ELECTROCHEMICAL DEPOSITION OF BITE FILMS FROM CHOLINE CHLORIDE – MALONIC ACID MIXTURE AS IONIC LIQUID

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A study of bismuth telluride electrodeposition on platinum and copper electrodes in an ionic liquid based on choline chloride and malonic acid mixture (1:1 moles) bath containing 1-50 mM BiCl₃ and 10-50 mM TeO₂ at 50-85°C is reported. The mechanism of Bi, Te and BiTe electrodeposition on Pt electrode was comparatively investigated by cyclic voltammetry. From cyclic voltammograms carried out in order to characterize the cathodic process it was found that singular tellurium deposition is performed at more positive potentials than bismuth deposition. The deposition of BiTe from ionic liquid occurs on a Te-covered Pt. Also, Nyquist and Bode impedance spectra showed differences in Pt behavior due to its polarization at various cathodic potentials. The bismuth telluride films were deposited on copper plates by electrolysis under potentiostatic conditions. The morphology of these BiTe films was determined by AFM, SEM and TEM microscopy.

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1. Introduction

In recent years it was shown that bismuth telluride and its ternary compounds with selenium or antimony are the most widely used thermoelectric materials for room temperature applications [1]. By varying the composition from its stoichiometric composition (Bi₂Te₃), bismuth telluride can be tailored to be n-type (Bi₂₋ₓTe₃₊ₓ) or p-type semiconductors (Bi₂₊ₓTe₃₋ₓ)[2]. Bi₂Te₃ and its derivatives may be prepared as thin films using a number of traditional techniques as sputtering, metalorganic vapour deposition and electrodeposition. Electrodeposition has certain advantages, including the fact that composition of BiTe films can be controlled by adjusting the electrolysis parameters, its cost-effectiveness, low deposition temperature and relative ease in controlling film thickness from nanoscale to a few millimetres[3,4].

The electrodeposition of Bi₂Te₃ in aqueous electrolytes has mostly been carried out from nitric acid baths [5-11], hydrochloric acid [12], perchloric acid [13,14] and sulphuric acid [15]. Ionic liquids can provide an alternative for metal electrodeposition. Abbott et al. [16] recently showed that an ionic liquid can be formed by mixing a quaternary ammonium salt, choline chloride (2-hydroxy-ethyl-trimethyl-ammonium chloride), with a hydrogen-bond donor species such as a glycol (ethylene glycol), amide (urea) or carboxylic acid (malonic acid). Previously [17] we investigated BiTe electrodeposition from a ionic liquid consisting in 1:2 moles eutectic mixture of choline chloride (ChCl) with urea as a hydrogen bond donor species. The eutectic mixture of ChCl-malonic acid (1:1 moles) was also found by us in preliminary experiments [18, 19] as an appropriate ionic liquid for BiTe electrodeposition.

In the present work it is investigated comparatively the deposition of Bi, Te and BiTe compound films using ionic liquid consisted in a mixture of choline chloride (ChCl) and malonic acid (MA). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were

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chosen as electrochemical techniques in order to evidence the interface processes. BiTe films were obtained on Cu substrate by electrolysis in potentiostatic conditions at various cathodic potentials and their surface was characterized.

2. Experimental

The supporting electrolyte was prepared by mixing ChCl (Aldrich 99%, used as purchased, without recrystallization or drying) with malonic acid (Aldrich 99%) by heating the two components in a 1:1 mole ratio at above 90°C for 30 min, a homogeneous colourless ionic liquid is formed. The precursors for Bi³⁺ and Te⁴⁺ ions were respectively BiCl₃ and TeO₂ reagents (Alfa Aesar 99%). In order to calculate the solution molarities, we used density values of ChCl malonic acid (1:1) mixture determined in our laboratory at the working temperatures. An AUTOLAB PGSTAT 12 Ecochemie potentiostat provided with a frequency response analyzer was used for cyclic voltammetry and impedance spectroscopic measurements. During the study of cathodic process, a platinum sheet (0.5 cm²) was used as a working electrode, whereas the auxiliary electrode was a platinum mesh. A platinum wire immersed in the working electrolyte constituted from ionic liquid containing tellurium and bismuth ions was used as a quasi-reference electrode. The Pt working electrode was polished with alumina paste, rinsed, and dried before every measurement. Cyclic voltammograms were recorded at scan rates from 2 mV s⁻¹ to 100 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was carried out in the 5×10⁻² Hz < f < 10⁵ Hz frequency range with an ac voltage amplitude of ±10 mV by gradually polarizing Pt cathode in the range of -0.15 V to -0.65 V (versus Pt quasi-reference electrode).

BiTe films were prepared on commercial copper sheets in ChCl–MA based baths, without stirring, by potential control electrolysis. The Cu cathode had an exposed area of 1-2 cm²; a parallel Pt sheet was the anode and a Pt wire was the quasi-reference electrode. Film morphology was studied using AFM microscope (Quesant Scope -350). Micrographs were obtained using SEM microscope (Bruker AXS Microanalysis provided with EDX) and TEM microscope (EM-410 Philips, 60 kV).

3. Results and discussion

A typical voltammogram (not shown) of ChCl–MA supporting electrolyte has a potential window of more than 1.1 V [22].

![a](image1.png) ![b](image2.png)

**FIG 1.** Cyclic voltammograms on Pt in ChCl +MA (1:1 mol) ionic liquid, 85°C; (A) with10 mM Te and (B) with different Te ions concentrations, scan rate 5mVs⁻¹.

Typical cyclic voltammograms of the separately investigated ions recorded on Pt electrode in the absence of solution stirring are presented in Figures 1-2. 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 0.6 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 presents some examples of cyclovoltammograms for tellurium ions. All CV curves for 10mM Te ions concentration are characterized by a reduction peak at ca. -0.2 V versus Pt quasireference electrode and an oxidation peak at ca. 0.2 V at all scan rates (Fig. 1A). With higher scan rates the peak separation for this couple increases from 100mV to ca. 200mV. Similar results can be also found in the CVs measured for other Te ion concentrations (Fig. 1B). It can see that both cathodic and anodic peak currents increase with scan rate and concentration.

During the examination of the electrochemical behaviour of Bi ionic species (Fig. 2) also a couple of reduction/oxidation peaks can be observed at all scan rates. The reduction peak (Fig. 2A) is attributed to deposition of bismuth film; also the single anodic peak corresponds to the stripping of deposit. At lowest scan rate and 85°C temperature the cathodic peak and the anodic peak are located in the potential range from -0.6V to -0.8V vs. Pt quasi-reference electrode. With higher scan rates the peak separation for this couple increases. Fig. 2B shows that both cathodic and anodic peak currents increase with scan rate and concentration.

Cyclic voltammetric behavior of Bi, Te, and Bi + Te ionic species in ChCl– malonic acid is shown in Figs. 3 and 4.
A comparison between singular Te, Bi and binary BiTe deposition is presented in Figures 3 and 4. From Figs.3 and 4 we can observe that, Bi and Te as singular ions have reduction peaks at very different potential values: −0.85 V for Bi and −0.08 V for Te, whereas CV curve for BiTe indicates a simultaneous codeposition in the range of −0.1 V to −0.6 V. The pronounced peak (at −0.68 V) in Fig.4 is attributed to a BiTe deposit which is very rich in Bi. The pre-deposited Te layer facilitates the co-reduction of Te and Bi as a binary compound.

Nevertheless, for a 50 mM Bi + 40 mM Te mixture, the peak current does not reach the value for pure Te deposition, which may be an indication of partial participation of Bi ions even in this potential range. The corresponding anodic peaks are observed, due to consecutive dissolution of pure Bi (or Bi-rich deposit), binary BiTe compound, and pure Te.

The first peak form Figure 5A attributed to tellurium deposition increases linearly with tellurium concentration in bath containing both Bi and Te ions. The second peak attributed to BiTe compound co-deposition increases, too. The corresponding anodic peaks have similar behaviour.

FIG 5. Cyclic voltammograms on Pt using ChCl–malonic acid (1:1) ionic liquid; 85°C, scan rate 50 mV s⁻¹. Curves for: 50 mM BiCl₃; 50 mM TeO₂; 50 mM BiCl₃ + two concentrations of TeO₂.

Quite similar behaviour is for the case of Figure 5B; now, the first of tellurium ion reduction remains almost constant in its potential value, but the peak current is a little bit smaller when the Bi ion concentration is increased.
The influence of temperature is shown in Figure 6. It is evident the increase of peak current and a shift of both peak potentials for cathodic and anodic processes.

**FIG 6.** Comparative voltammograms on Pt using ChCl–malonic acid (1:1) ionic liquid with 50 mM BiCl₃ + 10 mM TeO₂ showing temperature influence, scan rate 10 mV s⁻¹.

Regarding the mechanism of cathodic processes, literature indicates that ions are present in ionic liquid as complex ions, bringing the reduction potentials of bismuth and tellurium ions close to each other, in spite of differences in the standard electrode potentials. It has been shown that in the basic (chloride-rich) ionic liquid, it is possible for Bi and Te ionic species to exist as BiCl₄⁻ and TeCl₆²⁻ complex ions [18, 22, 23], and this may also be true in the ionic liquid In chloride-rich medium, BiCl₄⁻ and TeCl₆²⁻ complex species may be formed, therefore the following electron transfer processes were proposed:

\[
TeCl₆^{2-} + 4e^- \rightarrow Te + 6Cl^-
\]  
\[
BiCl₄^{-} + 3e^- \rightarrow Bi + 4Cl^-
\]  
\[
(1-x)BiCl₄^{-} + xTeCl₆^{2-} + (3+x)e^- \rightarrow Bi_{1-x}Te_{x} + (4+2x)Cl^-
\]

**FIG 7.** Nyquist (a) and Bode (b) plots at different potentials of Pt (0.5 cm²) in ChCl–malonic acid containing 50 mM BiCl₃ + 40 mM TeO₂; temperature 85°C.

In Fig. 7 we present comparatively Nyquist and Bode impedance spectra for BiTe deposition when Pt was polarized at various cathodic potentials; the onset of BiTe massive deposition (cathodic peak and diffusion-limited current domain) is evidenced. The plots show two
time constants, the first being related to a capacitive behaviour at high frequencies (semicircle) and the second one to a diffusion-limited process, corresponding to a sloping line extended to low frequency. From Bode diagram it results than tellurium film has a highest positive phase angle, followed by BiTe compound and Bi-riches BiTe films that are probably porous.

In another series of experiments, BiTe films were grown on commercial copper sheets using ChCl-MA ionic liquid containing Bi and Te ions, in the temperature range 40-85°C. Experiments were performed under controlled potentials with values in the range of −0.35 to −0.5V (vs. Pt quasi-reference electrode). The electrolysis time was 10-60 minutes. AFM images for BiTe deposited films at constant potential of -0.35 V for 60 minutes are presented in Figure 8. For this sample which is 2-2.3 mm thick the determined roughness had values of Ra = 59.3 nm and Rms= 81.4 nm.

**FIG 8.** AFM micrography for BiTe films deposited using the ChCl-MA ionic liquid containing 2.5 mM Bi + 2.5 mM Te, at constant potential of -0.35V for 1 hour; temperature 50°C.

**FIG 9.** The SEM image (A) and mapping image of elements (B) for BiTe films deposited on copper substrate using the ChCl-MA ionic liquid with 2.5 mM Bi + 2.5 mM Te, at constant potential of -0.35V, 1 hour; temperature 50°C.
The SEM images for BiTe films deposited using ChCl-MA ionic liquid containing 2.5 mM Bi + 2.5 mM Te and similar operating parameters as previous sample (analysed by AFM) are presented in Fig. 9. As can be observed, the deposit is relatively irregular with clusters of crystal sizes around 300 nm. EDX chemical analysis revealed a 50-64 % Te in the BiTe deposit. A uniform distribution of Te and Bi elements along to entire surface of analysed sample is shown by SEM mapping image. However, TEM micrographies (Fig. 10) reveal a size of single crystallites of the order of 8-18 nm.

**FIG 10. TEM images for BiTe films deposited using the ChCl-MA ionic liquid containing 2.5 mM Bi + 2.5 mM Te, at constant potential of -0.35V for 1 hour; temperature 50°C.**

4. Conclusions

Cyclic voltammetry and electrochemical impedance spectroscopy were successfully used for a comparative investigation of separate deposition of pure components (Bi or Te) and BiTe compound. Both techniques results indicate that BiTe films could be deposited from ChCl–MA based ionic liquid and they occur on a Te-covered substrate, at less negative potentials than for deposition of singular Bi films.

The electrodeposition of BiTe is diffusion controlled but, has degree of irreversibility with respect to singular Te and Bi deposition.

The morphology of BiTe films is less dependent on the applied potential during electrodeposition on copper substrate.

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References