A Novel Deep Eutectic Solvent Developed as a Medium for Ni Electrodeposition

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Abstract

The study involved preparing a deep eutectic solvent containing a 1:4 stoichiometric mixture of lithium chloride and 1, 2-propandiol to investigate Nickel electrodeposition. The electrochemical characteristics of nickel electrolytes in the absence and addition of additives have been studied using electrochemical techniques such as cyclic voltammetry measurement. In addition, in the absence and presence of additives, the effect of the deep eutectic solvent in the electroplating process on a copper substrate was investigated. Using atomic force microscopy, scanning electron microscopy, and X-ray diffraction, the deposited nickel's roughness, thickness, and surface morphology were identified, revealing that additives function as a very efficient brightener, permitting the development of homogenous and flat nickel deposits.

Keywords: lithium chloride, deep eutectic solvent, nickel, electrodeposition

1. Introduction

Nickel electrodeposition procedures utilized an estimated 105 metric tons of nickel and nickel salts globally in 2011. Electrolytic nickel coatings are frequently used in electroforming techniques and as aesthetic and/or functional coatings. Corrosion resistance, electrocatalysis, and usage in magnetic applications are some of the functional benefits of Ni coatings, which are deposited predominantly from aqueous solutions [1]. Bottager produced the first workable Ni plating recipe in 1843 [2], and since then, techniques have been discovered to give additional functionality to the resultant coatings, such as increased hardness, improved throwing power, decreased coating stress, improved adherence, and leveling/brightening [3].

Typically, additives that vary the deposition process to produce the desired influence on the resulting coating are used to enhance surface morphology (uniform coatings with minimal surface roughness) leveling/brightening of Ni coatings. The ability of an electroplating solution to deposit preferentially in recesses inside a coating rather than protrusions is known as levelling, and levelling agents often exhibit quick absorption and desorption. Polyethyleneglycol and coumarin are two common leveling agents used in Ni plating. The capacity of an electroplating solution to create thin deposits with a grain size smaller than visible light wavelengths and a directed grain structure while generating a smooth and uniform surface is known as brightening. Brighteners and levellers, for the most part, work through absorption onto the substrate surface in a certain way. Aromatic compounds containing polar functional groups, such as benzenesulfonic acid and saccharin, are commonly used as brighteners for Ni electroplating (o-benzoic sulphonamide). Although it is widely use aqueous deposition methods have a number of drawbacks, including low current efficiency, coating embrittlement, [1]. As a result, innovative ionic liquid [4] (IL) media and deep eutectic solvents [5] (DES) are becoming increasingly popular. These solvent/electrolyte media may increase process control/efficiency, environmental sustainability, and functionality, as well as provide access to reactive metal deposition that was previously unavailable (for example Al).

Ionic liquids (ILs) have attracted significant attention in many areas of chemistry in the last two decades, including materials [1], gas separation [6], electrochemistry [7], biomass evaluation [4], and catalysis. They have been of interest for more than 40 years as alternative media for a wide variety of applications [8] lectrochemistry,4↘Metals including aluminum, tin, and zinc were utilized to make early-generation ILs, which were employed as liquid catalysts for Lewis acid-catalyzed processes. These procedures were essentially solvent-free when the reagents and products were liquids. After then, more study was done to develop metal-free alternatives, which maintained the required solvent properties were combined with many coordinating and non-coordinating anions, such as Cl, BF4, PF6, and NTf2, to create a novel class of ILs [9].

species that melted below 100 degrees Celsius, but this definition has gradually been expanded to accommodate a broader spectrum of fluids in which ionic character dominates solvent–solute interactions [10]. Deep eutectic solvents (DESs) are a type of ion-dominated system that Deep eutectic solvents (DES) are a popular study area [11] , owing to the demand for environmentally friendly alternatives to traditional solvents as well as their versatility. This opens the door to a variety of applications, including electrolytic, electroless deposition, electropolishing [12], biomass removal [13], electrochemical energy storage [14], and pharmaceutical formulation [15]. The components, usually an ammonium salt and a hydrogen bond donor (HBD) are easily mixed to make DESs . Because DESs have the toxicological qualities of both components, choosing benign beginning materials can result in low-toxicity compounds. The bulk of these materials are both inexpensive and biodegradable [16, 17]. Choline chloride (ChCl), one of the most prevalent ammonium salts, is one of the most regularly utilized components. Because it is a pro-vitamin, it is widely employed in a range of commodities items, including as an animal feed addition. As a result, it is biodegradable, inexpensive, has minimal toxicity, and may be obtained from biomass. When choline chloride is

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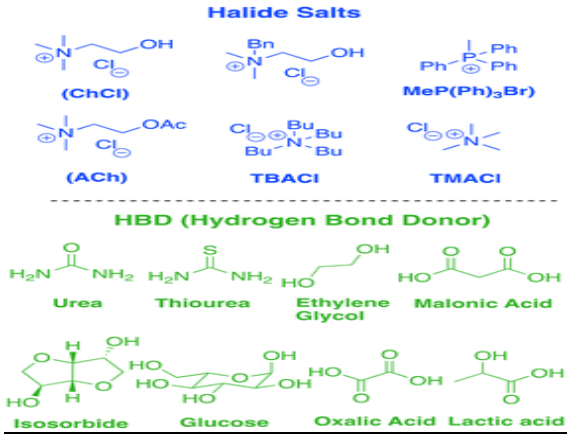
combined with an HBD like urea, glucose, or oxalic acid, it generates a eutectic combination. The HBDs lower the lattice energy of both homocouples, therefore lowering the freezing point. A multitude of HBDs have been published in the literature in recent years, resulting in a big library of ChCl-based DESs with a diverse range of physical and chemical properties. Furthermore, numerous alternatives to ChCl have been offered, and adjusting the two components appears to be the key to creating the appropriate medium for each procedure. Some examples of salts and HBDs are summarized in Table1 [18, 19]

Table 1 Common halide salts and HBDs used in the preparation of DESs



While the original definition of DESs included mixes of quaternary ammonium salts and hydrogen bond donors, they may now be defined more broadly as Brnsted and Lewis acids and bases. Strong hydrogen bonds form in all of these systems, and they diverge from perfect mixes, lowering the freezing point significantly. Natural DESs have been coined to describe similar mixes of Bronsted and Lewis acids and bases that are often found in nature, albeit this term should only be applied to naturally existing mixtures rather than those produced from naturally occurring starting ingredients [19, 20]. Table 2 lists the different types of Brønsted and Lewis acid and base mixtures which have been studied together with examples of the components used.

Table 2 Classification of deep eutectic solvents depending on their composition

Eutectic	Acid	Base
1	Lewis	Lewis
	MClx M = Zn, Sn [17], Fe Al [21], Ga, In	R4NCl
2	Lewis	Lewis
	MClx·yH2O, M = Cr, Co, Cu, Ni, Fe [20]	R4NCl
3	Brønsted	Lewis
	RZ, Z = CONH2, COOH, OH [22]	R4NCl
4	Lewis	Lewis
	MClx or MClx·yH2O M = Al, Zn Cr [23]	RZ, Z = CONH2, COOH, OH
5	Brønsted	Lewis
	ROH RZ, Z = COOH [24]	RZ, Z = CONH2, COOH, OH

In general, a considerable freezing point depression is seen, with the amount of that depression being proportional to the strength of the bond established between the two components, i.e. AlCl3 will have a higher freezing point depression than an alcoholic HBD such as glucose. DESs have been employed in a variety of applications, including the synthesis of metal–organic frameworks (MOFs), the creation of nanoparticles, the desulfurization of gasoline, and as a medium for organic processes [25, 26]. In previous studies there are very limited researchers discuss lithium chloride as salt to formation DESs [27].

In this work, We tested the novel DES as a medium for electrodeposition copper metal on nickel substrates made from LiCl and 1,2 propanediol in this study. Due to the smaller size of lithium ions compared to choline ions, we have replaced choline chloride with lithium chloride, which will reduce the conductivity of DES and improve electrodepositions of metals

2. Experimental

(DES) was prepared by mixing LiCl and 1,2-Propandiol in a 1:4 molar ratio, respectively. After that, the mixture was placed on a hotplate at 50°C and stirred until a colorless and homogenous electrolyte was obtained. Then it was added nickel chloride (NiCl2.6H2O) (Aldrich99%) to (DES) which has been prepared. Then it is added other materials such as (H2O), (Triton X100) (Sigma Aldrich, ≥ 99.5%), (Boric acid)(Aldrich99.8%), and (Nicotinic acid) (Aldrich 98%). Cyclic voltammetry GPES2 software was used to drive an Autolab/PGSTAT12 potentiostat for cyclic voltammetry experiments. A platinum working electrode (1 mm diameter), a platinum flag counter-electrode, and a silver wire pseudoreference electrode were employed in this study. Prior to each experiment, the working electrode was polished with 0.05 m-alumina paste and cleaned by washing with deionized water followed by acetone. Cyclic voltammetry was measured at different temperatures and different concentrations and different scan rat. The electroplating was carried out on a copper plate in DES containing 0.2 M NiCl2.6H2O, it was also painted with the addition of materials (H2O, Triton X100, Boric acid and Nicotinic acid) Bulk electrolysis was performed using copper cathodic plates that had been manually polished, washed with acetone, and rinsed with water, as well as a dried oxide-coated titanium mesh electrode that had been manufactured in the same way. The substrates were taken from the solution and cleaned with water and acetone in all of the tests, where the solution temperature was 90 °C and deposition was carried out using a continuous current (0.50A) for 1 hour. Scanning electron microscopy (SEM) was used to investigate surface characteristics, while metals analysis of plating compositions was carried out (EDAX). The XRD pattern of Ni deposit was studied using a powder X-ray diffraction method.

3. Results and Discussion

Cyclic Voltammetry

A. Effect of Concentrations on the CVs of Ni with DES

As shown in Figure 1, electrodeposition of NiCl2.6H2O from new DES (LiCl+1, 2-Propandiol) was accomplished at various concentrations (0.07, 0.1, 0.2, 0.3, and 0.4) M. The cyclic voltammetry of different concentrations of NiCl2.6H2O in DES was studied at an elevated temperature of 75°C, where the voltammetry was carried out in the potential range 0.8 V to -0.8 V and a scan rate of 30mVs-1, using a Pt disc (1 mm diameter) electrode as the counter-electrode and Ag wire as the reference

electrode, using a Pt disc (1 mm diameter) electrode as the counter-electrode.

Previous research into the electrodeposition of metals in ionic liquids at high temperatures has discovered that the enhanced pace and efficiency of metal deposition leads to better deposits than at room temperature; hence, this research was carried out at high temperatures [28, 29]. From the graphs below we can see that the reduction peak currents were increased due to the increased amount of NiCl2.6H2O in the electrolyte. The presence of high concentrations of NiCl2.6H2O, which considerably created [NiCl4]-2 in the solution, resulting in a considerable quantity of Ni deposition, is clearly associated to the rise in current peaks, and vice versa for low concentrations of [NiCl4]-2. Because there are many [NiCl4]-2 and few Cl anions on the electrode's surface, just a modest amount of energy is required to decrease the Ni+2 ions. As seen in figure 1, large concentrations of NiCl2.6H2O resulted in an increase in the number of stripping peaks, resulting in a positive shift in the Ni deposition potential.

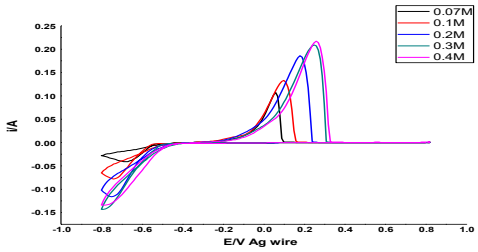


Figure 1. Effect of Concentration on NiCl2.6H2O in New DES.

B. Effect of Trmpretures on the CV of Ni with DES

Figure 5 shows the electrodeposition of Ni from new DES (LiCl+1,2-propandiol) at various temperatures (40,50,60,70,80, and 90 C). At various temperatures, cyclic voltammetry of NiCl2.6H2O in DES was investigated. Figure 2 illustrates the cyclic voltammetry of DES containing 0.2 M NiCl2.6H2O at various temperatures all experiments were recorded at a scan rate of 30mVs-1. When NiCl2.6H2O cyclic voltammograms were obtained at 90°C, they showed a considerable increase in Ni deposition and dissolution of the present peak of Ni, compared to those recorded at other temperatures. This was expected for many reasons: first, when the temperature was raised, the viscosity of the Ni electrolyte reduced, allowing the rate of mass transfer toward the electrodes to rise. This was attributed to the increased free void volume in the solution as a result. Second, the Ni electrolyte includes a large number of Cl^- anions, which may obstruct the approach of [NiCl4]-2 to the electrode surface via adsorption into the electrode surface. The number of adsorbed Cl^- anions on the electrode surface decreased as the temperature of the electrolyte increased, allowing the concentration of [NiCl4]-2 at the electrode surface to rise. This, in turn, would encourage Ni decrease. Figure 2 shows the cyclic voltammetry of NiCl2.6H2O. It is possible that the electrodeposition of Ni from DES at raised temperatures is significantly better than at ambient temperatures due to the increased rate of Ni deposition, and therefore the deposition efficiency will be improved.

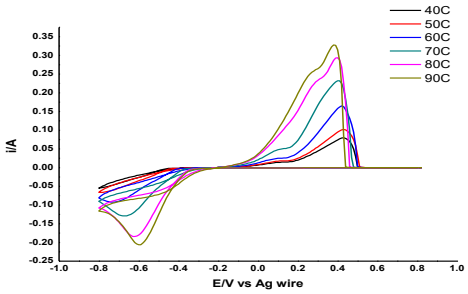


Figure 2.Effect of Temperature on NiCl2.6H2O in New DES.

C. Effect of Scan Rate on the CVs of Ni with DES

As shown in Figure 3, electrodeposition of Ni from a new DES (LiCl+ 1, 2-Propandiol) was accomplished at various scan speeds (10, 20, 30, 40, 50, and 60) mVs-1. At various scan speeds, cyclic voltammetry of NiCl2.6H2O in DES was investigated. Figure 3. Compares the cyclic voltammetry of DES containing 0.2 M NiCl26H2O at various scan speeds. All tests were conducted at 75°C. When NiCl2.6H2O cyclic voltammograms were recorded at 60mVs-1, they showed a considerable increase in Ni deposition and dissolution of the present peak of Ni, compared to those recorded at other Scan rates. This research found that in the presence of the additive, the amplitude of the oxidation peaks for Ni deposition increased along with the scan rate. However, unlike oxidation processes, the rise in cathodic currents at high scan speeds is not as great. It's possible that the electrodeposition of Ni from DES at higher scan rates is significantly better than at lower scan rates, owing to the increased rate of Ni deposition, and therefore deposition efficiency will be improved [30].

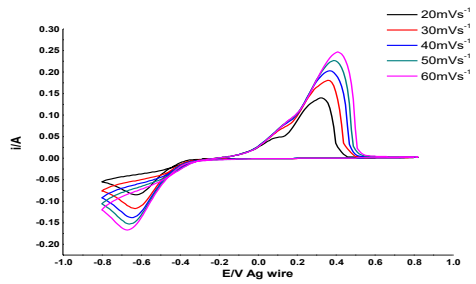


Figure 3. Effect of Scan Rate on NiCl2.6H2O in New DES.

D. Effect of Additives on the Voltammetry Behavior of Ni

Because of the increased efficiency and rate of Ni deposition at 75°C, the electrodeposition of Ni from DES is significantly better than at room temperature. As a result, performing Ni electrodeposition from DES at high temperatures is recommended. Figure 6 depicts cyclic voltammetry of 0.2 M NiCl2.6H2O in DES at 75°C in the presence of various additives concentrations: (a) Boric acid, (b) Nicotinic acid, (c) H2O, and (d) TritonX100. The

cyclic voltammograms were recorded at a scan rate of 30mVs-1 using platinum as working electrode (1.3 mm diameter); a platinum flag counter electrode, and an Ag wire reference electrode. The effects of different additions on the electrochemical behavior of DES were investigated only at 75 °C, as illustrated in figure 4. The CV of AN additive has definitely changed to the negative side. It is possible that NA is hindering the deposition process and increasing the stripping process due to the change in peak shape due to the decreased currents. [2].

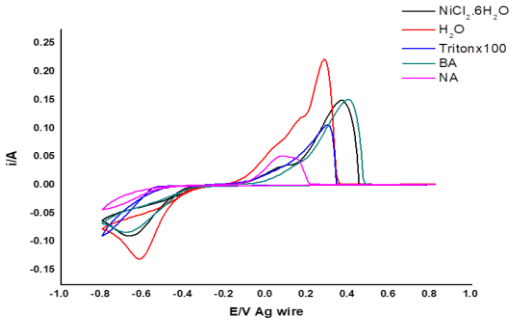


Figure 4.Cyclic Voltammogram at 75 °C of 0.2 M NiCl2.6H2O in a 1:4 Molar Mixture of Lithium Chloride and 1,2-Propandiol with varying amounts of additives BA , NA, H2O, and TritonX100. Measured Using a 1.3 mm Pt Disc Working Electrode, Pt Flag Counter Electrode, and Referenced against Ag Wire at 10 mV s-1.

Surface Characterization

A. AFM Study

AFM was used to investigate the topography and roughness of Ni growth (0.2 M NiCl2.6H2O) from new DES at 75 °C in the presence and absence of additives. as illustrated in figure 5. The morphologies of Ni coatings has clearly different when adding additives such as %10 H2O, 0.02M Tritonx100, 0.4M Boric Acid and 0.016M Nicotinic Acid. The roughness of the deposited Ni in the absence of the additives was very high, whereas when adding additives the roughness decreased significantlyIt is obvious that the surface of the electrodeposited Ni film from the additive-free electrolyte was a rough layer with a greater grain size, however in the presence of additives, the surface morphology becomes considerably smoother and extremely homogenous. The fact that the additive was significantly adsorbed into the Cu substrate during Ni electroplating [31].

Table 1. In the presence and absence of additives, the smoothness of Ni films produced in DES.

Metal Salt	Additives	Roughaness Ra/nm	Avarage Partical Size /pm
NiCl2.6H2O	None	80.11	3.103
NiCl2.6H2O	H2O	32.68	1.407
NiCl2.6H2O	BA	27.79	7.815
NiCl2.6H2O	Tritonx100	34.62	1.377
NiCl2.6H2O	NA	43.03	5.087

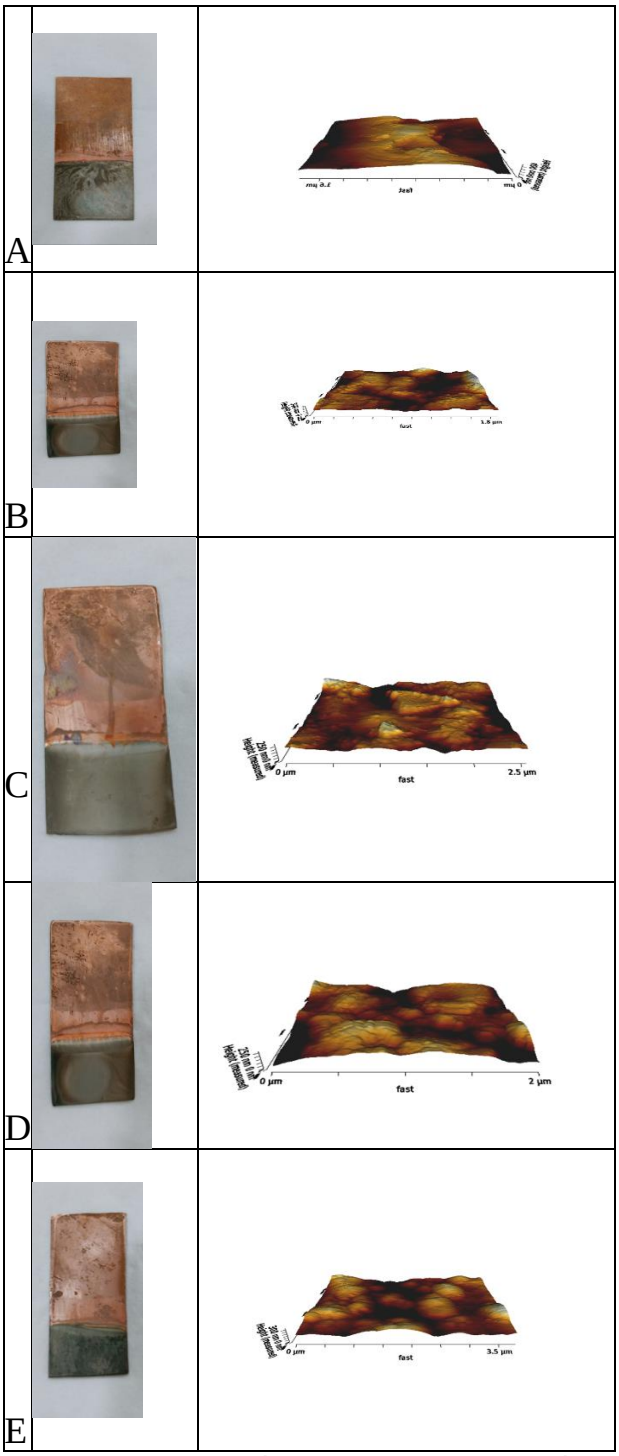


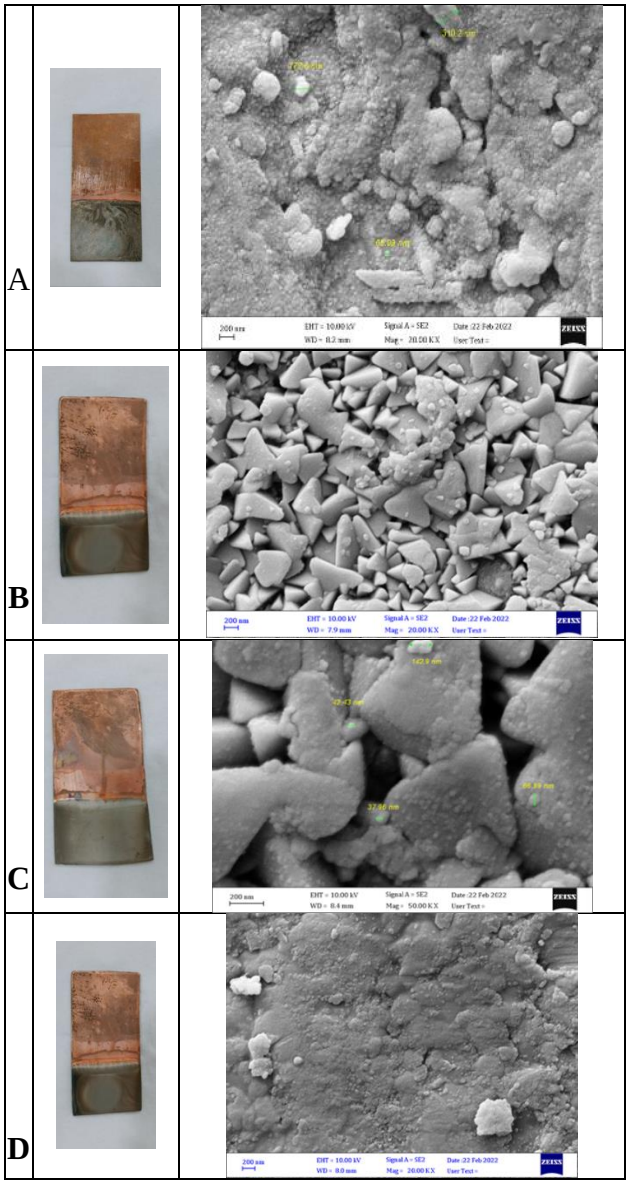
Figure 5.AFM Images for the Coatings Obtained from 0.2M NiCl2.6H2O in DES in the Absence and Presence of additives at a Current Density of 50 mA cm−2 for 1 h on a Cu Substrate at 75 °C. The Deposition was (a) DES + NiCl2.6H2O (b) with H2O,

(c) BA (d) Tritonx100 and (e) NA.

B. SEM Study

The effect of the additive on the surface morphology and deposition quality for 0.2 M Ni with and without additive in the novel DES electrolyte at 75 °C and a current density of 50 mA cm-2 for 1 h on Cu substrates was studied using scanning electron microscopy (SEM). Figure 6 shows optical images and SEM morphologies for Ni with and without additive. Ni coatings with excellent adhesion and uniformity were deposited in all systems. According to certain research, a tiny grain size is a necessary but not

sufficient prerequisite for brightness [32]. This illustration also demonstrates that the Ni layer is not microcrystalline, as would be expected from electrolytic Ni deposition from other molecular solvents. This proves that nanocrystalline development occurs as a result of immediate nucleation under such circumstances, resulting in flat and brilliant metallic mirrors. Metals with a high negative reduction potential have an immediate nucleation mechanism, whereas metals with a higher electropositive reduction potential have a sequential nucleation process [28]. When the additives were added, the grains became nanocrystalline, especially when TritonX100 was added at a concentration of 0.02 M, also when add %10 H2O, with an associated decrease in grain size. This results in a finer-grained deposit, implying that the Ni phase formed by TritonX100 and H2O is slower to develop than the Ni phase formed by the additive-free electrolyte or other additives. As a result, in the case of Tritonx100 and H2O, the average size of the crystallites is lower than, as well as being smooth and consisting of homogenous crystals.



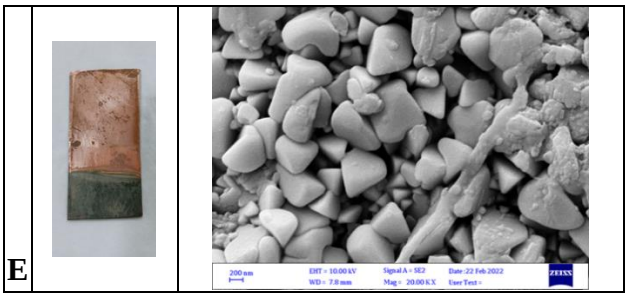


Figure 6: Optical Photographs, SEM Morphologies, of 0.2M NiCl2.6H2O Coatings Obtained from new DES in the Absence and Presence of Additives at a Current Density of 50 mA cm−2 for 1 h on a Cu Substrate at 75 °C. Images (a) for the Deposition without Additives, while (b) H2O, (c) BA, (d) Tritonx100, and (e) NA.

C. X-ray diffraction

The crystal orientations for Ni patterns generated from DES at 75 °C in the presence and absence of additives were investigated in this research [29, 33]. gives data for Ni samples deposited on the Cu substrate from 0.2M NiCl2.6H2O in DES at 75 °C in the presence and absence of additives at a current density of 50 mA cm-2 for 1 hour. In the absence of additives, the diffraction peaks for the Ni pattern emerge at 2θ= 43.339° , 44.50° , 50.451° , 51.856° , 54.14° , 74.173° and 76.51° as attributed to the (111), (200), (220) [19]. Nickel hexagonal planes, respectively, and as identical to those shown in previous researchs. Furthermore, the Cu substrate's XRD peaks were found at 2θ= 44.5° , 51.49° , 76.51° clearly in both solutions H2O and Boric acid. While these peaks disappear in pure solutions, Tritonx100 and nicotinic acid. Also Obviously the XRD spectrum direction of Ni coating shows lower intensities at 2θ= 43.3° , 50.4° , 74.1° in solutions H2O and BA , while the intensity of these peaks in solutions NA and Tritonx100 .

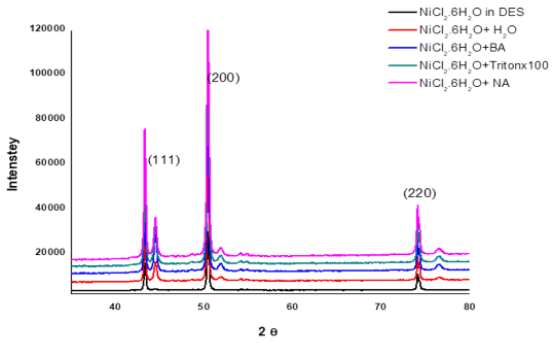


Figure 7: XRD Peaks for the Zn Patterns Deposited from 0.4M ZnCl2 in DES in the Absence and Presence of Additives.

4. Conclusions

The purpose of this study was to see how adding additives to the electrodeposition of nickel from an ionic liquid based on a eutectic solvent of Lithium Chloride and 1,2-Propandiol affected the results (stoichiometric ratio of 1:4, respectively). The additives were shown to have distinct effects on the electrochemical Ni coating in this study. According to the findings of this study, these additives considerably increased Ni deposition in this

system when compared to the similar system without the addition. When the additive was introduced to Ni-containing electrolytes, clear changes in cyclic voltammetry of Ni were observed. These tests showed that the additive may be adsorbed on the active areas of the electrode surface during Ni coating, thereby preventing Ni deposition at cathodic potentials. Furthermore, the system with the additives showed a significant improvement in the morphology and surface appearance of the Ni coating as compared to the system without additives. When electrodeposition was carried out in the presence of the additive in the electrolyte, the subsequent deposition indicated a considerable decrease in surface roughness and grain sizes of the Ni crystallites. The XRD results showed that when additives were added to the Ni deposit, new diffraction peaks were produced, indicating that a change in the structure of the Ni film had occurred. It can be concluded that this is the first time a uniform morphological, hard adherent Ni coating has been created from deposition in DES at 75 °C on a copper substrate including various additives, and the use of additives was beneficial to the final coating.

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