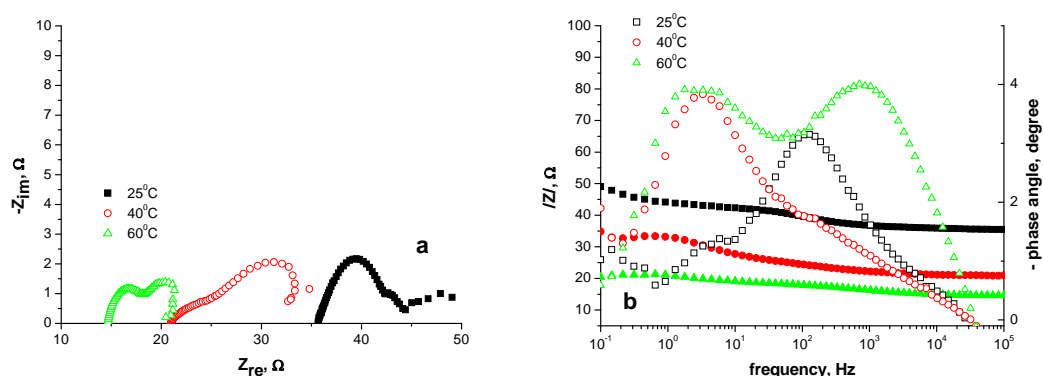

Fig12. Nyquist (a) and Bode (b) diagrams recorded at OCP for samples obtained at different temperatures of Pt electrode in ChCl-urea (1:2 moles) eutectic containing 50 mM $CdCl_2$ and 0.5mM TeO_2; polarization potential -1.3V, 60 minutes

In a another series of experiments we obtained samples by performing electrolysis at 25^0C by keeping the potential at constant value of -1V *vs.* platinum quasireference electrode and recording Nyquist and Bode diagrams. The obtained results for 50 mM $CdCl_2$ + 0.5mM TeO_2 dissolved in ChCl-urea (1:2 moles) ionic liquid system and different electrolysis times are presented in Figure 13. Nyquist spectra for samples prepared at prolonged time led to gradually decreased diameters of semicircles proving an increase of charge transfer rate during thickening of deposit. Correspondigly, Bode diagrams presented a decrease of impedance modulus together with a decrease from -20^0 to -10^0 of maximum phase angle. This behavior may be explained by an amplified porosity of CdTe film during the prolonged electrolysis.
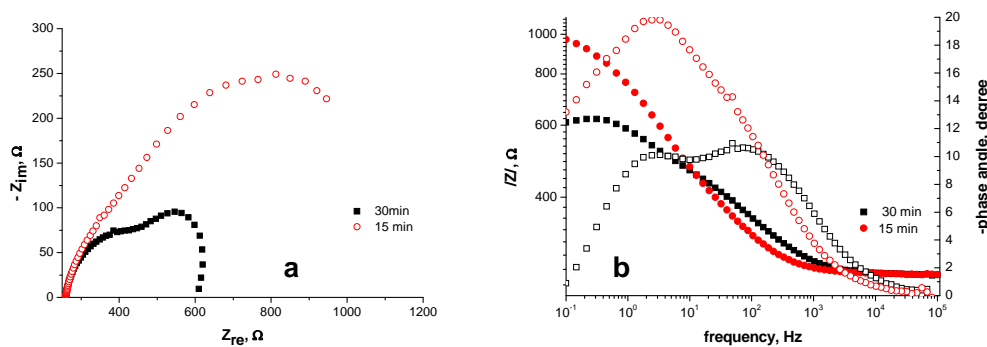
Fig. 13. Nyquist (a) and Bode (b) diagrams recorded at OCP potential for samples obtained at different electrolysis time of Pt electrode in ChCl-urea (1:2 moles) eutectic containing 50 mM CdCl$_2$ and 0.5mM TeO$_2$; temperature:25^{0}C, polarization potential -1V vs. Pt quasireference electrode

4.Conclusions

Cyclic voltammetry and electrochemical impedance spectroscopy were successfully used for a comparative investigation of separate deposition of pure component (Cd) and CdTe compound. Both techniques gave information about the potentials of deposition and dissolution of CdTe and its pure components, as well as about the mechanism.

In the case of Cd behaviour, only one couple of reduction/oxidation peaks, corresponding to Cd^{2+}/Cd couple, was observed. Their values increases with temperature.

The CV 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 Cd ions, with a certain degree of irreversibility. Decreasing the Cd^{2+} concentration in the electrolyte led to a significant decrease of amplitude of both cathodic and anodic peaks.

In the case of simultaneous presence of Cd^{2+} and Te^{4+} ions in ChCl-urea ionic liquid as supporting electrolyte the recorded cyclic voltammograms had more complex shapes. A current crossover is observed on the cathodic branches in the -1.15 ÷ -1.45 V potential region indicating a typical nucleation process. It is also found in voltammograms from previous Figures that nucleation overpotential is increased by scan rate. Electrolytes very concentrated in cadmium ions, do not exhibit a pronounced cathodic peak and a shift of peak potentials for both cathodic and anodic processes towards positive direction when the system is gradual riched in Cd ionic species.

In a series of experiments we studied the electric conductive properties of CdTe films freshly prepared.The electrolyses for films deposition were also carried out using platinum sheets in ionic liquid without stirring.

The novelty of this work consists in using the choline chloride:urea (1:2 moles) ionic liquid as supporting electrolyte. From cyclic voltammetry and impedance experiments carried out using Pt electrode it was possible to predict the potential range at which deposition of CdTe films take place. The deposition of CdTe from ionic liquid occurs on a Te-covered Pt substrate. Also, these films were formed at less negative potentials than for deposition of singular Cd films.

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