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Studies of antimony telluride and copper telluride films electrodeposition from choline chloride containing ionic liquids

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ABSTRACT

Cyclic voltammetry and electrochemical impedance spectroscopy were used to investigate the deposition of antimony telluride or copper telluride from ionic liquid consisting in mixture of choline chloride with oxalic acid. In addition, the cathodic process during copper telluride formation was studied in the mixture of choline chloride with ethylene glycol. The results indicate that the Pt electrode is first covered with a Te layer, and then the more negative polarisation leads to the deposition of Sb_xTe_y or Cu_xTe_y semiconductor compounds. Thin films were deposited on copper and carbon steel at 60–70 °C and were characterised by scanning electron microscopy, energy X-ray dispersive spectroscopy (EDS), and X-ray diffraction (XRD). Their stoichiometry depends on the bath composition and applied potential. EDS and XRD patterns indicate the possible synthesis of stoichiometric Sb_2Te_3 phase and Cu_2Te, Cu_5Te_3, and $Cu_{2.8}Te_2$ phases, respectively, by controlling the ratio of ion concentrations in ionic liquid electrolytes and deposition potential.

1. Introduction

Antimony tellurides, Sb_xTe_y (named also Sb–Te alloys) are narrow band-gap semiconductors used as thermoelectric material in solid state refrigerators, thermal sensors and micro-coolers [1–3]. In addition, thin films of Sb_2Te_3 compound are considered potential candidates for non-volatile phase change memory devices (rewritable compact or digital versatile discs) replacing the more complex $Ge_2Sb_2Te_5$ compound [4]. Semiconductor copper tellurides, Cu_xTe_y, have also a wide range of applications [5] in thermoelectricity and optoelectronics, photothermal conversion, microwave shielding coating, including photoelectrodes in solar cells, photodetectors and super ionic conductors.

Electrodeposition is a suitable technique used to prepare a wide range of thin or multilayer films. It is technologically simple and provides numerous advantages over other physical and chemical techniques such as low investment cost and the possibility of deposition over flat or complicated shaped substrates. The drawbacks refer to the need of specialised personnel in electrochemistry and conducting preliminary experiments to establish the optimal electrolysis conditions.

In general, thin films of tellurides have been mostly electrodeposited from aqueous electrolytes, particularly acidic solutions (with nitric or hydrochloric acid) in order to have a sufficiently high content of Te species despite their poor solubility. Studies describing the electrochemical synthesis of antimony telluride [5–13] in these solutions with a pH 1.0–3.5 were carried out in recent years. Also, the codeposition of copper and tellurium is usually carried out in chloride [14,15], sulphate [16–19], and nitrate [20] aqueous solutions. Very recently, the electrochemical deposition was used to show how the surface properties of $Cu_{2-x}Te$ thin films can be varied quasi-continuously by controlling the amount of Cu in the film *via* the intercalation of Cu metal into Te [21]. However, nonaqueous electrolytes such as low-temperature molten salts or ionic liquids exhibit many advantages over aqueous media because they are able to dissolve relatively high concentrations of precursor salts. In general, the codeposition of two metals in ionic liquids is rarely practised although it is easier than in aqueous solutions due to more narrow separation of reduction potentials or even their overlapping. $AlCl_3$ containing melts and ionic liquids based on imidazolium or pyrrolidinium derivatives were extensively used for the deposition of metals such as Sb [22–25] or Cu [26–34]. Elemental Te [35–37] and Sb_xTe_y [23,25,38] semiconductor electrodeposition was also reported in such media.

However, in terms of technological application, the traditional ionic liquids with methylimidazolium or methylpyrrolidinium derivates

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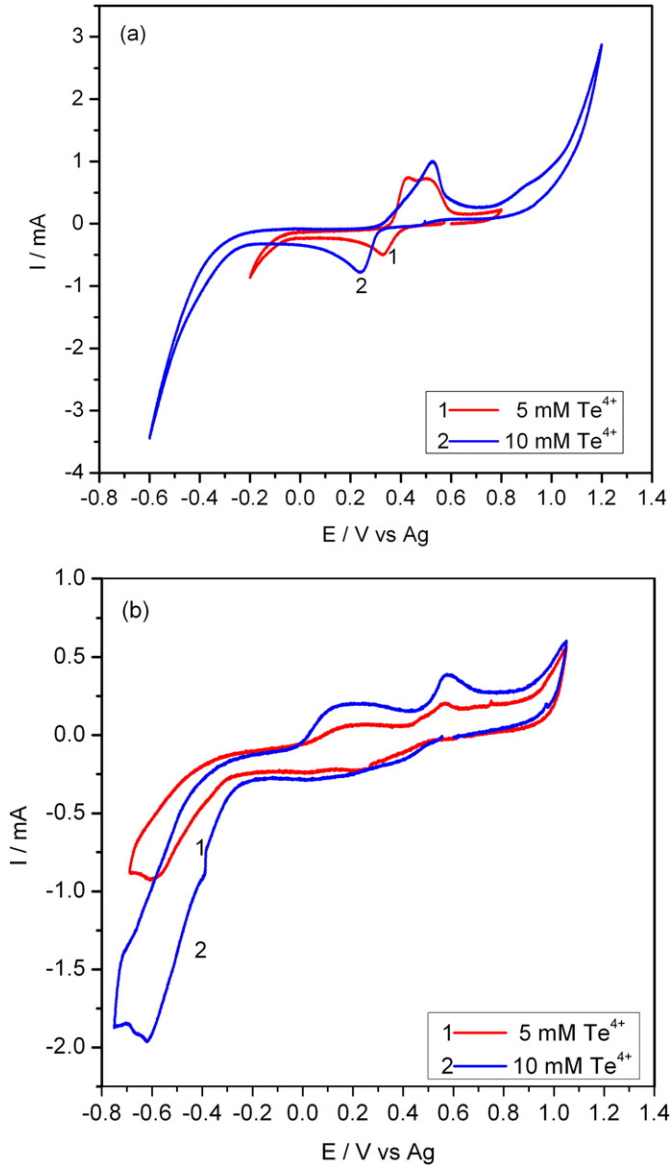

Fig. 1. CVs on Pt at 60 °C from ionic liquids containing 5 and 10 mM Te^{4+}: (a) ChCl–OxA + TeO_2, 50 mVs^{-1}; (b) ChCl–EG + TeO_2, 100 mVs^{-1}.

come with some economical and potential toxicological and purity issues. Very recently, ionic liquids containing choline chloride (*hydroxyethyl-trimethyl ammonium chloride*, ChCl) were also used as the electrolyte to investigate the electrodeposition of metals and semiconductors. These ionic liquids named DES (deep eutectic solvents) are formed as eutectic mixtures of quaternary ammonium salts (the one most often used is choline chloride) with amides, glycols, or carboxylic acids as hydrogen bond donors. Such media have the advantages of being easily prepared, water- and air-stable and nontoxic. Only few studies on the electrodeposition of Cu in DES based on choline chloride have been conducted [39–43]. We have reported experiments regarding the possibility of electrodeposition of individual Sb or Te and as binary or ternary (BiSbTe) compounds using eutectic mixtures of choline chloride with urea [44–46], malonic acid [47,48], and oxalic acid [49].

In this paper, we report the codeposition of Sb with Te from choline chloride–oxalic acid (ChCl–OxA) mixture and Cu with Te from either ChCl–OxA or choline chloride–ethylene glycol (ChCl–EG) mixtures.

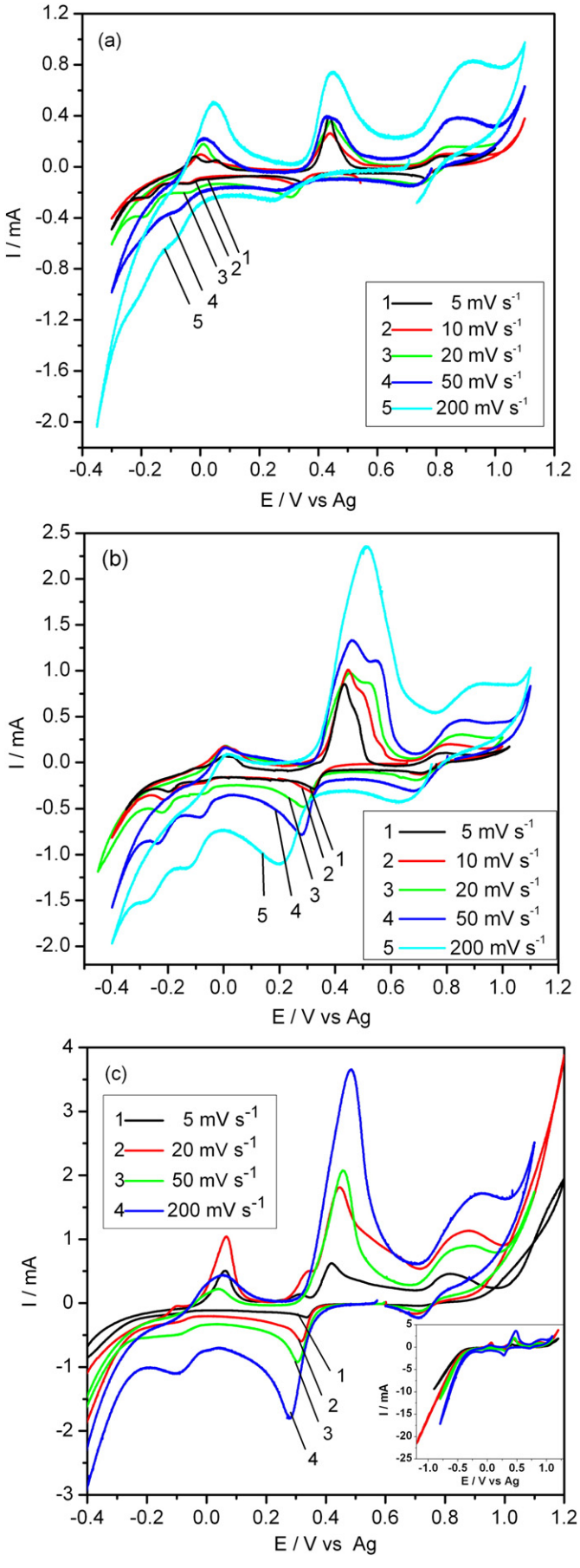

Fig. 2. CVs on Pt in ChCl–OxA + $SbCl_3$ + TeO_2 electrolyte at 60 °C; Sb^{3+} and Te^{4+} concentrations: (a) 8 mM + 3 mM; (b) 8 mM + 8 mM; (c) 3 mM + 8 mM.