

CATHODIC DEPOSITION OF COMPONENTS IN PbTe COMPOUNDS USING CHOLINE CHLORIDE-ETHYLENE GLYCOL IONIC LIQUIDS

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This paper reports the electrodeposition of Pb, Te and PbTe films on Pt using ionic liquids based on choline chloride: ethylene glycol eutectic mixture (ChCl-EG, 1:2 moles) in the 45-65°C temperature range. Lead and tellurium ionic species were dissolved in ChCl:EG ionic liquid at concentrations in the range of 1-10mM. The mechanism of Te, Pb and PbTe electrodeposition was investigated by cyclic voltammetry and electrochemical impedance spectroscopy. The results indicated that the PbTe compound films were obtained by induced codeposition of Pb and Te onto the previously deposited Te on Pt substrate. Two or three dissolution (stripping) anodic peaks were observed by reversing the potential scanning. Nyquist and Bode impedance spectra show differences in Pt behavior due to its polarization at various cathodic potentials.

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1. Introduction

In the recent years, room temperature ionic liquids are increasingly applied for cathodic deposition of numerous metals, alloys or semiconductor compounds [1,2]. The advantages of these novel baths include: electroplating of electronegative metals, *e.g.* Mg, Al, Ta, Nb, Mo, W and their alloys; significantly reduced hydrogen evolution as compared with the acidic aqueous baths conventionally employed; lower electrical energy consumption comparing with aqueous solutions. 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.

The lead chalcogenides PbX (X = S, Se, and Te) are IV–VI compound semiconductors that exhibit unique electronic properties relative to conventional III–V and II–VI compounds, such as very narrow energy gaps, high carrier mobilities, and high dielectric constants. They are mainly applied for infrared diodes lasers [3] and photovoltaic infrared sensors or converters [4,5].

Lead telluride, PbTe, has a band gap of 0.31eV at 300K [6] and may be either n-type or p-type as a result of deviation from stoichiometry: PbTe riched in Pb is a n-type semiconductor and PbTe having an excess of Te is a p-type semiconductor. It may be used in thermoelectric devices working in 500-600K temperature range [7].

In the specialty literature, the electrodeposition of lead telluride films on a variety of substrates using aqueous solutions was extensively reported. Saloniemi *et al.* [8,9] have investigated the electrodeposition of PbTe on Cu and ITO glass electrodes. Mondal *et al.* [10] employed an electrochemical galvanic technique to deposit PbTe on transparent conducting oxide coated glass substrates. The effect of electrodeposition conditions on the composition and structures of the PbTe films on silicon substrate was systematically investigated in several studies [11-13].

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Reports of the electrodeposition of lead chalcogenide semiconductors from ionic liquid media are relatively fewer, in spite of its many advantages, including cost-effectiveness, large-scale production, low temperature processing, and precise control of composition and thickness of materials [14]. 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 [15].

We report in the present work the deposition of Pb, Te and PbTe films using the eutectic of choline chloride and ethylene glycol (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.

In spite of the lack of data of solubility of inorganic salts, it is expected for Pb and Te precursors to dissolve in a large amount in ChCl based ionic liquids. Previously we have shown [16,17] that TeO_2 dissolve in ChCl-malonic acid and ChCl-urea eutectics. Also, TeCl_4 dissolves in 1-ethyl-3-methylimidazolium chloride/tetrafluoroborate (EMI-Cl- BF_4 ionic liquid) in the range 80-140 $^\circ\text{C}$ [18]. In the present study, PbCl_2 and TeO_2 were dissolved in ChCl: ethylene glycol (1:2 moles) eutectic. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were chosen as electrochemical techniques in order to evidence electrochemical couples of deposition/dissolution of Pb, Te, and PbTe, respectively.

2. Experimental details

The background electrolyte was prepared by mixing choline chloride (Aldrich 99%, used as purchased, without recrystallization or drying) with ethylene glycol (EG, Aldrich 99%); by heating the two components in 1:2 molar proportions at above 80 $^\circ\text{C}$ for 30 min, a homogeneous colorless liquid is formed. PbCl_2 (Merck) and TeO_2 (99%, Alfa Aesar) reagents as precursors of Pb^{2+} and Te^{4+} ions were also used as received, being dissolved in the supporting electrolyte ChCl-EG. In order to calculate the solution molarities we used a density value of ChCl-EG of 1.09 g cm^{-3} , determined in our laboratory in the temperature range of 45-65 $^\circ\text{C}$.

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 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 lead and/or tellurium ions was the quasi-reference electrode [19]. 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 10 to 100 mVs^{-1} . EIS characterization was carried out in $10^{-1} \text{ Hz} \leq f \leq 10^5 \text{ Hz}$ frequency range with an *ac* voltage amplitude of $\pm 10 \text{ mV}$.

3. Results and discussion

The investigation of lead telluride electrodeposition was carried out by comparing the cyclic voltammograms and impedance spectra for ChCl-EG ionic liquid containing ions of single components (Pb or Te) with the presence of both precursor ions in ChCl-EG ionic liquid.

Figure 1 presents an example of the voltammogram in ChCl-ethylene glycol (1:2 moles) eutectic as supporting electrolyte. It was noticed the large domain of potentials (from -0.8V to +1.2 V representing the *potential window* of more than 2V for selected ionic liquid, which is about 2 times wider in comparison with similar parameter of aqueous solutions (1.23V).

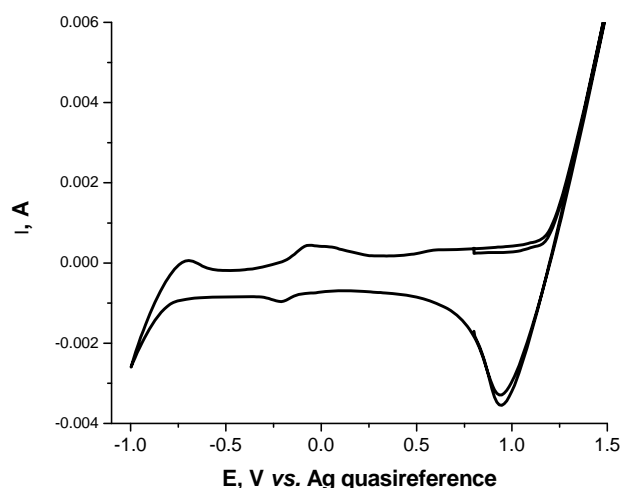


Fig. 1. Cyclic voltammogram within extended potential range on Pt (0.5 cm^2) for ChCl-ethylene glycol (1:2 moles) eutectic; scan rate 100 mVs^{-1} ; temperature 45°C

Electrodeposition of lead films

Figures 2a and 2b show the experimental results of application of cyclic voltammetry technique for Pt electrode in ChCl-ethylene glycol eutectic. As Figure 2a illustrates, for 10mM Pb^{2+} concentration the metallic Pb started to deposit at -0.37V , and displayed an increasing current during the negative going scan, with a cathodic peak at $-0.42\div -0.45\text{V}$ followed by a limiting current up to -0.8V . The electrode process may be described by the simple reduction of lead ions:

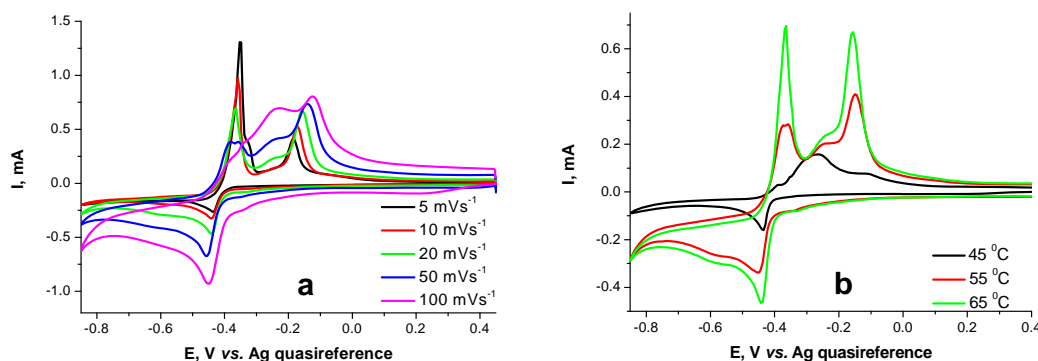
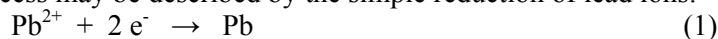


Fig. 2. Cyclic voltammograms for 10mM PbCl_2 dissolved in ChCl-EG (1:2 moles) eutectic, showing the influence of: (a) scan rate at constant temperature of 65°C and (b) temperature at constant scan rate of 20mVs^{-1}

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.

In the corresponding positive going scan, two or three anodic peaks were successively noticed and their behavior is more complex. Thus, a very sharp oxidation peak at -0.35V at slowest scan rate (5mVs^{-1}) is followed by a second anodic peak of smaller amplitude at -0.17V . Increasing the scan rate to 10mVs^{-1} , the current of first peak was diminished and of second peak was increased; a broader shape of the second peak together with a shift towards positive direction

was recorded. This behavior was similar for faster scans, but with occurrence of a new shoulder or even anodic peak situated at intermediary potential (-0.25V).

The interpretation of this anodic branch of voltammogram is difficult. We may assigned the first anodic peak to the desorption process of lead deposited onto electrode surface, a process that is evidently less intense during fast scans. The second anodic peak may correspond to the dissolution of bulk Pb layer formed onto Pt surface. The shoulder (or peak) appeared prior to the second peak may be due to a partial oxidation phenomenon of metallic Pb into Pb^+ univalent ions which are then converted into Pb^{2+} ions during the last anodic peak.

Figure 2b presents comparatively the voltammograms at constant scan rate of $20mVs^{-1}$ and the same Pb^{2+} ion concentration for different temperatures. The shapes of cathodic branches are very similar, with increasing currents with temperature. In the anodic scan, first peak of desorption at $65^{\circ}C$ has a magnitude comparable with dissolution peak, whereas at $55^{\circ}C$ it decreased significantly and almost fully disappeared at $45^{\circ}C$.

In a quantitative analysis of lead voltammograms, it has be seen that both cathodic and anodic peak currents increase with scan rate and temperature. As Figure 3a shows, linearly dependences of cathodic current with square root of scan rate are obtained for three Pb^{2+} concentrations at $55^{\circ}C$ constant temperature; also, the slopes of the straight lines obtained in all three cases increase with Pb^{2+} concentration, proving a diffusion-controlled deposition process of lead. This fact should allow us to calculate the diffusion coefficients of Pb^{2+} ionic species using the well-known Randles-Sevcik equation for a metal deposition [20]:

$$I_{pc} = 0.6401 n F A c \sqrt{\frac{nF}{RT}} \nu D \quad (2)$$

In Eq. (2), n is the number of electrons changed in electrode process ($n=2$); F , R and T are the Faraday number, ideal gas constant and absolute temperature, respectively; A – the surface area of electrode ($A=0.5 \text{ cm}^2$); ν – the scan rate; D – the diffusion coefficient of ionic species.

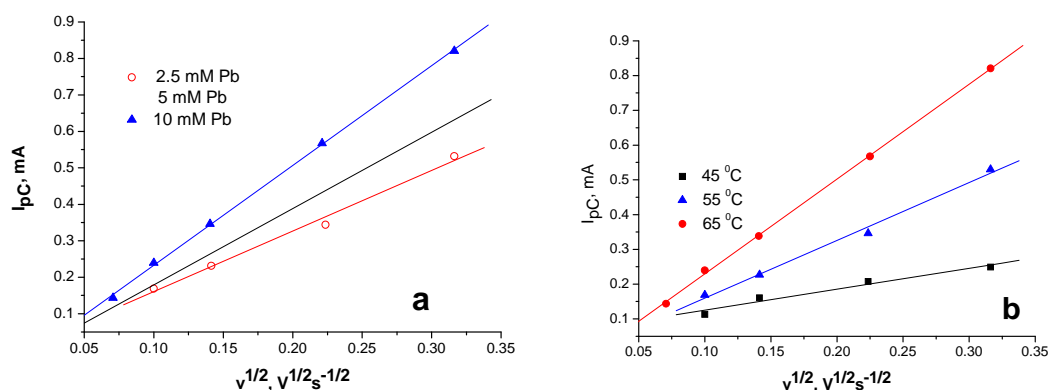


Fig. 3. $I_p - \nu^{1/2}$ linear plots for cathodic deposition of Pb films on Pt (0.5 cm^2) using ChCl-EG (1:2 moles) eutectic as electrolyte; (a) three Pb^{2+} ion concentrations; temperature $55^{\circ}C$ and (b) $10mM Pb^{2+}$ ion concentrations; three temperatures

Using the above equation and the slopes of $I_{pc} - \nu^{1/2}$ linear dependences, reliable results for diffusion coefficient may be obtained by performing a series of cyclic voltammetry experiments with various lead ion concentrations and scan rates under a severe control of temperature.

From our preliminary investigations we obtained D values for Pb^{2+} ionic species of the order of 10^{-7} - $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in the temperature domain of 45 - $65^{\circ}C$. We mention that the order of magnitude for diffusion coefficient of Pb^{2+} ion ($0.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at $55^{\circ}C$) is generally much lower than in aqueous solutions (D about $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for Pb^{2+} ion), but this is expected for diffusion in such ChCl-ethylene glycol ionic liquid that has higher viscosity and density as aqueous media. Figure 3b shows the influence of increasing temperature on $I_{pc} - \nu^{1/2}$ linear dependences.

From the slope of linear dependence of Arrhenius semi-logarithmic plot (logarithm of diffusion coefficient *versus* reciprocal of absolute temperature) a value of 137 kJmol^{-1} of the activation energy of diffusion of Pb^{2+} ion in the selected ionic liquid was estimated.

More information about the cathodic process is obtained by applying the electrochemical impedance spectroscopy technique for the same $\text{Pb}^{2+}/\text{ChCl-EG}$ ionic liquid system. In the followings we present both Nyquist and Bode diagrams obtained experimentally by shifting the electrode potential toward more negative values. Figure 4 shows clearly that the gradual cathodic polarization from 0V to -0.4V results in decreasing of diameters of capacitive semicircles up to $500 \Omega\text{cm}^2$, suggesting an increased rate of deposition of metallic Pb with a maximum value at -0.4V potential. Correspondingly, the maximum of Bode angle for both Pb^{2+} concentrations decreases from -65° to *cca* -50° , a value attributed to a diffusion-controlled deposition process. By continuing the polarization at more negative potentials an increase of semicircle diameter was noticed proving the diminution of faradaic process in the potential range more negative than cathodic peak.

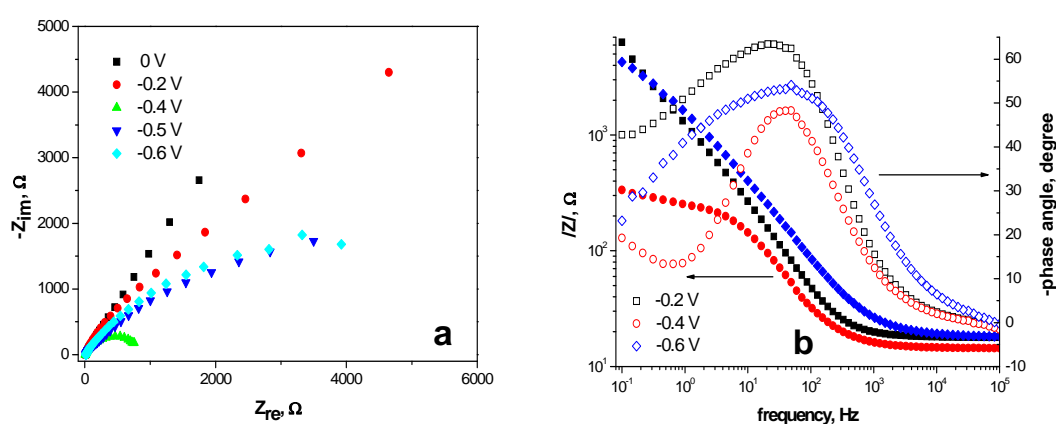


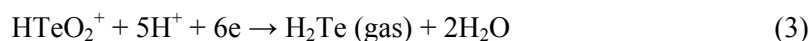
Fig. 4. (a) Nyquist and (b) Bode diagrams recorded at different polarizations of the Pt electrode (0.5 cm^2) in ChCl-EG (1:2 moles) eutectic containing 5 mM PbCl_2 ; temperature 55°C .

Electrodeposition of tellurium 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 [16] and malonic acid [17]. The voltammograms for singular Te ion reduction on Pt in ChCl-EG ionic liquid shown in Figure 5a exhibit a start of tellurium deposition at $+0.2\text{V}$, identified as Te UPD reaction. Along the cathodic curve it follows a series of two or three small reduction peaks and finally a main reduction peak at about $-0.63\text{V} \div -0.65\text{V}$, attributed to massive deposition of tellurium. At reverse scan, two consecutive anodic peaks were recorded at $+0.2\text{V}$ and $+0.6\text{V}$, respectively. Certainly, they may be attributed to separate dissolution processes of massive deposition layers and UPD layers (these being the first layers onto Pt surface).

The same shape of cathodic branch of voltammograms was observed for lower concentrations of tellurium ion (Figure 5b). In spite of this, on the anodic branch only a single oxidation peak was observed which may be a superposition of the above described anodic peaks.

The mechanism of tellurium electrodeposition was extensively investigated in aqueous media [21]. A general scheme proposed an electrochemical step of HTeO_2^+ electroreduction from which H_2Te gas results:



In a second step, tellurium deposit is formed by a chemical reaction between H_2Te and HTeO_2^+ ion:



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 [18]. In the absence of water a direct discharge to elementary Te is expected to be carried out on Pt electrode:



Thus, a simple electrode process described by reaction (5) is supposed to take place in ChCl-EG (1:2 moles) eutectic, where TeO_2 is dissolved in this ionic liquid as supporting electrolyte. It was noticed that the behavior of main cathodic peak situated more negatively than -0.6V is quite reversible, its peak current increasing with scan rate and tellurium ion concentration.

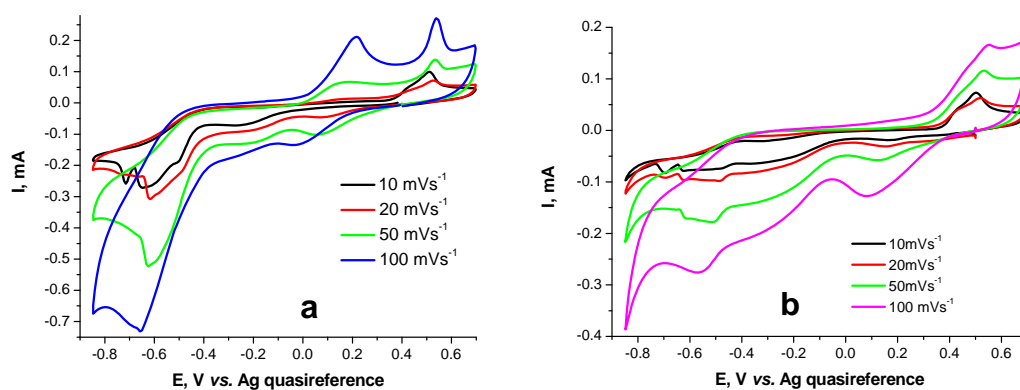


Fig. 5. Cyclic voltammograms for (a) 5mM TeO_2 and (b) 2.5mM TeO_2 dissolved in ChCl-EG (1:2 moles) eutectic at different scan rates; Pt electrode (0.5 cm^2), temperature 55°C

We tried to make a quantitative analysis of tellurium voltammograms, supposing also a diffusion-control of cathodic process, because both main cathodic peaks and anodic peak have currents increasing with scan rate and temperature. Linearly dependences of cathodic current with square root of scan rate are obtained for three temperatures. This fact should allow us to calculate the diffusion coefficients of Te^{4+} ionic species using the well-known Randles-Sevcik equation (eq. 2) and also the activation energy for diffusion of tellurium ion in ChCl-EG ionic liquid.

The estimated value of diffusion coefficient for Te^{4+} ion at 55°C was of around $10^{-6} \text{ cm}^2/\text{s}$; also, the diffusion coefficients at other temperatures are generally slightly higher than for Pb ionic species, while the activation energy for diffusion (around 50 kJmole^{-1}) is lower than for Pb species.

Nyquist and Bode impedance spectra (data recorded at 45°C and presented in Fig. 6) illustrate the massive deposition of tellurium that starts at -0.4V potential and has a peak around -0.6V. Thus, the gradual decreasing of diameters of Nyquist semicircles up to -0.6V polarization demonstrates the most intense cathodic process at this potential value. A confirmation is found in Bode diagrams, where the lowest impedance modulus is at -0.6V polarization with the lowest negative phase angle (-55°) at the same potential.

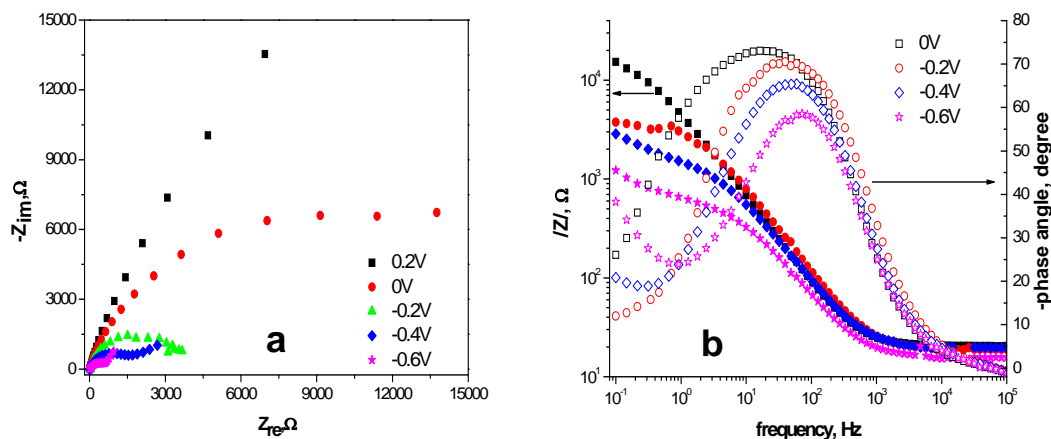


Fig. 6. (a) Nyquist and (b) Bode diagrams recorded at different polarizations of the Pt electrode (0.5 cm^2) in ChCl-EG (1:2 moles) eutectic containing 5 mM TeO_2 ; temperature 45°C .

Electrodeposition of lead telluride films

The mechanism of PbTe compound obtaining consists in a co-induced electrodeposition of components of this semiconductor. Co-induced deposition was explained by Kröger [22,23] who stated that the deposition potential of compound is determined by the electronegative component and is positively shifted that the equilibrium reduction potential of this less noble component. For PbTe, the reduction of chalcogen ion induces the reduction of Pb metal at a more positive value than that given by Nernst equation; thus the PbTe compound deposits at a potential prior to that given by Nernst equation. The observed potential difference due to induced co-deposition, ΔE , is related to the very negative value of standard Gibbs free energy of PbTe formation, ΔG^0 :

$$\Delta G^0 = -z F \Delta E \quad (6)$$

where z is the charge of metallic ion (Pb^{2+}) and F –Faraday number.

For PbTe, the order of magnitude of ΔG^0 value is around -100 kJ/mole at 25°C . First, a Te layer is deposited on platinum and subsequently the underdeposition of lead telluride taken place followed by the massive deposition. The cathodic process may be written as:



In the case of simultaneous presence of Pb^{2+} ion and Te^{4+} ion in ChCl-EG ionic liquid as supporting electrolyte the recorded cyclic voltammograms had more complex shapes. An example is given in Figure 7 where a comparison of systems with a single precursor dissolved separately with systems with both precursors jointly dissolved was made.

In the case of single precursor dissolved one be observed clearly a difference between the peak potential and the peak currents for reduction of Pb and Te ionic species, especially regarding the massive deposition. In Figure 7, the voltammogram recorded in the jointly presence of both Pb and Te species seems to be a summation of separate voltammograms. It starts with UPD deposition of Te as a monolayer onto Pt electrode on which the PbTe binary compound began a UPD process with an evident peak at -0.2V . If the cathodic scan is continued, the massive deposition of PbTe took place exhibiting a peak at -0.57V , a value that is intermediary between -0.4V and -0.6V of simple component depositions. On the anodic branch of this voltammogram two oxidation peaks occur evidently, the first one being certainly due to the dissolution of PbTe

compound deposit. The second anodic peak is probably a dissolution of a PbTe compound riched in Te or even a dissolution of pure tellurium deposited as UPD.

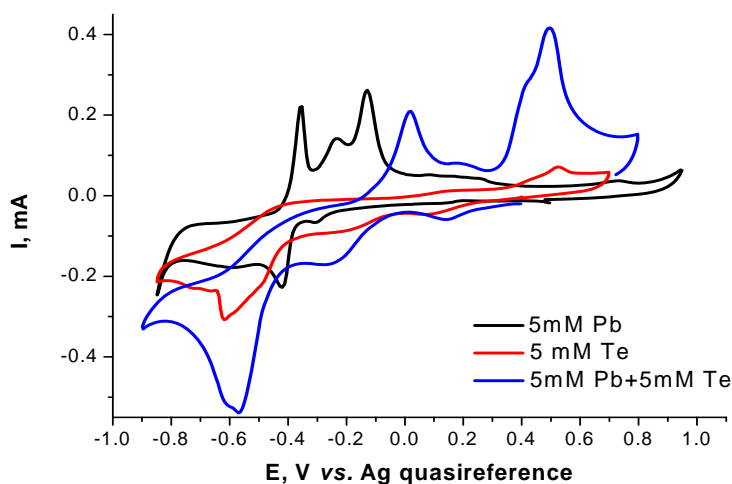


Fig.7. Cyclic voltammograms for 5mM PbCl₂ and 5mM TeO₂ dissolved separately and dissolved together in ChCl-EG (1:2 moles) eutectic; Pt electrode (0.5 cm²), temperature 55^oC, 20mVs⁻¹ scan rate

A comparison of systems with both precursors jointly dissolved but in different ratios of Pb and Te concentrations is presented in Figures 8 and 9. Regarding the Figure 8, for ionic liquid less riched in Pb ions (1mM PbCl₂) the voltammogram has the smallest peak current whereas for the most riched system (5mM PbCl₂) the peak current increased most significant. Correspondingly, the same tendency is for anodic peaks, where the highest current was recorded for system with 5mM PbCl₂. It is worth to mention that a shift towards positive potential is observed for cathodic peaks by increasing PbCl₂ concentration in ionic liquid, while the anodic peaks also shift towards positive potential, thus keeping a constant ΔE_p .

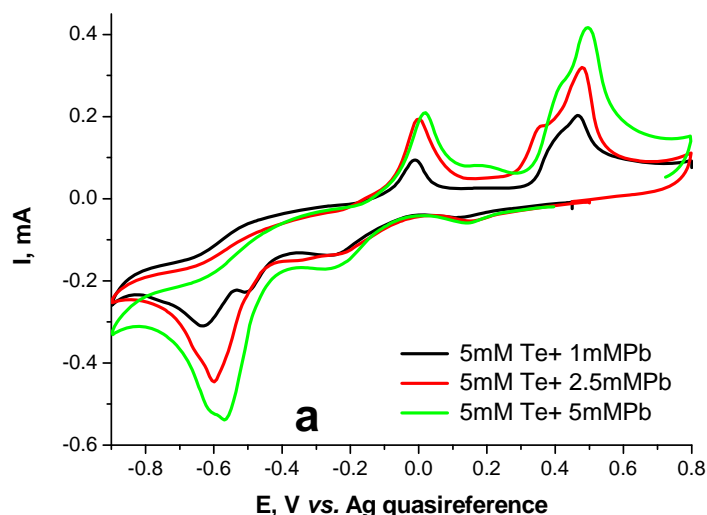


Fig. 8. Cyclic voltammograms for x mM PbCl₂ and 5mM TeO₂ jointly dissolved in ChCl-EG (1:2 moles) eutectic; x = 1mM, 2.5mM and 5mM PbCl₂, Pt electrode (0.5 cm²), temperature 55^oC, 20mVs⁻¹ scan rate

In general, Figure 9 illustrates the same behavior of systems of increase the peak current for more concentrated solutions. However, on contrary of Figure 8, Figure 9 shows a shift of peak

potentials for both cathodic and anodic processes towards negative direction when the system is gradual riched in Te 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 PbTe compound, but the explanation of this phenomenon requires more experiments to be performed.

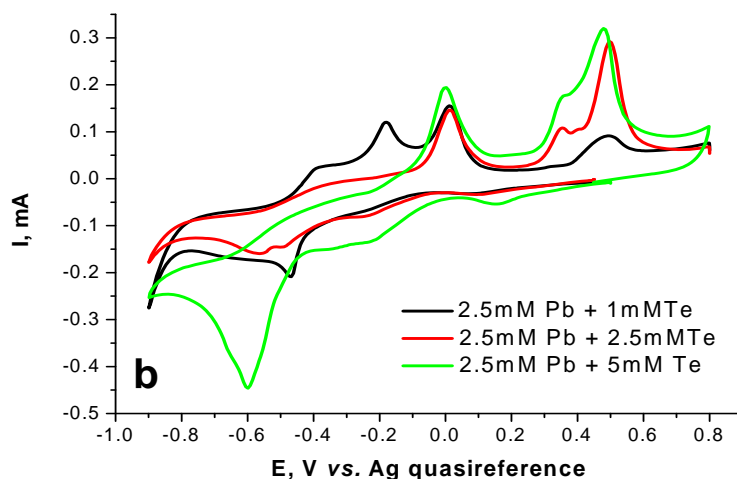


Fig. 9. Cyclic voltammograms for 2.5 mM PbCl₂ and x mM TeO₂ jointly dissolved in ChCl-EG (1:2 moles) eutectic; x = 1mM, 2.5mM and 5mM TeO₂, Pt electrode (0.5 cm²), temperature 55^oC, 20mVs⁻¹ scan rate

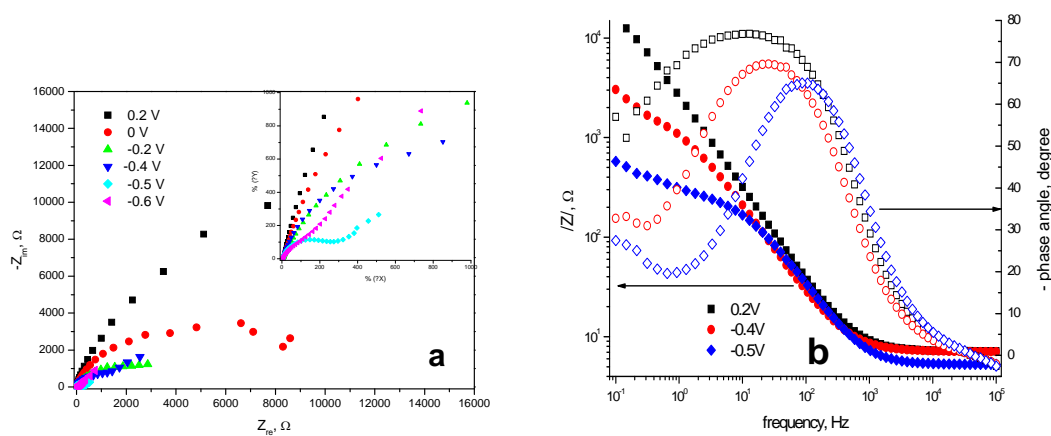


Fig. 10.(a) Nyquist and (b) Bode diagrams recorded at different polarizations of Pt electrode (0.5cm²) in ChCl-EG (1:2 moles) eutectic containing 5 mM PbCl₂ and 5mM TeO₂; temperature: 55^oC. **Inset:** high frequency data on an enlarged scale.

The impedance spectra of PbTe formation confirm the above evidences described by cyclic voltammograms. Figure 10 give some examples of experimental results by applying the electrochemical impedance spectroscopy for systems containing both Pb and Te precursors. From the inset of Figure 10-a it is obvious that the smallest diameter of Nyquist semicircles is recorded by -0.5V and -0.6V polarizations, where the massive deposition of PbTe compound takes place. The order of magnitude of these diameters is of 300-400 Ωcm². However, the maximum phase angle from Bode spectra reaches the minimum value at -65^o, only a fact that demonstrates the semiconductor character of PbTe compound. In Figure 11 were selected for comparison some Nyquist plots for systems with variable content in Te, the component which is first deposited onto Pt surface by UPD process. This Figure demonstrates that by polarizing Pt electrode at -0.2V the

increase of Te content in electrolyte led to a smaller diameter of Nyquist semicircles, a fact that suggested a faster electrochemical process (UPD) of tellurium deposition.

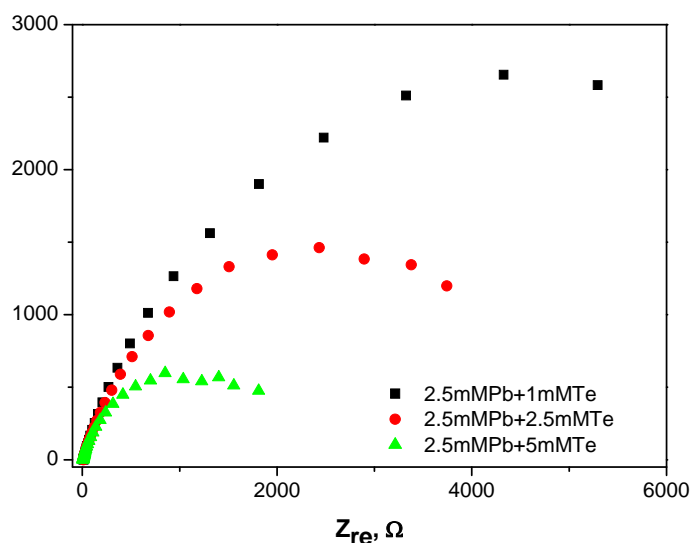


Fig. 11 Nyquist spectra recorded at $-0.2V$ polarization of Pt electrode ($0.5cm^2$) in ChCl-EG (1:2 moles) eutectic containing 2.5 mM PbCl_2 and $x\text{ mM TeO}_2$; $x = 1\text{ mM}; 2.5\text{ mM}; 5\text{ mM TeCl}_2$, temperature: 55°C

4. Conclusions

Cyclic voltammetry and electrochemical impedance spectroscopy were successfully used for a comparative investigation of separate deposition of pure components (Pb or Te) and PbTe compound. Both techniques gave information about the potentials of deposition and dissolution of PbTe and its pure components, as well as about the mechanism. The massive formation of PbTe is previously accompanied by a Te underpotential deposition and even a PbTe compound underpotential deposition as a result of co-induced effect.

The novelty of this work consists in using the choline chloride : ethylene glycol (1:2 moles) eutectic as supporting electrolyte. Working in the $45\text{-}65^\circ\text{C}$ temperature range we demonstrated that electrodeposition of Pb and Te are cathodic processes controlled by diffusion, a fact that allow to estimate the diffusion coefficients of both Pb^{2+} and Te^{4+} ionic species as well as their activation energies of diffusion.

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