

## Influence of Media on Electrodeposition of Zn Using New DES

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### ABSTRACT

The research involved preparing a deep eutectic solvent containing a 4: 1 stoichiometric mixture of ethylene glycol and lithium chloride to investigate zinc electrodeposition. Electrochemical methods such as cyclic voltammetry measurement have been used to understand the electrochemical properties of zinc electrolytes in the absence and presence of additives. Likewise, the deep eutectic solvent's physical properties (density and conductivity) were studied in the absence and presence of additives. Also, the effect of the deep eutectic solvent in the electroplating process on a copper substrate was studied in the absence and presence of additives. The resulting roughness, thickness, and surface morphology of the deposited zinc were distinguished using atomic force microscopy, scanning electron microscopy, and X-ray diffraction, indicating that additives, act as a highly effective brightener allowing the formation of homogeneous and flat zinc deposits.

### KEYWORDS

Green Chemistry, Ionic Liquids, Deep Eutectic Solvent, Zinc Electrodeposition.

### Introduction

Green chemistry, also known as sustainable chemistry, refers to products and chemical processes that minimize or eliminate the use and processing of hazardous substances. It aims to minimize or eliminate the use of hazardous chemicals in chemical processes, as well as get rid of harmful and toxic materials, as a new branch of chemistry with environmental methods. Green chemistry includes nearly all parts of chemistry such as organic and inorganic chemistry, analytical chemistry, biochemistry, polymer, ecology, and toxins. Through the many prevailing trends of the green program such as catalysis, bio-catalysis, reaction solution (such as water, ionic fluids, supercritical liquids), and reaction conditions (microwave radiation), environmental protection goals and economic benefits can be achieved. One of the ways in which green chemistry reduces the impact of chemical processes and technologies on the environment [1][2][3]. Ionic liquids (ILs) are chemical compounds that belong to the group of salts composed of ions and have a melting point below 100 degrees Celsius. A large organic cation and a smaller organic or inorganic anion make up these compounds. They're known for their high thermal stability and the fact that they can be liquid at a wide range of temperatures [4]–[6][7]. ILs are interesting solvents of increasing technical significance due to their characteristics. One of these characteristics is a low vapor pressure, which is associated with low combustibility and high thermal stability, making ILs widely regarded as "environmentally friendly." A wide variety of ions allows for the production of a compound with unique properties (solubility, selectivity, etc.) for a specific application. Solubility, melting point, volatility, thermal stability, electric conductivity, viscosity, and flammability are only a few of the physical and chemical properties that can be formed with the right ions. The development of ILs is complex, and they are increasingly used in industry and a variety of fields of science and technology due to their diverse properties and relatively simple synthesis [8], [9]. Scientists concentrated on forming ionic liquids by mixing metal salts, such as zinc, aluminum, tin, and iron chlorides, with quaternary ammonium salts. Despite the fact that both salts have extremely high melting points, proper mixing aids in the formation of a liquid phase, known as eutectic solvents [10]. Since they share certain properties with ionic liquids, deep eutectic solvents (DESs) are now commonly accepted as a new class of IL analogs. In the literature, the words DES and IL have been used interchangeably, but it must be pointed out that these are essentially two distinct forms of solvent. DESs are made up of a eutectic mixture of Lewis or Brnsted acids and bases that may contain a variety of anionic and/or cationic species, while ILs are made up of structures that contain only one type of distinct anion and cation. The chemical properties of DESs suggest application areas that are substantially different from those of other ILs, despite the fact that their physical properties are identical to those of other ILs [11][12]. Deep eutectic solvents (DES), introduced by Abbott et al. in 2001, have proven to be very interesting and useful alternatives to non-aqueous solvents and room temperature ionic liquids (IL), with applications in a wide range of fields. Many reports on the synthesis of DES, their properties and applications, recent examples being Less attention was given to the materials aspects until the publication of a recent review, which discussed advances in the fields of polymer science, metal processing, and nanotechnology [13][14]. DESs are novel solvents, similar to RTILs, which are made by combining two substances in different molar ratios: hydrogen bond donors (such as alcohols, acids, and amides) and quaternary ammonium salts (such as choline

chloride)[15]. Electropolishing[16], polymer preparation[17], and electroplating[18], are some of the industries that use DESs. Several authors have recently recorded the effects of various additives (organic and inorganic) on the electrodeposition baths of various metals in general, and Zn in particular, from aqueous and non-aqueous electrolytes to improve grain size, electrochemical stability, morphology, corrosion resistance, adhesion, composition, brightness, and roughness of the deposit[19], [20][21]. Several researchers have studied the effects of electrodeposition of additives on copper from aqueous solutions. However, some studies have looked at the role of additives in the electrodeposition of copper from eutectic solvents. This study investigated the effect of substituting choline chloride with lithium chloride as well as the effect of different media on zinc electrodeposition. The research will also study the new DES's (LiCl<sub>2</sub>+ Ethylene glycol) electro-deposition at elevated temperatures using additives that work with copper, for example. In H<sub>2</sub>O, TritonX100, oxalic acid, NH<sub>3</sub>. The initial goal was to understand the active additives in new DES, how they affect the physical properties of a solution and the mechanism by which they illuminate the surface. Finally, the properties of the copper film were distinguished by various additives.

## Experimental

### A. Materials

(DES) was prepared by mixing LiCl<sub>2</sub> and EG in a molar ratio of 1:4, respectively. This mixture was then placed on a hotplate at 50°C with stirring until a colorless and homogeneous electrolyte was achieved. Other materials such as zinc chloride (ZnCl<sub>2</sub>, Sigma Aldrich, ≥ 98%), (Triton X100) (Sigma Aldrich, ≥ 99.5%), ammonium persulphate (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Aldrich ≥98%), Oxalic acid (Aldrich 99%), NH<sub>3</sub> (Aldrich 98%), and Acetamide (Aldrich ≥95%), were all used as received.

### B. Electrochemical Analysis and Electrodeposition

An IVIUM potentiostat/galvanostat, controlled via the GPES2 software was used to run the cyclic voltammetry (CV). The cell used in these experiments was composed of three electrodes: a Pt electrode (1.5 dia.), and an Ag wire electrode were used as the working, counter, and reference electrodes, respectively. For each experiment, the working electrode was polished with 0.05 μm γ-alumina paste and subsequently rinsed with distilled water. All cyclic voltammograms of ZnCl<sub>2</sub> with/without additive were carried out in DES at identical temperatures (70 °C) using a potential window of 2.0 to -1.6 V using different concentrations, temperatures, additives, and scan rates. The electrochemical coatings of Zn were formed on a copper surface in DES at 70 °C containing 0.4 M ZnCl<sub>2</sub> with/without additives at a current density of 50 mA cm<sup>-2</sup> for 1 h. In this work, the anode was a Ti mesh (50 mm × 60 mm) coated with iridium oxide. Prior to the start of the experiment, the Cu substrate (cathode electrode) was etched with 0.87 M ammonium persulfate aqueous solution, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 0.2 M H<sub>2</sub>SO<sub>4</sub> solution, cleaned by washing with distilled water, and then completely dried.

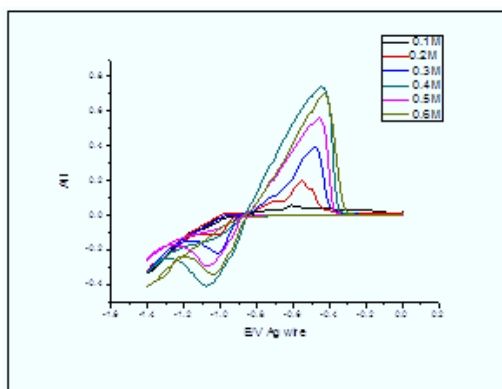
## Results and Discussion

### Cyclic Voltammetry

#### A. Effect of Concentrations on the CVs of Zn (II) with DES

In this work, electrodeposition of ZnCl<sub>2</sub> from new DES (LiCl<sub>2</sub>+Ethylene glycol) was achieved at different concentrations (0.1, 0.2, 0.3, 0.4, 0.5, and 0.6) M as shown in this **figure 1**. It is interesting to study the cyclic voltammetry of different concentrations of ZnCl<sub>2</sub> in DES at an elevated temperature of 70°C°, where the voltammetry was carried out in the potential range 0.2 V to -1.6 V and a scan rate 30mVs<sup>-1</sup>, using a Pt disc (1 mm diameter) electrode; the counter-electrode and Ag wire as the reference electrode. Previous studies that have explored the electrodeposition of metals in ionic liquids at high temperatures have found that this leads to improved deposits as a result of the increased rate and efficiency of metal deposition than at room temperature; therefore, this study was performed at high temperature[20], [22]. From the graphs below we can see that the reduction peak currents were increased due to the increased amount of ZnCl<sub>2</sub> in the electrolyte. Moreover, a shift in the reduction peaks of Zn toward the positive side was achieved with increasing amounts of Zn in the electrolyte, for example, the Zn was deposited at -1.4 V when using a concentration of 0.6 M ZnCl<sub>2</sub> and at -1.7 V when using 0.5 M ZnCl<sub>2</sub>. It is apparent from these data that the increase in the current peaks is related to the presence of high concentrations of ZnCl<sub>2</sub>, which largely produced [ZnCl<sub>4</sub>]<sup>2-</sup> in the solution, leading to a large amount of Zn deposition that occurred and vice versa for

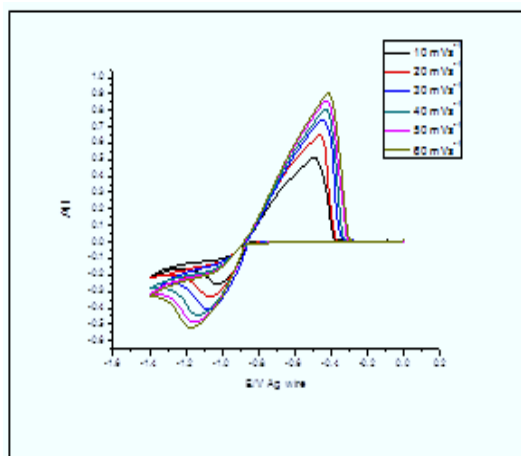
low concentrations of  $[\text{ZnCl}_4]^{2-}$ . A large number of  $[\text{ZnCl}_4]^{2-}$  and a small number of  $\text{Cl}^-$  anions at the surface of the electrode means only low amounts of energy are needed to reduce the  $\text{Zn}^{+2}$  ions. Thus, a positive shift in the Zn deposition potential can be achieved, as shown in **figure1**, the high concentrations of  $\text{ZnCl}_2$  led to an increase in the number of stripping peaks, which is quite apparent when comparing the 0.1 M and 0.3/0.6 M  $\text{ZnCl}_2$  solutions.



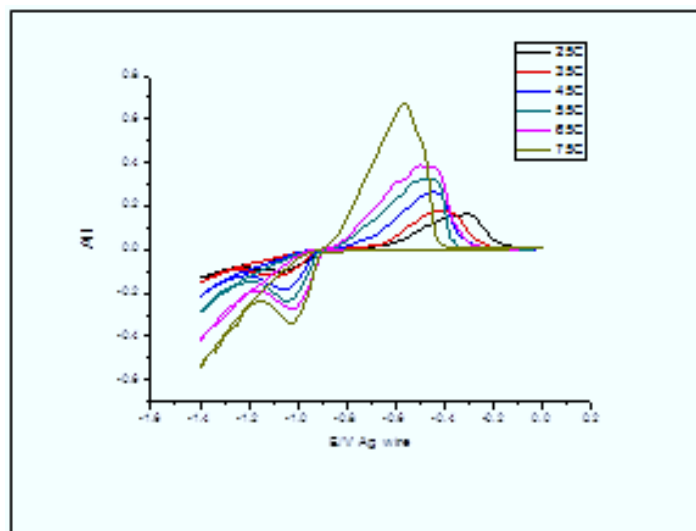
**Figure 1.** Effect of Concentration on  $\text{ZnCl}_2$  in New DES (1 $\text{LiCl}_2$ : 4Ethylene Glycol)

### B. Effect of Temperature on the CV of Zn with DES

In this work, electrodeposition of Zn from new DES ( $\text{LiCl}_2$ +Ethylene glycol) was achieved at different temperatures (25, 35, 45, 55, 65, and 75)  $^\circ\text{C}$  as shown in **figure2**. cyclic voltammetry of  $\text{ZnCl}_2$  in DES has been studied at different temperatures. **Figure2**. shows a comparison of the cyclic voltammetry of DES containing 0.4 M  $\text{ZnCl}_2$  at different temperatures all experiments were recorded at a scan rate of  $30\text{mVs}^{-1}$ . The cyclic voltammograms of  $\text{ZnCl}_2$  recorded at  $75^\circ\text{C}$  differed significantly from those recorded at other temperatures, showing a remarkable increase in Zn deposition and dissolution of the current peak of Zn when performed at  $75^\circ\text{C}$ . This was anticipated for various reasons: firstly, as the temperature was increased, the viscosity of the Zn electrolyte decreased, allowing an increase in the rate of mass transport toward the electrodes. This was due to the consequent increase in the free void volume in the solution. Secondly, the Zn electrolyte contains a high number of  $\text{Cl}^-$  anions which, through adsorption into the electrode surface, may thus impede the approach of  $[\text{ZnCl}_4]^{2-}$  towards the electrode surface. As the temperature of the electrolyte was increased, the number of adsorbed  $\text{Cl}^-$  anions on the electrode surface was reduced, allowing an increase in the concentration of  $[\text{ZnCl}_4]^{2-}$  at the electrode surface. This would in turn act to promote Zn reduction. From the cyclic voltammetry of  $\text{ZnCl}_2$  **figure 2**. it could be suggested that the electrodeposition of Zn from DES at elevated temperature is considerably better than at room temperature due to the increased rate of the Zn deposition, and thus the efficiency of deposition will be increased at a higher temperature.



**Figure 2.** Effect of Scan Rate on  $\text{ZnCl}_2$  in New DES (1 $\text{LiCl}_2$ : 4Ethylene Glycol)



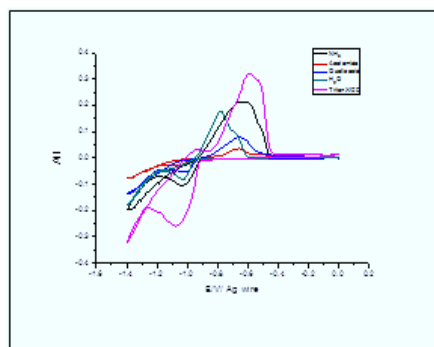
**Figure 3.**Effect of Temperature on  $\text{ZnCl}_2$  in New DES (1 $\text{LiCl}_2$ : 4Ethylene Glycol)

### C. Effect of Scan Rate on the CVs of Zn with DES

In this work, electrodeposition of Zn from new DES ( $\text{LiCl}_2$ +Ethylene glycol) was achieved at different scan rates (10, 20, 30, 40, 50, and 60)  $\text{mVs}^{-1}$  as shown in this **figure3**. cyclic voltammetry of  $\text{ZnCl}_2$  in DES has been studied at different Scan rates. **Figure3**. shows a comparison of the cyclic voltammetry of DES containing 0.4 M  $\text{ZnCl}_2$  at different Scan rates all experiments were recorded at  $70^\circ\text{C}$ . The cyclic voltammograms of  $\text{ZnCl}_2$  recorded at  $60\text{mVs}^{-1}$  differed significantly from those recorded at other Scan rates, showing a remarkable increase in Zn deposition and dissolution of the current peak of Zn when performed at  $60\text{mVs}^{-1}$ . This study shows that there was an increase in the magnitude of the oxidation peaks for Zn deposition in the presence of the additive associated with an increased scan rate. However, the increase in cathodic currents at high scan rates is not that large, as observed in the oxidation reactions[23]. It could be suggested that the electrodeposition of Zn from DES at elevated Scan rates is considerably better than others Scan rates due to the increased rate of the Zn deposition, and thus the efficiency of deposition will be increased at higher Scan rates.

### D. Effect of Additives on the Voltammetry Behavior of Zn (II)

The electrodeposition of Zn from DES at  $70^\circ\text{C}$  is considerably better than at room temperature due to the increased efficiency and rate of deposition of Zn. Therefore, it is recommended to perform the electrodeposition of Zn from DES at high temperatures. **Figure4**. shows the cyclic voltammetry of 0.4 M  $\text{ZnCl}_2$  in DES at  $70^\circ\text{C}$  in the presence of different concentrations of the following additives: (a)  $\text{NH}_3$ , (b) Acetamide, (c) Oxalic acid, (d)  $\text{H}_2\text{O}$ , and (e) TritonX100. The cyclic voltammograms were recorded at a scan rate of  $30\text{mVs}^{-1}$  using a 1.3 mm Pt disc electrode, a counter-electrode, and an Ag wire reference electrode. concentrations used were influenced by the work by Juma which in turn were limited by solute solubility[22]. The effects of the addition of various additives on the electrochemical behavior of DES only at  $70^\circ\text{C}$  were examined, as illustrated in **figure4**. a reduction peak at 2.0 to -1.6 V. The reduction peaks of DES with TritonX100 additive were observed at about -0.5 V,  $\text{NH}_3$  additive was observed at about -0.6,  $\text{H}_2\text{O}$  additive was observed at about -0.8 while the peaks of Acetamide and Oxalic acid were very weak. This can be attributed to increasing Zn deposition of the current peak of Zn when performed at TritoneX100,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ , whereas, zinc deposition decreased to the current peak of zinc when it was combined with Acetamide and Oxalic acid.

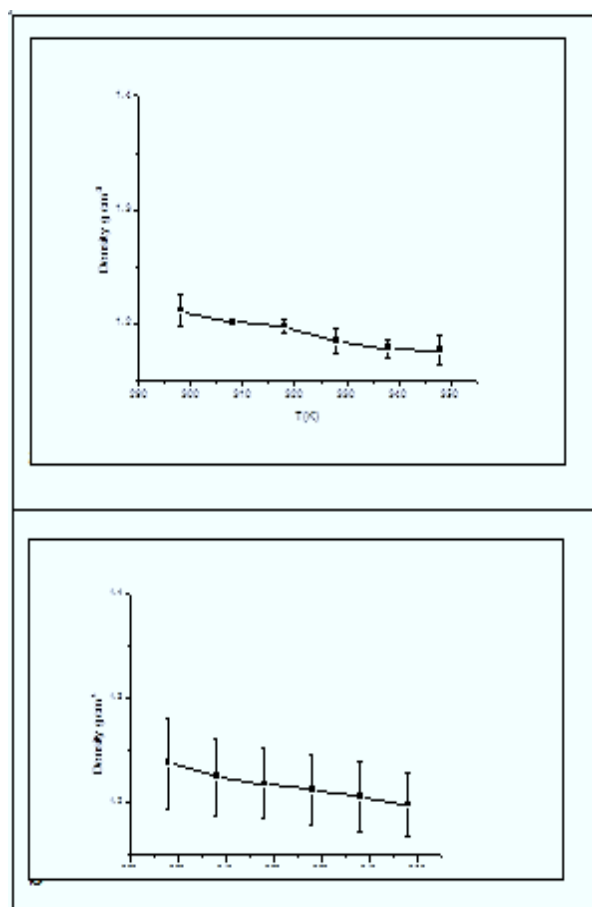


**Figure 4.** Cyclic Voltammogram at 70 °C of 0.4 M  $\text{ZnCl}_2$  in a 1:4 Molar Mixture of Lithium Chloride and Ethylene Glycol with Varying Amounts of Additives  $\text{NH}_3$ , Acetamide, Oxalic Acid,  $\text{H}_2\text{O}$ , and TritonX100. Measured Using a 1.3 mm Pt Disc Working Electrode, Pt Flag Counter Electrode, and Referenced against Ag Wire at  $10 \text{ mV s}^{-1}$

## Physical Properties

### A. Density

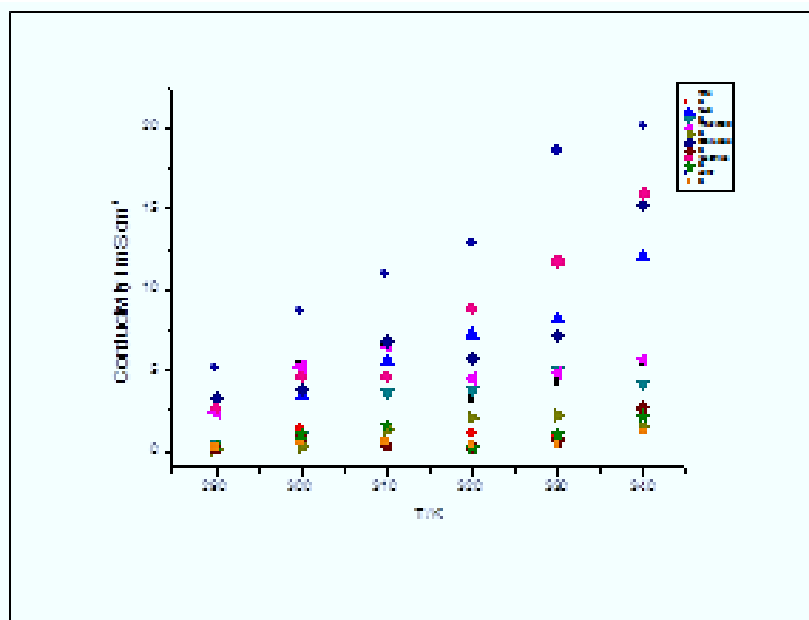
The density data for the pure DESs are shown in **figure 5** the density decreases with increasing temperature. **Figure 5-a** shows that the density of DES pure decreases in this study, usually, when the temperature increases the free volume also increases which leads to a decrease in density. Likewise, **figure 5-b** shows that the eutectic liquid to which  $\text{ZnCl}_2$  is added, we notice that the density decreases with increasing temperature, and thus the free volume increases.



**Figure 5.** Density of (a) Three DESs (b) and Three  $\text{ZnCl}_2$ +DES as a Function of Temperature. Error Bars Indicate oneStandard Deviation

## B. Conductivity

The conductivities of the DESs used in this study were measured using a conductivity meter as follows: the conductivity meter probe was immersed in a liquid over a range of temperatures (25°C- 75°C), with the conductivity recorded at least three times at each temperature, from which the average was determined for each sample. As the viscosity of the Zn solution was increased with the additives, the conductivity of the liquid was according to decreased, as is clear from **figure6**. The increase in the viscosity of Zn in DES in the presence of  $\text{NH}_3$  caused a decrease in the conductivity of the electrolyte, as is clear in **figure6**. Additionally, a slight decrease in the conductivity of the Zn bath, **figure6**, was achieved as a result of individually adding Triton X100, Oxalic acid, Acetamide,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  to the Zn solution. (The ionic liquid group in Leicester) has recently published the effects of nicotinic acid and boric acid on the electrodeposition of Ni from Ethaline 200. Also, they found that these additives increased the viscosity and decreased the conductivity of the Ni electrolyte[20].

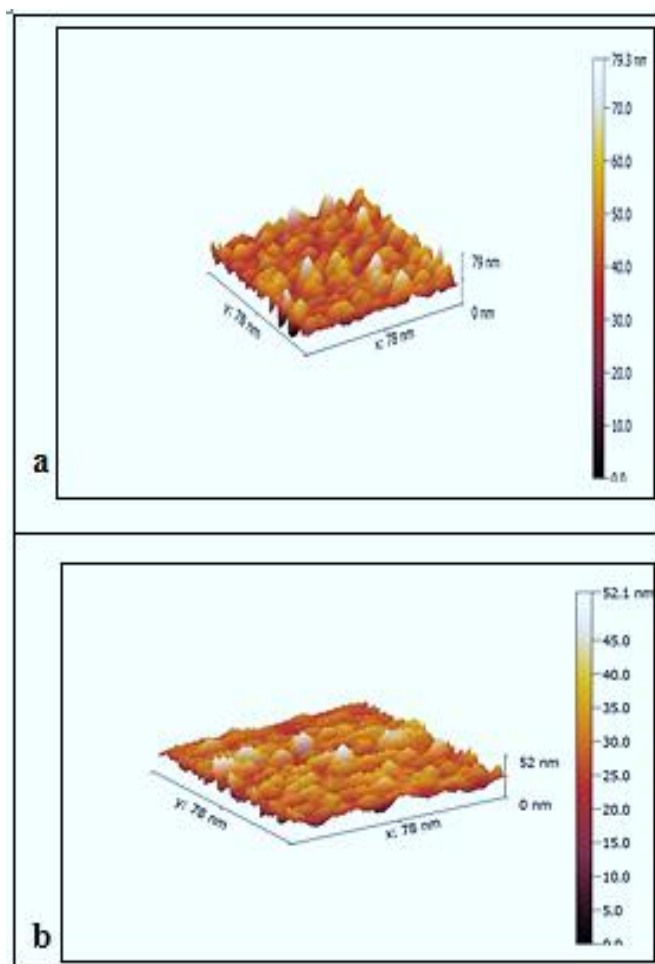


**Figure 6.** The Conductivity of 0.4 M  $\text{ZnCl}_2$  in DES as a Function of Temperatures and Different Additives

## Surface Characterization

### A. AFM Study

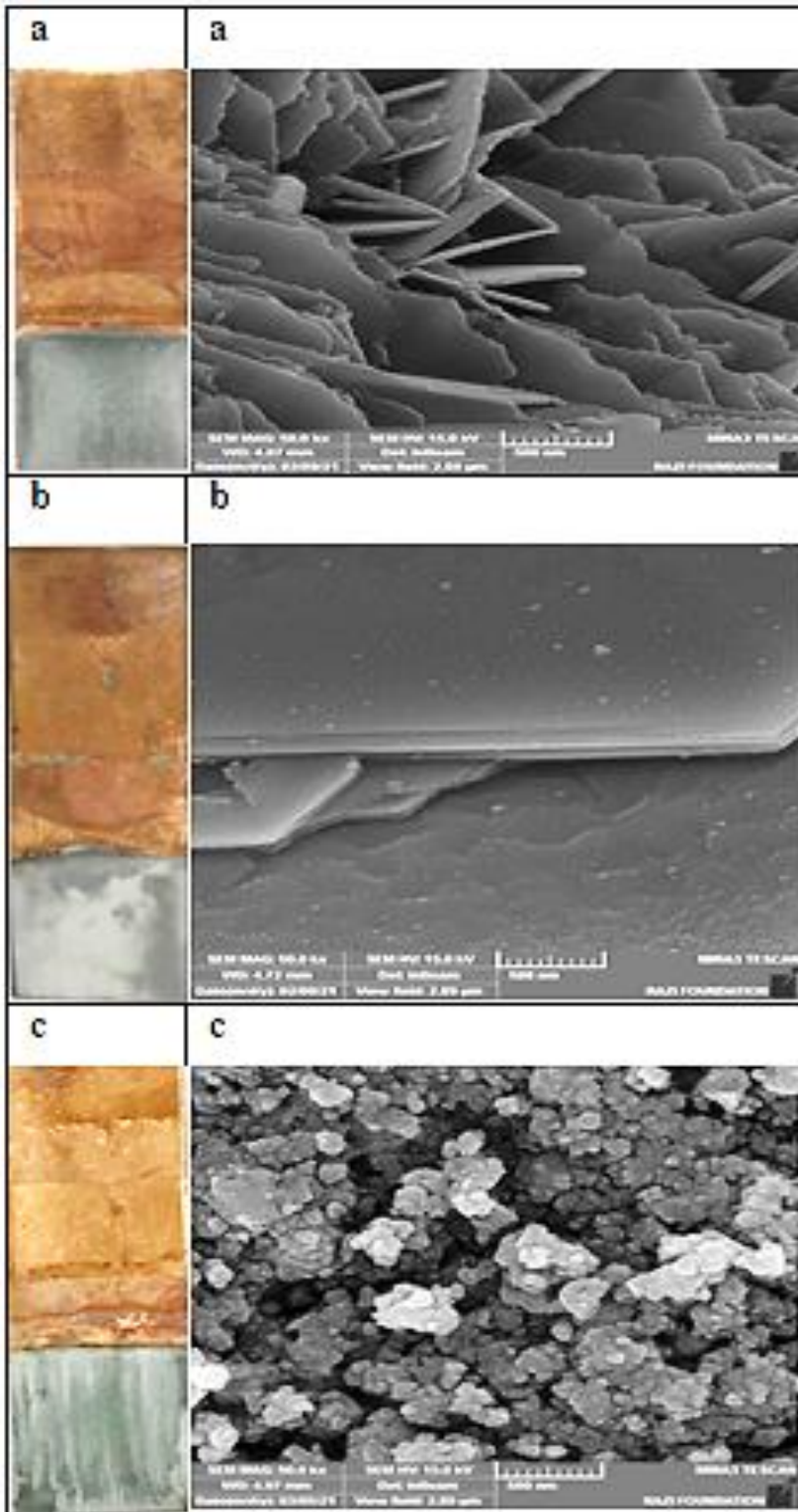
AFM was utilized to characterize the topography and roughness of the Zn growth (0.4 M  $\text{ZnCl}_2$ ) from new DES at 70 °C in the presence and the absence of a TritonX100 additive (0.01 M), as illustrated in **figure7.a**. The roughness of the deposited Zn in the absence of the TritonX100 additive was approximately 79 nm, whereas in **figure7.b** roughness was only approximately 52 nm in the presence of the TritonX100 additive. It is clear that in the electrodeposited Zn film from the additive-free electrolyte, the surface of the film was a rough layer with a larger grain size, while the surface morphology becomes much smoother and highly homogeneous in the presence of TritonX100. This further supports the supposition that the additive was strongly adsorbed onto the Cu substrate during Zn electroplating.



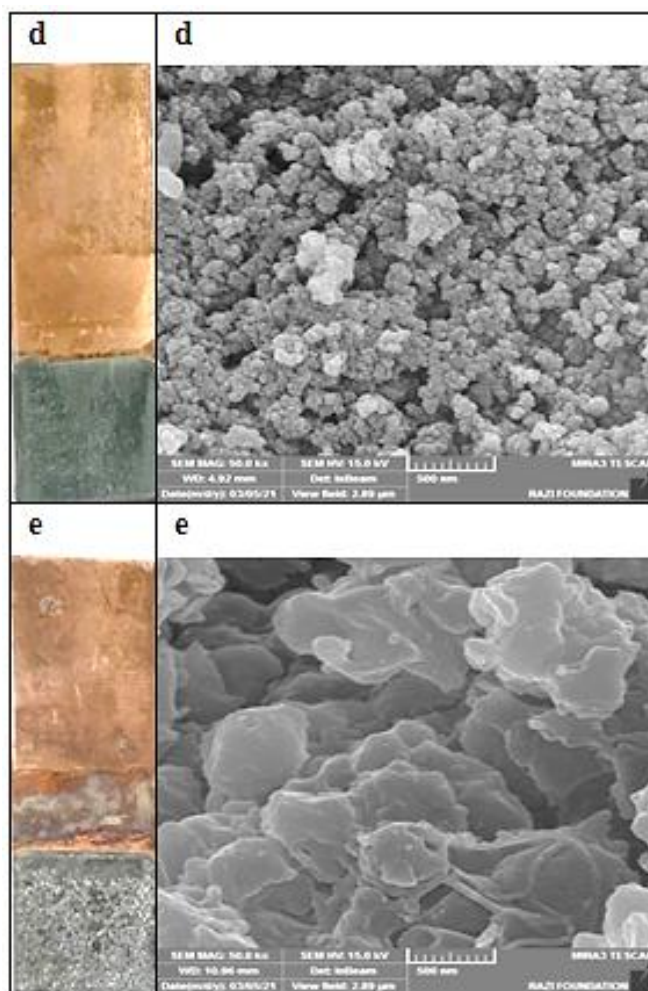
**Figure 7.** AFM Images for the Coatings Obtained from 0.4M  $\text{ZnCl}_2$  in DES in the Absence and Presence of 0.01M TritonX100 at a Current Density of  $50 \text{ mA cm}^{-2}$  for 1 h on a Cu Substrate at  $70^\circ\text{C}$ . The Deposition was (a) DES and (b) with TritonX100

## B. SEM Study

Scanning electron microscopy (SEM) was also used in this research to study the additive's influence on the surface morphology and deposition quality for 0.4 M Zn with and without additive in the new DES electrolyte at  $70^\circ\text{C}$  and a current density of  $50 \text{ mA cm}^{-2}$  for 1 h on Cu substrates. Optical photographs and SEM morphologies for Zn with/without additive are shown in **figure 8**. In all systems, Zn coatings were deposited that showed good adherence and were highly uniform. Some studies have found that a small grain size is an important, but not a sufficient, condition for brightness[24]. In this work, the Zn deposits are microcrystalline in nature, and accordingly have grain sizes on the order of a few micrometres; however, the grains became nanocrystalline on addition of the additives especially when addition TritonX100 at a concentration of 0.01 M, with an associated reduction in grain size (in nanometres ranges), as shown in inset of **figure 8-b**. This results in a finer grained deposit, suggesting that the Zn phase with TritonX100 is slower to form than the phase of electrodeposited Zn film from the additive-free electrolyte or the other additives. Therefore, the average size of the crystallites is smaller in the case of TritonX100, as well as being smooth and consisting of uniform crystals. The results of this study are in agreement with to the findings reported in previous work[25].



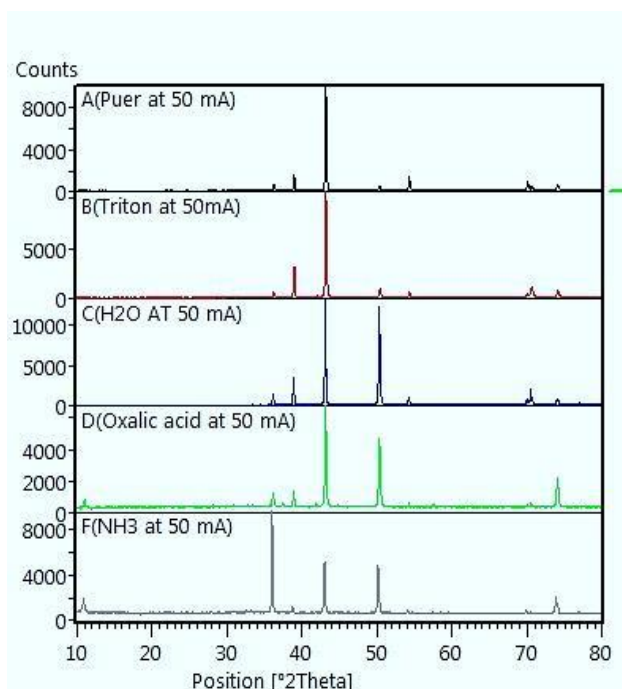




**Figure 8.** Optical Photographs, SEM Morphologies, of 0.4M  $\text{ZnCl}_2$  Coatings Obtained from new DES in the Absence and Presence of Additives at a Current Density of  $50 \text{ mA cm}^{-2}$  for 1 h on a Cu Substrate at  $70^\circ\text{C}$ . Images (a) for the Deposition without Additives, while (b) TritonX100, (c)  $\text{H}_2\text{O}$ , (d) Oxalic acid, and (e)  $\text{NH}_3$

### C. XRD Study

In this paper, the crystal orientations for the Zn patterns obtained from DES at  $70^\circ\text{C}$  in the presence and absence of the additives were studied[22], [26]. **Figure9.** provides the results for the Zn samples deposited from 0.4M  $\text{ZnCl}_2$  in DES at  $70^\circ\text{C}$  on the Cu substrate in the presence and absence of the additives at a current density of  $50 \text{ mA cm}^{-2}$  for 1 h. The diffraction peaks for the Zn pattern in the absence of additives appear at  $2\theta=36.3^\circ$ ,  $39.1^\circ$ ,  $43.24^\circ$ ,  $50.25^\circ$ ,  $71.10^\circ$ ,  $72.10^\circ$ , and  $74.65^\circ$ , as attributed to the (002), (100), (101), (102), (103), (105), (110) hexagonal planes of zinc, respectively, and as identical to those observed in earlier studies [18,20]. In addition, the XRD peaks of the Cu substrate were observed at  $2\theta = 43.2^\circ$ ,  $50.4^\circ$ , and  $74.14^\circ$ [25], [27]. Obviously, the XRD spectrum direction of zinc coating shows lower intensities at  $2\theta = 39.1$  degrees (100) for Oxalic acid, TritonX100, Pure and  $\text{H}_2\text{O}$ , and  $71.10$  degrees (103) in the presence and disappearance of additives, while the peak crystal growth is in the direction (002) and (101) show greater density at Oxalic acid, TritonX100, Pure and  $\text{H}_2\text{O}$  compared to that observed for zinc  $\text{NH}_3$  at (002) due to changes in crystal growth, and we also notice peaks at (102) in both  $\text{H}_2\text{O}$  and Oxalic acid. And  $\text{NH}_3$ , confirming the absorption of additives on the copper substrate during zinc deposition from DES. Interestingly, some of the zinc XRD peaks disappeared when the additive was Oxalic acid, TritonX100, Pure, and  $\text{H}_2\text{O}$  at  $2\theta = 36.3$  degrees (002), and  $50.25$  degrees (102) at the additive TritonX100 and at pure zinc, thus shifting the peak trend Preferably to (110) at  $2\theta = 36.3^\circ$  (002) in  $\text{NH}_3$  while at  $2\theta = 43.24^\circ$  (101) in Oxalic acid, TritonX100, Pure and  $\text{H}_2\text{O}$ .



**Figure 9.** XRD Peaks for the Zn Patterns Deposited from 0.4M  $\text{ZnCl}_2$  in DES in the Absence and Presence of Additives. (a) Is without Additives, (b) TritonX100, (c)  $\text{H}_2\text{O}$ , (d) Oxalic Acid and (f)  $\text{NH}_3$ . All Patterns were Carried out for 1 h at 70 °C and at a Current Density of  $8 \text{ mA cm}^{-2}$

## Conclusions

The present study was designed to investigate the effects of adding additives to the electrodeposition of zinc from an ionic liquid-based on a eutectic solvent of Lithium Chloride and ethylene glycol (stoichiometric ratio of 1:4, respectively). Herein, the additives were observed to have different influences on the electrochemical Zn coating. The results of this investigation have found that these additives significantly developed the Zn deposition in this system compared to the corresponding system in the absence of the additive. Clear changes in the cyclic voltammetry of Zn were obtained when the additive was added to the Zn-containing electrolytes. These experiments confirmed that the additive can be adsorbed on the active sites of the electrode surface during the Zn coating and strongly limit Zn deposition at cathodic potentials. Furthermore, a remarkable improvement in the morphology and surface appearance of the Zn coating was observed for the system containing the additives in comparison to the system without. The resultant deposition revealed a significant reduction in surface roughness and grain sizes of the Zn crystallites when electrodeposition was carried out in the presence of the additive in the electrolyte, showing the roughness of the Zn deposit was 95 nm thick in the absence of additive, while in its presence was only 130.8 nm thick. From the XRD results, the crystal orientation in the (002) and (102) planes was found to disappear for Zn deposition from the system containing the additive. Thus, the orientation of the (103) plane at  $2\theta = 71.10^\circ$  was preferentially shifted to (110) at  $2\theta = 74.65^\circ$ . It can be concluded that this is the first time uniform morphology, and hard adherent Zn coating was formed from the deposition taking place in DES at 70 °C on a copper substrate containing different additives, and the act of using of additive was good for the resultant coating.

## Conflicts of Interest

“There are no conflicts to declare”.

## Formatting of Funding Sources

Self.

## Acknowledgments

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