



## Electrochemical tin deposition from an ethaline (choline chloride: ethylene glycol 1:2)

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### Abstract

In this work, we have undertaken the electrodeposition of tin in deep eutec solvent consisting of a mixture of choline chloride-ethylene glycol. The objective is to determine the potential at which tin (Sn) can be electrodeposit with a view to its recovery and recycling in electrical, electronic and electrotechnical waste. Cyclic voltammetry experiments were performed to study the electrochemical behavior of the tin redox system. By application of Randles-Sevcik equation, the coefficient of diffusion reflecting the mobility of Sn(II) ions at the surface of the electrode is  $105.10^{-4} \text{ cm}^2/\text{s}$ . From the CV obtained, a window of synthesis potential is defined in which the electrodeposition of Sn was studied. The analysis of the deposits obtained by chronoamperometry at a fixed potential of -0.61V on a glassy carbon electrode indicates the presence of a tetragonal phase of metallic tin. SEM images of the surfaces of deposits obtained shows a butterfly microstructure.

*Keywords:* electrodeposition, tin, cyclic voltammetry, deep eutectic solvents.

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## 1. Introduction

Most of the refined tin ingots placed on the market supply a whole series of industries including the steel industry (flat steel products or castings in pearlitic cast iron), mechanical construction (bearings, sintered parts, tools, pumps), in the automotive industry (radiators, tanks, seats, bearings, engine blocks), electronics (printed circuits, connections), glassware (float-glass, bottles), ceramics (tiles), organic chemistry (reagents, catalysts, PVC), agrochemicals (fungicides, insecticides, pesticides), electrical engineering (contactors, windings) [1]. In addition, electrosynthesis is one of the most widely used methods to develop materials. It is an interesting method to prepare advanced materials in the form of coatings or thin layers, due to its many advantages: economic and ecological [2]. In this method, the most used process is carried out in an aqueous medium. However, this medium has a significant defect because of the hydrogen discharge which disturbs the electrodeposition of the very electronegative elements, reducing the efficiency of the deposit. In addition, this phenomenon has destructive effects on the quality of the deposits, causing the appearance of pitting and dendritic morphologies [3]. The electrodeposition of tin in an aqueous medium has been studied by several authors. In their work, Melani De Vos and all [4] used aqueous electrolytes in which sodium oxalate was added in order to stabilize the electrochemical bath and prevent the precipitation of SnO<sub>2</sub>. Other authors have used aqueous solutions of sodium gluconate in an acidic medium and have underlined, despite everything, the formation of tin chloride or the tin gluconate complex [5]. An alternative to its problems is to use low cost non-aqueous electrolytes such as Deep Eutectic Solvents (DES) based on combinations of choline chloride with oxalic acid, urea or ethylene glycol in a well-defined molar ratio. Indeed, these solvents have important properties including high conductivity, electrochemical stability, a relatively wide potential range, low vapor pressure and an ability to solvate many metal salts [6]. These properties make these solvents good candidates for use as electrolytes for the electrodeposition of metals [7, 8, 9] alloys [10, 11] and semiconductors [12, 13].

The present work consists in exploring the use of a non-aqueous electrolyte which is a eutectic mixture of choline chloride: ethylene glycol (1:2) (Deep Eutectic Solvent). The deposition conditions of Sn thin films and the structural properties will be studied.

## 2. Materials and methods

### 2.1. Electrochemical measurements

During this work, the electrochemical measurements were carried out in a cell with three electrodes and connected to an Autolab PGSTAT 20. A glassy carbon electrode with an area of 0.0707 cm<sup>2</sup> was used as the working electrode. A large-area glassy carbon plate served as the auxiliary electrode. A

silver wire is the reference electrode. Data acquisition and processing is done using Nova software version 2.1.5. The working electrode is polished using a suspension of alumina particles 1  $\mu\text{m}$  in diameter in ultrapure water, before being washed with acetone and ethyl alcohol. It is then treated with an ultrasound bath for 5 min and then dried under a current of hot air before being inserted into the electrochemical cell. For each experiment, the potential is initiated in the cathodic direction from the OCP (Open Circuit Potential).

The precursor used for the preparation of electrochemical baths is tin chloride dehydrate  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (98%, Aldrich). The eutectic solvent is a mixture (ChCl-EG) of choline chloride (Sigma 99%; MW: 139.62 g/mol) and ethylene glycol (Merck 99.0%; MW: 62.07 g/mol) in the proportions 1:2 in moles. Solution concentrations were calculated based on density values from Ciocirlan and all [14]. The mixture is heated at 70°C for 2 hours using a heating plate until complete fusion and mixing of all the components. Finally, a colorless solution is obtained.

The coefficient of diffusion was determined by applying the Randles-Sevcik equation [15].

$$i_{pic} = (2,7 \times 10^5) n^{\frac{3}{2}} A D^{\frac{1}{2}} C_0 v^{\frac{1}{2}} \quad (1)$$

A is the electrode surface in  $\text{cm}^2$ , n the number of electrons,  $C_0$  the concentration in  $\text{mol}/\text{cm}^3$ , v the scanning rate in V/s and D the coefficient of diffusion in  $\text{cm}^2/\text{s}$ .

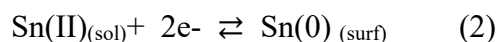
## 2.2. Characterizations

After deposition of the Sn films at fixed potential, the nature of the phases present in the samples was determined using a Bruker D8 Advance Diffractometer (DRX) X-ray device with a  $\text{Cu-K}\alpha$  radiation source ( $\lambda = 1.54182 \text{ \AA}$ ). A 2SBU scanning electron microscope (SEM) was used to study the microstructure of the deposits obtained.

## 3. Results and discussion

### 3.1. Electrochemical behavior of tin in ethaline

Cyclic voltammetry curves were performed on the Sn(II) solutions (Fig 1). They made it possible to detect a cathodic peak C1 at -0.6V corresponding to the change from Sn(II) to Sn(0) at the surface of the electrode. An anodic peak A1 corresponding to the redissolution of Sn(0) to Sn(II) is also reported. The redox equation of the reversible system involved is at the equilibrium potential of -0.55V/AgCl/Ag/Ethaline is indicated as follows:

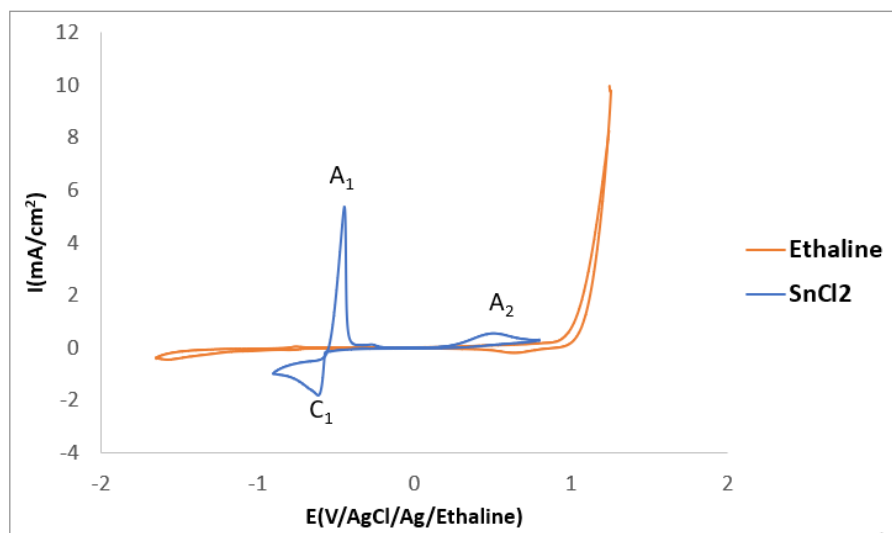


In addition, it should be noted the appearance of a second, smaller anodic peak A2 at +0.4V

corresponding to the oxidation of Sn(II) to Sn(IV). This peak can be explained by the formation of SnO<sub>2</sub> according to equation 3:



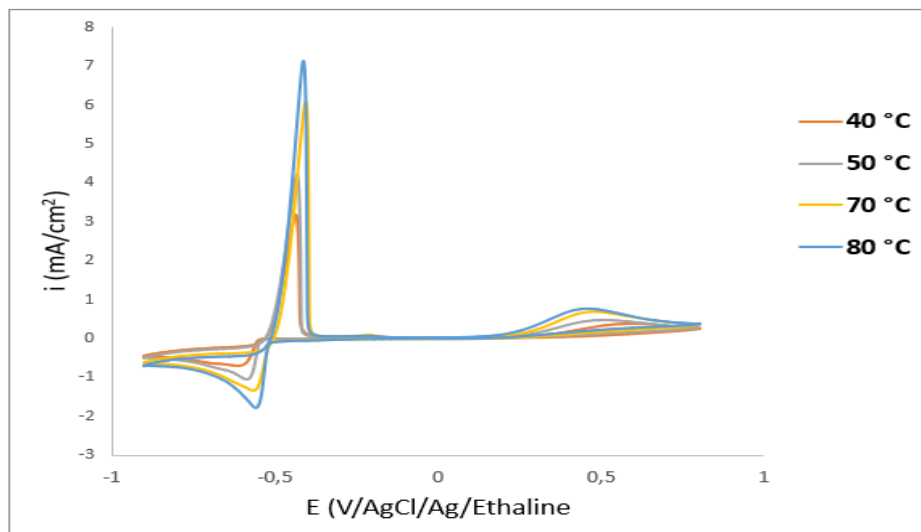
These results agree with those of some authors listed in the literature [4] who have studied Sn electrodeposition in an aqueous medium.



**Fig 1.** Cyclic voltammogram obtained with a solution of ethaline +20 mM SnCl<sub>2</sub>.2H<sub>2</sub>O on glassy carbon electrode at  $v = 10$  mV/s and at  $T = 80^\circ\text{C}$

### 3.2. Study according to temperature

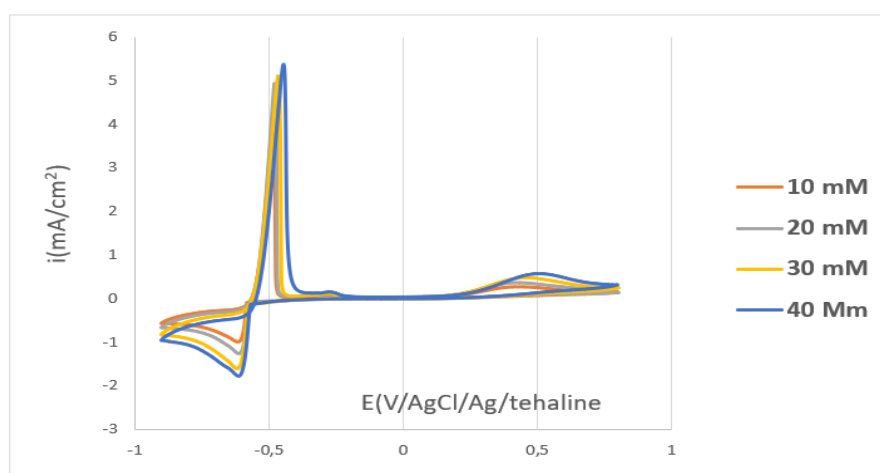
Various measurements as a function of temperature were carried out (**Fig 2**) in order to better understand the behavior of tin in ethaline as a function of temperature. For this, the temperature of the electrolytic bath was varied from 40°C to 80°C and the speed was kept constant at  $v = 10$  mV/s. The voltammograms obtained are similar. There is an improvement in the density of the cathodic current when the temperature increases. Similarly, the amount of Sn electrodeposited on the electrode surface increases. This fact is illustrated by an improvement in the height of the A1 anodic dissolution peaks. This fact is illustrated by an improvement in the height of the A1 anodic dissolution peaks. In fact, the ionic conductivity increases with the temperature which facilitates the transport of Sn(II) species by diffusion in the electrolyte both for the electrodeposition of the Sn and for its return to solution after the oxidation of the deposit. Moreover, in general, we note that the characteristics of the voltammograms obtained are well defined at the investigated temperatures. These results corroborate those of certain authors listed in the literature. Bougouma M and all [16] studied the electrodeposition of selenium in reline and obtained an improvement in the density of the cathodic current by increasing the temperature from 70°C to 100°C.



**Fig 2.** Cyclic voltammogram obtained with a solution of ethaline +20 mM  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  on glassy carbon electrode at  $v = 10 \text{ mV/s}$  : study as a function of temperature

### 3.3. Study according to concentration

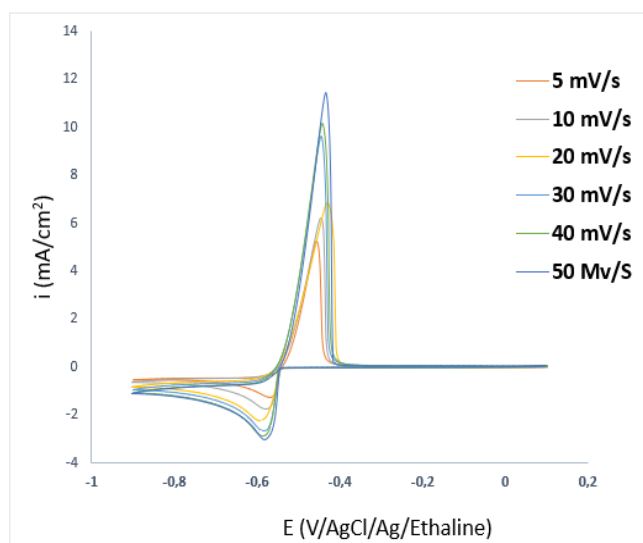
The study according to the concentration made it possible to obtain the voltammograms indicated in **Fig 3**. This study was carried out on different solutions of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  at the speed of  $20 \text{ mV/s}$  and at the temperature of  $70 \text{ }^\circ\text{C}$ . The two peaks (A1 and C1) highlighted on the voltammograms are always similar. As the concentration of the solutions increases, the cathodic and anodic current densities increase. However, a very slight displacement of the cathodic wave in the direction of the more negative potentials and of the anodic wave in the direction of the more positive potentials is observed. Similar results have been obtained by some authors. Ousmane MS and all [17] studied anodic dissolution solutions of single crystals of  $\text{MoSe}_2$  in an aqueous medium and obtained an improvement in the densities of the cathodic current by increasing the concentration of the solutions.



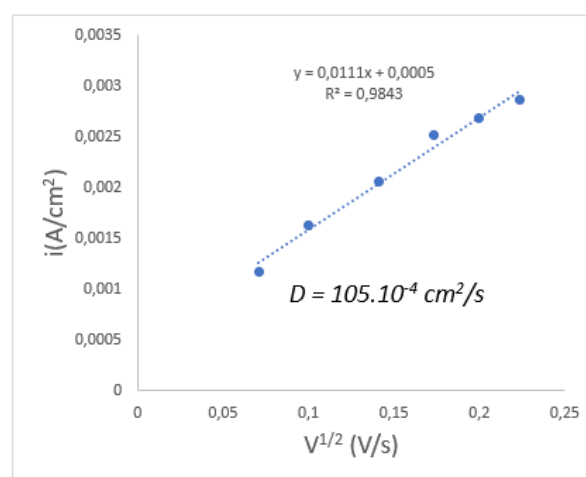
**Fig 3.** Cyclic voltammogram obtained with a solution of ethaline +  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  on glassy carbon electrode at  $v = 10 \text{ mV/s}$  : study as a function of concentration

### 3.4. Study as a function of scan rate

In order to determine the diffusion coefficient of Sn(II) ions at the surface of the electrode, different measurements depending on the scan rate were investigated (Fig 4a). The measurements were carried out on a solution of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  at a temperature of  $70^\circ\text{C}$  and at several scan rates. The results obtained show the same characteristics. There is an increase in the charge density of the cathodic current when the scan rate increases. From the slope of the curve of the cathodic current densities as a function of the square root of the scan rate (Fig 4b) and by application of the Randles-Sevcik equation, the diffusion coefficient is  $105 \cdot 10^{-4} \text{ cm}^2/\text{s}$ . This coefficient translates the mobility of the Sn(II) ions at the surface of the electrode. These results are better than those obtained by Mélanie De Vos et al [4] who obtained a coefficient of  $2.89 \times 10^{-5} \text{ cm}^2/\text{s}$  at  $50^\circ\text{C}$  in an aqueous medium. Furthermore, this variation as a function of the square root of the sweep rate shows a good linear correlation (Fig. 4b) indicating a diffusion-controlled process for the reduction of Sn(II) as observed by Zhou and all [18] and Karar [19]. On the other hand, it indicates that the phenomena take place on the surface of the electrode [20, 21].



**Fig 4a.** CV of a solution of ethaline +  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  on glassy carbon electrode at  $v = 10 \text{ mV/s}$ : study as a function of the scan rate

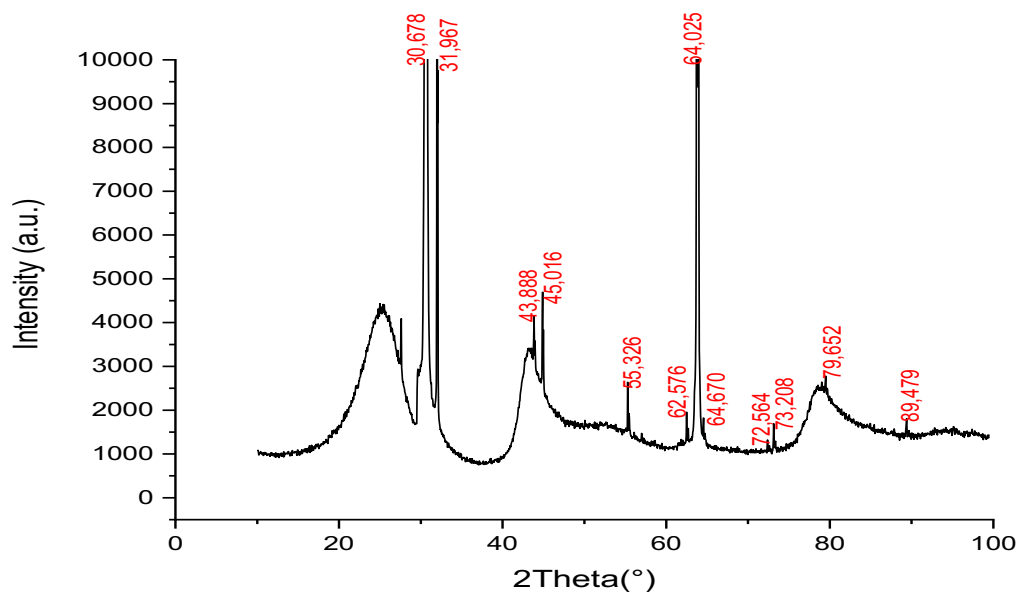


**Fig 4b.** Curve of cathodic current densities as a function of the square root of the scan rate

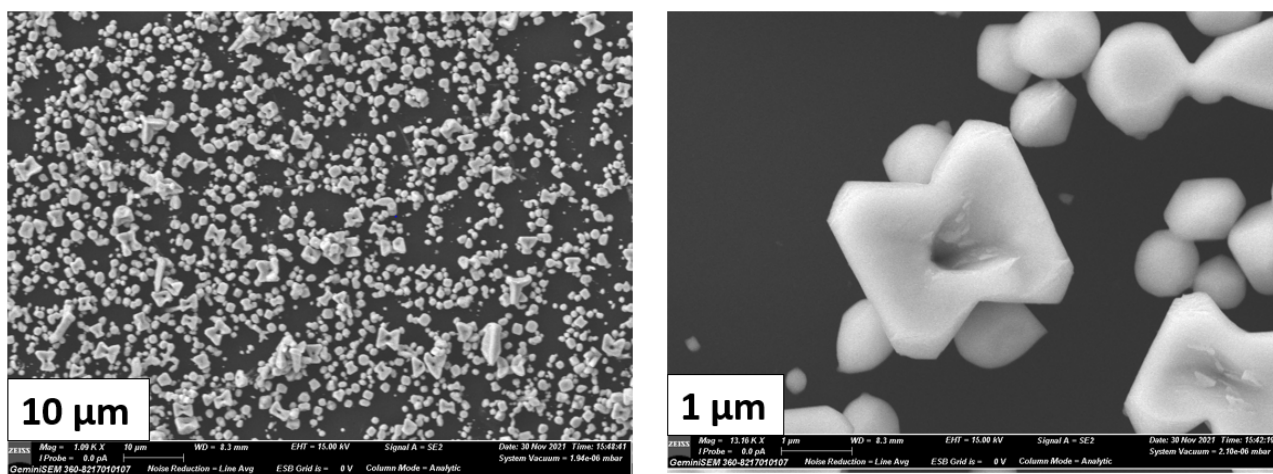
### 3.5. XRD analysis and SEM microscopy of the deposits obtained

In order to show the formation of metallic tin, thin film deposits were made by chronoamperometry at a fixed potential of  $-0.61\text{V}$  on a glassy carbon electrode. Then the thin films obtained were washed with ultrapure water and then with ethanol before being dried. Analysis of the deposits by X-ray diffraction indicates the presence of a tetragonal phase of pure metallic tin (Fig 5). Moreover, the layers present a homogeneous surface morphology with some porosities and a butterfly microstructure

is observed (Fig 6).



**Fig 5.** XRD diagram of Sn deposits on glassy carbon electrode



**Fig 6.** SEM images of Sn deposits obtained at -0.61V on glassy carbon electrode

## Conclusion

The electrodeposition of the thin layers of tin was carried out in the deep eutectic solvent (choline chloride-ethylene glycol 1:2). The influences of an increase in temperature and concentration have been studied. The results obtained indicate an increase in the yield of deposits. The analysis by X-ray diffraction and the morphology of the deposits obtained were carried out. The results indicate crystallizing metallic tin in the tetragonal phase with a butterfly microstructure. The results of this study could open a way for the recovery of metallic tin present in electrical and electrical electronic waste. This is an advantage from an environmental and industrial point of view.

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## Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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