

Electrodeposition of metals and their alloys using different deep eutectic solvents based on choline chloride

Masoud mahamad salah Rahim Zankana¹ and Azeez Abdullah Azeez Barzinjy^{2*}

¹ Department of Chemistry, University of Garmian, Sulaimani-Iraq
masoud.mahamad@garmian.edu.krd

² Department of Physics, College of Education, University of Salahaddin, Erbil -Iraq
*azeez.azeez@su.edu.krd

Abstract

Ionic liquids with discrete anions are deep eutectic solvents can be utilized for metals electroplating. In this investigation various types of deep eutectic solvents have been utilized such as Reline, Ethaline and Hybrid as solvents for the electrodeposition of Sn, Zn and Zn-Sn alloys. Ethaline and Reline displayed identical voltammetric profiles for the reduction of Zn^{+2} and Sn^{+2} . Reline possess high viscosity which lead to decreasing the quality of electroplating, therefore the process needs higher temperature or longer electroplating time. The surface morphology and compositions have been characterized using scanning electron microscopy (SEM) and elemental analysis by energy dispersive X-ray Spectroscopy (EDX). These techniques lead to detecting the metal alloy that have been added to the ionic liquids. Pure ionic liquids preparation was another aim of this investigation, which utilized as a standard scale for comparison with the metal based liquids. Analysis of cyclic voltammetry in all systems indicated differences in the reactivity and mobility of species in solution which affected the growth mechanism and resulted in changes in deposit morphology.

Keywords: Electrodeposition, Deep eutectic solvent, ionic liquids, Zn-Sn alloy, voltammogram.

1. Introduction

Ionic liquids (ILs) are known as salts that are liquid at room temperature in contrast to high-temperature molten salts [1]. They have a unique array of

physico-chemical properties which make them suitable in numerous applications in which conventional organic solvents are not sufficiently effective or not applicable [2]. ILs have been known for a long time, but their extensive use as solvents in chemical processes for synthesis and catalysis has recently become significant. The number of research on ILs and their specific applications is increasing rapidly in the literature. The number of patent applications in ionic liquids field increased to 100 and finally by 2004, there were more than 800. This is a clear indication of the high affinity of the academia and industry to the ILs [3].

Ionic liquids (ILs) are considered to be a relatively recent magical chemical due their unique properties, have a large variety of applications in all areas of the chemical industries. The areas of application include metal electroplating, electrolyte in batteries, lubricants, plasticizers, solvents and catalysis in synthesis, extraction, gas absorption agents, etc. Non-volatility and non-flammability are their common features giving them an advantageous edge in various applications [4]. This common advantage, when considered with the possibility of tuning the chemical and physical properties of ILs by changing anion-cation combination is a great opportunity to obtain task-specific ILs for a multitude of specific applications [5]. There are numerous studies in the related literature concerning the unique properties, preparation methods, and different applications of ILs in the literature [6].

Deep Eutectic Solvents (DESs), which are the last generation of ionic liquids, are eutectic mixtures of simple salts with either Lewis acidic or Bronsted acidic complexing agents. While they do not have the same chemical inertness of some of the ionic liquids with discrete anions they are simple to prepare, are insensitive to water content, do not need to be registered as their toxicological properties are known and probably most importantly for large scale applications like electroplating they are inexpensive [7].

Researchers explained that ILs remain liquid at room temperature due to the reason that their ions do not pack well [8]. Combination of bulky and asymmetrical cations and evenly shaped anions form a regular structure namely a liquid phase. The low melting points of ILs are a result of the chemical composition. The combination of larger asymmetric organic cation and smaller inorganic counterparts lower the lattice energy and hence the melting point of the resulting ionic medium. In some cases, even the anions are relatively large and play a role in lowering the melting point [9].

In fact, the electrodeposition of most metals and alloys is almost exclusively performed from aqueous solutions. They can be obtained from aqueous solutions that in some cases are based on toxic components (e.g., cyanide) and using processes that have rather low current efficiencies (e.g., chromium). ILs have now caught the attention of electroplaters, hitherto mostly in the research labs. ILs consist of an organic cation and an inorganic or organic anion. They have a wide range of solubility and miscibility; for example, some of them are hydrophobic, while others are hydrophilic [10].

For electrodeposition of zinc, tin and zinc-tin alloys choline chloride as a quaternary ammonium halide salt has been utilized. In this systems whether urea or ethylene glycol have been added as a hydrogen bond donor. Moreover, the consideration of the reduction potential and the potential window were the first step to start the electrodeposition rather than thinking about which kinds of ionic liquids should be utilized. The coordination geometry of the anions has partial impact on reduction potential [2]. However, the great role has been noticed from the amount of redox potential in relation to the coordination geometry. Another crucial factor that can change the potential window is the acidity of metal halides which are added to ionic liquids during the electrodeposition electrodeposition process. With increasing the Lewis acidity the negativity of reduction potential will rise up due to the direct relationship between them. Finally, it is slightly significant to mention the amount or ratio of the metals and

quaternary ammonium salts that take part in potential window [11]. In this study three different ionic liquids have been utilized explicitly; Reline, Ethaline and Hybrid.

2. Experimental

This study has been done using three different ionic liquids which are:

- (i) The first ionic liquid, Reline, was simply prepared by heating choline chloride and urea (ChCl/Urea) with a molar ratio of 1:2 at 353 K until a homogeneous liquid was formed. Samples were dried under a vacuum at 333 K for 72 h. The water content of dried ChCl/Urea (1:2) was determined by Karl Fischer titration analysis, which was 1200 ± 100 ppm. Later the metal halides namely; Zinc chloride, Tin chloride and zinc-tin chloride alloy have been added to three identical volumes with 50 ml of the ionic liquid. Table 1 demonstrates the details of these preparations. The amount of the metal halides were used was 1.13g SnCl₂ and 3.407g ZnCl₂ for each mixture either as separated metal chloride or as mixed alloy, in whole process and with all three ionic liquids.

Table 1: the electrodeposition process using Reline ionic liquid.

Sample	T/ °C	Applied potential /V	Applied current density A/cm ²	Plating period/ mints
Reline+ ZnCl ₂	40-50	5	0.5	45
Reline + ZnCl ₂ +SnCl ₂	50-60	5	0.05	60
Reline + SnCl ₂	40-50	5	0.06	30

- (ii) The second ionic liquid, Ethaline, were simply prepared by heating choline chloride and ethylene glycol (ChCl/EG) with a molar ratio of 1:2 at 353 K until a homogeneous liquid was formed. Later the metal halides namely; Zinc chloride, Tin chloride and zinc-tin chloride alloy have been added to three identical volumes with 50 ml of the ionic liquid. Table 2 demonstrates the details of these preparations. The amount of the metal halides were used

was 1.13g SnCl₂ and 3.407g ZnCl₂ for each mixture either as separated metal chloride or as mixed alloy, in whole process and with all three ionic liquids.

Table 2: the electrodeposition process using Ethaline ionic liquid.

Sample	T/ °C	Applied potential /V	Applied current density A/cm ²	Plating period/ mints
Ethaline + ZnCl ₂	60-65	5	0.25	45
Ethaline + ZnCl ₂ +SnCl ₂	60-65	5	0.368	20
Ethaline + ZnCl ₂ +SnCl ₂	60-65	3	0.204	3
Ethaline + ZnCl ₂ +SnCl ₂	60-65	4	0.423	2.5

(iii) The last ionic liquid was formed by adding the same relative of choline chloride (139.63g) with one mole to (60g urea + 62g ethylene glycol), Hybrid, with one mole for each component. Later the metal halides namely; Zinc chloride, Tin chloride and zinc-tin chloride alloy have been added to three identical volumes with 50 ml of the ionic liquid. Table 3 demonstrates the details of these preparations. The amount of the metal halides were used was 1.13g SnCl₂ and 3.407g ZnCl₂ for each mixture either as separated metal chloride or as mixed alloy, in whole process and with all three ionic liquids.

Table 3: the electrodeposition process using Hybrid ionic liquid.

Sample	T/ °C	Applied potential /V	Applied current density A/cm ²	Plating period/ mints
Hybrid + SnCl ₂	50-60	2.5	0.5	35
Hybrid + ZnCl ₂ +SnCl ₂	50-60	2.5	0.23	35
Hybrid + ZnCl ₂	50-60	2.5	0.12	3

The surface morphology and compositions have been characterized using scanning electron microscopy (SEM) and elemental analysis by energy dispersive X-ray Spectroscopy (EDX) using a Phillips XL30 ESEM instrument with an accelerating voltage between 15 and 20 keV, giving an average beam current of ca. 120 μA.

Cyclic voltammetry was carried out using an Autolab PGSTAT20 potentiostat (Ecochemie, Holland) which is controlled by GPES2 software. A 3-electrode system consisting of a working electrode (platinum/GC disc electrode; 1mm diameter), counter electrode (platinum flag; area 1cm²) and pseudo-reference electrode (silver wire) was used for all experiments. The working electrode was first cleaned electrochemically and then mechanically polished with 0.3 μm alumina paste followed by rinsing with deionized water and dried before every single measurement. All cyclic voltammogram were made at a scan rate of 20 mV s⁻¹. The peak analysis of the voltammogram was performed by using the GPES ver. 4.9.

3. Results and discussions

Initially, the plating was run using 4V for a potential difference, however the results were unsatisfactory. Then the potential difference was increased to 5V with some enhancement in the morphology of plating and the method of removing the useless spots before starting the electrodeposition, after that the convenient results were observed.

Before describing the SEM images of the plated samples it seems relevant to demonstrate information regarding cyclic voltammetry of the liquids in pure conditions. The all 9 solutions were prepared have been tested by utilizing a voltammogram.

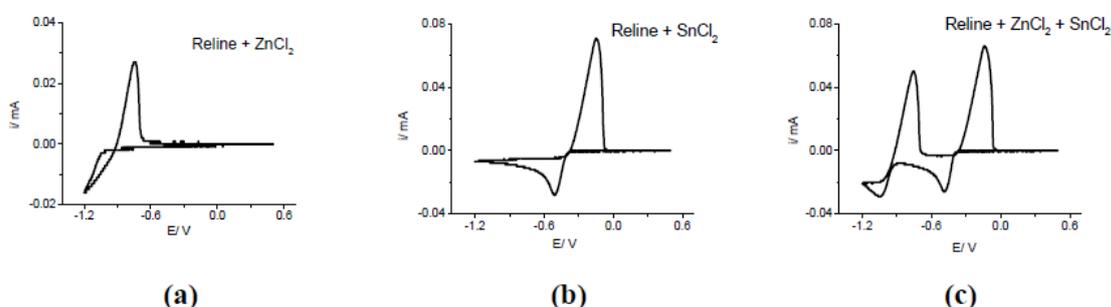


Figure 1: Cyclic voltammogram for (a) Reline with ZnCl_2 ; (b) Reline with SnCl_2 and (c) Reline

Ethaline with ZnCl_2 - SnCl_2 systems at 313 K on a Pt microelectrode, at a sweep rate of 20 mV s⁻¹. Figure 2 displays three parts which are Ethaline with ZnCl_2 , Ethaline with SnCl_2 and Ethaline with ZnCl_2 - SnCl_2 alloy. Figure 2a regarding ZnCl_2 condition seems identical to Figure 1a in terms of the potential window which is about -1.2 V and the reduction area without any peak, however the oxidation process of Zn^{+2}/Zn to some extent shifted just next to -1V which is around -0.8V. These result are comparable with Gollas and his co-workers [14]. Figure 2b, provide knowledge about SnCl_2 with Ethaline solution. Interestingly, only one peak around -0.45V appeared which is related to the deposition process, while two peaks are illustrating the stripping condition (or oxidation) at approximately -0.1V and -0.3V [15]. The potential window range is almost similar to the condition of the previous figures, 0.5V to -1.2V. To end with, Figure 2c represents the redox potential of Ethaline with ZnCl_2 - SnCl_2 alloy. In the reduction area only one peak can be observed. However three oxidation peaks can be observed for Zn/Zn^{+2} and Sn/Sn^{+2} in -0.1V, -0.25 V and -0.9V refers to strong oxidation due to Ethaline existence. These results are relatively in a good agreement with Alhaji's [16] results.

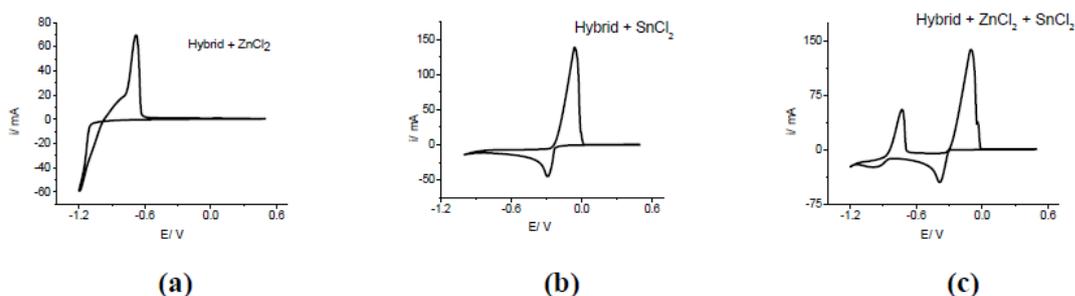


Figure 3: Cyclic voltammogram for (a) Hybrid with ZnCl_2 ; (b) Hybrid with SnCl_2 and (c)

Hybrid with ZnCl_2 + SnCl_2 systems at 313 K on a Pt microelectrode, at a sweep rate of 20 mV s⁻¹. Figure 3 in some extent is different than the previous figures. The difference is mainly due to the using Hybrid solvent, Reline with Ethaline. The method of the Hybrid preparation has been explained in the experimental section beforehand. Figure 3a shows the cyclic voltammogram condition of ZnCl_2 in Reline and Ethaline solvents. The potential window, inexistence of

peak in reduction area and a single peak in oxidation part of the redox potential. Figure 3b is comparable with those reported by Abbott et. al. [17] for the negative going scan, but varies in the oxidative scan since our data only shows one oxidation peak corresponding to the tin oxidation. It is obvious that the nature of the liquid does not have any significant influence on the voltammetric profile of Zn^{+2} and Sn^{+2} in the solution. The clear difference is basically on the value of the peak current density, which may be related to the difference on the viscosity of the liquid [18]. The peak current is lower for the deposition in Reline which is the liquid with higher viscosity. Figure 3c shows the cyclic voltammetric response of a Hybrid solution containing a mixture of $ZnCl_2$ and $SnCl_2$. It is obvious that the deposition of tin and zinc occurs practically at the same potential as in the individual solution of the metals and therefore the deposition of zinc occur on tin electrodeposit. The removal of both metals occurs at well-divided potentials with peak potentials comparable to those attained for the isolated metals. These explanations are comparable to those stated by Abbott et al. [19].

After electrodeposition of Zn, Sn and Zn-Sn alloy on the mild-steel substrate, the Scanning electron microscopy have been utilized. Figure 4 shows the surface morphology of Reline + $ZnCl_2+SnCl_2$, Ethaline + $ZnCl_2+SnCl_2$ and Hybrid + $ZnCl_2+SnCl_2$ electroplating samples which have been taken within the condition stated in the experimental section. SEM images illustrate that zinc-tin alloy; crystallization may change with changing the electroplating solution. It can be noted from Figure 4 that, there is not any cracks in the electroplated samples. Similar results using different solvent obtained by Wu et at.[20]. With higher magnification, it is possible to detect that the particles have quasi spherical shape spatially in the Reline + $ZnCl_2+SnCl_2$ case. Similar images were reported by Wang et al. [21]. In contrast, the morphology is totally different in the Ethaline + $ZnCl_2+SnCl_2$ and Hybrid + $ZnCl_2+SnCl_2$ cases.

in the Ethaline + $ZnCl_2+SnCl_2$ and Hybrid + $ZnCl_2+SnCl_2$ cases.

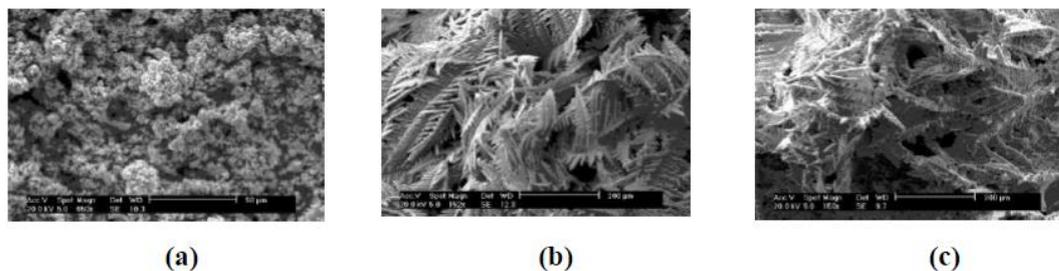


Figure 4: SEM micrographs of deposits obtained on mild-steel electrode for (a) Reline with $ZnCl_2+ SnCl_2$; (b) Ethaline with $ZnCl_2+ SnCl_2$ and (c) Hybrid with $ZnCl_2+ SnCl_2$ systems.

4. Conclusion

Despite of high instruction, using ionic liquids in electrodeposition process can decrease considerable difficulties such as toxicity, volatility and many other problems. Different ionic liquids give different results in electroplating. Zn-Sn deposition could be obtained from DES based on a choline chloride mixture. Reline was chosen in this study as a high viscos medium, while Ethaline was selected due to their lower viscosity. The voltammogram results show that morphology and composition of the Zn-Sn electrodeposits is solution dependent. Finally, morphological and voltammogram description of the deposits shows that alloy deposition produces a very uniform Zn-Sn deposit. The results obtained in the study are relatively in good agreement with the results obtained by other authors.

Acknowledgment

The authors would like to thank Dr Jamil Juma at Materials Centre/ University of Leicester, Leicester-UK, for his insightful ideas, suggestions, and time for serving in our discussions. The authors also thank people in Materials Centre/ University of Leicester, Leicester-UK who give us opportunity to use available techniques.

References

1. Endres, F., D. MacFarlane, and A. Abbott, *Electrodeposition from Ionic Liquids*. 2008: Wiley.
2. Zhang, Q., et al., *Deep eutectic solvents: syntheses, properties and applications*. Chemical Society Reviews, 2012. **41**(21): p. 7108-7146.
3. Short, P.L., *Out of the ivory tower*. Chem. Eng. News, 2006. **84**(17): p. 15-21.
4. Keskin, S., et al., *A review of ionic liquids towards supercritical fluid applications*. The Journal of Supercritical Fluids, 2007. **43**(1): p. 150-180.
5. Smith, E.L., A.P. Abbott, and K.S. Ryder, *Deep eutectic solvents (DESs) and their applications*. Chemical reviews, 2014. **114**(21): p. 11060-11082.
6. Heintz, A., *Recent developments in thermodynamics and thermophysics of non-aqueous mixtures containing ionic liquids. A review*. The Journal of Chemical Thermodynamics, 2005. **37**(6): p. 525-535.
7. Abbott, A.P., et al., *Preparation of novel, moisture-stable, Lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains* Electronic supplementary information (ESI) available: plot of conductivity vs. temperature for the ionic liquid formed from zinc chloride and choline chloride (2: 1). Chemical Communications, 2001(19): p. 2010-2011.
8. Renner, R., *Ionic liquids: an industrial cleanup solution*. Environmental science & technology, 2001. **35**(19): p. 410A-413A.
9. Yang, Q. and D.D. Dionysiou, *Photolytic degradation of chlorinated phenols in room temperature ionic liquids*. Journal of Photochemistry and Photobiology A: Chemistry, 2004. **165**(1): p. 229-240.
10. Han, D. and K.H. Row, *Recent applications of ionic liquids in separation technology*. Molecules, 2010. **15**(4): p. 2405-2426.
11. Abbott, A.P. and K.J. McKenzie, *Application of ionic liquids to the electrodeposition of metals*. Physical Chemistry Chemical Physics, 2006. **8**(37): p. 4265-4279.

12. Voegel, P.D., W. Zhou, and R.P. Baldwin, *Integrated capillary electrophoresis/electrochemical detection with metal film electrodes directly deposited onto the capillary tip*. Analytical chemistry, 1997. **69**(5): p. 951-957.
13. Huang, J.-F. and I.-W. Sun, *Electrochemical studies of tin in zinc chloride-1-ethyl-3-methylimidazolium chloride ionic liquids*. Journal of The Electrochemical Society, 2003. **150**(6): p. E299-E306.
14. Pözlner, M., A.H. Whitehead, and B. Gollas, *A study of zinc electrodeposition from zinc chloride: choline chloride: ethylene glycol*. ECS Transactions, 2010. **25**(39): p. 43-55.
15. Tang, B. and K.H. Row, *Recent developments in deep eutectic solvents in chemical sciences*. Monatshefte für Chemie-Chemical Monthly, 2013. **144**(10): p. 1427-1454.
16. Alhaji, A.I., *Electrodeposition of alloys from deep eutectic solvents*. 2012, University of Leicester.
17. Abbott, A.P., K. Ryder, and U. König, *Electrofinishing of metals using eutectic based ionic liquids*. Transactions of the IMF, 2008. **86**(4): p. 196-204.
18. Kölle, P. and R. Dronskowski, *Synthesis, crystal structures and electrical conductivities of the ionic liquid compounds butyldimethylimidazolium tetrafluoroborate, hexafluorophosphate and hexafluoroantimonate*. European Journal of Inorganic Chemistry, 2004. **2004**(11): p. 2313-2320.
19. Abbott, A.P., et al., *Electrodeposition of zinc–tin alloys from deep eutectic solvents based on choline chloride*. Journal of Electroanalytical Chemistry, 2007. **599**(2): p. 288-294.
20. Zhou, W.-H. and S.-X. Wu, *Solution-Based Synthesis of Cu₂ZnSnS₄ Materials for Energy Related Applications*. Materials Focus, 2012. **1**(3): p. 175-190.
21. Wang, K., H. Pickering, and K. Weil, *EQCM studies of the electrodeposition and corrosion of tin–zinc coatings*. Electrochimica acta, 2001. **46**(24): p. 3835-3840.