IONIC LIQUIDS AS ADDITIVES ON THE ELECTRODEPOSITION OF COBALT, NICKEL AND ITS ALLOY ONTO COPPER IN ACIDIC SULFATE BATH

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ABSTRACT

The electrocatalytic properties of nickel (Ni), cobalt (Co) and nickel-cobalt (Ni-Co) alloy coating qualified them to be utilized in industrial applications. Traditional organic additives have been used to enhance the deposits properties but some of them are not eco-friendly and obtained low deposits quality. Green ionic liquids (ILs) have become an alternative additive to be used in the electrodeposition due to their excellent properties. In the present study, the influence of two new ILs, namely, 1-methyl-3-((2-oxo-2-(2,4,5 trifluorophenyl) amino)ethyl)-1H-imidazol-3-ium iodide ([MOFIM]I) and 1-(4-fluorobenzyl)-3-(4- phenoxybutyl)imidazol-3-ium bromide ([FPIM]Br) were investigated as green additives for Ni, Co and Ni-Co alloy electrodeposition from acidic sulfate bath on a copper substrate. The resultant surface morphologies demonstrated that both studied ILs served as effective leveling agents but [MOFIM]I was more effective than [FPIM]Br owing to their molecular structures. Both studied ILs led to the formation finer-grained, more ordinated crystals, compact, free-cracked and highly uniform Ni, Co and Ni-Co alloy deposits compared to that obtained from free ILs bath as shown by scanning electron microscopic (SEM) studies. Atomic force microscopic (AFM) analyses exhibited that the roughness of all films deposited with [MOFIM]I were lower than that with [FPIM]Br. Both ILs led to a homogeneous distribution of the Ni and Co elements and confirmed the Ni-Co formation, as shown by the EDX-mapping. The X-ray diffraction (XRD) patterns exhibited the fcc crystal structures with (2 2 0) was preferred growth orientation of the Ni, Co and Ni-Co alloys crystallites without and with both studied ILs. The average crystallite size of the Ni, Co and Ni-Co alloy films decreased by 30%, 12% and 27% respectively with [MOFIM]I and by 25%, 5% and 18% respectively with [FPIM]Br. The microhardness of the Ni, Co and Ni-Co alloys increased in the presence of both ILs. All voltametric measurements indicated that the inhibition of Co^{2+} and Ni^{2+} reduction in the presence of both ILs occurred *via* their adsorption on the cathode surface, which obeyed the Langmuir adsorption isotherm. The optimal bath conditions that led to the highest CCE% values involved a current of 20 mA cm^{-2}, deposit potential of 6.5 V, pH of 4.5, temperature of 25°C and deposit time of 10 min. The percentage current efficiency (CCE%) values of Ni, Co and Ni-Co alloy electrodeposition were very high (nearly 100%) in the presence of both studied ILs. The highest corrosion resistance was for Ni deposit in the NaCl solution with [MOFIM]I, compared to that with [FPIM]Br. However, Co deposit exhibited lowest corrosion resistance with [MOFIM]I and [FPIM]Br respectively. Ni-Co2 and Ni-Co3 alloys deposited at the optimal conditions were the two best alloys to resist corrosion among all the Ni-Co alloys examined in the current study. The co-deposition of Ni-Co alloy obeyed the anomalous type. This anomalous behavior was alleviated after [MOFIM]I and [FPIM]Br were introduced in the Ni-Co deposition baths. Quantum chemical calculations were performed at the B3LYP/6-311++G(d,p) level of the density functional theory (DFT). Several quantum parameters and natural atomic charges were calculated. The results showed that the calculated values of the quantum parameters and natural atomic charges were consistent with the experimental findings.

ABSTRAK

Sifat elektromangkin nikel (Ni), kobalt (Co) dan aloi nikel-kobalt melayakkan mereka digunakan dalam aplikasi industri. Bahan aditif organik tradisional telah digunakan untuk menambahbaik sifat enapan tetapi sebahagiannya tidak berkualiti dan tidak mesra persekitaran. Cecair ionik (IL) hijau telah menjadi alternatif untuk digunakan dalam menghasilkan elektroenapan yang sangat baik. Dalam kajian ini kesan dua cecair ionik, iaitu, 1-metil-3-((2-okso-2-(2,4,5-trifluorofenil)amino)etil)-1H-imidazol-3-ium iodida ([MOFIM]I) and 1-(4-fluorobenzil)-3-(4-fenoksibutil)imidazol-3-ium bromida ([FPIM]Br) dikaji sebagai bahan tambahan hijau untuk elektroenapan Ni, Co dan aloi Ni- Co di atas substrat kuprum daripada media sulfat. Hasil morfologi permukaan menunjukkan kedua IL berperanan sebagai agen pelaras tetapi [MOFIM]I adalah lebih berkesan daripada [FPIM]Br disebabkan oleh struktur molekulnya. Kedua IL menyebabkan pembentukan butiran halus berkristal yang tersusun, padat, bebas retak dan endapan Ni, Co dan Ni-Co yang seragam seperti ditunjukkan oleh kajian mikroskopi imbasan elektron (SEM). Analisis mikroskopi daya atom (AFM) menunjukkan penurunan kekasaran permukaan yang diendap oleh [MOFIM]I berbanding [FPIM]Br. Kedua IL menyebabkan penyerakan Ni, Co yang lebih seragam selain pembentukan aloi Ni-Co yang ditunjukkan oleh pemetaan EDX. Corak pembiasan sinar-X (XRD) menunjukkan Ni, Co dan Ni-Co terendap berstruktur hablur fcc dengan (2 2 0) sebagai orientasi tumbuh terpilih samada dengan kehadiran IL atau tidak. Purata saiz hablur dalam filem Ni, Co dan aloi Ni-Co berkurangan masing-masing sebanyak 30%, 12% dan 27% dengan [MOFIM]I dan masing-masing 25%, 5% dan 18% dengan [FPIM]Br. Kekerasan mikro Ni, Co dan aloi Ni-Co juga bertambah dengan kehadiran kedua IL. Semua pengukuran voltametrik menunjukkan bahawa penghalangan penurunan Co^{2+} and Ni^{2+} dengan kehadiran IL berlaku melalui penjerapan di atas permukaan katod yang mematuhi isoterma penjerapan Langmuir. Keadaan mandian optimum yang memberikan %CCE tertinggi melibatkan arus 20 mA cm^{-2}, keupayaan endapan 6.5 V, pH 4.5, suhu 25°C dan masa endapan selama10 min. Nilai %CCE elektroendapan Ni, Co dan aloi Ni-Co adalah sangat tinggi (hampir 100%) dengan kehadiran kedua IL yang dikaji. Rintangan kakisan tertinggi adalah untuk endapan Ni di dalam larutan NaCl dengan [MOFIM]I berbanding [FPIM]Br. Walau bagaimanapun, endapan Co menunjukkan rintangan kakisan terendah di dalam [MOFIM]I dan [FPIM]Br. Aloi Ni-Co2 and Ni-Co3 yang dimendapkan pada keadaan optimum adalah dua aloi terbaik untuk menghalang kakisan di kalangan semua aloi Ni-Co yang diselidiki dalam kajian ini. Ko-enapan aloi Ni-Co mematuhi jenis anomali. Sifat anomali ini ditingkatkan setelah [MOFIM]I dan [FPIM]Br digunakan di dalam mandian endapan Ni- Co. Pengiraan Kuantum Kimia dilakukan pada aras teori fungsi ketumpatan (DFT) B3LYP/6-311++G (d, p). Beberapa parameter kuantum dan cas atom tabii telah dikira. Keputusan menunjukkan nilai pengiraan parameter kuantum dan cas atom tabii adalah konsisten dengan dapatan eksperimen.

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LIST OF ABBREVIATIONS

AFM	-	Atomic Force Microscopy
ALSV	-	Anodic Linear Stripping Voltammetry
CCE	-	Cathodic Current Efficiency
CE	-	Counter Electrode
CP	-	Cathodic polarization
CPE	-	Constant phase element
CPP	-	Cathodic Polarization Potential
Cu	-	Copper
CV	-	Cyclic Voltammetry
3D	-	Three Dimensional
2D	-	Two Dimensional
DFT	-	Density Functional Theory
EDX	-	Energy Dispersive X-Ray Spectroscopy
EIS	-	Electrochemical Impedance Spectroscopy Method
E_{HOMO}	-	The highest occupied molecular orbital energy
E_{LUMO}	-	The lowest unoccupied molecular orbital energy
fcc	-	Face Center Cubic
[FPIM]Br	-	1-(4-fluorobenzyl)-3-(4-phenoxybutyl)imidazol-3-ium bromide
GCE	-	Glassy Carbon Electrode
H_{ads}	-	Adsorbed Hydrogen
HER	-	Hydrogen Evolution Reaction
HOMO	-	The highest occupied molecular orbital
ILs	-	Ionic Liquids
LUMO	-	The lowest unoccupied molecular orbital
[MOFIM]I	-	1-methyl-3-((2-oxo-2-(2,4,5 trifluorophenyl) amino)ethyl)-1H-imidazol-3-ium iodide
NOP	-	Nucleation Over Potential
OCP	-	Open-Circuit Potential
Pt	-	Platinum
R_a	-	Average roughness
R_{ct}	-	Charge transfer resistance
RE	-	Reference Electrode
R_s	-	Solution resistance
R_t	-	Total roughness
SCE	-	Saturated Calomel Electrode
SEM	-	Scanning Electron Microscopy
W_{Co}	-	Practical weight of the cobalt deposit
WE	-	Working Electrode

W_{Ni}	-	Practical weight of the nickel deposit
W_p	-	Practical weight of the deposit
W_t	-	Theoretical weight of the deposit
XRD	-	X-Ray Diffraction Analysis

LIST OF SYMBOLS

a	-	Constant
A	-	Electron affinity
A	-	Electrode area
b_c	-	Cathodic tafel slope
C	-	Additive concentration
D	-	Diffusion coefficient
ΔE	-	Energy gap
F	-	Faraday's constant
ΔG^o_a	-	Standard free energy of adsorption
I	-	Ionization potential
i	-	Current density in the absence of the additive
i_{add}	-	Current density in the presence of the additive
i_c	-	Cathodic current
i_{pc}	-	Cathodic peak current
K	-	Equilibrium constant of the adsorption reaction
n	-	Number of electrons
ΔN	-	The fraction of electrons transferred from the inhibitor to the metal surface
R	-	The gas constant
S	-	Softness
T	-	Absolute temperature
$v^{1/2}$	-	Proportional to the square root of the scan rate
W	-	Warburg impedance
χ	-	Electronegativity
α_c	-	Electron transfer coefficient
η	-	Hardness
θ	-	Surface coverage
μ	-	Dipole moment

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The formation of metallic films and coatings is an important technology and has been applied in many industries. Several coating methods which are commercially available such as vapor deposition, plasma spray, hot metal processes, painting, thermal spraying and metallizing including electrodeposition (1–4) can be used to extend the component's life and protect surface functionality. Ni-Co alloy is commonly produced through electrochemical reduction, leaching process, mechanical alloying, and solgel method (5). Electrodeposition or electroplating is the process by which an applied current or potential is used to deposit a film of metal or alloy by the reduction of metallic ions onto a conductive substrate.

Electroplating finds numerous applications as thin films and three- dimensional, thick structures in micro devices due to its interesting advantages. The main advantages of electrodeposition process are rapid deposition rates, cost effectiveness, requires simpler operating conditions and instrumentation, obtaining a homogenous deposit film. Moreover, many other desirable properties of electrodeposition are simplicity of high level control over the thickness of the films, possible to prepare material that could not be prepared by other methods such as thermal spraying, painting, hot metal processes, and evaporation (1–3). The investigation of more beneficial properties as well as high deposit qualities was conducted using electrodeposition. The deposit exciting qualities are large area deposition, excellent corrosion protection, high strength formability, attractive bright appearance, ease of process ability, and relatively low temperature contrary to the physical systems usually required high temperature (6).

Among the wide range of electroplating materials available, nickel (Ni), cobalt (Co) and Ni-Co alloy are essential engineering material employed widely in several industrial applications. In industrial production, it is usually prepared by means of electrodeposition.

1.2 Properties, Corrosion Resistance and Structure of Nickel, Cobalt and Ni-Co Alloy Electrodeposits:

Nickel (Ni) is silvery-white, hard, malleable, ductile metal and good conductor of heat and electricity. Ni and Ni-based alloy films obtained by electrodeposition approach are widely manufactured to improve the corrosion resistance in engineering application due to their good physical properties, high chemical stability and heat resistance, high current efficiency (>90%) (7) and attractive appearance. Moreover, the appropriate adsorption strength between Ni and adsorbed hydrogen (Ni-H_{ads}) gave Ni deposit high electrocatalysts activity. The addition of additives is considered as responsible for strengthening the passivation phenomenon and enhancing the oxidation resistance of the Ni and its alloy phase in the coating. A reasonable cost of Ni and Ni alloy coatings compared with noble metals makes it an industrially desirable product (8–12). The mechanical properties of Ni deposited are high tensile strength, low ductility, high hardness and high internal strength (13,14).

In electrodeposition technique, mechanic, magnetic, structure and morphological properties of deposits depend on the electrodeposition parameters. The refinement of crystal structure, for example by the use of organic addition agents, is accompanied by increased hardness and tensile strength, and reduced ductility (13,14). The Ni and its alloy coatings which are follow face-centered cubic (fcc) structure, is usually bright, pore-free and crack-free with fine and compact grains coatings. Addition of supporting agent such as Na_2SO_4 to the electrodeposition bath increases the conductivity of the solution, thus facilitating the mass transfer of metal ions towards the cathode surface.

Cobalt (Co) is a hard ferromagnetic, silver-white, lustrous and brittle element. It is stable in air and does not react with water and it can also be magnetized (13,14). The Co properties as good corrosion resistance, high coercivity and high saturation magnetization make Co useful and feasible material for potential applications in magnetic media devices. The special properties of Co electrodeposit, including good strength and thermal stability, high heat conductivity, strong hardness, good resistance to corrosion, good wear resistance, strong adhesion, optical properties, and high catalytic properties (15–17) qualified Co deposit to be very essential engineering material. Co can take two different crystalline structures which are hexagonal closed packed (hcp; ε-Co) at T < 417 °C, and fcc; α-Co) at 417 °C < T < 1493 °C (melting point) (18).

The electrodeposition of iron family-based alloys, including Ni and Co alloy, has been the subject of continuous investigations due to the high magnetic, mechanical chemical, physical and electrocatalytic properties of such coatings (1). Ni-Co alloy possesses an excellent adhesion and wear resistance, good hardness, high corrosion resistance, and heat conductivity. Therefore, Ni-Co alloy coatings are used in various magnetic devices, especially in micro-technology for the manufacture of sensors, actuators, and memory devices (2)(5). The bath composition deposition affects the Ni-Co alloy properties. The cobalt introduction in nickel alloys, ≤ 40%, causes an increase in their hardness and strength and corrosion resistance (16)(19).

The bath composition deposition potential and the current density strongly influence the deposit growth mechanism and morphological characterization including surface roughness, microstructure and grain size. If the Ni content is higher than that of Co in the bath, (up to 50wt.%, rich nickel deposit) (2)(20) at high overpotentials, the deposit has lower roughness and finer grain size with face center cubic-close packed structure (fcc) solid solutions of Ni and Co. In contrast, while at low overpotentials, and at higher content of cobalt in the electrolyte (rich cobalt deposit), hexagonal-close packed (hcp) structure, higher surface roughness, bigger grain size of deposits was formed. Moreover Ni-Co alloy deposit with lower Co content exhibits higher hardness and strength (21).

1.3 Mechanism of Ni, Co and Ni-Co alloy electrodeposition

Ni, Co and Ni-Co alloy coatings are constructed using the electrodeposition method through applying the electrical current in the electrochemical cell. The following steps, Figure 1.1, illustrated the mechanism of the formation Ni, Co and Ni-Co alloy electrodeposits from aqueous system (22):

1- The divalent Co and/or Ni ions are surrounded by hydration shells. The solvated ions move towards the negative charged cathode electrode after applying the electrical current on metal substrate cathode.
2- The ions get reduced and neutralized, as the following Eqs. (1.1-1.2):

$$Co^{+2} + 2e^{-} \rightarrow Co \quad (1.1)$$

$$Ni^{+2} + 2e^{-} \rightarrow Ni \quad (1.2)$$

3- The attractive interaction between water molecule and neutral Co and Ni ions is zero, so hydrated water molecules are displaced and neutral metal atom gives an intermetallic phase according to the following chemical reaction (Eq.1.3 only related to Ni-Co alloy):

$$Co + Ni \rightarrow CoNi \quad (1.3)$$

4- Then Co and/or Ni diffuse to the surface sites where it incorporates into the metal lattice.
5- After the incorporation into the metal lattice, the Ni, Co and Ni-Co alloy deposits are formed.

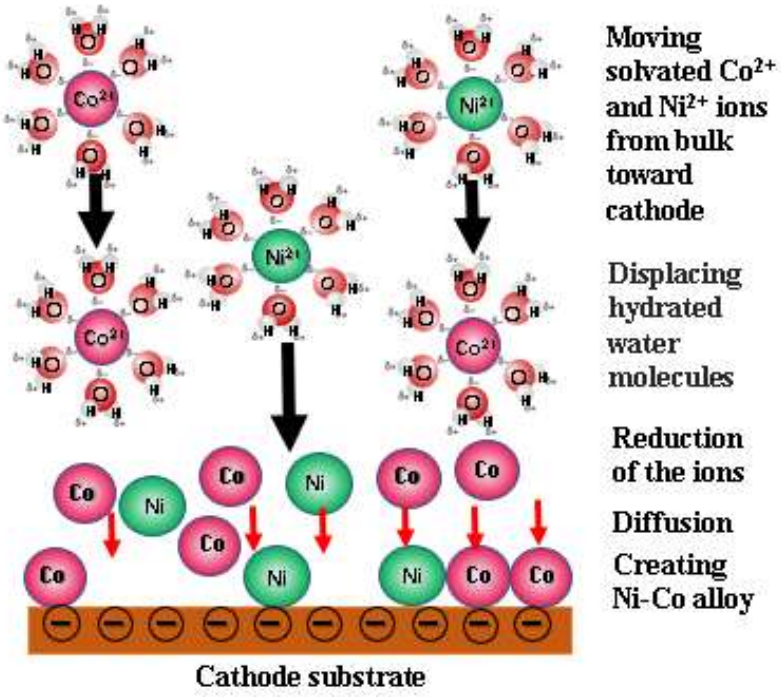

Figure 1.1 Schematic steps illustrated the mechanism of the formation Ni, Co and Ni-Co alloy electrodeposits.

1.4 Applications of Nickel, Cobalt and Ni-Co Alloys in Industry

1.4.1 Application of Nickel

Nickel and nickel alloys are important industrial materials as their wide variety of utilizations, as shown in Figure 1.1. The majority of these applications require heat resistance and high corrosion resistance, (such as nuclear power systems, power stations, steam turbines, and aircraft gas), medical applications, and petrochemical and chemical industries (1–3)(23–25). Being highly resistant to tarnish and high hardness, nickel and nickel alloys have become alternatives for chromium electrodeposition in hardware, automotive, electrical and electronics accessories. Currently, Ni film is considered to be one of the most promising hydrogen evolution reaction (HER) electrocatalysts among high-activity electrocatalysts due to the appropriate adsorption strength between Ni and adsorbed hydrogen (Ni-H_{ads}). Moreover, the significant Ni and its alloy coating properties include stability, high efficiency and reasonable cost of Ni

and Ni alloy coatings compared with noble metals (8–12). Other Ni alloy film applications are in the fabrication of anodes for Li–ion batteries (1–3) and protein microarray fabrication technologies (26). Moreover, because of its favorable mechanical properties, Ni deposits are used for printing, phonography, foils, tubes, screens and many other articles (27).

1.4.2 Application of Cobalt

In engineering, cobalt and its alloys are regarded as essential materials and are commonly used in many industrial applications. This is due to their special characteristics, including good strength and thermal stability, high heat conductivity, strong hardness, good resistance to corrosion, good wear resistance, strong adhesion, optical properties, and high catalytic properties (15–17). Co and its alloys are also used in the manufacture of nanostructural materials such as nanowires and nanotubes and in various storage and magnetic equipment (28). Moreover, Co and its alloys are applied in microsystem technology for the manufacture of sensors, actuators, micro relays, inductors and magnetic devices in the computer industry (16)(29,30), as shown in Figure 1.1. Additionally, it is used in modern accumulators and advanced batteries, as well as in microelectronics for the semiconductor industry (28).

1.4.3 Application of Ni-Co Alloys

Ni-Co alloy deposits are very important due to their industrial applications (such as electronics, computers, automotive and energy storage devices, particularly in the computer field), technological (space, rocketry) applications (1–3)(31,32), biotechnological applications (26) and powerful fabrication applications (33). These significant applications are due to Ni-Co alloys having suitable magnetic, mechanical, chemical, physical and electrocatalytic properties, Figure 1.1. In addition, electrodeposited Ni-Co alloys are widely used as active materials for hydrogen and oxygen evolution reactions in water electrolysis, as anode materials for lithium

batteries, and as catalysts for H_2O_2 decomposition (31)(34). Ni-Co films have been prepared via electrodeposition due to their low cost, easy to maintain equipment, control of film thickness, preparation of high-quality alloys, and capability of handling complex geometries. The method is environmentally friendly compared with other coating technologies including chemical and physical deposition by vapor (1–3).

Figure 1.2 Examples of different Ni, Co and Ni-Co alloy coatings applied on components in various industries.

1.5 Additives in the Electrodeposition Process:

1.5.1 Organic and Inorganic Additives:

The electrodeposition of metals and alloys employed usually by using solutions contain one or more organic or inorganic addition agents which have effective functions

in the electrodeposition processes (35–39). In the aqueous electroplating solutions, it is considerably important to use additives in order to improve the surface morphology of the deposit, produce more precision, durability and stability for coating (40–43), owing mainly to the desirable influences produced on the structure and growth of deposits (44). The increasing in current density range, enhancing potential brightening the deposit, promoting leveling, reducing grain size and the tendency to tree, reducing stress and pitting in the deposited film, and improving physical and mechanical properties, can be achieved by using additives. The additives may even be organic and metallic, ionic and non-ionic, and adsorbed onto the plated surface (6). Organic additives actually seem to enhance the creation of some dominant textures of most crystallites, often inhibiting crystallization process towards the other crystallographic axes (45). These additives influence the processes of deposition and crystal building as adsorbate on the cathode surface (46). The deposit form obtained at a constant current density can depend on the surface coverage value of the additive. Therefore, the adsorbed additives may affect both the kinetics and mechanism of electrodeposition. Organic additives can also elevate surface polarization, increase cathodic overpotential, and suppress the kinetics of electrodeposition reaction (47).

1.5.2 Mechanism of Additives

One of the two main brightener categories is additives. Brighteners are organic or inorganic, ionic or non-ionic compounds that added to the electrodeposition for enhancing the morphological structure of deposit obtained and improving its quality and properties. In aqueous solutions, there are mainly two mechanisms for the brighteners to affect the deposits during the electroplating. One is called leveling agent additive or additive (common name). It is performed by the adsorption of an organic species on the electrode surface, blocking nucleation and hindering growth of metal nucleus. The other is carried through coordinating to the metallic species called complexing agent. Complexing with metal ions leads to decreasing their reduction potential for making it more difficult to nucleate metal clusters (48).

On the other hand, it is important to study the nucleation and growth mechanism of the film structure during electrodeposition. The nucleation mechanism of the conducting metals growth was investigated via the theory model of metal growth (5)(49). The nucleation mechanism includes instantaneous and progressive nucleation was developed by Scharifker and Hills, and the direction of nucleation includes two-dimensional (2-D) and three-dimensional (3-D) growth (5)(49). In an instantaneous nucleation process, the model assumes the rate of nucleation is high and that coverage of all active sites by nuclei, i.e., nucleus grow. In the progressive nucleation mechanism, the rapid growth of a large number of active sites is achieved throughout the reduction, i.e., the number of nuclei increases (5)(44).

The nucleation mechanism of the metal or alloy deposited on the surface is affected significantly by the category of the brighteners used. The leveling agent additive, which is adsorbed on the cathode surface and exhibited the change in the cathodic current density, follows a 3D-progressive nucleation/growth mechanism. The morphology of the deposited metal or alloy is getting leveled (5)(44)(50). However, since the coordination environment of the metal ions in electrodeposition bath was changed by addition of a complexing agent and led to change in the cathodic current density, the electrodeposition of metal or alloy follows a 3D-instananeous nucleation/growth mechanism (5)(44)(50). With the instantaneous nucleation model, the number of nuclei is constant, and they grow on their former positions on the bare substrate surface without formatting new nuclei. Hence the radii of the nuclei is larger and the surface morphology is rougher. Addition of leveled additive into electrodeposition bath, the nuclei not only grow on their former positions but also on new nuclei, which form smaller nuclei particles and the surface morphology becomes smoother, less granular, flatter and lower roughness (51).

1.6 Ionic Liquids (ILs):

Ionic liquids (ILs) are an interesting challenge for new chemicals with the potential to enhance chemical technology development and stimulating considerable field research. Ionic liquids are organic salts composed of organic cations and

organic/inorganic anions that are liquids at room temperature (39). ILs are synthesized by combining organic cations such as pyridinium, imidazolium, ammonium, phosphonium, and guanidinium with a wide variety of anions including halides (Cl^-, Br^-), hexafluorophosphate (PF^{6-}), tetrafluoroborate (BF^{4-}), trifluoroacetate (CF_3COO^-), bis- (trifluoromethylsulfonyl) amide (NTf_2), and dicyanamide (DCA) (52). The amount of literature concerning ILs has significantly increased over the past few decades (53). ILs are considered as an efficient alternative to conventional organic solvents. Air and water-stable ILs systems have been emerged because of their unique properties, including such better organic and inorganic solvents, non-volatile, less poisonous, non-flammable, thermal stability (can be used over a wide temperature range up to 400 °C) and negligible vapor pressures (10^{-11} - 10^{-10} mbar) (54). In addition, the most important advantage of ionic liquids is their wide electrochemical windows (> 5V) which offers access to elements which cannot be electrodeposited from aqueous or organic systems (46)(55). Some of the crucial factors that can cause ILs to differ towards aqueous systems are conductivity, viscosity, density, dissolving ability from metal salts, polarity, and potential window. In conclusion, ILs are inevitably sophisticated and advanced solvents which can be formulated to fit the specific application. In addition, eco-sustainable, recyclable material for synthetic organic chemistry, separation sciences and other chemical and engineering sciences have been fully justified for ILs. Due to the multitude of useful properties and abilities of ILs, ILs have now become alternatives for several industrial applications including (54):

- Electrochemistry.
- Synthesis and extraction processes.
- Electrodeposition.
- Liquid crystals.
- Photochemistry.
- Fuel desulfurization.
- CO_2 capture.
- Lubrication.
- Enzymatic synthesis.
- Thermal storage systems.
- Rocket propulsion.

The ionic liquid is defined as an ionic material consists cation and anion with a melting point below 100 °C. Low melting point of ILs arises due to a large, non-symmetrical organic cations and hence low lattice energies of ILs structure (48). It is generally accepted that the cation is more important in controlling the physical properties of the salt whereas the anion has a greater effect upon the stability and chemical reactivity. The majority of ILs systems used for metal deposition have been based on nitrogen-based cations. Imidazolium based cations, which are chosen in the current work, have been favored due to their superior fluidity and conductivity. The other important role that the cation probably plays in electrodeposition is controlling the structure and most importantly the Helmholtz layer thickness. Anions also affect the conductivity and viscosity of the electrolyte. Anions could decrease the Helmholtz layer thickness considerably and should make metal ion reduction easier (48).

1.6.1 Ionic Liquid as Additives

Due to special properties of ionic liquids, such as undetectable vapor pressure, a wide range of liquids, fast recovery and reuse, ionic liquids are a strong alternative to traditional molecular organic solvents in recent years (53). Scientists are currently interested in ionic liquids applications, including imidazolium-ionic liquids as additives (36). Ionic liquids reporting in the liquid chromatography (56), sustainable solutions (57), organic synthesis, catalytic reactions, and ILs used as lubricants and corrosion inhibitors (53).

1.7 Quantum Chemical Calculation:

The investigation of ionic liquid additives performance in the electrodeposition processes are conducted experimentally. In addition, computational chemistry can be used to provide theoretical explanation for the experimental findings. Experimental measurements to achieve the effect of ionic liquid as additives in Ni, Co and Ni-Co alloy electrodeposition process are conducted using various techniques which are

studied deeply in the experimental section. Traditionally, experimental techniques are mainly used to investigate the additives performance in the electrodeposition field. However, employing the experimental methods only is harmful to the environment, expensive and time consuming (58). With the improvement in computer hardware and software as well as in theoretical chemistry, computational chemistry has been increasingly used in the design and development of addition agents in the electrodeposition field (43)(59–61) and corrosion inhibitors (58)(62–65). As reported in (59) "Density functional theory (DFT) has become an active field of research to envisage the mechanism arising between additives and surface of the metal at the molecular level".

1.8 Problem Statement

An organic or inorganic compound is considered as one of the main components of electrodeposition solution of single metal or alloy due to a positive and beneficial effects of specific functions of additives on the deposit's properties. Adding additives in Ni, Co and Ni-Co alloy electrodepositions processes is not very common. Moreover, glycine, acetonitrile and choline chloride–urea (1:2 molar ratio) which were used as additives in the Ni-Co alloy electrodeposition exhibits granular, no uniform deposits (1)(66–68). An extensive micro-cracked deposits were produced by adding glycine, thiourea, sodium gluconate, boric acid, coumarin and saccharin due to hydrogyn evolution (23,24)(15)(59–62). Non-brightness, low corrosion resistance Ni-Co alloy deposit obtained by using nano Al_2O_3 particles as additive (32). Moreover, the hardness and the strength of deposits (27)(16) and the cathodic current efficiency (CCE%) of some studies were very low (15)(36)(39,40). Insufficient thermal stability and poor throwing power were achieved in other studies (23)(27)(7).

In addition, Ni, Co and Ni-Co alloy crack free films were produced in the presence of glycine and sodium citrate (67)(69) as additives but these studies required high temperature and high current density. Moreover, some studies used an expensive substrate such as gold, Pt, Si (25)(29)(66). The others consumed high concentration of

metal sources and additives (16)(29)(66). Some studies used non environmentally friendly, toxic such as Cd^{2+} (70) and cyanides (71), highly flammable and volatile substances, acetone, (50) and health hazards substance, thiourea (50), as additives. Moreover, some works lack for hardness and corrosion resistance measurements (36)(72–74).

Ionic liquids have been applied as a media of electrodeposition process by many researchers (24)(34)(50,51)(67)(75) but some of them obtained micro-cracked, granular films, and low CCE% (24)(31)(44)(46) (50,51)(67,68). However, using ionic liquids as addition agents in the electrodeposition processes attracted only few researchers (39)(53). This means that study the effect of ILs as additives during electrodeposition process is insufficient.

Many investigations into Ni induced from different baths including, sulfamate, chloride, citrate, acetate, gluconate, glycine, and Watts-type nickel electrodeposition bath, without or with additives were recorded (76–78). Moreover, cobalt deposits has been obtained from different baths containing chloride (79), chloride & sulfate (80), gluconate (81), acetate (82) and citrate (83) electrolytes. Unfortunately, some of these coating deposited in industry from electrolytic baths contains toxic solutions such as the cyanide anions (71)(84). A distinguished feature of cyanide-based systems is obtained fixable and soft deposits, strong adhere to alloys, good electrical conductivity, easily buffed, good solderability and obtaining decorative, bright and attractive antique finishes (84). Cyanide process is being prohibited due to its health and environmental pollution hazards as well as high cost involved to treat the effluent. Therefore, demanding to use green and more environmentally friendly electrolytes in the industrial fields become extremely necessary to decrease the problem of pollution in the world. Using acid sulfate bath is attracted many attentions due to pollution control characteristics, its safety features and relatively low cost (85). Moreover, finer grained and smoother surface was obtained from sulfate bath than that which was obtained from other baths (38).

On the other hand, employing experimental approaches only for investigating the additive's role in the electrodeposition is not eco-friendly, costly and time

consuming. Therefore, applying computational techniques, including quantum chemical calculations as predictive techniques, is more environmentally friendly, time saver and more economic (64). The practical investigations are complemented through computational systems. These systems are effective tools to propose the effective ionic liquids as additive among an enormous group of additives using in the electroplating field. Quantum chemical calculations are used to support the experimental investigations. Al-Fakih et al (64) reported that "Density functional theory (DFT) is a quantum chemical approach that is considered a powerful tool to investigate the quantum parameters of molecules theoretically with reasonable accuracy". Moreover, the natural atomic charge, i.e., Mulliken population analysis, has been calculated to determine the active sites and the adsorption mode of additives or inhibitor molecules, which can offer or accept electrons (86). As reported in (86) "There is a general consensus that the more negatively charged the heteroatom is, the more adsorption centers there are on the metal surface through donor–acceptor interactions". The use of Mulliken population analysis has been widely reported for calculation of the charge distribution over the whole skeleton of inhibitor molecules (64)(59).

Most of studies which used the quantum chemical parameters were conducted for organic compounds as additives in the electrodeposition field (43)(59) (60,61)(87) or as corrosion inhibitors (62)(64)(86)(88). Moreover, many other researchers calculated the natural atomic charge and determined the active sites and the adsorption mode of organic compounds as corrosion inhibitors (62)(64) or as additive in the electrodeposition (59).

Although some studies used ionic liquids as electrodeposition electrolytes (72)(89) or as corrosion inhibitors (90,91). However, very limited studies have used the quantum chemical parameters for clarifying the behavior of ionic liquids which are used as additives during the electrodeposition processes. It could be said that the studies regarding the use of quantum chemical calculations on ionic liquid compounds as additive in Ni, Co and Ni-Co alloy electroplating are not many and very poor.

According to the gaps in all previous research in the Ni, Co and their alloys electrodeposition, the main aim of the current study is improving the qualities of Ni, Co

and Ni-Co alloys deposits by investigating the influence of two new green eco-friendly imidazolium ionic liquids using as addition agents in the electrodeposition of Ni, Co and Ni-Co alloy from acidic baths.

Furthermore, in the current work, the quantum chemical calculations as theoretical tools are used to explain the adsorption performance of two studied ionic liquids additives based on their molecular structure properties. Moreover, electronic properties and molecule orbital information were obtained by quantum chemical calculation to further analyze the interaction between studied ionic liquid and metal surface. In addition, the natural atomic charge was calculated and employed to investigate the active sites of two imidazole derivatives ionic liquids molecules which can offer or accept electrons.

1.9 Research Objectives

As stated by all previous research gaps, obtaining Ni, Co and its alloy via electrodeposition by applying a novel green ILs become very essential to achieve it in current study. Therefore, the objectives of the present study are as follows:

1. To study the electrodeposition of Ni, Co and Ni-Co alloy in the absence and the presence of [MOFIM]I and [FPIM]Br ionic liquids as new additives.
2. To characterize the surface morphology and microstructure of Ni, Co and Ni-Co alloy deposits in the presence of the studied new ionic liquids as additives from acidic sulfate bath.
3. To optimize the ionic liquids as additives in the electrodeposition of Ni, Co and Ni-Co alloy by using density functional theory (DFT).
4. To study the structure and properties relationship of Ni, Co and Ni-Co alloy deposits prepared by electrodeposition with the presence of the studied new ionic liquids.

1.10 Scope of the Research

Figure 1.3. illustrated the molecular structure of two new studied ionic liquids namely:

1- Imidazolium iodide incorporating aromatic amide (name: 1-methyl-3-(2-oxo-2-((2,4,5trifluorophenyl)amino)ethyle)-1H-imidazol-3-ium iodide [MOFIM]I ionic liquid.
2- Imidazolium bromide (name: 1-(4-fluorobenzyl)-3-(4-phenoxybutyl)imidazol-3-ium bromide [FPIM]Br ionic liquid.

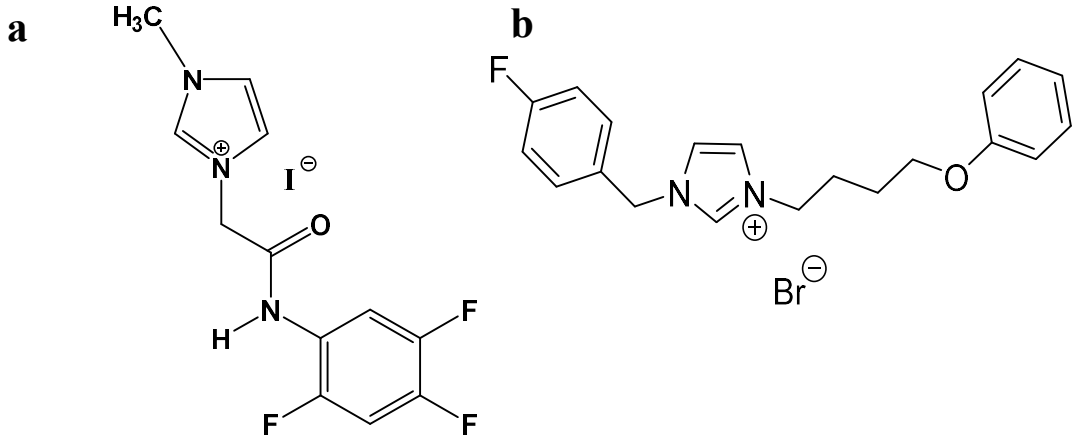

Figure 1.3 The molecular structure of the ionic liquids namely (a) 1-methyl-3-(2-oxo-2-((2,4,5 trifluorophenyl) amino) ethyl)-1 imidazol-3-ium iodide ([MOFIM]I), (b) 1-(4-fluorobenzyl)- 3-(4-phenoxybutyl)imidazol-3-ium bromide ([FPIM]Br).

The effect of many important factors will be studied in the electrodeposition of Ni, Co and Ni-Co alloy. The first factor is concentrations of two studied ILs in the range from 1×10^{-7} to 1×10^{-3} M, The other factors that will be studied in the electrodeposition of Ni, Co and Ni-Co alloy are including pH ,in the range from 3.5 to 4.5, electroplating time, in the range from 5 to 15 min, current density, in the range from 6 to 24 mA/cm^2, and electroplating potential, in the range from 3 to 9 V. Three different bath compositions for co-electrodeposition of Ni-Co alloy ,as illustrated in Table 3.2 in chapter 3, will be investigated. These selected range of all previous factors are due to

the pest coating qualities and high cathodic current efficiency (CCE%) are obtained, as reported in (1)(3)(15)(7)(49). Moreover, the CCE% during electrodeposition processes will be investigated at all these factors.

Characterization the surface morphology, elemental compositions, roughness, microstructure and microhardness of Ni, Co and Ni-Co alloys deposited in the absence and the presence of two studied ILs will be obtained by using microscopic analysis such as scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX), EDX mapping, atomic force microscopy (AFM) and X-ray diffraction analysis (XRD). Moreover, the mechanical properties such as micro-hardness of Ni, Co and Ni-Co alloy deposits will be measured.

The mechanism of the electroplating process of Ni, Co and Ni-Co alloys in absence and presence of additives will be achieved experimentally by using voltametric analysis such as (potentiodynamic cathodic polarization curves, cyclic voltammetry (CV), In situ-anodic linear stripping voltammetry (ALSV)). The electrochemical corrosion behavior in a saline environment (3.5% NaCl solution) will be investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques.

Optimization of the neutral and cationic forms of both [MOFIM]I and [FPIM]Br ionic liquids used as additives in the electrodeposition of Ni, Co and Ni-Co alloy will be investigated by using quantum chemical calculations. Quantum chemical calculations using DFT was conducted to calculate quantum parameters and discuss the relationship with the experimental findings. Several quantum parameters, such as highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), ionization potential (I), electron affinity (A), electronegativity (χ), hardness (η), softness (S) and fraction of electrons transferred (ΔN), and the natural atomic charge will be calculated using DFT (44). The results of the quantum chemical calculations will be served as a theoretical confirmation for the experimental data based on the quantum chemistry of the ionic liquids molecules.

1.11 Significance of the Study

In the current study, two new [MOFIM]I and [FPIM]Br ionic liquids will be added in Ni, Co and Ni-Co alloy electroplating baths to enhance the qualities, the surface morphology, hardness and the corrosion resistance of Ni, Co and Ni-Co alloy deposits. It is hopeful to overcome these defects of traditional additives and toxic organic corrosion inhibitors and help to realize additives with good stability and inhibitors with a virulence by using ILs as metal electrodeposition additives and corrosion inhibitors, respectively. This study will provide our industry with new ionic liquids for producing good quality Ni-Co alloy deposits from environmentally friendly solutions.

The use of quantum chemical calculations in this study complements the experimental measurements. The calculations provide theoretical descriptions for the effect of ionic liquid behavior on structures and mechanical properties of Ni, Co and Ni-Co alloy. The implementation of these procedures is useful to predict potential efficient ionic liquids additives, and thus will reduce the cost and time of testing inefficient ionic liquids. Based on our research, quantum chemical calculations are used effectively for the prediction of ionic liquids as addition agents in Ni, Co and Ni-Co alloy electroplating. This efficient and versatile method thus opens a new window to study or design ionic liquids for generalized metal electroplating and will vigorously promote the level of this research region.

1.12 Outline of the Thesis

The dissertation is split into seven chapters. **Chapter 1** provides a summary of the research, a brief history on the advantages of the electrodeposition process, the applications of industrial deposits of Ni, Co and Ni-Co alloys, the mechanism of Ni, Co and Ni-Co alloy electrodeposition, the effective role of additives in improving the consistency of deposited films, the advantages of using ionic liquid as additives in the field of electrodeposition and experimental measurement methods, and theoretical

approaches. It also includes the present study's problem statement, aims, importance and scope. The related literature of the present study is discussed in **Chapter 2**. The literature was reviewed on the basis of four key subjects, previous studies in electrodeposition of Ni, Co and Ni-Co alloys, organic compounds as additives, mechanism of additives in the electrodeposition, the nucleation mechanism of deposit, ionic liquid including synthesis, description, structure, properties and utilities of electrodeposition processes, mechanism of Ni, Co and Ni-Co alloy electrodeposition in the presence of ionic liquid as additive, the principle of adsorption isotherm and quantum chemical calculations of additives and corrosion inhibitors. The details and specifics of the experimental methods are given in **Chapter 3**. An overview of the key experimental procedures used to investigate the current efficiency, voltametric behavior and mechanism, surface morphology, hardness and corrosion resistance of deposited Ni, Co and Ni-Co alloys from acidic baths is included. The findings result from the experimental work, discussion, and derived conclusions are discussed. **Chapter 4** is split into two sections (A and B). The findings and discussion of the Co and Ni electrodeposition measurements in the absence and presence of different concentrations of [MOFIM]I and [FPIM]Br were included in both sections. **Chapter 5** describes the outcomes and discussion of the Ni-Co alloy electrodeposition experimental study with three primary compositions of Ni^{2+} and Co^{2+} ions without and with [MOFIM]I and [FPIM]Br. Then, the main results are presented from all experimental measurements. The details of the quantum chemical calculation are given in **Chapter 6**. An overview of the procedures used and the quantum parameters measured and the natural atomic charge is given. The key conclusions of the present work and a brief description of this study are given in **Chapter 7** and some suggestions for future work are provided.

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APPENDIX F

LIST OF PUBLICATIONS

1. Omar, I.M.A., Emran, K.M., Aziz, M., and Al-Fakih, A.M. A novel viewpoint of an imidazole derivative ionic liquid as an additive for cobalt and nickel electrodeposition. *Royal Society of Chemistry Advance*. (2020). 10, 32113-32126. RSC Adv Impact Factor: 3.119. Journal Ranking in *Royal Society of Chemistry Advance*: Q2.

2. Omar, I.M.A., Emran, K.M., and Aziz, M. Part I: Ni-Co alloy foils electrodeposited using ionic liquids. Arabian Journal of Chemistry (2020) 13, 7707–7719. *Arabian Journal of Chemistry* Impact Factor: 4.762. Journal Ranking in Arabian Journal of Chemistry: Q2.

3. Omar, I.M.A., Emran, K.M., Aziz, M., and Al-Fakih, A.M. Part II: Impact of Ionic Liquids as Anticorrosives and Additives on Ni-Co Alloy Electrodeposition: Experimental and DFT study. *Arabian Journal of Chemistry* (2021) 14(1), 102909 . Impact Factor: 4.762. Journal Ranking in Arabian Journal of Chemistry: Q2. Accepted.

4. Omar, I.M.A., Emran, K.M., and Aziz, M. Electrodeposition of Ni-Co Film: A Review. *International Journal of Electrochemical Science* 16 (2021) 150962, doi: 10.20964/2021.01.16. Impact factor: 1.573. Journal Ranking in Int. J. Electrochem. Sci: Q4.

5. Omar, I.M.A., Emran, K.M., and Aziz, M. Impact of Ionic Liquid [FPIM]Br on the Electrodeposition of Ni and Co from an Aqueous Sulfate Bath. *Journal of Materials Research and Technology* (2021) 12,170-185. Impact factor: 5.289. Journal Ranking in Journal of Materials Research and Technology: Q1.