As the existing methods of aqueous electroplating have limitations, researchers have been seeking alternative fluid systems that are free from toxicity, non-corrosive and cost-effective. In the present work, we introduce a promising approach towards efficient electroplating of cobalt from a deep eutectic solvent (DES) mixture of choline chloride and ethylene glycol (1:2 mol ratio). The presence of hydantoin (HD) as an additive may contribute to an improved quality of electroplating in terms of the formation of a dense and adherent film.

The electroplating process was carried out at a constant current density of 2.8 mA cm\(^{-2}\) for one hour at 90 °C. A range of electrochemical, spectroscopic and microscopic techniques were utilized to characterize the deposition process. The film thickness of Co was calculated and found to be 8.31 and 23.54 µm in the absence and presence of hydantoin, respectively. The hardness test indicates the dense Co film formation on copper sheet. The mirror-like Co film will be shown using SEM and photograph.

**Keywords**: Mirror finishing, hydantoin, cobalt, deep eutectic solvent, UV-vis study; Morphology; Electrochemical analysis

1. **INTRODUCTION**

Surface finishing technology comprises electrodeposition (electroplating) and electropolishing processes. The processes of surface finishing are implemented to modify the metallic surfaces in an attempt to prevent from corrosion, decorate and catalysis [1-4]. In aqueous solutions, the electrodeposition of a series of metals nickel and silver were carried out [5,6]. However, low efficiency, quality and toxicity of aqueous electrolytic baths encourage researchers to find alternatives.
Recently, ionic liquids (ILs) in particular deep eutectic solvents (DESs) appear as interesting electrolytes for electrodeposition of precious metals, such as nickel, silver, and chromium [7-9].

The mechanism of electrodeposition processes in aqueous media has been well-studied. However, in ILs and DESs, the mechanism of electrodeposition has still been poorly understood, requiring further investigation. Dealing with the detail of electrodeposition process in ionic media is to answer the questions about the nature of mass transport, speciation, and achievement of exceptional surface morphology [10].

The high-quality surface finishing is desired and of great importance fundamentally and industrially in the presence of additives. For example, a bright surface of Ni can be achieved with addition of additives into an electrolytic bath that based on urea-ChCl and EG-ChCl DESs. Surface finishing also comprises surface modification via anodisation, electropolishing and nanoporous formation [11-15].

In this work, the electroplating of cobalt on Cu sheet has been examined in an attempt to implement at the large scale. It has also dealt with the mechanism of the process in ChCl-EG eutectic electrolytic bath in the presence of hydantoin (HD) as an efficient additive using electrochemical techniques.

2. EXPERIMENTAL

2.1. Raw materials

From Sigma Aldrich, all chemicals were purchased, including choline chloride; HOC2H4N(CH3)3Cl (ChCl) (99%), ethylene glycol (EG) (≥ 99%), cobalt salt; CoCl2.6H2O (≥ 98%), hydantoin (HD) (≥ 99.5%), ammonium persulphate, (NH4)2S2O8. Only chemical obtained from fisher is sulphuric acid, H2SO4.

2.2. Preparations

The liquid mixture was prepared from mixing choline chloride and ethylene glycol in a 1: 2 mol ratio of ChCl: ethylene glycol) at 60 °C until a homogeneous, colourless liquid was formed. The cobalt concentration (CoCl2.6H2O) in all electrolytic baths was 0.40 mol L⁻¹; otherwise, it will be specified. The concentration of hydantoin (HD) as an additive was 0.40 mol L⁻¹ that accompanied with cobalt concentration.

2.3. Uv-visible measurements

A Shimadzu model UV-1601 spectrophotometer with a cuvette cell (a path length of 1 cm. λmax) was used in the acquisition of UV-visible spectra for a set of samples.
2.4. Electrochemical measurements

Three electrode-based cell and the electrochemical perturbation using Autolab PGSTAR12 potentiostat controlled via the GPES2 software were used. A platinum disk (1 mm² Pt), a Pt flag and an Ag wire were used as working, counter and pseudo-reference electrodes, respectively. The working electrode was polished mechanically using a 0.05 µm γ-alumina paste followed by washing using deionized water and dried with acetone prior to measurements.

In the bulk electrolysis of co electroplating, a Cu sheet (50 mm × 42 mm × 1 mm) was used as a substrate that degreased with anopol for five minutes to make sure of gaining clean surface. Further treatment was performed as surface activation by removing the thin oxide layer over Cu sheet using aqueous solution of 0.87 mol L⁻¹ (NH₄)₂S₂O₈ and 0.20 mol L⁻¹ H₂SO₄ solution. As anodic pole, iridium oxide-coated Ti mesh was used. All electrochemical experiments were performed by holding the current density at 2.8 mA cm⁻² for one hour at 90 ºC. Ultimately, the coated Cu substrate was removed from the electrolytic bath and cleaned by rinsing with water followed by drying with acetone.

2.5. Surface morphology

The scanning electron microscope (SEM) images were acquired using a Philips XL-30 Field Emission Gun equipped with a Bruker AXS X Flash 4010 EDS detector. The operating conditions comprised a holder (five mm in diameter) and an accelerating voltage of 20 kV. After covering in Conductomount (Met-Prep) on a Struers Labopress-3 with heating at 180 °C for three minutes at 25 kN, samples were exposed followed by cooling with water for three minutes.

3. RESULTS AND DISCUSSION

3.1 Spectrophotometric study

Fig.1a shows the Uv-Vis spectra of Co(II) in the mixture containing choline chloride-ethylene glycol. It is strongly supposed that the [CoCl₄]²⁻ is formed in the such environment that enriched in chloride ion. It is seen that the addition of hydration could not change the complexation of Co(II) ion that evidenced from the main feature of spectra as well as obtaining the same colour for the baths in the presence and absence of hydantoin as shown in Fig.1b. It crucial to notice that some interesting peaks can be seen in the wavelength ranges from 600 to 730 nm. These bands have first been allocated to a metal-ligand charge transfer complexes.
"Figure 1. shows (a) Uv-Visible spectra of 0.015 M Co(II) at 25 and (b) photographic picture of Co(II) in the mixture containing choline chloride-ethylene glycol.

It is also seen that addition of hydantoin causes a tiny increasing in intensity of the absorption peak. This can be correlated to formation of an association between the [CoCl\(_4\)]\(^{2-}\) complex and hydantoin molecule which then increases the molar absorptivity of the whole system. The tetrahedral complex of cobalt has already been confirmed in the current electrolytic bath via Extended X-ray Absorption Fine Structure (EXAFS) [16, 17].

3.2 Cyclic Voltammetry

Fig.2a shows voltammograms of 0.40 mol L\(^{-1}\) M CoCl\(_2\).6H\(_2\)O solutions at various sweep rates at 90 °C. It is clearly seen that the behavior of CoCl\(_2\).6H\(_2\)O is described qualitatively as quasi-reversible process. Over reduction sweep scan, there is peak lies on -0.60 V and the oxidation peak localizes at -0.1 V. The Randles-Sevcik equation relates Faradaic current \(i\) to square root of scan rate as shown below:

\[ i_p = (2.69 \times 10^5)n^{3/2}ACD^{1/2}v^{1/2} \quad (1) \]

Where \(n\) is the number of electron involved in the process, \(A\) is the geometric surface area) in cm\(^2\), \(C\) is the concentration (in mol cm\(^{-3}\)), \(D\) is the diffusion coefficient (in cm\(^2\) s\(^{-1}\)) and \(v\) is the scan rate (in V s\(^{-1}\)).

The reduction process obeys the above equation in which \(i\) is proportional to \(v^{1/2}\) as shown in Fig. 2b (inset) [18]. In the presence of HD with various concentrations, the Co (II) ion in the form of [CoCl\(_4\)]\(^{2-}\) undergoes reduction with obvious kinetic difference where the electrochemical reaction is faster in the absence of hydantoin as shown in Fig. 2a and Fig. 2b. This could be due to an association between [CoCl\(_4\)]\(^{2-}\) and hydantoin molecule; in other words, the mass transport becomes sluggish in the existence of hydantoin.
Figure 2. shows CVs of CoCl$_2$.6 H$_2$O in the ethylene glycol-Choline chloride electrolytic bath in the absence and presence of hydantoin at various concentrations at 90°C (a) and CVs CoCl$_2$.6 H$_2$O in the ethylene glycol-Choline chloride electrolytic at various sweep rate (b).

It is also noticed that HD causes lowering the current values as expected of both reduction and oxidation peaks of cobalt ion. This is ascribed to the increasing the viscosity of electrolytic bath in the presence of HD. Finally, at relatively high concentration of there is a couple of peaks which can be ascribed to reduction of hydantoin.

3.3 Conductivity and viscosity

Fig. 3(a-d) shows influence of temperature on two crucial important physical properties; viscosity and conductivity of 0.40 mol L$^{-1}$ CoCl$_2$.6H$_2$O with HD in ChCl-EG eutectic mixture. In general, it is seen that as hydantoin is added, the viscosity increases. The composition of ChCl-EG-HD is little different from ChCl-EG where stronger hydrogen bonding exists in the former eutectic mixture. This increase in viscosity leads to slowness of the mass transport; thereby, the mechanism of the process is controlled to some extent by the additive molecule.
Figure 3 exhibits the viscosity (a) and (b) and conductivity (c) and (d) of 0.4 M CoCl₂·6H₂O, as a function of temperature in the ethylene glycol-Choline chloride electrolytic bath in presence and absence of 0.4 M HD.

As expected the conductivity decreases in the existence of hydantoin. It is well-defined that there is an inversely proportionality between viscosity and conductivity [19]. The conductivity decreasing as shown in Fig. 3c, d.

3.4 Chronocoulometry

Chronocoulometry as one of electrochemical techniques is used to study the mass transport. In this technique, the over potential (relatively high charge transfer) is implemented to monitor the mass transport and to estimate the charge transfer using Cottrell equation in two forms, as shown in Eq. 2 and Eq. 3:

\[
I = \frac{nFAC_0\sqrt{D}}{\sqrt{\pi\tau}} \quad \text{(2)}
\]

\[
Q = \frac{2nFAC_0D^{3/4}\tau^{1/2}}{\pi^{1/2}} \quad \text{(3)}
\]

Where; \(D\) is the diffusion coefficient, \(n\) is the number electron involved, \(C_0\) is the initial concentration, \(\tau\) is time in s, \(A\) is the surface area of the electrode and \(F\) is the Faraday constant. Herein, the reduction process was studied where higher charge transfer was counted for 0.40 mol L⁻¹ CoCl₂·(H₂O)₆ in the case of absence of HD. The non-linear behavior in both cases can be correlated to a large quantity (bulk analysis) of CoCl₂·(H₂O)₆ in the electrolytic baths. Fig. 4 shows chronocoulometry by holding potential at -0.8 V. It is clearly noticed that the number of charge consumed in the Co (II) electrodeposition is much high relatively in the absence of 0.4 M HD. This case can be interpreted on the basis of high current efficiency when hydantoin exists as supported by the SEM images.
In dealing the mechanism of electrodeposition of Co (II) ion, Scharifker and Hills models were applied in an attempt to show the dominating mechanism of the electrochemical reduction process. Accordingly, there are two different nucleation processes, namely instantaneous and progressive [20].

After fitting, it is observed that in the absence of HD, Co (II) ion electrodeposition process much close to instantaneous mechanism while in the presence of HD, the process is quite close to progressive mechanism as shown in Fig. 5. From the fitting, it is concluded that in case of existence of HD, the nucleation is faster than in the absence one. This might be the reason of obtaining mirror-like surface of Co film.

Figure 4. Chronocoulometry of cobalt electrodeposition with a concentration of 0.4 mole L⁻¹ CoCl₂·6H₂O in the ethylene glycol-ChCl bath (red) and in the presence of 0.4 mole L⁻¹ HD (black). The potential was held at -0.8 V for 10 s, followed by a step to -0.4 V for ca. 30 minutes.

Figure 5. The experimental $i$-$t$ transient plot of 0.4 M CoCl₂·6H₂O in ethylene glycol-ChCl bath (a). The experimental $i$-$t$ transient plot of 0.4 M CoCl₂·6H₂O in ethylene glycol-ChCl bath (b). All experiments were carried out on a Pt disc (1 mm dia.) at 25 °C versus a silver wire reference electrode where the potential was first held at -0.8 V for 10 s.
3.5 Surface morphology

Fig. 6a exhibits micrographs of coated copper substrate by Co film from ethylene glycol-ChCl mixture in the absence of any additive, showing dark film produced whereas in the presence of hydantoin as an additive at 25 °C for 1 hr. at a current density of 2.8 mA cm$^{-2}$, it is seen that the additive produces a mirror-like Co film as shown in Fig. 6b. From the SEM, it is seen that in the absence of additive, there is a huge number of discrete protrudes, in contrast, relatively extremely smooth surface (bright surface) is achievable when hydantoin is added as shown in Fig. 6c and Fig. 6d, respectively.

![Figure 6a](image1)
![Figure 6b](image2)
![Figure 6c](image3)
![Figure 6d](image4)

**Figure 6.** photographs of Cu-sheet coated by cobalt; the dark and mirror-like surface of (a) and (b) with respect to absence and presence of hydration. The SEM images of Cu-sheet coated by cobalt; in the absence (c) and presence of hydantoin (d). The cross section film of Co layers; in the absence (e) and presence of hydratoin (f). All results were obtained at 2.8 mA cm$^{-2}$ for 1 hr. at 25°C.
It is also recorded that the electrodeposited layer of Co is much thicker by almost three times when hydantoin is added as presented in Fig. 6e and Fig. 6f, respectively. This can be mainly related to changing composition of the interfacial region.

4. CONCLUSIONS

Summarily and descriptively, the followed methodology is promising in terms of fundamental and applied aspects of Co electrodeposition and the followings are concluded:

- From fundamental point of view, the mechanism of nucleation of reduced Co (II) ion is progressive in nature in the presence of used additive.
- From the practical view point. The use of relatively benign electrolytic bath of ChCl-EG in the electrodeposition of Co in the presence of hydantoin at relativelyon copper substrate can be implemented at the large scale.
- The change of electrochemical mechanism of Co plating on copper sheet in the presence of hydantoin is achieved via interfacial composition and mass transport rate changing’s using hydantoin as a potential alternative to ethylene glycol via forming hydrogen bonding with ChCl in an attempt to achieve a desired metallic surface.
- The addition of hydantoin as an effective additive results in obtaining mirror-like Co surface via altering the mechanism of electrodeposition of Co ion.

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CONFLICTS OF INTEREST
The authors declare no conflict of interest

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