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# **DEVELOPMENT OF AN ELECTROCHEMICAL PROCESS FOR THE SELECTIVE SEPARATION OF CO AND NI TO BE APPLIED IN LI-ION BATTERIES**

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# Master in Chemical Engineering

## *Development of an electrochemical process for the selective separation of Co and Ni to be applied in Li-ion batteries*

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of

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## **Abstract**

Through conventional recycling processes of batteries, a portion of metals are not able to be recovered. This small percentage of metals, such as cobalt and nickel, represents a significant loss at industrial scale, amounting to tons. Electrodeposition emerges as an electrochemical method to be applied at the final stage the of recycling process, aiming to recover the remaining cobalt and nickel.

In this work, various parameters that may affect the electrochemical separation of cobalt and nickel were studied, including electrolyte concentration, cobalt and nickel ratio in solution, stirring, temperature, concentration of the metals in solution and surface modification of the working electrode.

Chloride-based electrolytes demonstrated a wider potential separation window and increasing the electrolyte concentration contributed to better separation of cobalt and nickel metals. Higher ratios of cobalt in the solution resulted in improved separation, with the best Co/Ni ratio in the deposited film being 5.4 to -0.55 V. Introducing stirring in equimolar solutions significantly enhanced selectivity, achieving a Co/Ni ratio of 5.6. Stirring facilitated the diffusion of cobalt ions, reducing the diffusion layer thickness and thereby improving cobalt deposition. Temperature did not improve selectivity; in fact, it improved nickel deposition while maintaining anomalous codeposition.

A tenfold increase in metal concentration in the solution further improved selectivity, with an average increase of approximately 2 in the Co/Ni ratio across all potentials. Tests controlling the electrode surface showed that cobalt coating provided no advantages in enhancing selectivity. However, further experiments should be conducted to account for the potential influence of the aged copper electrode on these results.

**Keywords (theme):** Electrodeposition, Metal recovery, Cobalt, Nickel, Lithium-ion batteries

## **Resumo**

Através dos processos convencionais de reciclagem de baterias, uma parte dos metais não pode ser recuperada. Esta pequena percentagem de metais, como o cobalto e o níquel, representa uma perda significativa à escala industrial, na ordem das toneladas. A eletrodeposição surge como um método eletroquímico a ser aplicado na fase final do processo de reciclagem, com o objetivo de recuperar o cobalto e o níquel remanescentes.

Neste trabalho, foram estudados vários parâmetros que podem afetar a separação eletroquímica de cobalto e de níquel, incluindo a concentração do eletrólito, a proporção de cobalto e níquel na solução, a agitação, a temperatura, a concentração dos metais em solução e a modificação da superfície do eletrodo de trabalho.

Os eletrólitos à base de cloreto demonstraram uma janela de diferença de potencial de separação mais ampla e o aumento da concentração do eletrólito contribuiu para uma melhor separação dos metais cobalto e níquel. Rácios mais elevados de cobalto na solução resultaram numa melhor separação, tendo-se atingido o melhor rácio Co/Ni no filme depositado de 5,4 a -0,55 V. A introdução de agitação em soluções equimolares melhorou significativamente a seletividade, atingindo um rácio Co/Ni de 5,6. A agitação facilitou a difusão dos iões de cobalto, reduzindo a espessura da camada difusiva e melhorando assim a deposição de cobalto. A temperatura não melhorou a seletividade; na realidade, melhorou a deposição de níquel, mantendo a deposição anómala de cobalto.

Um aumento de dez vezes na concentração de metal em solução melhorou ainda mais a seletividade, com um aumento médio de aproximadamente 2 no rácio Co/Ni em todos os potenciais. Os testes de controlo da superfície do eletrodo mostraram que o revestimento de cobalto não proporcionou vantagens no aumento da seletividade. No entanto, devem ser realizadas mais experiências para ter em conta a potencial influência do envelhecimento do eletrodo de cobre nestes resultados.

## Declaration

I hereby declare, under word of honour, that this work is original and that all non-original contributions is indicated and due reference is given to the author and source

*Eduardo Elipe Torres Santos*

*Sign and date*

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## Notation and Glossary

|     |                                                      |                      |
|-----|------------------------------------------------------|----------------------|
| $F$ | Faradaic constant (96 485.3321 C mol <sup>-1</sup> ) | C mol <sup>-1</sup>  |
| $M$ | Molar concentration                                  | mol dm <sup>-3</sup> |
| $N$ | Sum of cobalt and nickel mols                        | mol                  |
| $n$ | Electron number                                      |                      |
| $Q$ | Charge                                               | C                    |
| $V$ | Potential difference                                 | V                    |

### List of Acronyms

EDX - Energy Dispersive X-ray

EV - Electric Vehicle

GDP - Gross Domestic Product

ICP-MS - Inductively Coupled Plasma Mass Spectrometry

LCO - Lithium Cobalt Oxide

LFP - Lithium Iron Phosphate

LIBs - Lithium-ion Batteries

LMO - Lithium Manganese Oxide

LSV - Linear Sweep Voltammetry

NCA - Nickel Cobalt Aluminum Oxide

NMC - Nickel Manganese Cobalt Oxide

PDADMA - Poly(diallyldimethylammonium chloride)

SEM - Scanning Electron Microscopy

SHE - Standard Hydrogen Electrode

# 1. Introduction

## 1.1. Framing and presentation of the work

The rapid growth of the global population raises concerns about the availability of resources, in particular, what concerns the production and supply of energy. Natural resources, like metals, once abundant and unproblematic, are now becoming scarce and harder to access. Consequently, this results in rising resource prices. Moreover, the rising cost of fossil fuels, as well as the severe environmental impact they can cause, have led to increased research and development of alternatives for energy production and storage in recent years. The goal of decarbonizing the energy sector is another motivation for the transition to cleaner forms of energy production.

Lithium-ion batteries (LIBs), despite being a technology with early origins, emerge as an option for energy storage that plays an important role in the future decarbonization of society, mainly because of their relevant use in electric vehicles (EVs). Electric vehicles are an important step in the decarbonization of the transportation sector, as its electrification means a reduction in greenhouse gas emissions. This demonstrates the high importance of lithium-ion batteries as a societal tool, besides their massified application in, many other electronic devices used in everyday life.

Despite the benefits of LIBs, they contain a diverse array of metals, including cobalt, manganese, nickel, and others. As the production of these batteries increases, the demand for these metals is expected to rise, potentially leading to economic and environmental constraints. Some of these metals are quite costly and scarce, and their extraction can be complex and increases the strain on natural resources. Thus, the recovery of metals is crucial for a circular economy of batteries. Besides, reducing the need for mining new materials, a proper recovery of metals from batteries prevents hazardous waste from accumulating in landfills, which can lead to soil and water contamination. Finally, from an economic point of view, recovering metals typically requires less energy than extracting and processing of virgin materials, and many of the critical metals used in batteries are sourced from regions with geopolitical instability.

Currently, the two most widely used processes for the treatment of spent LIBs are hydrometallurgical and pyrometallurgical. Pyrometallurgical methods are likely used because they allow flexibility in battery feedstock and due to fixed investment in existing facilities. [1] However, this process is highly energy-demanding. On the other hand, the hydrometallurgical method allows for a high recovery of elements with lower energy consumption, significantly lower greenhouse gas emissions, and minimal air emissions. [2] The main disadvantage is the large consumption of chemical reagents and the generation of

wastewater. As an alternative, the electrochemical recovery method has been demonstrated to be a very viable process to produce high-quality metallic films and allows controlled structure and morphology. This process is very efficient and environmentally friendly, with lower energy consumption when compared to the pyrometallurgical process and consumes much lower reagents when compared to hydrometallurgical methods.

Among the metals used in batteries, cobalt and nickel are two metals whose recovery is of high interest due to their importance in today's world. For this reason, the optimization of the electrodeposition process for selective recovery of cobalt and nickel is the main objective of this dissertation. This process is intended to complement the recycling processes already established for lithium-ion batteries and help retrieve a slightly greater quantity of metal.

## **1.2. Contribution of the author to the work**

All the experimental work was carried out by the author based on procedures already implemented in the host laboratory but fully optimized within this work. In particular, all solutions and respective calculations were performed by the author. The author did not perform SEM and ICP characterization but was responsible for preparing all the samples for analysis and accompanied all experiments. Finally, the experimental data was treated and interpreted by the author and the main conclusions were discussed with the supervisors.

## **1.3. Organization of the dissertation**

This dissertation is divided into 6 chapters. Chapter 1, Introduction, presents the motivation behind the proposed work and introduces the main objective which is the selective recovery of cobalt and nickel using an electrochemical process.

In Chapter 2, Context and State of the Art, the dissertation topic is presented in greater depth, along with the motivation behind it. Topics such as the increase in demand for lithium-ion batteries, their composition, and different recycling methods are discussed. The fundamentals of the main technique used in this dissertation, the electrodeposition, as well as other electrochemical methods, are presented. Characterization techniques used throughout the work are also described.

Chapter 3, Materials and Methods, describes the three-electrode electrochemical cell system used for the Linear Sweep Voltammetry and electrodeposition tests. The conditions and

equipment used for each of the tests are also identified. A description of the procedure used for the preparation of samples for characterization analysis is also presented in this chapter.

In Chapter 4, Results and Discussion, the results achieved in the different studies developed within this work and the methodologies employed are presented. Furthermore, a critical analysis of the results obtained is presented, along with a literature background.

Chapter 5, Conclusion, displays the main conclusions and deductions of the dissertation.

For last chapter, Chapter 6, Assessment of the Work Done, addresses the work done and how the work contributes to the Sustainable Development Goals (SDGs).

## 2. Context and State of the art

We live in a world with finite resources, such as fossil fuels and minerals. As global development and population growth accelerate, the consumption of these resources increases accordingly. This trend leads to a higher demand for energy and increased extraction of raw materials for various industries. The overuse of fossil fuels, mining activities, and exploration of raw materials are critical issues that need to be addressed. The planet's resources are limited, and a prime example of this is the fact that in 2023 the resources produced by the Earth for that same year were exhausted on the 2<sup>nd</sup> of August. [3]

To combat the use of fossil fuels, which are limited and harmful to the environment, the development of various technologies that enable alternative energy sources is essential. A prominent example of such technology is the lithium-ion battery, which is widely used for energy storage.

### 2.1. Lithium-ion batteries (LIBs)

The concept of LIBs first emerged in the 1970s and has been a topic of great interest and research ever since. [4, 5, 6]

The use of LIBs has been increasing due to the goal of decarbonization of the energy sector, as they are the primary energy source for electric vehicles. Additionally, these batteries are extensively used in numerous electronic devices, such as mobile phones, laptops, etc. [6, 7] Figure 1 illustrates the increasing demand for batteries as a power source for electric vehicles.

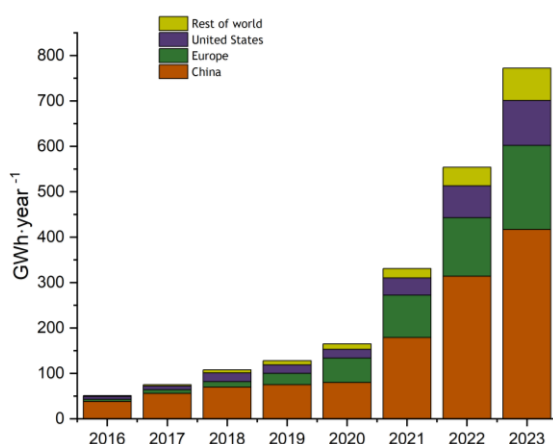


Figure 1. Electric vehicle battery demand by region, 2016-2023. [8]

What makes this type of battery so attractive is the fact that lithium has a highly reductive nature with a standard reduction potential of -3.04 V vs standard hydrogen electrode (SHE).

Lithium has the lowest atomic weight of all metals and the best energy density per unit mass and has a small ionic radius, which leads to fast ion transport. [5, 9, 10]

### 2.1.1. Lithium-ion batteries components and composition

The main elements that constitute a LIB are the cathode, the anode, the electrolyte, the separator and the current collector, as shown in Figure 2. [11, 12] The battery's operation relies fundamentally on each of its components, which can be made from different materials. Over the years, extensive research and testing have been conducted on different materials to optimize battery components, balancing both energy efficiency and economic considerations.

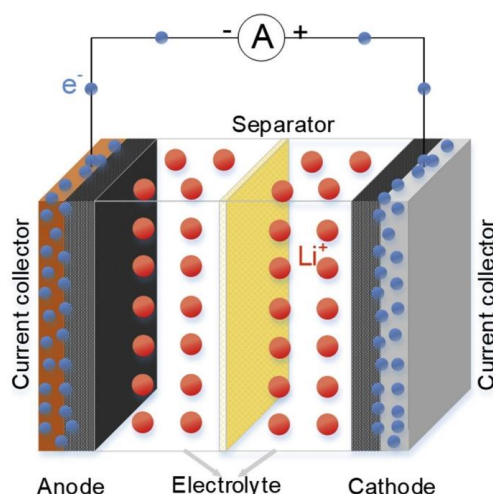


Figure 2. Schematic diagram of a typical LIB. [12]

The anode, operating as the negative electrode where oxidation (loss of electrons) takes place, is traditionally made from graphite and other carbon materials, although newer silicon-based materials and lithium titanate are also increasingly used. These different materials offer different specific volumetric and gravimetric capacities, as well as different associated costs. [11, 13]

Different materials can also be used for the cathode, the positive electrode where the reduction (gain of electrons) takes place. Some of the most commonly used cathodes are Lithium Cobalt Oxide - LCO, Lithium Manganese Oxide - LMO, Nickel Manganese Cobalt Oxide - NMC, Nickel Cobalt Aluminium Oxide - NCA and Lithium Iron Phosphate - LFP [10, 11, 13]. The different cathodes provide different levels of specific energy and power density, along with differences in lifespan and charging speed. These characteristics make them suitable for different applications.

As it was stated before, a wide variety of elements are used to fabricate the different lithium-ion battery components, and some of the elements used are relatively rare and quite valuable. For instance, lithium can represent up to 7%, cobalt can go from 5 to 20% and nickel can range from 5 to 10% of the battery's content. [14, 15]

The quantity of these elements being utilized is rising along with the use of LIBs, which raises concerns about the availability and reserves of these metals. For example, the demand for lithium exceeded the supply in 2022, and the same happened for cobalt and nickel in 2021, as can be seen in Figure 3. [7]

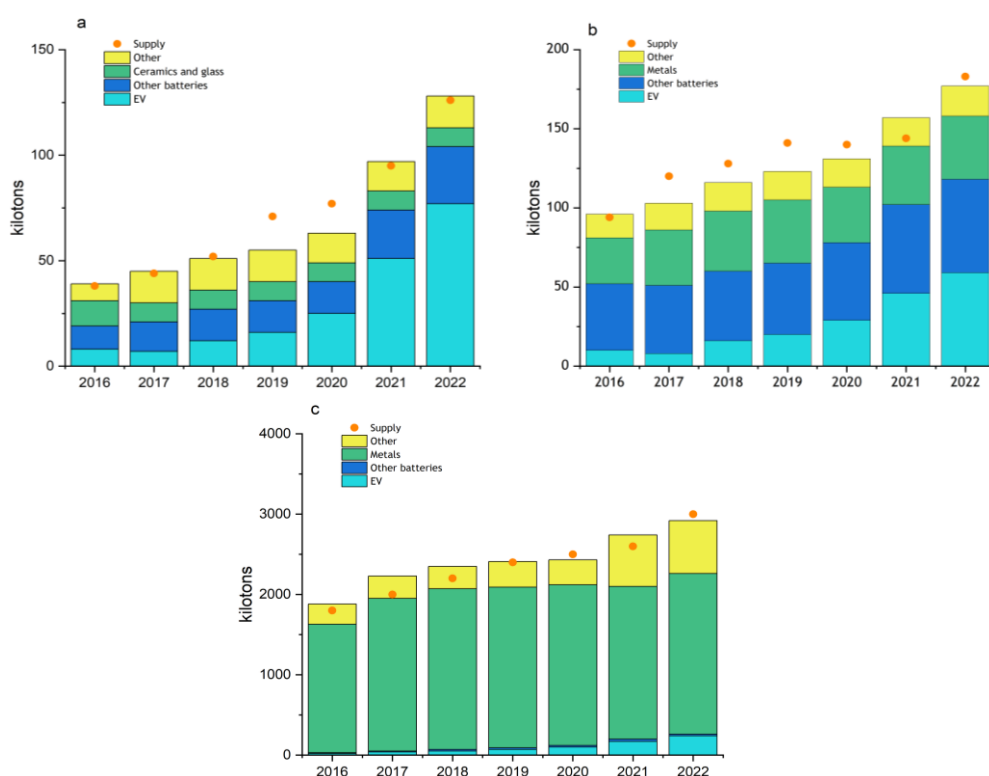


Figure 3. Supply and demand by sector from 2016 to 2022 for lithium (a), cobalt (b) and nickel (c).

[7]

The increasing demand for LIBs raises concerns about future metal reserves and the environmental impact related to the end of life of these batteries. The potential political impact also represents a real concern since these metals are not equally distributed across the planet. As an example, most of the cobalt comes from the Democratic Republic of Congo, as for lithium the largest reserves are in South America. [4, 15, 16]

To address these challenges, recovery of metals contained in batteries emerges as a crucial opportunity for the circularity of these valuable metals. The lithium-ion batteries are associated with a relatively average short lifetime, making the constant use of primary resources, from metal mining, an inadequate strategy to ensure the sustainability and prosperity of LIBs. [5]

By using different recycling techniques and processes, it is possible to address the environmental harm caused by discarded batteries and recover valuable materials, creating a secondary supply chain with recycled elements and creating a path towards a sustainable circular economy. Additionally, using recycled materials can reduce dependency on imported metals such as cobalt and nickel and potentially lower associated costs. [4, 17, 18]

## **2.2. Lithium-ion battery recycling methods**

Recycling batteries is a difficult process mainly because of their complex structure and the wide variety of elements used. There are three main approaches to recycling LIBs: direct recycling, pyrometallurgical and hydrometallurgical methods.

### **2.2.1. Direct recycling**

In direct recycling, the battery is first dismantled, whereby the different components are separated. These components can then be reconditioned and reused in new batteries. This method allows the reuse of several components present in LIBs, as the recovered cathode material often retains its intact crystalline structure. [4] Direct recycling is the most environmentally friendly recycling process, as it uses fewer reagents and has lower energy costs compared to other methods. Moreover, it is also advantageous from an economic point of view due to the lower installation costs and gives added value to an already non-functional battery. However, this method has some drawbacks: it depends on the condition and composition of the batteries, relies heavily on manual labor since it is not possible to automate the disassembly and recognition of the different types of LIBs, and requires extensive pretreatments to avoid possible contamination from different battery families and impurities accumulated during the battery's lifespan. [4, 19]

### **2.2.2. Pyrometallurgical recycling**

Pyrometallurgical is another method for battery recycling. [20] In this process, high temperatures are used to recover the metal elements of interest in the form of metal alloys. The batteries undergo a relatively simple pre-treatment process in which they are shredded and/or crushed. The resulting battery elements are then placed in a furnace at high temperature, with a reductant agent, usually graphite due to its stability. [4, 20] Through high temperatures and a controlled atmosphere, the elements undergo chemical and physical transformations that result in the formation of alloys and slags containing the

elements of interest to be recovered. Metals recovered as alloys include cobalt, nickel and copper. Lithium can be also recovered from the slag. [4, 21, 22, 23]

The pyrometallurgical method shows several advantages, such as the flexibility of the starting material, which enables the recycling of batteries with different compositions and sizes, and ease of implementation, which requires simpler pretreatment. On the other hand, the energy requirement of this type of process is relatively high, which is associated with high costs, and the process results in the emission of environmentally harmful gases. [4, 21, 22]

### **2.2.3. Hydrometallurgical recycling**

Another method for recycling lithium-ion batteries is the hydrometallurgical process. This method mainly consists of two stages: leaching and recovery. In the leaching step, solid materials, after pre-treatment, are leached into an aqueous solution using leaching agents, such as inorganic and organic acids. This process produces a leachate solution containing the elements of interest. The most commonly used leaching agents include  $\text{H}_2\text{SO}_4$  with  $\text{H}_2\text{O}_2$ ,  $\text{HCl}$ , and  $\text{HNO}_3$ . [4, 17, 21, 22] In the second step, different techniques can be used to recover the elements dissolved in the aqueous solution from the leaching process. Some techniques involve ion exchange, precipitation, adsorption, and solvent extraction. [17, 21]

The main advantage of the hydrometallurgical process is its lower energy consumption, which leads to lower energy costs. However, this process has some limitations, such as the difficulty of scaling the process, the selectivity of the recovery process, the high usage of reagents and water, and the need to treat the produced wastewater. [4, 19, 21]

## **2.3. Electrochemical techniques**

Besides the shortcomings of hydrometallurgical and pyrometallurgical processes, these are established processes for recycling electronic waste with good metal recovery rates at competitive costs. Moreover, in recent years, many works have focused on hydrometallurgical greener processes by using organic acids, but with diminished recovery levels, limited up to approximately 95%. [16, 24, 25] Technologies that can complement or assist these complex purification routes are needed, especially if they can lower either thermal/chemical consumption or waste generation and improve the quality of the recovered metal. So, this work proposes a new electrochemical metal recovery process from LIBs, that avoids the use of hazardous and expensive reducing agents, shows convenient and precise control of the final products, reduces energy consumption, and has low

environmental impacts. [26] The electrochemical process will be the last step in the value chain of battery recycling, to be applied after the green hydrometallurgical recycling process. So, the idea of having a final recycling process that can be used to fine-tune the recovery levels of these important metals means that the recycling process can theoretically reach 100 %, with significant economic and environmental impact. The electrochemical-assisted process may include electrodeposition, electrodialysis, electrosorption, and electrocoagulation (Figure 4). [17, 24]

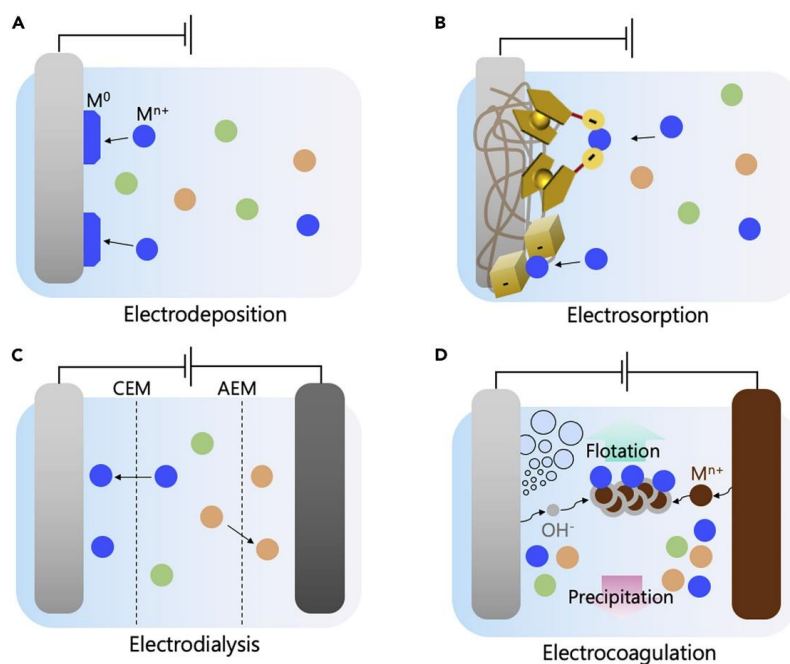


Figure 4. Schematic representation of the different electrochemical approaches for metal recovery: (A) electrodeposition, (B) electrosorption, (C) electrodialysis and (D) electrocoagulation. [17]

### 2.3.1. Electrodeposition

Within this work, electrodeposition is the selected electrochemical technology, which has been studied for metal recovery since 1972 [27], being a simple and safe technique that allows obtaining metals from solutions. [17]

The electrodeposition consists of applying a constant potential difference (potentiostatic analysis) or a constant current (galvanostatic analysis) to an electrode submerged in a solution containing metal ions. This process results in the reduction of metal ions,  $M^{n+}$ , dissolved in the solution, forming a coating of metal,  $M$ , on the surface of the electrode - Equation 1. [17, 24, 25]

al



Figure 5 shows a schematic representation of the electrodeposition process, where  $M$  is cobalt.

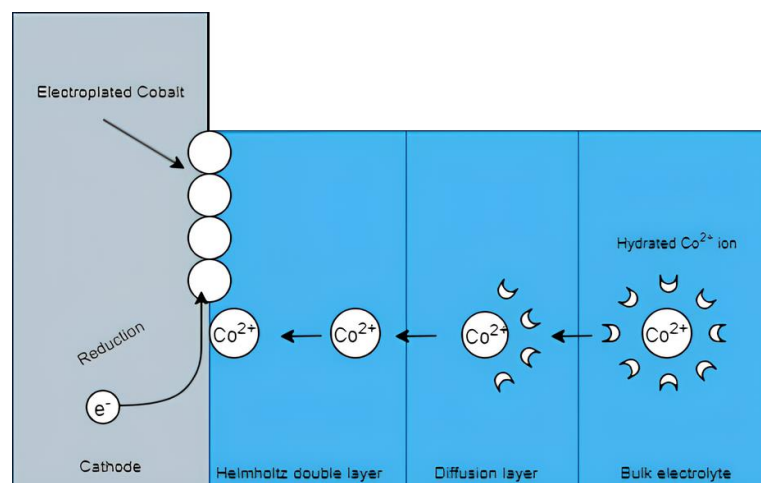


Figure 5. Schematic representation of the electrodeposition process of cobalt in the surface of the electrode (cathode). Reprinted from the reference [25].

The electrodeposition setup requires an electroplating bath, an electrolyte, inert electrodes (a counter electrode that acts as the anode and a working electrode that acts as the cathode) and a reference electrode. [17, 25]

The main factor influencing the electrodeposition of metals is their reduction potential. [14, 16] Other parameters, such as pH, the concentration of metals in solution, electrolyte, temperature, and electrode material, also affect the electrodeposition process' efficiency. This method has the advantage of being applicable to aqueous solutions, which allows its application on a large scale at a low cost. However, water possesses a low breakdown voltage, affecting the range of the accessible potential window. Alternatively, non-aqueous solutions or ionic liquids can be used, as they have a higher breakdown voltage. [25] Despite the advantages, electrodeposition for the recovery of high purity metals can be complicated when working with very heterogeneous mixtures. [15, 17] To achieve selective recovery, the difference between the potentials of the metal species involved must be large enough. This means that codeposition will occur when the metal to be recovered has a reduction potential that is very close to that of the other metal present in the solution.

This is what happens in the case of cobalt and nickel. The reduction potentials of both species are very close ( $E^{\circ}_{Co} = -0.277V$  and  $E^{\circ}_{Ni} = -0.250V$  versus standard hydrogen electrode), leaving a very tight window for the selective electrodeposition. [15]

Different studies on the electrodeposition of cobalt and nickel have already been conducted, focusing on the investigation of the codeposition of both metals using different electrolytes and operation parameters. Tebbakh *et al.* [28] studied the effect of cobalt content in the electrolyte, using a chloride bath, and how it affected the electrodeposition process and the

composition of the deposited film. Properties such as surface morphology and corrosion resistance were also studied. In their work, cobalt showed preferential deposition for all tests realized and showed that an increase in the cobalt ratio in the electrolyte also increases its percentage on the final deposited film. Regarding parameters such as temperature, the literature contains inconsistent and occasionally contradictory information. Schweckandt *et al.* [29] demonstrated the behavior of anomalous codeposition in electrodepositions with different proportions of cobalt and nickel in solution. In most electrodepositions, even those with higher nickel content in solution, cobalt was preferentially deposited.

Studies such as the one from Vazquez and Pritzker [30] investigated the performance of different electrolytes and the effect of stirring on the electrodeposition of cobalt and nickel. Kim *et al.* [15] also studied different electrolytes for the electrodeposition of cobalt and nickel. They investigated the influence of a polymer-coated electrode using PDADMA (poly(diallyldimethylammonium chloride)) and how this could change the selectivity of the process. Their investigations showed that a chloride-based electrolyte leads to better selectivity than a sulphate-based electrolyte. A low loading of polymer additionally leads to better cobalt deposition, however, a higher polymer content in the electrode gradually decreases the amount of cobalt.

Most studies on the electrodeposition of cobalt and nickel focus on creating metal alloys for various applications. These include use in electrocatalysts, the computer industry, fuel cells, anti-corrosion coatings, magnetic applications, and others. [31]

Equations 2 and 3 show the reactions that occur during the electrodeposition of cobalt and nickel, respectively.



Cobalt can also be deposited on the working electrode through the formation of cobalt hydroxide if the hydrogen evolution reaction occurs simultaneously, according to equation 4 and 5. [15]



Some of the most used electrolytes are chloride, sulfamate and sulphate bath solutions. Different baths offer different advantages and lead to different results according to the deposition and content of cobalt and nickel. [15, 30]

## 2.4. Characterization techniques

Characterization techniques such as Linear Sweep Voltammetry (LSV) analysis, Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Scanning Electron Microscopy (SEM) and Energy dispersive X-ray (EDX) were used in this dissertation to study the selectivity of cobalt and nickel electrodeposition process here developed.

### 2.4.1. Linear Sweep Voltammetry (LSV)

Linear Sweep Voltammetry is an electroanalytical method that allows the study of redox reactions, providing information about the steps involved in the electrochemical processes. It is one of the most used electrochemical techniques, due to its simple use and basic equipment requirements, as well as the speed in obtaining results. [32]

In LSV measurements, the potential of the working electrode is swept linearly over a range of values as a function of time. During this potential sweep, the current is measured as a function of the applied potential. Figure 6 illustrates both the variation of potential over time (A) and the current as a function of the applied potential (B). [31, 32]

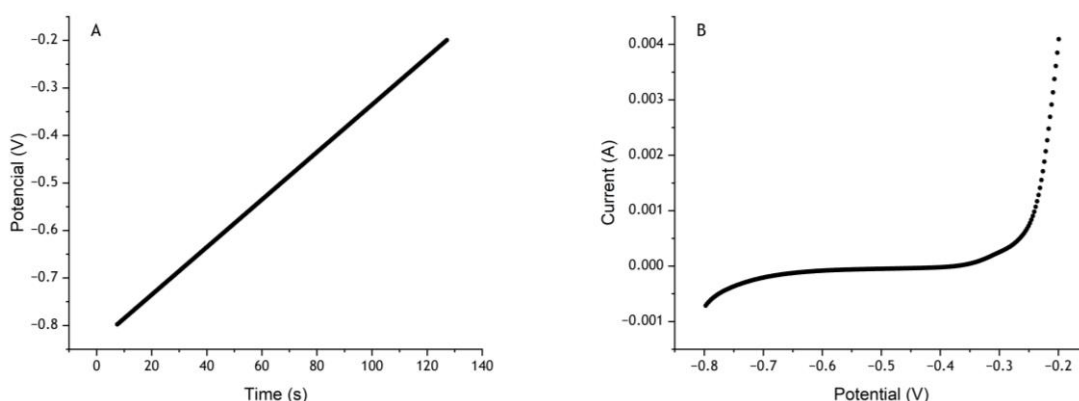


Figure 6. Examples of LSV curves for 0.01 M cobalt chloride in 10 M lithium chloride as electrolyte: (A) variation of potential over time, (B) current as a function the of applied potential. Data taken from the present work.

The curves obtained depend on several factors such as the voltage scanning rate, the speed of the electron transfer reaction and the chemical activity of the electroactive species. [33]

### 2.4.2. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively Coupled Plasma Mass Spectrometry is a technology used for trace elements analysis. In this technique, liquid samples are turned into an aerosol that is transferred into an argon plasma; an electric field is applied for the ionization of gas and to maintain plasma. The plasma, at high temperatures, subsequently ionizes the sample generating ions that are

directed into a series of electrostatic lenses that focus and guides the ion beam into a mass analyzer. The mass analyzer separates the ions based on their mass and charge ratio. The ions, after being separated, are measured in a detector. [33, 34] Figure 7 illustrates a schematic diagram of an ICP-MS analysis system. [35]

This technique offers the advantages of multiple elements quantification, a low detection range, low sample volume and simple sample preparation. However, the equipment and the analysis can be expensive. [34]

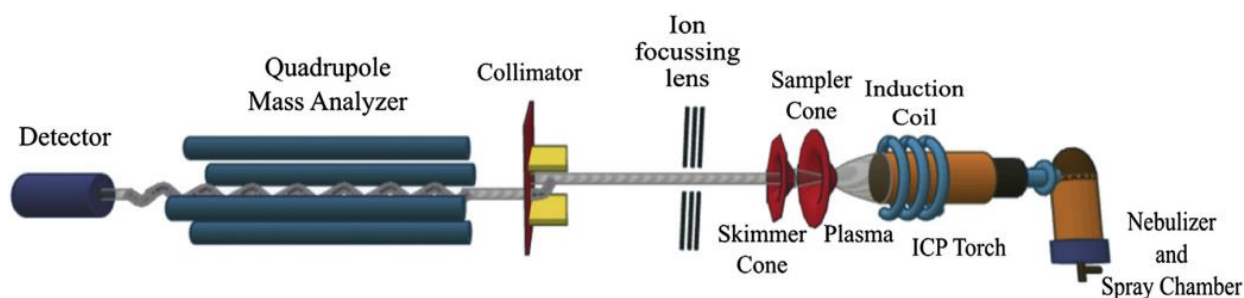


Figure 7. ICP-MS schematic diagram. [35]

#### 2.4.3. Scanning Electron Microscopy (SEM)

SEM analysis is a technique used in a variety of fields to obtain images on a nanometer to micrometre scale. SEM is mainly used for the analysis of the surface morphology of the samples.

In SEM analysis, a high-energy electron beam is generated by an electron gun and directed to a specific area. The electron beam then scans the sample line by line. The sample interacts with the electrons, generating a signal that is subsequently detected by the detectors. Through the intensity of the various signals detected throughout the sample, an image is formed. The analysis occurs under vacuum to minimize the interaction between the electrons and the particles of air. [35, 36]

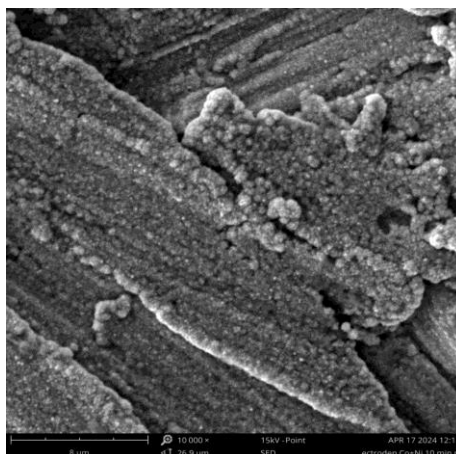


Figure 8. Example of a top view SEM image showing cobalt and nickel film deposited on a copper foil. Data taken from the present work.

#### 2.4.4. Energy dispersive X-ray (EDX)

EDX is a characterization technique used together with SEM for the elemental identification and quantitative compositional information in nanomaterial surfaces. The energy emitted by the sample when it is exposed to the electron beam varies depending on the elements present, allowing for the analysis of the composition of the sample. The electron beam is directed across the sample to create an image of the elements within it. [38] This technique is particularly effective for detecting heavy metals, but it is challenging to detect elements with an atomic number lower than 11. [39]

### 3. Materials and Methods

The experimental procedure outlined in this dissertation is divided in two parts. The first part focuses on the electrodeposition tests using different parameters for assessing Co/Ni selectivity, while the second part considers the characterization of the electrodeposited samples.

Both electrodeposition setup and conditions used, as well as the sample preparation and conditions for characterization, are described in this section.

#### 3.1. Setup Assembly

To carry out the Linear Sweep Voltammetry (LSV) curves and the electrodeposition tests, an electrochemical setup was assembled. As can be seen in Figure 9, the system consists of a three-electrode electrochemical cell, with the reference electrode being an Ag/AgCl electrode, a platinum wire as the counter electrode, and a copper foil being the working electrode.

The copper foils used were  $1 \times 2 \text{ cm}^2$  in size and had to be properly cleaned and washed with a 10 % v/v nitric acid solution in an ultrasonic bath before use. To ensure reproducibility, the working electrode (copper foil) was 1 cm immersed in the solution, meaning a  $1 \text{ cm}^2$  available area for the metal electrodeposition, and an insulating tape was attached to the back of the area of the copper foil immersed in the solution to guarantee that the electrodeposition only occurred in one surface.

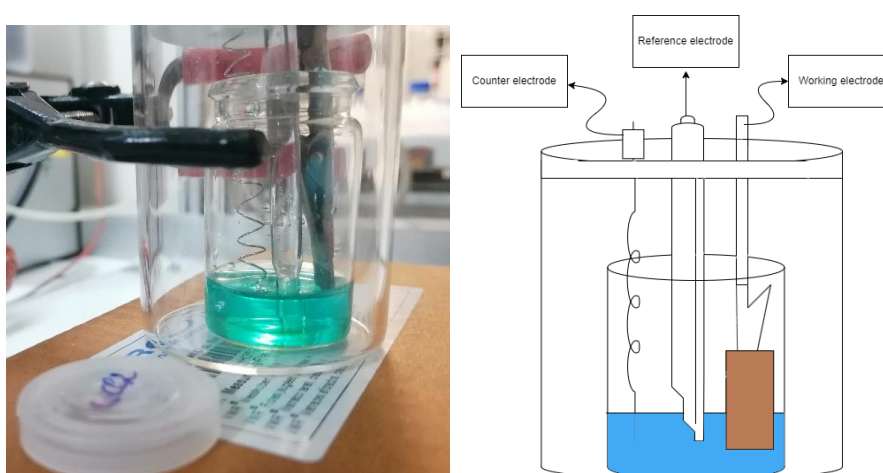


Figure 9. Picture of the electrochemical setup used (left side) and schematic representation of the three-electrode electrochemical cell (right side).

A hot plate equipped with a thermocouple was used to measure and control the solution's temperature, allowing continuous temperature monitoring. A magnetic stirrer was used to ensure a homogeneous temperature distribution in the solution and to improve the transport of the metal ions to the electrode surface.

All tests were conducted using a potentiostat/galvanostat station (Autolab PGSTAT302N). This device has 3 connection cables that should be connected to the electrodes of the electrochemical cell. To make the connections between the cables of Autolab and the setup electrodes, gold-plated clips were used.

### 3.2. Preparation of electrolyte solutions

Before starting the electrodeposition tests, different electrolyte solutions were prepared for testing. The two chosen electrolytes were lithium chloride (LiCl) and lithium sulfate ( $\text{Li}_2\text{SO}_4$ ). Various concentrations in the range of 0.1 M to 10 M were tested for both electrolytes.

For the preparation of the 10 M LiCl solution, due to its limited solubility in water, a different approach was taken. This electrolyte solution was prepared as described:

- i) 21.195 g of LiCl were weighed in a small beaker using an analytical balance (Radwag AS 220/X).
- ii) approximately 40 mL of ultrapure water was added and then placed under stirring at room temperature for about 1-2 hours to ensure complete dissolution of the solute.
- iii) when the solute was totally dissolved, the solution was transferred to a 50 mL volumetric flask and subsequently filled up to the mark with ultrapure water.

For testing both electrolytes, the metal sources considered were: 0.01 M solutions of cobalt chloride ( $\text{CoCl}_2$ ), nickel chloride ( $\text{NiCl}_2$ ), cobalt sulfate ( $\text{CoSO}_4$ ), and nickel sulfate ( $\text{NiSO}_4$ ).

### 3.3. LSV procedure

Before starting the LSV measurements, each new solution was degassed with a stream of nitrogen for 35 seconds.

LSV experiments with a potential difference between -0.80 V and -0.20 V were carried out to determine the onset potential at a scanning rate of  $0.005 \text{ V}\cdot\text{s}^{-1}$ .

The LSV curves were performed before each electrodeposition test to ensure reproducibility between experiments.

### **3.4. Electrodeposition tests**

Five potentials were defined for the electrodeposition tests (-0.55, -0.59, -0.64, -0.68, -0.72 V vs Ag/AgCl), for each the current was measured over 3600 seconds. For each electrodeposition test, the copper foil was replaced with a clean one.

Once the test was completed, the copper foil was removed from the setup, washed with distilled water, dried with a N<sub>2</sub> flow and stored for future SEM and ICP-MS analysis to determine the composition and the ratio of the electrodeposited metals.

The tests were conducted using a 5 mL mixture of 0.01 M NiCl<sub>2</sub> and CoCl<sub>2</sub> in a 50:50 % v/v ratio, at different temperatures (25 °C, 35 °C, 40 °C and 45 °C). 5 mL mixtures of NiCl<sub>2</sub> and CoCl<sub>2</sub> in a 75:25 % v/v and 25:75 % v/v ratio were also used for tests at room temperature. Tests using higher metal concentrations (0.1 M) were also performed at room temperature using 50:50 % v/v mixtures.

### **3.5. ICP analysis**

The cobalt and nickel deposited on the copper foil were quantified by ICP-MS. The corresponding metal solutions were prepared as described next.

First, the insulating tape placed on the back of the copper foils was removed carefully to avoid touching the electrodeposited area. Then, the back of the copper foil was cleaned with a cotton bud and a bit of acetone to remove any leftover glue residues, avoiding organic contaminants that could interfere with the ICP measurements to be performed.

The copper foils were placed in a 5 mL plastic flask, to which 3 mL of 10 % v/v HNO<sub>3</sub> was added. After the plates were immersed in the acid, they were left to metal digest overnight.

After that, the copper foils were removed from the flasks, leaving only the solution with the metals dissolved. In the final step, 1 mL of each sample solution was transferred to a 15 mL Falcon tube. Then, 4 mL of ultrapure water was added to each tube to dilute the HNO<sub>3</sub> concentration by about 2 % v/v.

For each electrodeposition test, two aliquots were taken, which means that two samples were analyzed on ICP.

## 4. Results and discussion

### 4.1. Background electrolyte selection

The close reduction potentials of cobalt and nickel present intrinsic difficulties in selectively electrodepositing one metal over the other. The role of electrolyte in metal deposition efficiency and selectivity is critical. Background electrolytes such as  $\text{Li}_2\text{SO}_4$  and  $\text{LiCl}$  are proposed, and the corresponding working potentials were optimized. Various concentrations were tested for both electrolytes. Table 1 shows the different solutions prepared, along with their concentrations and solvent used. For  $\text{Li}_2\text{SO}_4$  due to the difficulty in dissolving in ultrapure water, it was not possible to create a 10 M solution; thus, this electrolyte was not tested at a 10 M concentration.

Table 1. Different electrolyte solutions prepared and their respective concentration and solvent.

| Solution                 | Concentration (M) | Solvent         |
|--------------------------|-------------------|-----------------|
| $\text{LiCl}$            | 0.1               | Ultrapure water |
|                          | 1                 |                 |
|                          | 10                |                 |
| $\text{Li}_2\text{SO}_4$ | 0.1               | Ultrapure water |
|                          | 1                 |                 |

As metal sources, solutions of cobalt sulphate ( $\text{CoSO}_4$ ), cobalt chloride ( $\text{CoCl}_2$ ), nickel sulphate ( $\text{NiSO}_4$ ), and nickel chloride ( $\text{NiCl}_2$ ), with concentrations of 0.01 M were prepared in the previously mentioned background electrolytes. Linear sweep voltammetry curves for cobalt and nickel solutions are shown in Figure 10. It is important to note that all potential differences mentioned in this chapter are referenced against Ag/AgCl electrode.

Upon analyzing the obtained curves, when lithium sulphate is used as the background electrolyte (Figure 10 b and d), the onset potentials of cobalt and nickel are close, meaning that, the reduction reactions of both will occur at similar potentials, leading to their codeposition. Even with a tenfold increase in concentration from 0.1 M to 1 M, the difference between the onset potentials remains consistently close.

When using lithium chloride as a background electrolyte, at lower concentrations (0.1 M and 1 M) the potential window for cobalt and nickel is wider than that observed for  $\text{Li}_2\text{SO}_4$  electrolytes, but it is still insufficient, offering little selectivity for electrodeposition (Figure 10a and c). On the other hand, a considerable difference can be observed for the 10 M  $\text{LiCl}$  solution. The LSV curves in the 10 M electrolyte, show more separated onset potentials and

both curves start at lower current values, indicating easier mobility of the ions in solution and higher conductivity.

In (Figure 10e), a slower increase in current during nickel electrodeposition is observed providing some insights into the electrodeposition mechanism. This slower increase is due to the slow dehydration process of the  $[\text{Ni}(\text{H}_2\text{O})_5\text{Cl}]^+$  complex, which limits the nickel ion's ability to receive electrons at the electrode.

According to the literature, the use of concentrated chloride electrolytes suppresses the hydrogen evolution reaction, leading to better efficiency of the process. [15]

With these results, it was concluded that the use of a 10 M LiCl solution as a background electrolyte would be the most advantageous to achieve the objective of selective recovery.

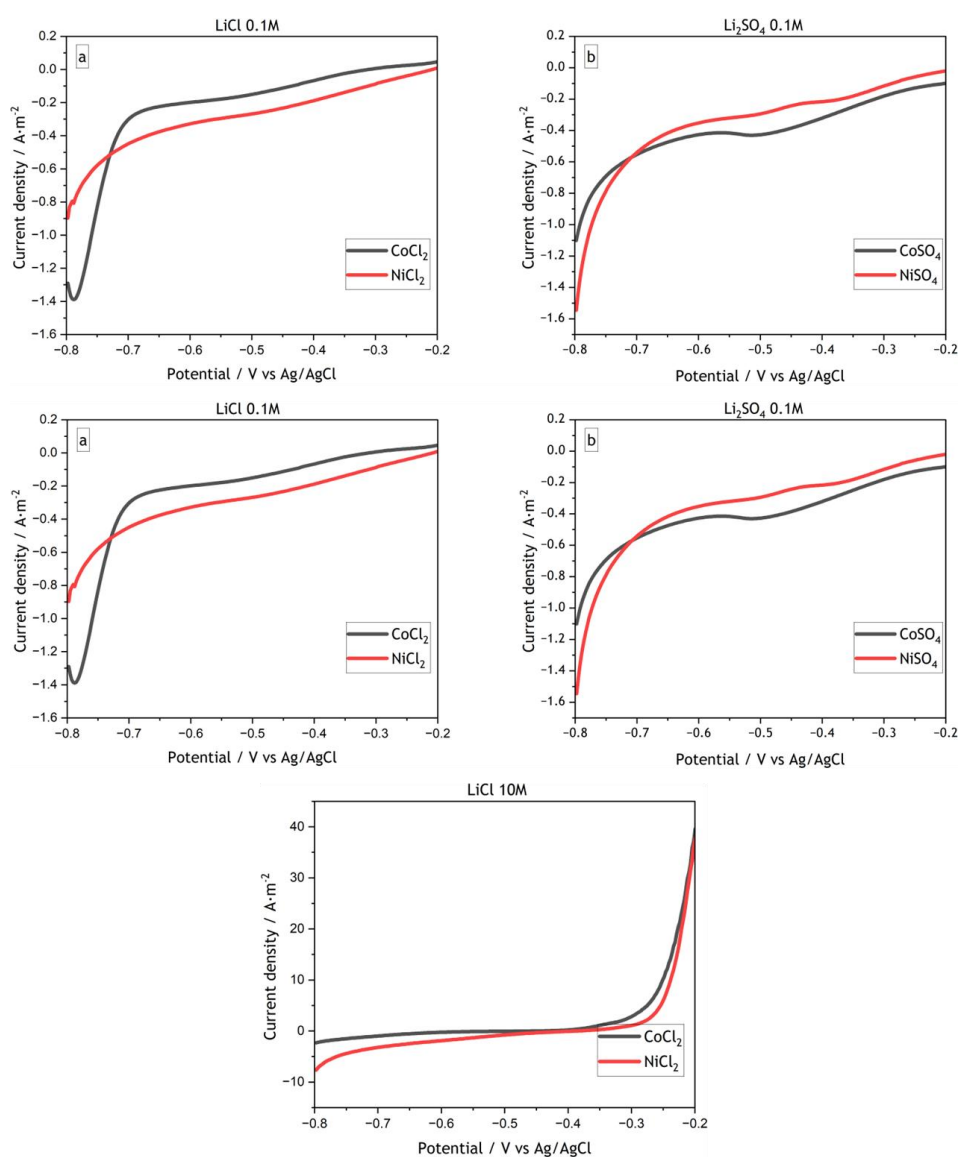


Figure 10. Linear Sweep Voltammetry using different background electrolytes: (a) LiCl 0.1 M, (b)  $\text{Li}_2\text{SO}_4$  0.1 M, (c) LiCl 1 M, (d)  $\text{Li}_2\text{SO}_4$  1 M, (e) LiCl 10 M.

## 4.2. Electrodeposition evaluation of pure cobalt and nickel samples

Since better onset potential separation was achieved with lithium chloride (10M), this was chosen as the background electrolyte for the subsequent experiments. Multiple electrodepositions were conducted to determine the onset potential of both metal sources:  $\text{CoCl}_2$  and  $\text{NiCl}_2$ . For that, electrodeposition tests at the potential differences mentioned in the previous sub-chapter 3.4, were conducted. Figure 11 shows the plots of the current over the time recorded for each of the electrodeposition tests conducted.

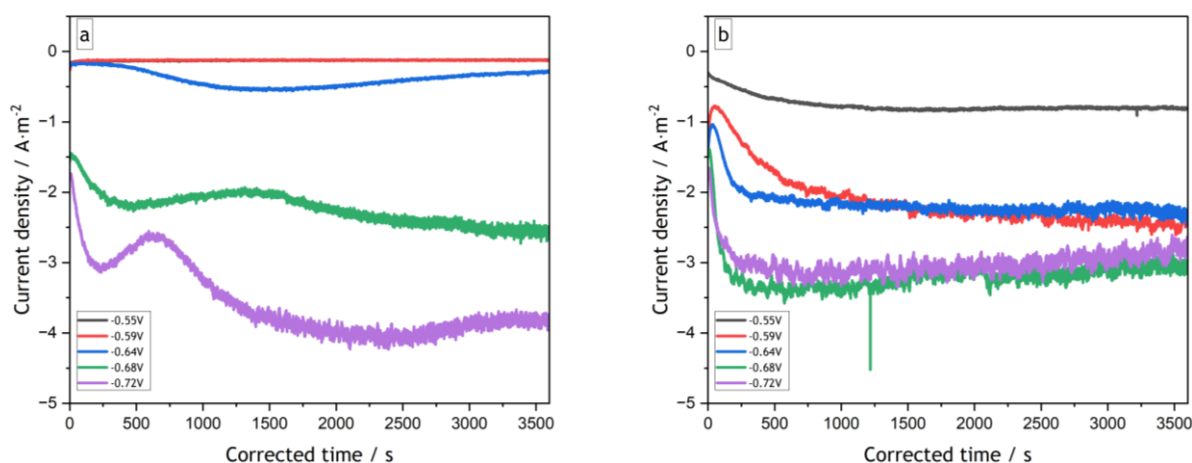


Figure 11. Plots of the current over the time recorded during the electrodeposition for (a)  $\text{CoCl}_2$  0.01 M and  $\text{NiCl}_2$  0.01 M.

Figure 11a, makes clear that at -0.72 V higher absolute current values are achieved, indicating greater deposition of cobalt. For nickel, Figure 11b, two potential differences with higher currents are observed; the most significant nickel deposition occurs at -0.68 V.

By calculating the total charge, determined by the area under the curve, the highest absolute values were indeed at -0.72 V and -0.68 V for cobalt and nickel, respectively. A higher total charge indicates a greater number of electrons being transferred during the electrodeposition process, signifying a higher rate of metal reduction.

Figure 12, which shows the results of the ICP-MS analysis of the metals deposited on the electrode from pure samples, corroborates this. At -0.72 V, a greater mass of cobalt is deposited, while at -0.68 V, a greater mass of nickel is deposited.

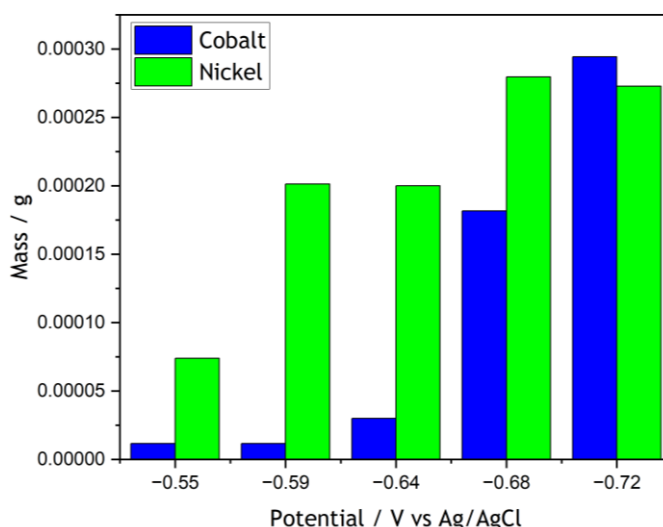


Figure 12. Amount of cobalt and nickel deposited as a function of potential difference.

### 4.3. Electrodeposition evaluation of $\text{CoCl}_2\text{:NiCl}_2$ mixtures

#### 4.3.1. 50:50 % v/v at room temperature and no stirring

After carrying out the electrodeposition process with pure solutions of cobalt and nickel, the next step was to test solutions containing both metals to assess selectivity. To this end, 0.01 M  $\text{CoCl}_2\text{:NiCl}_2$  mixture (50:50 % v/v) was prepared and subjected to electrodeposition experiments at the same potential differences mentioned previously.

Before sending the samples for ICP-MS analysis, SEM and EDX characterization of the electrodeposited films were made, (Figure 13a) to obtain a rapid and rough analysis of the electrodeposits. For the SEM and EDX analysis, three points in the electrodeposition zone were chosen, and the composition was analyzed at these points. Despite a higher level of uncertainty, the results obtained by EDX were in line with the ICP-MS results - Figure 13 b.

Table A1 presents all the ICP-MS results for each set of conducted electrodepositions. These results include the mass of deposited cobalt and nickel, Faradaic efficiency, and the cobalt to nickel concentration ratio. Each set of electrodepositions underwent analysis using ICP-MS to determine the mass of the electrodeposited metals. For understanding selectivity, Faradaic efficiency was also calculated using Equation 6.

$$\text{Faradaic efficiency} = \frac{n \cdot N \cdot F}{Q_{\text{total}}} \times 100 \quad (6)$$

In the equation,  $n$  represents the number of electrons involved in the reduction reaction that occurs during the process of electrodeposition ( $n = 2$ ),  $N$  is the sum of the number of mols deposited of cobalt and nickel,  $F$  is the Faraday constant ( $F = 95485 \text{ C} \cdot \text{mol}^{-1}$ ) and  $Q_{\text{total}}$  is the total charge registered during the electrodeposition test.

Figure 13 presents the plots related to the Co/Ni concentration ratio (b) and the electrodeposited mass of each metal (c) for the set of experiments with a 50:50 % v/v mixture of 0.01 M  $\text{CoCl}_2\text{:NiCl}_2$  at room temperature and with no stirring of the solution.

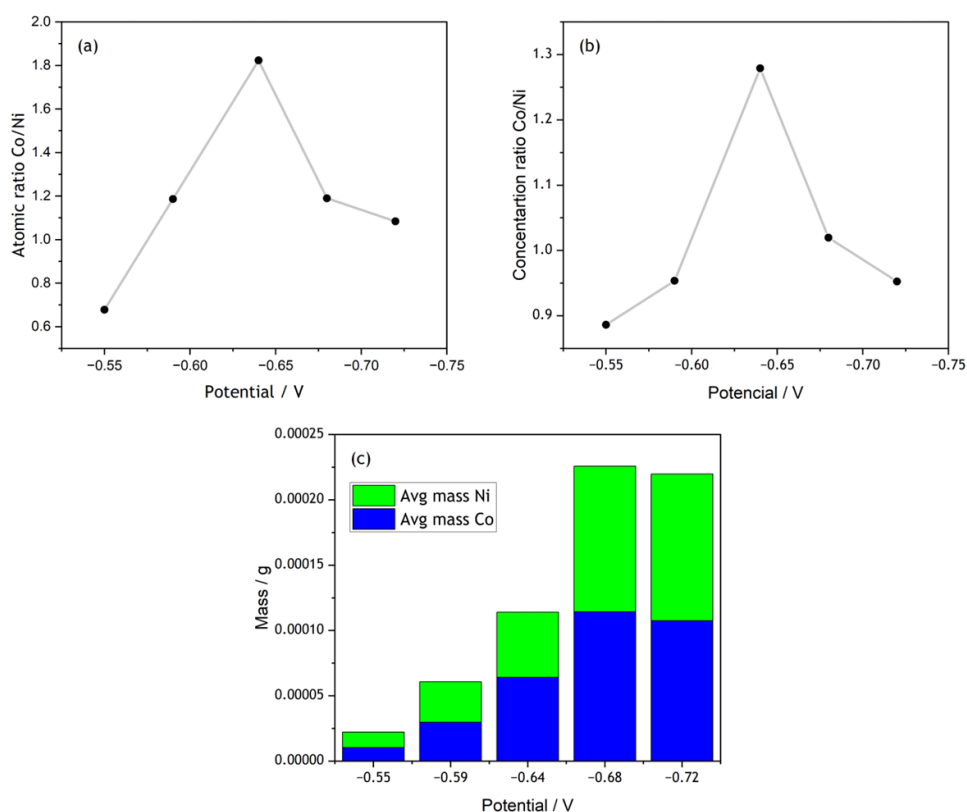


Figure 13. Electrodeposition data obtained for a 50:50 % v/v mixture of 0.01 M  $\text{CoCl}_2\text{:NiCl}_2$  at room temperature and no stirring: (a) the Co/Ni atomic ratio obtained by EDX, (b) the Co/Ni concentration ratio obtained by ICP-MS, (c) the quantity deposited for each metal.

At less negative potentials, -0.55 V and -0.59 V, nickel deposition occurs preferentially, with the Co/Ni ratio being less than one. At the intermediate potential difference (-0.64 V), the greatest difference was recorded, with a ratio of approximately 1.3, demonstrating a common behavior in the codeposition of cobalt-nickel known as anomalous electrodeposition. This type of codeposition is common with some elements, mainly cobalt, nickel and iron, and occurs when the less noble metal, in this case, cobalt, is deposited preferentially compared to the more noble metal, nickel. [15, 30, 39]

Indeed, in this type of codeposition, the presence of cobalt ions can inhibit the deposition of nickel. [31] Another possible reason for the greater cobalt deposition at -0.64 V may be related to hydrogen evolution. At -0.64 V, the hydrogen evolution reaction may be more significant, leading to an increase in pH and thus greater formation of cobalt hydroxide. Cobalt hydroxide can then deposit or adsorb on the cathode surface, impairing nickel deposition. [40, 41]

With the decrease in potential, there is a decrease in the Co/Ni ratio, and nickel becomes preferentially electrodeposited again at the potential difference of -0.72 V.

As the potential increases, there is also an increase in the total current and thus an increase in the total deposited mass, reaching a maximum at -0.68 V, followed by a slight decrease at the most negative potential.

#### 4.3.2. (75:25 %v/v) and (25:75 %v/v) at room temperature and no stirring

To understand the impact of different concentrations of cobalt and nickel, solutions with other metal ratios were prepared. The first experiment used a solution enriched with cobalt (Figure 14), while the second experiment used a solution enriched with nickel (Figure 15).

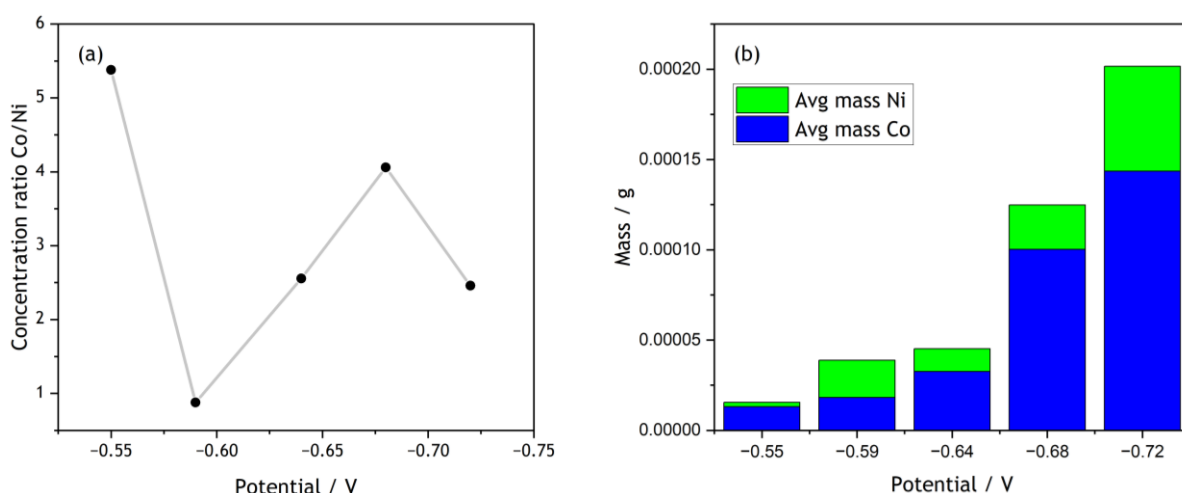


Figure 14. Electrodeposition data obtained for 75:25 % v/v mixture of  $\text{CoCl}_2:\text{NiCl}_2$  at room temperature and no stirring: (a) the Co/Ni concentration ratio obtained by ICP-MS, (b) the quantity deposited for each metal.

In the 75:25 %v/v of  $\text{CoCl}_2:\text{NiCl}_2$  mixture, the maximum Co/Ni concentration ratio observed was 5.4, at the less negative potential difference, -0.55 V. However, increasing the potential difference to -0.59 V led to a significant decrease in the ratio to 0.9. Increasing the potential further increases the ratio, with another peak at -0.68 V, which may be contradictory since this potential demonstrated the highest deposition of nickel for a pure solution. For these peaks, the anomalous electrodeposition is observed again, showing a higher percentage of cobalt relative to nickel on the plated surface compared to the electrolyte bath. For the remaining potential differences (-0.59 V, -0.64 V and -0.72 V), a smaller percentage of cobalt is deposited compared to its concentration in the solution, indicating that a normal electrodeposition occurs.

With an increase in the concentration of Co in the solution, greater selectivity is expected, as there will be a higher quantity of cobalt ions available for deposition. With larger amounts

of cobalt available, these can act as nucleation sites for the deposition of larger quantities of cobalt. Moreover, an increase in  $\text{Co}^{2+}$  concentration tends to attenuate the depletion of  $\text{Co}^{2+}$  ions in the cathodic diffusion layer and increases the efficiency of cobalt deposition, as explained by Kamel and Qiao [40, 43].

The higher concentration of cobalt can also amplify the impact on inhibiting nickel deposition at -0.55 V and -0.68 V. Greater quantities of cobalt may result in larger amounts of intermediate species, such as  $\text{Co(OH)}_2$  and  $\text{CoOH}^+$ , which are more likely to be adsorbed over nickel species,  $\text{Ni(OH)}_2$  and  $\text{Ni(OH)}^+$ . The  $\text{Co(OH)}_2$  species adsorbed to the cathode surface block nickel ion movement but allow  $\text{Co(OH)}^+$  to move through these species into the electrode surface where reduction into solid cobalt occurs, leading to a higher amount of cobalt deposited. [43, 44, 45].

Figure 14 b shows once more that increasing the potential leads to a greater total quantity of metal electroplated. When the current is increased, more electrons flow into the cell, causing more ions to be reduced, which speeds up electrodeposition. Thus, the concentration of species in the bath solution actually influences the behavior of the metals during electrodeposition process.

In the case of 25:75 %v/v of  $\text{CoCl}_2\text{:NiCl}_2$  mixture, the concentration of the metals in the solution demonstrates to have, again, a big influence on the composition of the material electroplated - Figure 15. Despite the solution having a 3 to 1 ratio in favor of nickel, the percentage of nickel deposited does not reach as high values as it was for the solution with a 3 to 1 ratio in favor of cobalt. In the cobalt-favoring solution, a cobalt percentage of 84.4 % was achieved in the deposited film at -0.55 V. However, in the 25:75 %v/v solution in favor of nickel, the maximum percentage of deposited nickel reached was 68.9% for -0.72 V. This indicates that despite being in smaller quantity, the inhibition of nickel deposition by the presence of cobalt still occurs.

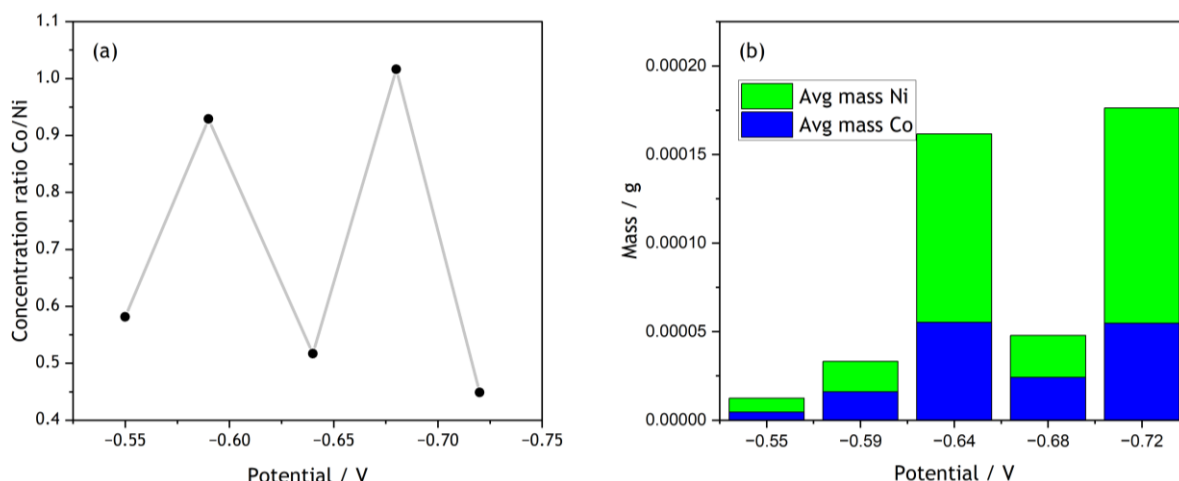


Figure 15. Electrodeposition data obtained for 25:75 % v/v mixture of  $\text{CoCl}_2\text{:NiCl}_2$  at room temperature and no stirring: (a) the Co/Ni concentration ratio obtained by ICP-MS, (b) the quantity deposited for each metal.

Varying the concentrations, the percentage of each deposited metal varied in a non-linear way, making it hard to predict the behavior of metal species during the process for non-equimolar solutions. Even though, the fluctuation in the percentages of cobalt and nickel electrodeposited, when using mixtures with different concentrations, illustrates the potential utility of the same element being used as a nucleation source for the metal in solution, for certain applied potentials, thereby providing a pathway for the selective separation of metals.

The total quantity of deposited metal did not show significant variation, with values in the same order of magnitude. The only exception was for the potential differences -0.64 V and -0.68 V.

As for the Faradaic efficiency of the non-equimolar solutions, it showed a large inconsistency in values, ranging from 96% to 201% in the 75:25 % v/v  $\text{CoCl}_2\text{:NiCl}_2$  and from 27% to 304% in the 25:75 % v/v  $\text{CoCl}_2\text{:NiCl}_2$ . The inconsistency in these values may be attributed to factors such as variations in electrode surface conditions, or unexpected side reactions occurring during the electrodeposition process.

#### 4.4. Operating conditions evaluation

By tuning the operational parameters, electrodeposition can be made more selective towards certain metals. This is crucial for reaching precise control over material composition, besides ensuring that the electrodeposition process is reproducible across batches. Consistent quality and performance are essential for meeting industry standards and customer expectations. Moreover, and more importantly, the assessment of the most relevant parameters limiting the electrodeposition process can improve efficiency by

maximizing the utilization of electrical energy and minimizing side reactions. For the subsequent experimental runs, 0.01 M mixtures of  $\text{CoCl}_2\text{:NiCl}_2$  50:50 % v/v were used.

#### 4.4.1. Stirring effect

For the size level of the electrochemical cells used, stirring might not be thought to play such an important role. Thus, this operating condition was further explored for studying metal recoveries during the electrodeposition of cobalt and nickel.

The tests with 50:50 % v/v mixtures of  $\text{CoCl}_2\text{:NiCl}_2$  were repeated, now using a magnetic stirrer at a speed of approximately 225 rpm.

Figures 16a and 16b show the results obtained for this set of tests.

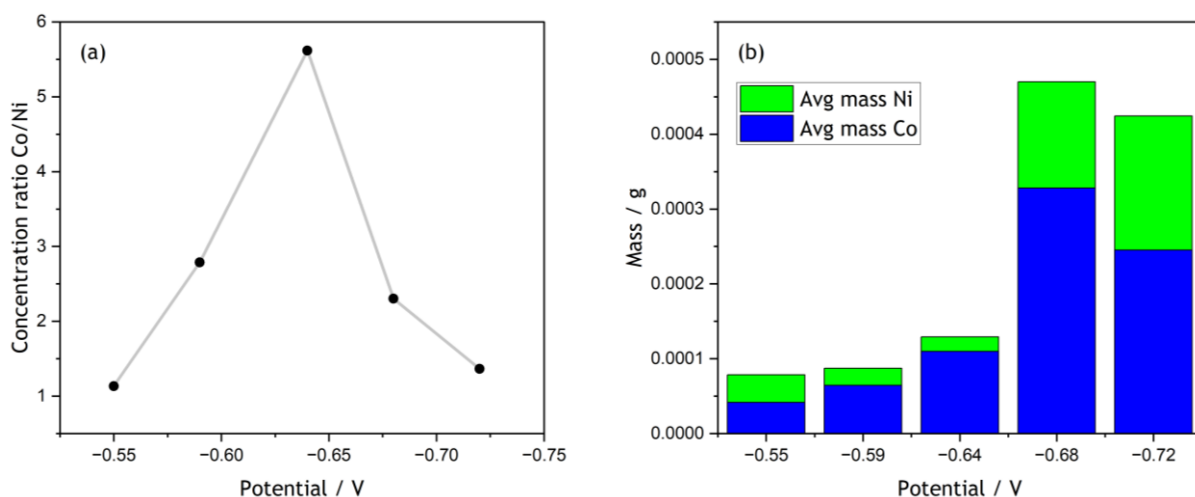


Figure 16. Electrodeposition data obtained for 50:50 % v/v mixtures of  $\text{CoCl}_2\text{:NiCl}_2$  at room temperature and with stirring: (a) the Co/Ni concentration ratio obtained by ICP-MS, (b) the quantity deposited for each metal.

Comparing Figure 16a with Figure 13b, it is evident that the Co/Ni ratio curves follow the same pattern, with an increase in cobalt deposition up to -0.64 V followed by a decrease. Stirring demonstrates greater selectivity in cobalt deposition, with a maximum ratio value of 5.6 at -0.64 V, corresponding to approximately 85 % cobalt in the deposited film. This marks a significant improvement compared to the non-stirred experiment, which achieved a ratio of 1.3 and only 56 % cobalt in the electrodeposited film. Indeed, with stirring, both selectivity and total amount of metal deposited increased, maintaining, for all potential differences, an anomalous codeposition.

These findings are largely consistent with reported literature. The increase in cobalt deposition is attributed to enhanced stirring, which reduces the thickness of the diffusion layer near the cathode surface, thereby increasing ion availability on it. Since cobalt is preferentially deposited in equimolar cobalt-nickel solutions, heightened ion concentration

in the diffusion layer favors cobalt deposition. [29, 42, 43] Similar results were reported by Vazquez-Arenas *et al.* [30]

Qiao *et al.* [43] and Zhang *et al.* [46], who also demonstrated increased cobalt deposition, albeit in jet-electrodeposition studies. Increasing the jet flow rate in their experiments is analogous to increasing stirring in an electrolyte bath.

Another contributing factor to increased cobalt deposition could be related to the greater rate of  $H^+$  ions reduction. [30, 41] At pH 3,  $H^+$  reduction is controlled by mass transport, therefore, increased stirring enhances the reduction of  $H^+$  ions and consequently promotes the formation of cobalt hydroxide, which conditions the nickel deposition.

This phenomenon typically results in reduced Faradaic efficiency due to increased electron consumption for  $H^+$  reduction instead of metal ion reduction. Notably, in this study, no decrease in efficiency was observed.

Additionally, as illustrated in Figure 16b, stirring affects the total amount of metal deposited as expected since there are more metal ions at the cathode surface provided by the stirring of the solution. At -0.68 V and -0.72 V, the total amount of metal deposited almost doubled. Excessive stirring, however, can diminish metal deposition due to strong hydrodynamic forces that sweep particles away, reducing their concentration in the final deposited layer. [31]

Based on these results, stirring is deemed crucial and was therefore implemented in subsequent experiments.

#### 4.4.2. Temperature dependence

The effect of the temperature was evaluated, submitting the electrolyte bath to heating during the electrodeposition test, using a hot plate and stirring. For this study, mixtures of 0.01 M  $CoCl_2:NiCl_2$  (50:50 % v/v) were maintained to observe temperature effects. Temperatures of 35 °C, 40 °C and 45 °C were tested.

Electrodeposition processes are usually sensitive to temperature variations. Optimal deposition conditions are achieved by carefully balancing the temperature to ensure a high deposition rate, good quality of the deposits, and efficient use of electrochemical energy. While higher temperatures generally improve deposition characteristics, they must be managed to avoid side reactions, like increased hydrogen evolution, and electrolyte evaporation.

For the experiments conducted at 35 °C (Figure 17a), the cobalt-nickel concentration ratio demonstrated a significant decrease compared to the experiments performed at room temperature (Figure 16a).

A maximum Co/Ni ratio of 2.25 was reached at -0.59 V. As the potential increased to more negative values, the selectivity progressively decreased, with values of 2.18, 1.58, and 1.22. Additionally, there was a shift in the maximum peak of cobalt content, from -0.64 V at room temperature to -0.59 V at 35 °C.

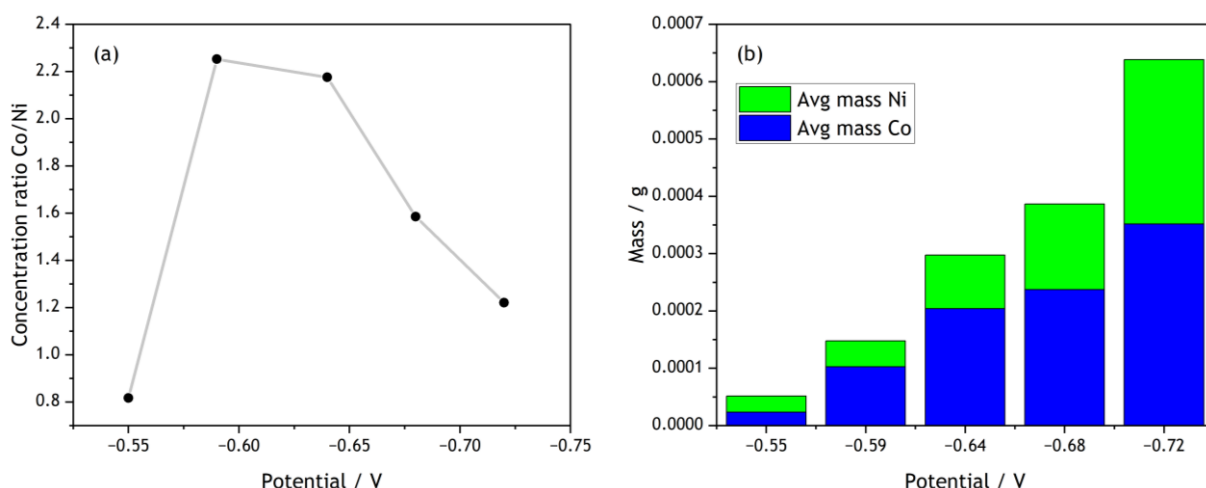


Figure 17. Electrodeposition data obtained for 50:50 % v/v mixture of  $\text{CoCl}_2\text{:NiCl}_2$  at 35 °C and with stirring: (a) the Co/Ni concentration ratio obtained by ICP-MS, (b) the quantity deposited for each metal.

For the experiments conducted at 40 °C, as illustrated in Figure 18 a, the concentration ratio follows the same pattern, with the higher cobalt content found at -0.59 V. Increasing the potential to more negative values again lead to a decrease in the Co/Ni ratio.

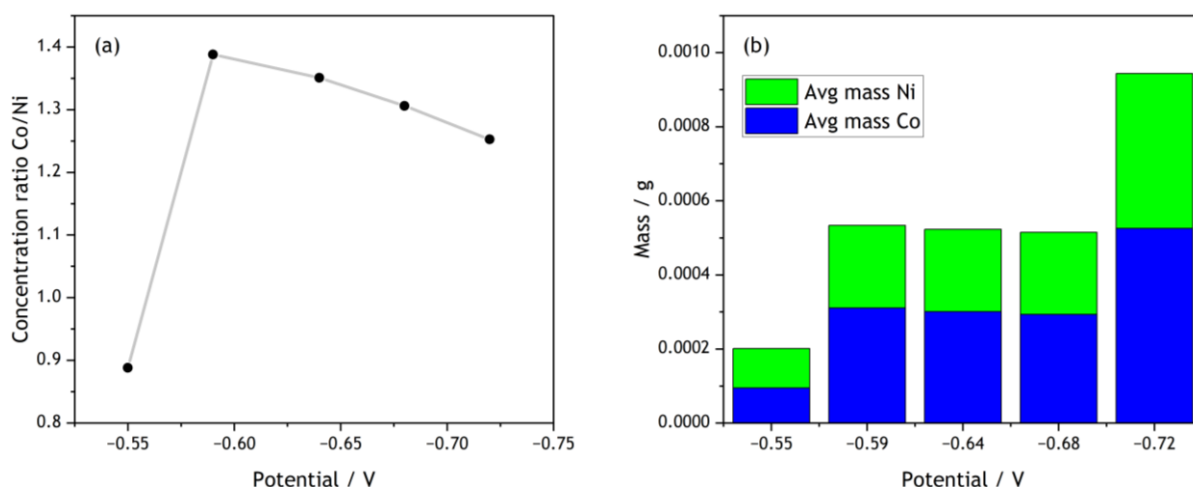


Figure 18. Electrodeposition data obtained for 50:50 % v/v mixture of  $\text{CoCl}_2\text{:NiCl}_2$  at 40 °C and with stirring: (a) the Co/Ni concentration ratio obtained by ICP-MS, (b) the quantity deposited for each metal.

Figure 19a, relating to the 45 °C tests, evidences a very similar pattern to the two previous temperature tests. In all cases, the highest ratio is observed at -0.59 V. The only potential difference at which nickel was preferentially deposited, for all temperatures, was -0.55 V. At the remaining potentials, anomalous codeposition was always present. The similar pattern in the ratio curve across all temperature tests demonstrates consistency across the temperatures tested, as the ratio maxima and minima occur at the same potentials.

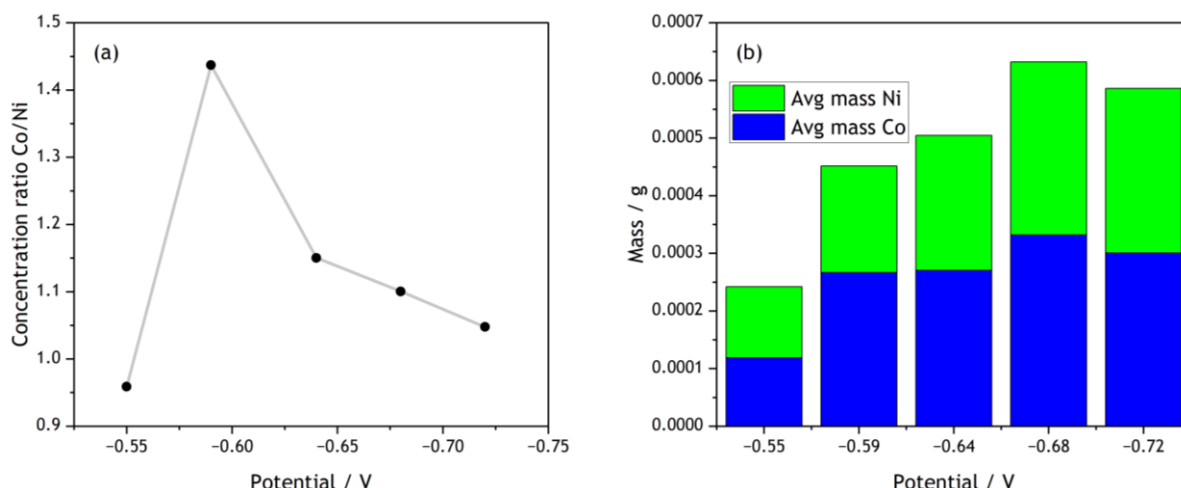


Figure 19. Electrodeposition data obtained for 50:50 % v/v mixture of  $\text{CoCl}_2\text{:NiCl}_2$  at 45 °C and with stirring: (a) the Co/Ni concentration ratio obtained by ICP-MS, (b) the quantity deposited for each metal.

Based on previous results, it can be concluded that temperature can influence the anomalous codeposition of cobalt and nickel through two competing mechanisms that are polarization and diffusion. Polarization refers to the deviation of the electrode potential from its equilibrium value due to the passage of current. It encompasses both activation polarization and concentration polarization. Activation polarization decreases with an increase in temperature. This is because the activation energy for electrochemical reactions is reduced at higher temperatures, facilitating easier charge transfer reactions at the electrode surface. Concentration polarization tends to decrease at higher temperatures, as it is directly related to diffusion. At higher temperatures, ions have greater mobility, enhancing the concentration of metal ions within the cathode diffusion layer. Increased ion mobility and diffusion rates reduce the concentration gradients near the electrode surface, minimizing the concentration polarization.

Bearing in mind the system under study, as a more noble metal, nickel experiences lower activation polarization inherently. With increased temperature, the reduction in activation polarization is more pronounced, favoring nickel deposition. Additionally, higher temperatures improve ion mobility and diffusion, which reduces concentration polarization. While higher temperatures may improve the ion diffusion of the less noble metal (cobalt),

the metal's higher activation polarization and susceptibility to hydrogen evolution will influence the overall deposition selectivity.[40] Enhanced diffusion helps to mitigate concentration polarization, but the deposition efficiency does not match that of nickel. Indeed, nickel, being more noble, benefits more from these improvements due to its lower inherent activation polarization and reduced susceptibility to hydrogen evolution. Cobalt, while also benefiting from increased diffusion, also faces increased activation polarization.

Qiao *et al.* [43] showed that increasing the bath temperature negatively affects the amount of cobalt deposited, confirming the effect of the temperature in the mechanism of anomalous codeposition presented in this study. The increase in temperature will amplify the influence of activation polarization over the diffusion in the process, improving further the deposition of nickel and so hindering the selectivity towards cobalt.

Important to mention that if the temperature is further raised to more extreme values, it might be possible to achieve selectivity biased towards nickel. However, this would make the process dependent on high operating temperatures, which are associated with high operating costs. Moreover, increasing the temperature to more extreme values would sacrifice one of the advantages of the electrodeposition method, which is the use of moderate temperatures. High operation temperatures could also lead to the evaporation of electrolyte. The ideal scenario is the development of a process based on aqueous solutions that are environmentally friendly, cost and energy-efficient.

Table 2. Comparison of cobalt percentage obtained in the electrodeposition tests using 0.01 M  $\text{CoCl}_2\text{:NiCl}_2$  (50:50 % v/v) at different temperatures with stirring.

| Potential<br>(V) | Co/(Co+Ni) (%)      |       |       |       |
|------------------|---------------------|-------|-------|-------|
|                  | Room<br>temperature | 35 °C | 40 °C | 45 °C |
| -0.55            | 53.27               | 45.05 | 47.14 | 49.05 |
| -0.59            | 73.68               | 69.34 | 58.23 | 59.07 |
| -0.64            | 84.94               | 68.60 | 57.56 | 53.60 |
| -0.68            | 69.80               | 61.41 | 56.92 | 52.49 |
| -0.72            | 57.82               | 55.07 | 55.71 | 51.27 |

Table 2 shows the percentage of cobalt in the electrodeposited film for electrodeposition tests performed at different temperatures. From room temperature to 45 °C, there is a progressive decrease in the cobalt content deposited, as evidenced by the percentage values. When the temperature reaches 45 °C, the values are very similar to those obtained at 40 °C. The peak value is substantially the same, around 59 %, and for the remaining potential differences where anomalous codeposition occurs, the values show a small, almost insignificant difference.

Another effect of temperature is the increase in the total amount of metal deposited (see Figure 19 b), which was observed for all potential differences. This suggests that, besides its effect on selectivity, temperature also affects the kinetics of the process, as predicted by the Arrhenius equation. The increase in temperature enhances the reaction rate in electrodeposition, meaning that as the temperature rises, the rate of metal reduction increases.

Despite the increase in the amount of metal deposited does not necessarily lead to an increase in selectivity, it can be an important factor in the possible future implementation of a large-scale electrodeposition-based process. The electrodeposition separation process of cobalt and nickel appears to be rather slow, meaning that any parameter capable of accelerating the process holds significance.

A decrease in Faradaic efficiencies was observed in the comparison between the experiments with stirring and temperature control. For the initial electrodeposition tests at room temperature, high efficiencies were obtained. However, for the three temperature groups of experiments, the efficiencies showed lower values, ranging from 77 % to 85.5 %, as illustrated in Figure 20.

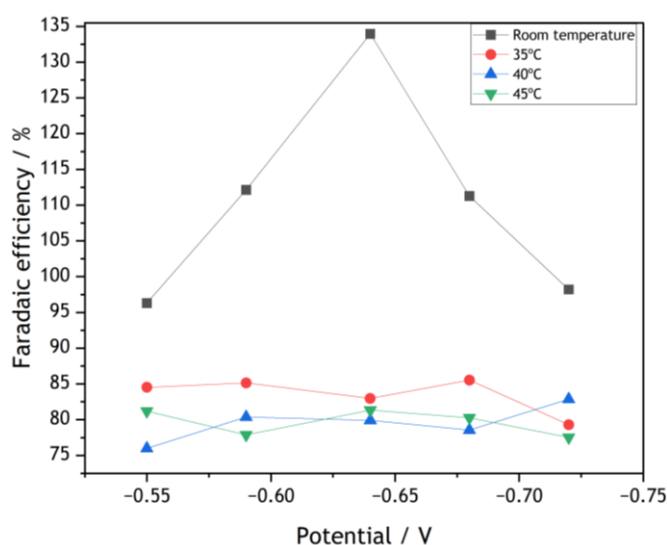


Figure 20. Faradaic efficiencies for the electrodeposition tests carried out with stirring and at different temperatures.

The decrease in efficiency for the temperature experiments indicates that part of the current is being used for secondary processes or reactions. Higher temperatures may lead to unwanted side reactions or changes in the system that reduce the efficiency of the electrodeposition process. In the electrodeposition of cobalt and nickel, this diversion of electrons to a secondary process is primarily due to the hydrogen evolution reaction (Equation 4). The increase in temperature could also enhance the kinetics of the hydrogen reaction, making it more dominant and thereby reducing current efficiencies. [15, 49]

Indeed, if the hydrogen evolution reaction becomes more relevant, it would compete with cobalt deposition. Higher temperatures exacerbate this issue, making it more challenging to achieve pure high-quality cobalt deposits. Electrolyte formulations may need more careful balancing to handle the higher polarization and hydrogen evolution issues. Additives that promote smoother deposits and reduce internal stress have to be used. [31]

Temperature proves to be a parameter with influence on the selective recovery of cobalt and nickel for values slightly above room temperature. Further increase leads only to better kinetics of the process and thus higher amounts of metal deposited but does not offer a better Co/Ni ratio for the conditions used in the presented experiments.

#### 4.4.3. Metal concentration

The subsequent tests aimed to assess the impact of a tenfold increase in the concentration of both metals in the solution. To achieve this, 50:50 % v/v solutions containing 0.1 M  $\text{CoCl}_2\text{:NiCl}_2$  were utilized. The operating conditions selected were those previously identified as optimal for improving selectivity, namely room temperature with continuous stirring of the solution. Figure 21 illustrates the outcomes obtained from these experiments.

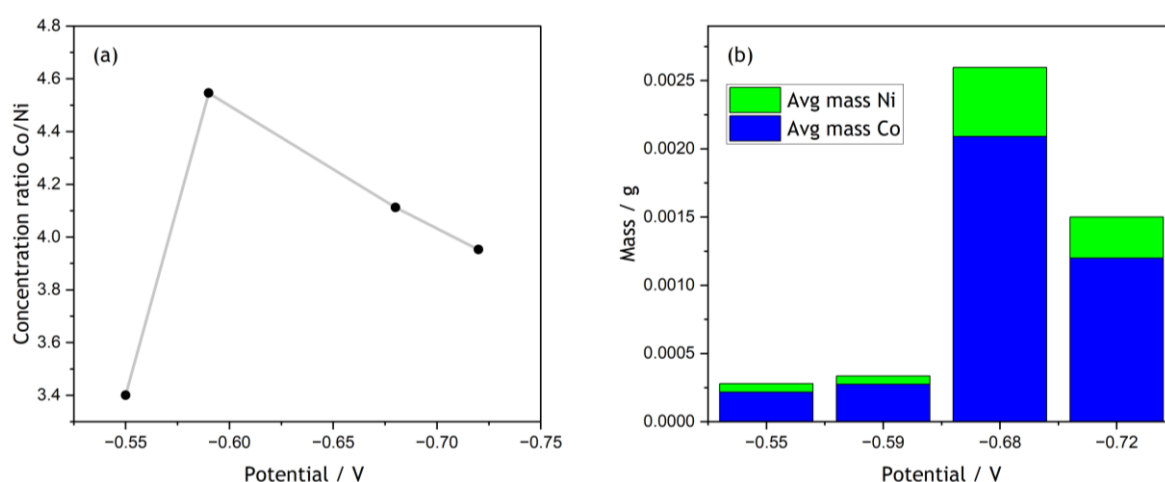


Figure 21. Electrodeposition data obtained for 50:50 % v/v mixture of  $\text{CoCl}_2\text{:NiCl}_2$  0.1 M at room temperature with stirring: (a) the Co/Ni concentration ratio obtained by ICP-MS, (b) the quantity deposited for each metal.

The best selectivity Co/Ni ratio observed was 4.5, achieved at a potential difference of -0.59 V. For all potentials tested, a significant difference is noticed, with an improvement in the Co/Ni ratio. The values are all above 3.4, and most are above 4.

Unfortunately, due to solution unavailability, the potential difference -0.64 V was not tested. However, it can be hypothesized that since ratios increased significantly at other potential differences, a similar increase would be expected at -0.64 V. For example, extrapolating from the average ratio increase observed at other applied potentials, a ratio of 7.7 could be anticipated at -0.64 V. This suggests that increased concentration enhances selectivity.

Nickel deposition never became preferential at any applied potential. Cobalt deposition was favored, consistent with its dependency on mass transfer. Increasing the total number of cobalt ions in solution enhances concentration within the diffusion layer at the cathode, thereby improving selectivity over nickel. [29, 39] Regarding the total amount of metal deposited, cobalt showed a substantial increase of 4 to 6 times, while nickel increased by 2 to 3 times.

Similarly Vazquez-Arenas *et al.* [48] demonstrated that higher concentrations of both metals lead to increased cobalt deposition in the film. Kim *et al.* [15] also reported an increase in cobalt selectivity, however, the increase was more significant achieving Co/Ni ratios greater than 10 for potential differences between -0.75 V and -0.60 V. This aligns with literature findings, indicating advantages in using more concentrated solutions, including reduced solvent usage.

#### 4.5. Electrode surface modification

The next objective was to investigate the influence of a cobalt-functionalized copper electrode on the selectivity of the electrodeposition process. For that, a small amount of cobalt was firstly electrodeposited onto a copper foil using 0.01 M  $\text{CoCl}_2$  solutions and a potential difference of -0.68 V. Four tests were carried out varying cobalt deposition times to assess its initial impact. Subsequently, a new electrodeposition lasting one hour was performed on the copper foils already coated with cobalt, using 50:50 %v/v  $\text{CoCl}_2$ : $\text{NiCl}_2$  0.01 M solutions at the same potential difference.

Figure 22 shows the amount of cobalt previously deposited. As expected, the deposition increased with longer deposition times.

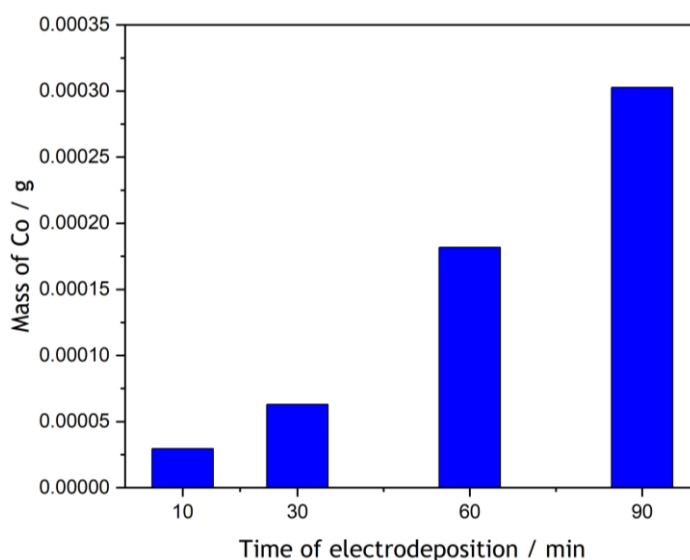


Figure 22. The amount of cobalt deposited with different deposition times at -0.68 V at room temperature.

Figure 23 shows the deposition results with solutions containing both metals but previously subtracting the amount of cobalt deposited for electrode functionalization.

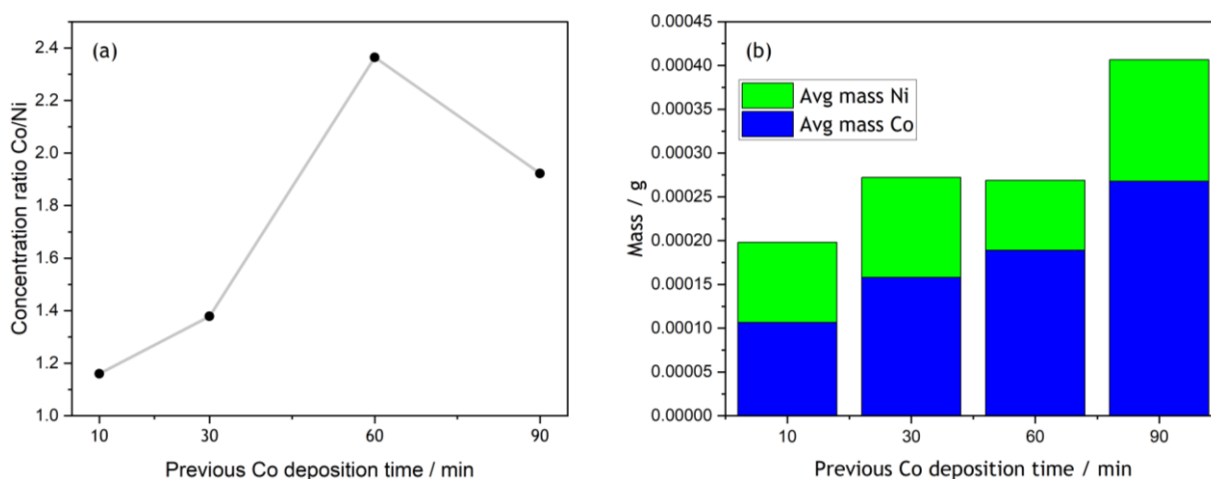


Figure 23. Electrodeposition data obtained with cobalt-functionalized copper electrode: (a) the Co/Ni concentration ratio obtained by ICP-MS, (b) the quantity deposited for each metal.

Figure 23a shows that the presence of pre-deposited cobalt on the electrode surface does not improve the selectivity of the process. The highest ratio obtained was only 2.4. According to the literature expectations [49, 50], pre-deposited cobalt should create nucleation sites on the electrode that promote preferential cobalt deposition when electroplating with solutions containing both metals. This study, however, did not demonstrate such benefits. Comparing these tests with control experiments conducted under identical conditions (stirring and room temperature) but without cobalt deposition, we concluded that selectivity did not improve.

Another notable observation from these tests is the variability in the amount of metal deposited, as depicted in Figure 23b. Despite all electrodepositions being conducted for one hour at -0.68 V, there are fluctuations in the deposited metal quantity across experiments under the same conditions. This variability could be attributed to the degradation of the working electrode, the copper foil, after repeated use in electrodeposition and subsequent acid washing. For future research, it is recommended to repeat these experiments with new copper foils to ensure consistent and reliable results.

## 5. Conclusion

Recycling batteries is crucial to reduce the reliance on raw materials and prevent the depletion of metals like cobalt and nickel, which are pivotal in various industries today. Conventional recycling processes are still limited to 95-96 % metal recovery. So, electrochemical techniques, particularly electrodeposition, have emerged as an assisting approach to selectively recover cobalt and nickel without excessive reagent usage or energy consumption.

In this study, multiple electrodeposition experiments were conducted to optimize the selective recovery process of cobalt and nickel. Initially, experiments comparing two electrolytes revealed that LiCl provides a wider deposition window for each metal and higher electrolyte concentrations enhance metal separation in solution.

Subsequent tests utilized 50:50 % v/v  $\text{CoCl}_2\text{:NiCl}_2$  solutions with the optimal electrolyte under room temperature and unstirred conditions, yielding limited selectivity with a maximum Co/Ni ratio of 1.3. Further investigations into different solution compositions (75:25 % v/v and 25:75 % v/v  $\text{CoCl}_2\text{:NiCl}_2$ ) demonstrated that increasing cobalt concentration improved selectivity, consistent with literature predictions. While higher nickel concentrations increased deposition, the extent of this increase was not as great as in the case of cobalt.

Stirring significantly improved selectivity by reducing diffusion layers, facilitating greater cobalt ion access to the electrode surface. Using stirring for solutions containing a higher concentration of cobalt in solution will surely increase selectivity even more. Tests at varying temperatures (35 °C, 40 °C and 45 °C) with continuous stirring showed that temperature did not enhance selectivity. It was concluded that an initial temperature increase from room temperature to 35 °C results in enhanced activation polarization having a greater influence than diffusion, leading to a decrease in cobalt content in the deposits and so hinder selectivity. With a further increase in temperature from 35 °C to 45 °C, the effect of polarization increases even more, resulting in an even bigger quantity of nickel content in the deposited film. By the end, increasing the temperature by approximately 20 °C, the ratio changed from 5.6 to 1.4. Indeed, higher temperatures exacerbated the hydrogen evolution reaction, lowering Faradaic efficiency.

Subsequent experiments with a tenfold increase in metal concentration maintained advantageous conditions and demonstrated enhanced metal deposition and selectivity across all potential differences tested. Higher metal concentrations not only increased deposition but also improved selectivity, underscoring its role in achieving more efficient metal recovery with reduced solvent usage.

As a final step, attempts to modify electrode surface by pre-depositing cobalt did not improve selectivity in subsequent electrodepositions with both metals. Results were inconsistent, possibly due to electrode degradation after repeated use.

In summary, stirring appears to be essential during the process, while temperature has the opposite effect and should therefore be avoided. In future work, solutions with a higher concentration of cobalt and nickel should be used, since they allow a higher percentage of cobalt to be obtained in the deposited film. Controlling the surface of the electrode is a potential method for modelling selectivity, but it should be repeated for fresh copper electrodes and tested with other types of materials.

## 6. Assessment of the work done

### 6.1. Objectives Achieved

This study represents the first exploration of electrochemical metal recovery within the host laboratory. Thus, the primary objective was to optimize the electrodeposition process for selectively recovering pure samples of cobalt and nickel, intended for subsequent application in real end-life battery cathodes. This objective was successfully achieved by testing various operating parameters and gaining insights into their influence on the electrodeposition process. Future work will focus on refining the process and extending its application to more complex solutions, aiming to fulfil the project's ultimate objectives.

### 6.2. Contribution to the Sustainable Development Goals

*Table 3. Sustainable Development Goals addressed by the dissertation*

| SDG | Goal | Contribution                                                                                                                    | Performance indicators and metrics                                                                                                                                                                                                                                         |
|-----|------|---------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 7   | 7.2  | Increase renewable energy share in the total final energy consumption                                                           | By recycling batteries, the availability of affordable and sustainable energy storage solutions is enhanced, thereby facilitating the integration of renewable energy into the grind.                                                                                      |
| 12  | 12.2 | Decrease the domestic material consumption, domestic material consumption per capita, and domestic material consumption per GDP | Instead of being discarded after use, batteries are collected, dismantled, and recycled to recover valuable components. By reintegrating these materials into the production process, recycling extends the lifespan of resources and reduces the need for new extraction. |
|     | 12.4 | Reduction of hazardous waste generated per capita; and increase the proportion                                                  | Improper disposal of batteries can lead to environmental pollution and soil contamination due to the leakage of hazardous chemicals.                                                                                                                                       |

|    |      |                                                                   |                                                                                                                                                                                                                                                                                                                                                  |
|----|------|-------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|    |      | of hazardous waste treated, by type of treatment                  | Recovering and reusing these resources at a very high level, helps to protect ecosystems, water resources, and human health from the adverse effects of pollution, contributing to climate change adaptation.                                                                                                                                    |
|    | 12.5 | Rise in the national recycling rate and tons of material recycled | Recycling based on electrochemical systems consumes less energy compared to the extraction and processing of raw materials. By incorporating recycled materials into battery production, manufacturers can reduce the energy intensity of the manufacturing process.                                                                             |
| 13 | 13.2 | Reduction of the total greenhouse gas emissions per year          | Recycling batteries reduces greenhouse gas emissions by recovering metals from used batteries with minimized environmental and energy impact when compared with traditional recycling processes. This reduction in energy consumption translates into lower carbon emissions, thereby contributing to global efforts to mitigate climate change. |

### 6.3. Final Assessment

The work carried out during this dissertation was engaging and allowed the development of my critical thinking and evaluative skills. Despite its challenges, the field of electrochemistry proved to be very interesting and broadened my perspective on its diverse applications in engineering, as well as its potential contributions to a more sustainable world.

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## Annex A - Supplementary information

Table A1. Electrodeposition results relating Co/Ni concentration ratio, the mass of cobalt, the mass of nickel, the total mass and the Faradaic efficiency.

| Mixture<br>CoCl <sub>2</sub> :NiCl <sub>2</sub> (% v/v) | Stirring | Temperature<br>(°C) | Potential (V) | Co/Ni<br>concentration<br>ratio | Mass of Co<br>(mg) | Mass of Ni<br>(mg) | Total mass<br>(mg) | Faradaic<br>efficiency<br>(%) |
|---------------------------------------------------------|----------|---------------------|---------------|---------------------------------|--------------------|--------------------|--------------------|-------------------------------|
| 50/50                                                   | No       | Room<br>temperature | -0.55         | 0.886                           | 0.010              | 0.012              | 0.022              | 104.939                       |
|                                                         |          |                     | -0.59         | 0.953                           | 0.030              | 0.031              | 0.061              | 108.010                       |
|                                                         |          |                     | -0.64         | 1.279                           | 0.064              | 0.050              | 0.114              | 109.552                       |
|                                                         |          |                     | -0.68         | 1.020                           | 0.114              | 0.050              | 0.164              | 102.324                       |
|                                                         |          |                     | -0.72         | 0.952                           | 0.107              | 0.112              | 0.220              | 104.532                       |
| 75/25                                                   | No       | Room<br>temperature | -0.55         | 5.381                           | 0.013              | 0.002              | 0.015              | 199.092                       |
|                                                         |          |                     | -0.59         | 0.878                           | 0.018              | 0.021              | 0.039              | 201.231                       |
|                                                         |          |                     | -0.64         | 2.557                           | 0.033              | 0.013              | 0.045              | 145.215                       |
|                                                         |          |                     | -0.68         | 4.059                           | 0.100              | 0.025              | 0.125              | 110.834                       |
|                                                         |          |                     | -0.72         | 2.459                           | 0.143              | 0.058              | 0.202              | 96.6545                       |
| 25/75                                                   | No       | Room<br>temperature | -0.55         | 0.582                           | 0.005              | 0.008              | 0.012              | 116.574                       |
|                                                         |          |                     | -0.59         | 0.929                           | 0.016              | 0.017              | 0.033              | 101.393                       |
|                                                         |          |                     | -0.64         | 0.517                           | 0.055              | 0.106              | 0.162              | 304.951                       |
|                                                         |          |                     | -0.68         | 1.016                           | 0.024              | 0.024              | 0.048              | 27.059                        |
|                                                         |          |                     | -0.72         | 0.449                           | 0.055              | 0.121              | 0.176              | 88.863                        |

|       |     |                  |       |       |       |       |       |         |
|-------|-----|------------------|-------|-------|-------|-------|-------|---------|
| 50/50 | Yes | Room temperature | -0.55 | 1.135 | 0.042 | 0.037 | 0.078 | 96.303  |
|       |     |                  | -0.59 | 2.787 | 0.064 | 0.023 | 0.087 | 112.138 |
|       |     |                  | -0.64 | 5.617 | 0.110 | 0.019 | 0.129 | 133.954 |
|       |     |                  | -0.68 | 2.302 | 0.328 | 0.142 | 0.470 | 111.277 |
|       |     |                  | -0.72 | 1.365 | 0.245 | 0.179 | 0.424 | 98.208  |
| 50/50 | Yes | 35               | -0.55 | 0.816 | 0.023 | 0.028 | 0.052 | 84.508  |
|       |     |                  | -0.59 | 2.252 | 0.102 | 0.045 | 0.148 | 85.141  |
|       |     |                  | -0.64 | 2.175 | 0.204 | 0.093 | 0.297 | 82.971  |
|       |     |                  | -0.68 | 1.585 | 0.237 | 0.149 | 0.386 | 85.533  |
|       |     |                  | -0.72 | 1.220 | 0.351 | 0.287 | 0.638 | 79.298  |
| 50/50 | Yes | 40               | -0.55 | 0.888 | 0.095 | 0.106 | 0.201 | 81.195  |
|       |     |                  | -0.59 | 1.388 | 0.311 | 0.223 | 0.534 | 77.865  |
|       |     |                  | -0.64 | 1.351 | 0.301 | 0.222 | 0.523 | 81.347  |
|       |     |                  | -0.68 | 1.306 | 0.293 | 0.222 | 0.515 | 80.266  |
|       |     |                  | -0.72 | 1.253 | 0.526 | 0.418 | 0.943 | 77.509  |
| 50/50 | Yes | 45               | -0.55 | 0.959 | 0.119 | 0.123 | 0.242 | 75.971  |
|       |     |                  | -0.59 | 1.437 | 0.267 | 0.185 | 0.451 | 80.369  |
|       |     |                  | -0.64 | 1.150 | 0.270 | 0.234 | 0.504 | 79.922  |
|       |     |                  | -0.68 | 1.101 | 0.335 | 0.300 | 0.632 | 78.551  |
|       |     |                  | -0.72 | 1.048 | 0.301 | 0.286 | 0.586 | 82.850  |

|        |     |                     |       |       |       |       |       |         |
|--------|-----|---------------------|-------|-------|-------|-------|-------|---------|
| 50/50* | Yes | Room<br>temperature | -0.55 | 3.400 | 0.216 | 0.063 | 0.279 | 123.887 |
|        |     |                     | -0.59 | 4.546 | 0.274 | 0.060 | 0.335 | 121.396 |
|        |     |                     | -0.68 | 4.113 | 2.090 | 0.506 | 2.596 | 155.650 |
|        |     |                     | -0.72 | 3.952 | 1.199 | 0.302 | 1.501 | 45.742  |

\* CoCl<sub>2</sub>:NiCl<sub>2</sub> 0.1 M

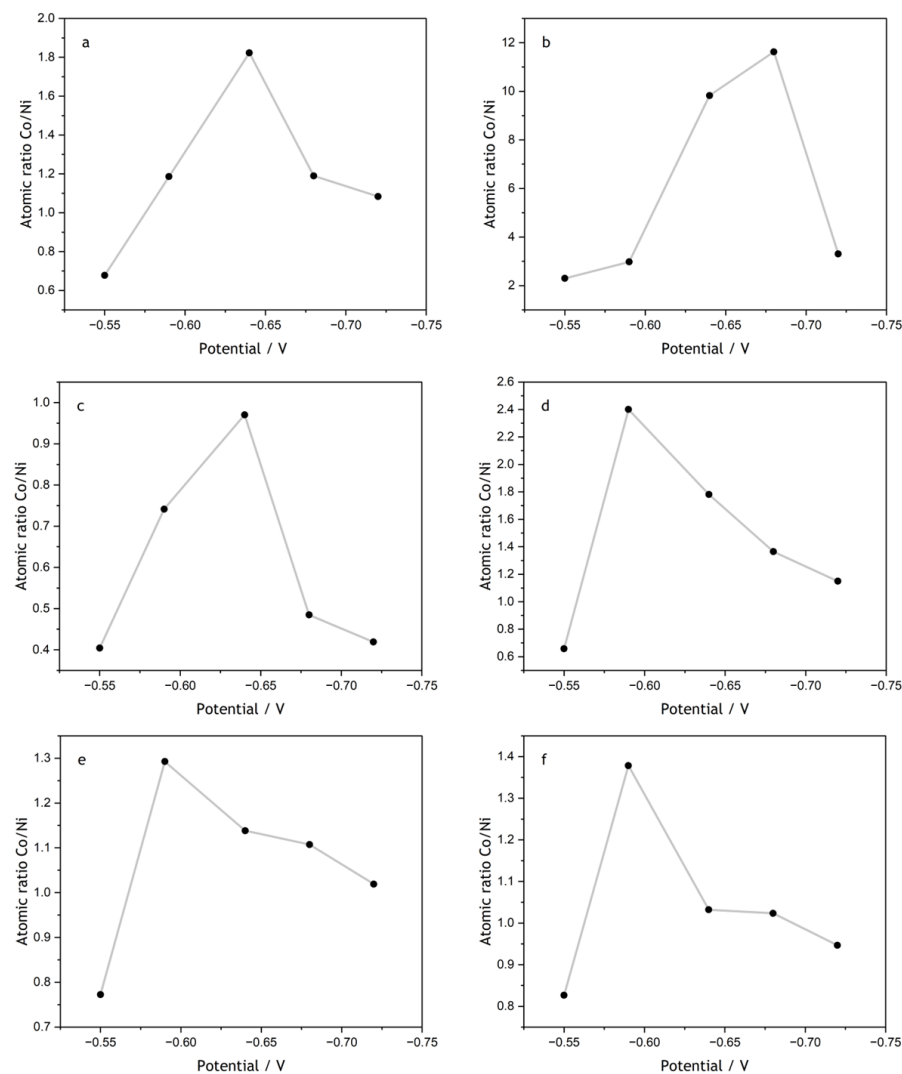


Figure A1. EDX analysis results for the electrodeposition tests carried out with (a) 50:50 %v/v mixture of  $\text{CoCl}_2\text{:NiCl}_2$ , (b) 75:25 %v/v mixture of  $\text{CoCl}_2\text{:NiCl}_2$ , (c) 25:75 %v/v mixture of  $\text{CoCl}_2\text{:NiCl}_2$ , (d) at 35 °C, (e) at 40 °C, (f) at 45 °C.