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By

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Theme:

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## **Elaboration and Electrochemical Study of Ni and Mn-Based Deposit: Application as an Electrode for Fuel Cells**

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## List of abbreviations

|                |                                                     |
|----------------|-----------------------------------------------------|
| <i>ALD</i>     | <i>Atomic layer deposition</i>                      |
| <i>AFC</i>     | <i>Alkaline Fuel Cells</i>                          |
| <i>AFM</i>     | <i>Atomic force microscopy</i>                      |
| <i>AMFC</i>    | <i>Alkaline Membrane Fuel Cell</i>                  |
| <i>CE</i>      | <i>Counter electrode</i>                            |
| <i>CV</i>      | <i>Cyclic voltammetry</i>                           |
| <i>DFT</i>     | <i>Density Functional Theory</i>                    |
| <i>ECSA</i>    | <i>Electrochemical surface area</i>                 |
| <i>ED</i>      | <i>Electrodeposition/Electrochemical deposition</i> |
| <i>EDX/EDS</i> | <i>Energy-dispersive X-ray spectroscopy</i>         |
| <i>EIS</i>     | <i>Electrochemical impedance spectroscopy</i>       |
| <i>ESCA</i>    | <i>Electron spectroscopy for chemical analysis</i>  |
| <i>FC</i>      | <i>Fuel Cell</i>                                    |
| <i>GGA</i>     | <i>Generalized Gradient Approximation</i>           |
| <i>HER</i>     | <i>Hydrogen evolution reaction</i>                  |
| <i>HOR</i>     | <i>Hydrogen Oxidation Reaction</i>                  |
| <i>LSV</i>     | <i>Linear sweep voltammetry</i>                     |
| <i>OCP</i>     | <i>Open circuit potential</i>                       |
| <i>OER</i>     | <i>Oxygen evolution reaction</i>                    |
| <i>ORR</i>     | <i>Oxygen reduction reaction</i>                    |
| <i>RE</i>      | <i>Reference electrode</i>                          |
| <i>RHE</i>     | <i>Reversible hydrogen electrode</i>                |
| <i>SEM</i>     | <i>Scanning electron microscopy</i>                 |
| <i>SHE</i>     | <i>Standard hydrogen electrode</i>                  |
| <i>TMs</i>     | <i>Transition metals</i>                            |
| <i>WE</i>      | <i>Working electrode</i>                            |
| <i>XRD</i>     | <i>X-ray diffraction</i>                            |

|                       |                                            |
|-----------------------|--------------------------------------------|
| <i>LSV</i>            | <i>Linear sweep voltammetry</i>            |
| <i>Ag/AgCl</i>        | <i>Silver/Silver chloride electrode</i>    |
| <i>RE</i>             | <i>Reference electrode</i>                 |
| <i>Ra</i>             | <i>Arithmetic Mean Roughness</i>           |
| <i>Rq</i>             | <i>Root Mean Square Roughness</i>          |
| <i>R<sub>K</sub></i>  | <i>Kurtosis of the Height Distribution</i> |
| <i>R<sub>Sk</sub></i> | <i>Skewness of the Height Distribution</i> |
| <i>Rz</i>             | <i>Mean Peak to Valley Height</i>          |
| <i>Rt</i>             | <i>Total Height of the Profile</i>         |
| <i>SCE</i>            | <i>Saturated Calomel Electrode</i>         |
| <i>EEC</i>            | <i>Electrical equivalent circuit</i>       |
| <i>Rs</i>             | <i>Solution Resistance</i>                 |
| <i>R<sub>ct</sub></i> | <i>Charge Transfer Resistance</i>          |
| <i>CPE</i>            | <i>Constant Phase Element</i>              |
| <i>j<sub>0</sub></i>  | <i>Exchange current density</i>            |
| <i>ECSA</i>           | <i>Electrochemical active surface area</i> |
| <i>C<sub>dl</sub></i> | <i>Double-Layer Capacitance</i>            |

## Abstract

The development of electrocatalysts with enhanced reactivity, stability, and cost-effectiveness is a critical challenge in advancing sustainable energy systems. Large-scale applications such as hydrogen production and fuel cells often rely on expensive precious metals to ensure performance and durability. Designing efficient and affordable electrodes for both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) is essential for improving the viability of hydrogen energy technologies. The development of high-performance electrocatalysts for overall water splitting and fuel cell processes remains a significant hurdle in this field.

This study investigated nonprecious metal-based electrodes, including Ni, Ni-Mn, Ni-Mn-Co, and Ni-Mn-Co-Fe thin films, as electrocatalysts for the HER, OER, and overall water splitting. The electrodes were synthesized via electrochemical deposition and characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray diffraction (XRD) to analyze their morphology, surface roughness, and phase structure. The electrocatalytic performance of these materials was evaluated through linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) under alkaline conditions.

The Ni-Mn-Co-Fe electrode demonstrated outstanding catalytic activity, requiring overpotentials of 436 mV for the HER and 447 mV for the OER to achieve a current density of 100 mA/cm<sup>2</sup>. This performance is attributed to its unique microstructure, enhanced electrochemically active surface area, and synergistic interaction with its components. The electrode also exhibited excellent stability, with a less than 4% increase in overpotential after 20 hours of continuous electrolysis at 100 mA/cm<sup>2</sup>. As a bifunctional electrode in water-splitting systems, it achieves a current density of 10 mA/cm<sup>2</sup> at a cell voltage of 1.57 V vs. RHE, highlighting its potential for practical applications.

Key deposition parameters, including the bath composition, scan rate, pH, current density, applied potential, deposition time, supporting electrolyte, and temperature, were systematically optimized for the Ni, Ni-Mn, and Ni-Mn-Co-Fe films. The electrocatalytic performance was assessed in alkaline KOH solutions at various temperatures and concentrations. Comparative analysis of the deposition conditions, including scan rates (5–50 mV/s), pH values (1.5–7.5),

bath temperatures (25°C–60°C), and applied potentials (-0.5 to -1.4 V vs. Ag/AgCl), enabled a comprehensive understanding of the factors affecting catalytic efficiency.

This study presents an effective strategy for producing active, stable, and cost-efficient electrocatalysts, demonstrating a scalable approach for renewable energy applications. These findings contribute to the development of high-performance catalysts for sustainable hydrogen production and fuel cell technologies.

## Résumé

Le développement d'électrocatalyseurs offrant une réactivité élevée, une stabilité améliorée et un coût réduit constitue un défi majeur pour le progrès des systèmes énergétiques durables. Les applications à grande échelle, telles que la production d'hydrogène et les piles à combustible, reposent souvent sur des métaux précieux coûteux pour garantir leurs performances et leur durabilité. Concevoir des électrodes efficaces et abordables pour les réactions d'évolution de l'hydrogène (HER) et d'évolution de l'oxygène (OER) est essentiel pour améliorer la faisabilité des technologies basées sur l'énergie d'hydrogène. La mise au point d'électrocatalyseurs performants pour le clivage total de l'eau et les processus liés aux piles à combustible reste un défi de taille.

Cette étude s'intéresse aux électrodes à base de métaux non précieux, notamment les films minces de Ni, Ni-Mn, Ni-Mn-Co et Ni-Mn-Co-Fe, en tant qu'électrocatalyseurs pour la HER, l'OER et le clivage global de l'eau. Ces électrodes ont été synthétisées par dépôt électrochimique et caractérisées par microscopie électronique à balayage (SEM), microscopie à force atomique (AFM) et diffraction des rayons X (XRD) pour analyser leur morphologie, leur rugosité de surface et leur structure de phase. Les performances électrocatalytiques ont été évaluées à l'aide de voltampérométrie linéaire (LSV) et de spectroscopie d'impédance électrochimique (EIS) en milieu alcalin.

L'électrode Ni-Mn-Co-Fe a montré une activité catalytique remarquable, nécessitant des surtensions de 436 mV pour la HER et de 447 mV pour la OER pour atteindre une densité de courant de 100 mA/cm<sup>2</sup>. Ces performances exceptionnelles sont attribuées à sa microstructure unique, à une surface électrochimiquement active accrue et aux effets synergiques de ses composants. De plus, l'électrode a démontré une excellente stabilité avec une augmentation de

surtension inférieure à 4 % après 20 heures d'électrolyse continue à 100 mA/cm<sup>2</sup>. En tant qu'électrode bifonctionnelle dans les systèmes de clivage de l'eau, elle a permis d'atteindre une densité de courant de 10 mA/cm<sup>2</sup> à une tension de cellule de 1,57 V vs RHE, soulignant son potentiel pour des applications pratiques.

Les paramètres de dépôt clés, tels que la composition du bain, la vitesse de balayage, le pH, la densité de courant, le potentiel appliqué, le temps de dépôt, l'électrolyte support et la température, ont été systématiquement optimisés pour les films de Ni, Ni-Mn et Ni-Mn-Co-Fe. Les performances électrocatalytiques ont été analysées dans des solutions alcalines de KOH sous diverses températures et concentrations. Une analyse comparative des conditions de dépôt, incluant les vitesses de balayage (5–50 mV/s), le pH (1,5–7,5), les températures de bain (25 °C–60 °C) et les potentiels appliqués (-0,5 à -1,4 V vs Ag/AgCl), a permis de comprendre les facteurs influençant l'efficacité catalytique.

Cette étude propose une stratégie efficace pour produire des électrocatalyseurs actifs, stables et économiques, offrant une méthode évolutive pour les applications énergétiques renouvelables. Les résultats contribuent au développement de catalyseurs performants pour la production durable d'hydrogène et les technologies des piles à combustible.

## المخلص

تطوير المحفزات الكهربية التي تتميز بنشاط عالٍ، واستقرار محسّن، وتكلفة منخفضة يُعد تحديًا كبيرًا لتطوير أنظمة الطاقة المستدامة. تعتمد التطبيقات واسعة النطاق، مثل إنتاج الهيدروجين وخلايا الوقود، غالبًا على معادن ثمينة ومكلفة لضمان أدائها واستدامتها. لذلك، يعد تصميم أقطاب كهربية فعالة ومنخفضة التكلفة لتفاعلات توليد الهيدروجين (HER) وتوليد الأكسجين (OER) أمرًا بالغ الأهمية لتعزيز جدوى تقنيات الطاقة الهيدروجينية. ومع ذلك، تظل تحقيق محفزات كهربية عالية الأداء لتقسيم الماء بالكامل ولعمليات خلايا الوقود تحديًا كبيرًا.

تركز هذه الدراسة على الأقطاب الكهربية المصنوعة من معادن غير ثمينة، مثل أفلام Ni و Ni-Mn و Ni-Mn-Co و Ni-Mn-Co-Fe الرقيقة، كمحفزات كهربية لتفاعلات HER و OER وتقسيم الماء بالكامل. تم تصنيع هذه الأقطاب باستخدام الترسيب الكهروكيميائي وتمت دراستها باستخدام تقنيات مثل المجهر الإلكتروني الماسح (SEM) والمجهر الذري (AFM) وحيود الأشعة السينية (XRD) لتحليل الشكل المورفولوجي وخشونة السطح وبنية الطور. وتم تقييم الأداء الكهروكيميائي باستخدام تقنيات الفولطية الخطية (LSV) وقياس الطيف الكهروكيميائي للمقاومة (EIS) في وسط قلوي.

أظهرت القطب Ni-Mn-Co-Fe أداءً محفّرًا متميزًا، حيث احتاج إلى تجاوز جهدي قدره 436 م.ف لتفاعل HER و 447 م.ف لتفاعل OER لتحقيق كثافة تيار قدرها 100 مللي أمبير/سم<sup>2</sup>. تُعزى هذه الكفاءة العالية إلى التركيب الميكروي

الفريد وزيادة المساحة السطحية النشطة كهروكيميائيًا والتأثيرات التآزرية لمكوناته. بالإضافة إلى ذلك، أثبت القطب استقراره العالي مع تغيرات طفيفة في الجهد) أقل من (4% بعد 20 ساعة من التحليل الكهربائي المستمر عند 100 مللي أمبير/سم<sup>2</sup>. وعند استخدامه كقطب مزدوج الوظيفة في أنظمة تقسيم الماء، استطاع تحقيق كثافة تيار تبلغ 10 مللي أمبير/سم<sup>2</sup> عند جهد خلية 1.57 فولت بالنسبة إلى RHE ، مما يبرز إمكاناته للتطبيقات العملية.

تم تحسين معلمات الترسيب الرئيسية مثل تكوين المحلول، سرعة المسح، درجة الحموضة، كثافة التيار، الجهد المطبق، وقت الترسيب، نوع الإلكتروليت الداعم ودرجة الحرارة بشكل منهجي للأفلام Ni و Ni-Mn و Ni-Mn-Co-Fe. وتم تقييم الأداء الكهروكيميائي في محاليل KOH القلوية تحت درجات حرارة وتركيزات مختلفة. كما أُجريت مقارنة تفصيلية بين معايير الترسيب، بما في ذلك سرعات المسح (5-50 م.ف/ثانية)، قيم درجة الحموضة (1.5-7.5) ، درجات حرارة المحلول (25-60 درجة مئوية) ، والجهود المطبقة (-0.5 إلى -1.4 فولت بالنسبة إلى Ag/AgCl) ، لفهم العوامل المؤثرة على الكفاءة التحفيزية.

تقدم هذه الدراسة استراتيجية فعالة لإنتاج محفزات كهربائية نشطة ومستقرة واقتصادية، مما يوفر طريقة قابلة للتطوير لتطبيقات الطاقة المتجددة. تساهم النتائج في تطوير محفزات ذات أداء عالٍ لإنتاج الهيدروجين المستدام وتقنيات خلايا الوقود.

# General Introduction

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## General Introduction

This chapter provides a comprehensive introduction to electrocatalytic water splitting and fuel cells, emphasizing the importance of energy storage technologies. The advantages of hydrogen and oxygen as clean energy carriers are discussed, and the benefits of producing them through water electrolysis powered by renewable energy sources are highlighted. This chapter further elucidates the motivation behind investigating nickel-based and manganese-based nonnoble compounds as electrocatalysts for water electrolysis, detailing the rationale for employing electrochemical deposition as the synthesis method. Finally, an overview of the thesis organization is presented, guiding readers through the structure and focus of the subsequent chapters.

### 1.1 Introduction

Since the Industrial Revolution of the 18th century, fossil fuels such as coal, oil, and natural gas have been the driving force behind technological advancements and transportation systems. However, the continuous increase in fossil fuel demand threatens our energy resources and places considerable strain on the environment. In response to global population growth and shifts in living conditions, the world's energy demand is projected to reach approximately 30 TW by 2050 and 46 TW by 2100. This increasing demand underscores the urgent need for sustainable energy solutions that minimize environmental impact and ensure energy security for future generations.[1, 2] As fossil resources are finite, shortages of oil and natural gas are anticipated within our lifetimes. Consequently, ensuring a reliable energy supply is becoming increasingly challenging. Moreover, the chemical and particulate pollution resulting from fossil fuel use poses serious health risks, while carbon dioxide (CO<sub>2</sub>) and other greenhouse gas emissions associated with global warming threaten the stability of the Earth's climate. Therefore, transitioning to renewable energy sources is essential for sustaining our society's

lifestyle and mitigating environmental impacts. Embracing renewables not only addresses energy security concerns but also contributes to a cleaner and more sustainable future.[3] There are several types of infinite (or semi-infinite) energy sources, including nuclear fission, geothermal, wind, solar, hydropower, and biomass. Nuclear fission, while a powerful energy source, poses significant challenges due to the handling, transportation, and storage of radioactive materials, all of which require specialized processes and equipment. In contrast, other renewable sources are subject to fluctuations over time due to natural variability. To address the growing energy demand, technologies that convert electrical energy from renewable sources into chemical energy for storage and later use, as well as those that directly convert a fuel's chemical energy into electricity, may be key solutions. Among these, hydrogen stands out as one of the most promising fuels. It can be produced from water through various methods, including electrolysis, radiolysis, thermolysis, the ferrosilicon process, photobiological water splitting, and photocatalytic water splitting.

Electrolysis is the most established method for the electrochemical production of hydrogen in industry. By using renewable energy as the power source for water electrolysis, water can be split into hydrogen and oxygen without emitting greenhouse gases, providing a clean and sustainable pathway for hydrogen production. This approach not only meets energy demands but also contributes to a reduction in the environmental impacts associated with traditional fossil fuels.[4, 5] The created hydrogen may then be stored and utilized in the chemical sector, or it can be used to generate power via fuel cells or internal combustion engines that emit no pollutants after combustion.[6, 7] Furthermore, high-purity oxygen is a beneficial byproduct. Its application in both medical care and the chemical sector might significantly reduce the nominal cost of water electrolysis.[7, 8]

The conversion of energy stored in hydrogen fuel is efficiently achieved through fuel cells, particularly with the development of solid alkaline fuel cells (SAFCs) based on anion-exchange membranes. SAFCs represent a novel type of polymer electrolyte membrane fuel cell that has several advantages over traditional systems. Compared with liquid electrolyte-based alkaline fuel cells (AFCs), they are more resistant to carbon dioxide (CO<sub>2</sub>) and do not rely on noble metals, making them a more cost-effective alternative. One significant advantage of SAFCs is their ability to use nonprecious materials, such as silver or transition metal oxides, as catalysts for the oxygen reduction reaction. This catalytic process is notably more efficient in alkaline environments than in acidic environments. However, the hydrogen oxidation reaction (HOR)

tends to proceed slowly under alkaline conditions due to substantial overpotential losses at the anode in SAFCs.

This challenge emphasizes the need for researchers to develop active and stable catalysts that can enhance the HOR. Moreover, the reverse reaction, the hydrogen evolution reaction (HER), is critical for the advancement of solid alkaline electrolyzers. Understanding and optimizing both the HOR and HER in alkaline electrolytes are essential for improving the performance of hydrogen-based energy systems. Consequently, effective electrocatalysts are needed to accelerate these reactions, lower the necessary overpotentials, and reduce overall energy costs. Currently, platinum (Pt) is recognized as the best-performing electrocatalyst for the HER; however, its high cost and scarcity necessitate the exploration of alternative materials. Research efforts are focused on discovering and developing nonprecious metal-based catalysts that can achieve similar or improved performance while being more sustainable and economically viable. This pursuit is crucial for advancing the commercialization of hydrogen fuel cells and electrolyzers, paving the way for a more sustainable energy future.[9, 10] However, ruthenium (Ru) and iridium (Ir) oxides are considered the most effective electrocatalysts for the oxygen evolution reaction. [10, 11] However, their limited abundance and high market price limit their use in large-scale industrial applications. Earth-abundant transition metals (Fe, Co, Mo, Ni, Mn, Cu, etc.) have attracted increasing interest in energy storage and conversion applications, particularly in electrocatalysis, as cost-effective and efficient alternatives to traditional noble metal-based catalysts (Pt, Pd, Au, Ag, Ir, and Ru).

Ni has emerged as one of the most promising components among these transition metal elements due to its fascinating electronic properties (multivalent oxidation states), abundance, low cost, good electrical conductivity, and heat conduction.[12] Many studies have been conducted on the development of active electrocatalysts to date. [13, 14]. These results led to the use of nonprecious materials for the HER, including transition metal phosphides, borides, carbides, selenides, and metal alloys, as well as transition metal oxides and hydroxides for the OER. These electrodes are also used as bifunctional electrodes to separate water. Among the many HER electrocatalysts studied under alkaline conditions are transition metal alloys [15-18]. Recent studies have shown an exciting strategy for improving the catalytic effectiveness of these electrodes. This includes supplementing them with more affordable metals, such as iron (Fe). [16] A separate investigation confirmed that nickel alloying with transition metals has a significant effect on the electrocatalytic activity during hydrogen evolution. Notably, this

alloy demonstrates a significant improvement in electrocatalytic activity.[16], [19] Metal alloys are a particular kind of electrocatalyst that might be employed to produce active and efficient electrodes. Overall, nickel-based electrocatalysts are considered excellent for hydrogen production in alkaline environments due to their superior corrosion resistance, strong electrical conductivity, and remarkable stability. [20-23] One of the most promising techniques for improving electrocatalytic activity is enhancing the electrical structure via nickel doping or alloying with other nonprecious metals.[24-26] The selection of catalytically active materials is based on two important properties: (a) intrinsic activity on the basis of the material's chemical composition and (b) the catalyst's active surface. Numerous investigations have demonstrated that various nickel-based alloys significantly improve the active surface area of catalysts.[27-29] Nickel alloys include cobalt, iron, molybdenum, and manganese. All of these studies revealed that alloying increases the electrocatalytic activity. Furthermore, the use of triple alloy systems such as Ni-Mn-Co improved the electrocatalytic activity. Ni-Fe-Mn triple alloys have been shown to be more electrolytically active than are Ni-Fe and Ni-Mn alloys. [30] This finding also suggests that the use of triple nickel-based alloys may increase the inherent electrocatalytic activity.[31-33] Increasing the electrocatalytic efficiency can also be achieved by expanding the active surface area through the design of three-dimensional nanostructures, including nanowires, nanocones, nanosheets, and nanotubes. [34],[35] These accomplishments not only enhance the application area of electrocatalysis but also provide the foundation for substantial advancements in this field. Innovative manufacturing procedures for engineering materials capable of producing desired structures have the potential to result in the creation of novel electrocatalysts. [36] ,[37]

There are various methods for synthesizing Ni-based electrocatalysts, including hydrothermal techniques, organic synthesis, chemical vapor deposition (CVD), physical vapor deposition (PVD), and atomic layer deposition (ALD). Among these methods, electrodeposition, also known as electrochemical deposition (ED), was selected as one of the most effective methods due to its unique intrinsic advantages. It is recognized as one of the most efficient and cost-effective techniques for electrode fabrication. [38],[39] This technique provides several notable benefits over other methods of electrocatalyst synthesis, such as being cost-effective, having a rapid synthesis time, and requiring inexpensive equipment. It can also be carried out under typical environmental conditions, including ambient temperature and pressure, making it ideal for large-scale industrial use. Additionally, by modifying the

parameters that influence the electrochemical deposition process, it is possible to achieve a variety of morphologies.

The aim of this study was to use electrochemical deposition to fabricate various electrocatalysts, including Ni-Mn, Ni-Fe, Ni-Co, Ni-Mn-Co, Ni-Mn-Fe, and Ni-Mn-Co-Fe alloys, and evaluate their effectiveness as electrocatalysts for the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and overall water splitting. The originality of this work lies in the novel application of electrochemical deposition to produce a Ni-Mn-Co-Fe alloy for the first time. By optimizing the bath conditions, we sought to thoroughly evaluate the electrocatalytic performance of the synthesized electrodes, focusing on both the HER and OER. Our results revealed a significant improvement in the electrocatalytic performance, which can be attributed to the surface nanostructure of the alloy and the synergistic effects from the combination of nickel with manganese, cobalt, and iron. This study not only enhances the understanding of electrocatalytic processes but also contributes to the development of advanced, nonnoble metal-based electrocatalysts for efficient water splitting and fuel cell applications.

## **1.2 Motivation**

The motivation for this study stems from the urgent need to address the dual challenges of energy sustainability and economic feasibility in hydrogen production. High-performance electrocatalysts, such as platinum-based materials, are widely recognized for their efficiency in hydrogen evolution reactions (HERs) and oxygen evolution reactions (OERs). However, their high cost and scarcity hinder their large-scale industrial application. This research aims to bridge the gap between performance and affordability by developing cost-effective, nonprecious metal-based electrocatalysts.

By focusing on the novel synthesis of multicomponent Ni-Mn-Co-Fe alloys through an optimized electrodeposition process, this study seeks to exploit the synergistic effects of transition metals to significantly increase their electrocatalytic activity. Electrodeposition offers a scalable, low-cost, and industrially feasible method for catalyst fabrication compared with conventional synthesis approaches such as chemical vapor deposition (CVD) and atomic layer deposition (ALD). The development of highly active and stable electrodes for water splitting could pave the way for efficient hydrogen production, contributing to the global transition toward clean and sustainable energy systems. Furthermore, this work has broader implications

for the integration of renewable energy sources into industrial hydrogen production, supporting energy security and reducing reliance on fossil fuels.

### 1.3 Novelty

The novelty of this work lies in the innovative application of electrodeposition to synthesize a quaternary Ni-Mn-Co-Fe alloy as an electrocatalyst for the first time. While binary and ternary nickel-based alloys have been widely studied, quaternary alloys present an untapped opportunity to harness the synergistic effects of multiple transition metals. By carefully optimizing electrodeposition parameters, such as the bath composition, pH, temperature, and deposition time, this research achieves a fine-tuned surface nanostructure that maximizes the active surface area and enhances the catalytic efficiency.

This study is significant because it thoroughly investigates the electrocatalytic performance of the Ni-Mn-Co-Fe alloy for both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) in alkaline media (1 M KOH). This work systematically compares the performance of quaternary alloys with that of their individual components (Ni, Co), binary alloys (Ni-Fe, Ni-Co), ternary alloys (Ni-Mn-Co, Ni-Mn-Fe), and benchmark commercial catalysts (Pt/C for the HER and RuO<sub>2</sub>/IrO<sub>2</sub> for the OER). The results demonstrate a remarkable improvement in the catalytic activity of the quaternary alloy, attributed to the following:

- **The synergistic effects** among nickel, manganese, cobalt, and iron led to an optimized electronic structure and increased intrinsic catalytic activity.
- **Surface nanostructuring** increases the electrochemically active surface area (ECSA), As a result facilitating efficient electron transfer and reaction kinetics.

The ability of the synthesized quaternary alloy to act as a bifunctional electrocatalyst for overall water splitting (HER and OER) makes it a promising candidate for integrated hydrogen production systems. Compared with conventional noble metal-based catalysts, which exhibit superior performance, cost efficiency, and stability, this study offers a step forward in the development of scalable, sustainable solutions for hydrogen production and renewable energy technologies.

## 1.4 Supplementary insights and technical details for the thesis

To provide a comprehensive evaluation of the synthesized electrocatalysts, this research also investigated the following:

1. **Electrodeposition mechanism:** A detailed study of the nucleation and growth process during electrodeposition is needed to understand the formation of alloy nanostructures.
2. **Structural and Morphological Characterization:** Techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM) are employed to analyze the crystal structure, morphology, and elemental composition of the deposited alloys.
3. **Electrocatalytic Performance Metrics:** Key parameters, including overpotential, Tafel slope, exchange current density, electrochemically active surface area (ECSA), and stability over long-term operation, are systematically evaluated.
4. **Stability Testing:** Long-term cyclic voltammetry (CV) and chronoamperometry (CA) tests were used to assess the robustness and durability of the quaternary alloy electrodes.

The results not only highlight the efficiency of the synthesized Ni-Mn-Co-Fe alloy but also provide insights into the structure-activity relationship, which is essential for further optimization and industrial application. This work serves as a foundation for the future development of advanced bifunctional electrocatalysts, contributing to sustainable hydrogen production technologies and the broader goal of clean energy solutions.

## 1.5 Scope of the Thesis

This thesis is organized as follows on the basis of the motivations outlined earlier:

**Chapter 2** provides a detailed exploration of the thermodynamic and kinetic factors involved in the electrolysis-based water-splitting reaction. It also reviews the current understanding of the mechanisms behind the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and hydrogen oxidation reaction (HOR) in fuel cells. This chapter places particular emphasis on the electrocatalytic properties of various nickel-based materials for both the HER and OER.

**Chapter 3** describes the methods and techniques used throughout the research.

Following the foundational discussions, the main research findings are presented in **Chapters 4 and 5**.

**Chapter 4** focuses on the single-step electrochemical deposition of Ni, Ni-Mn, and Ni-Mn-Co-Fe alloys as electrocatalysts for the HER and OER in alkaline media, employing cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The deposition method involves various bath parameters, such as the bath composition, scan rate, pH, temperature, supporting electrolyte concentration, and deposition time. The catalytic activity of the synthesized catalysts was examined under different electrolysis conditions, including various KOH temperatures and concentrations.

**Chapter 5** details the electrodeposition and characterization of optimized Ni, Ni-Mn, Ni-Mn-Co, and Ni-Mn-Co-Fe films as electrocatalysts for hydrogen and oxygen evolution reactions. The morphology, roughness, and phase structure of the synthesized electrodes were investigated via techniques such as scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray diffraction (XRD). The optimized catalysts are analyzed and compared, and their electrocatalytic performance for the HER and OER in alkaline media is evaluated via LSV and electrochemical impedance spectroscopy (EIS). The stability and bifunctionality of Ni-Mn-Co-Fe as an electrode in an overall water-splitting system is also discussed, alongside investigations of key deposition parameters such as the bath composition, scan rate, pH, and temperature. The electrocatalytic activity at different KOH temperatures and concentrations was explored through LSV.

The thesis concludes by summarizing the key findings and offering insights while also discussing potential future developments arising from this doctoral research.

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# Chapter 02

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## Chapter 2: Theoretical Background

This chapter provides a comprehensive theoretical foundation for contextualizing the key aspects of the research conducted in this thesis. The topics covered span from the general principles of thin films and electrodeposition to the electrochemistry of water splitting and the fundamentals of fuel cells. These interconnected subjects are critical for understanding the mechanisms, challenges, and innovations explored in this study.

Thin films and electrodeposition are fundamental to the fabrication of high-performance catalysts. This chapter begins with an exploration of thin film formation, discussing deposition techniques, structural properties, and their impact on catalytic activity. This is followed by an in-depth review of electrodeposition, a versatile and scalable method for synthesizing advanced materials. Key parameters, such as the bath composition, deposition potential, and substrate effects, are discussed to illustrate their influence on the film morphology and electrochemical properties.

The electrochemistry of water splitting forms the core of this chapter, which focuses on the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). These reactions are essential for hydrogen production through water electrolysis, a sustainable energy technology. The thermodynamic and kinetic aspects, including the activation energy, overpotential, and electrode dynamics, are discussed in detail to elucidate the fundamental challenges and opportunities in designing efficient catalysts.

The final section addresses the principles of fuel cell technology, highlighting its role in clean energy conversion. The mechanisms of the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) are examined, emphasizing the integration of electrocatalytic materials into fuel cell systems. Additionally, the interplay between water splitting and fuel cell operations is explored to highlight the broader implications of this research in advancing energy storage and conversion technologies.

By establishing a detailed theoretical framework, this chapter sets the stage for the experimental findings and discussions presented in subsequent chapters, offering insights into the principles and processes that underpin the development of innovative electrocatalytic materials.

## **2.1 General characteristics of thin films**

### **2.1.1 Introduction**

Thin film deposition technology involves applying a very thin layer of material onto a substrate, with thicknesses ranging from a few nanometers to micrometres or even just a few atoms. This process can also be used to add additional layers over previously deposited coatings. Thin film deposition methods are crucial for the production of modern electronic devices, including semiconductors, optical components, solar panels, disk drives, and CDs. These coatings can be applied through a variety of techniques, utilizing specialized tools and equipment that improve the efficiency and precision of the deposition process.[1]

### **2.1.2 Definition and Importance**

Thin film deposition is a process in which thin coatings are applied to a substrate material. A wide range of materials, including metals, oxides, and compounds, can be used to create these coatings. Thin films can possess various properties that modify or enhance specific characteristics of the substrate. For example, some thin films are transparent, others are strong and scratch resistant, and some can alter the electrical conductivity or improve signal transfer.[2]

Thin films are commonly used to enhance the surface properties of solids or bulk materials. These properties include but are not limited to transmission, reflection, absorption, hardness, abrasion resistance, corrosion resistance, permeation, and electrical behavior. As such, thin film deposition is a critical manufacturing step in the production of various solid-state, optoelectronic, and medical devices and products. These include consumer electronics, precision optics, compound semiconductors, semiconductor lasers, fiber lasers, microscopy and microanalysis slides, LED displays, optical filters, medical implants, and applications in nanotechnology.[2]

### **2.1.3 Basic Principles of Thin Film Deposition**

The methods used to produce thin films, such as evaporation, sputtering, ion beam deposition, or chemical vapor deposition, dictate the production process. The choice of a suitable thin-film deposition technique depends on several factors, including the application,

the target and substrate materials, the required uniformity of the film, and specific chemical and physical properties, such as corrosion resistance or high thermal conductivity.[2]

### 2.1.4 Materials Used for Thin Film Deposition

Metals, oxides, and compounds are key materials in thin film deposition, each chosen for specific properties like conductivity, protection, or tailored functionality. Material selection depends on the application's requirements.[1],[3]

### 2.1.5 Properties

A thin film is a layer of material with a thickness ranging from a nanometer to a few micrometers. Various industries use different deposition techniques to create thin films. These films are present in many everyday applications, such as the metal-coated glass used as mirrors in homes. Vac Coats, manufacturers, and designers of vacuum coating systems, utilize physical vapor deposition (PVD) methods, including sputtering, thermal evaporation, and pulsed laser deposition (PLD), to produce various types of thin films.

Depositing thin films onto solid materials helps enhance their surface properties. By forming a thin film on a bulk material, it is possible to achieve the desired mechanical, electrical, or optical properties on the material's surface, resulting in improved features such as increased conductivity, corrosion resistance, reflection, or hardness. [4],[5],[6]

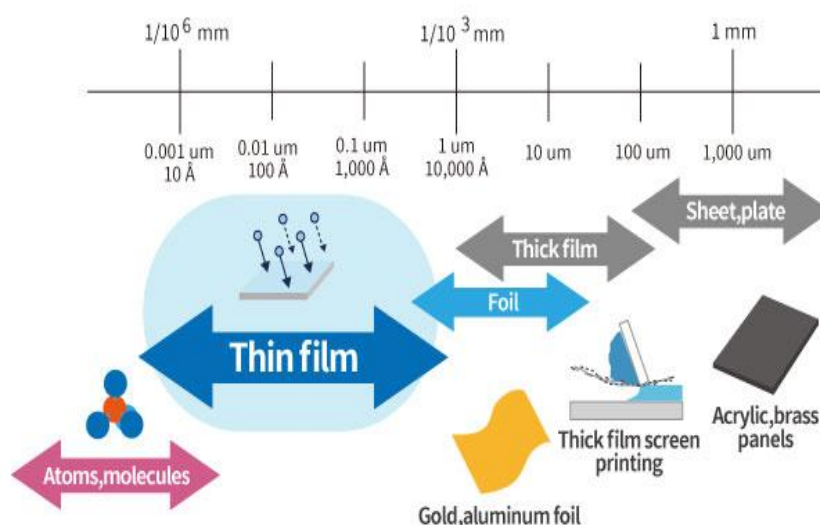


**Figure 2.1** Thin Film Thickness Range

### 2.1.6 Thin Film Deposition Process

The process of depositing a thin film onto a substrate involves several stages, including adsorption, surface diffusion, and nucleation. Each of these stages is influenced by factors such as the material properties, the characteristics of the substrate, the deposition technique, and the operating conditions. The way in which adsorbed species interact with the substrate surface plays a crucial role in determining the growth mode and structure of the final thin film.[7]

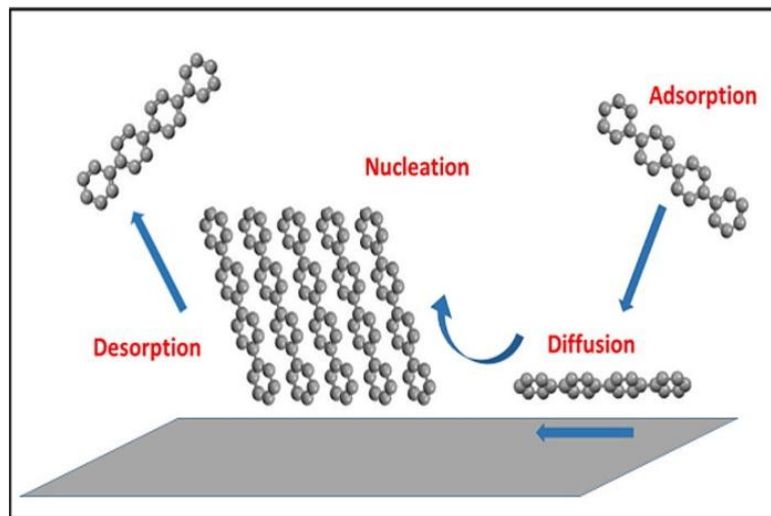


**Figure 2.2** Thin-film deposition process

The thin film deposition industry has experienced remarkable advancements, resulting in the creation of fast, scalable, and highly efficient deposition systems. In this review, we discuss the prevalent chemical vapor deposition and physical vapor deposition techniques and their applications.[8]

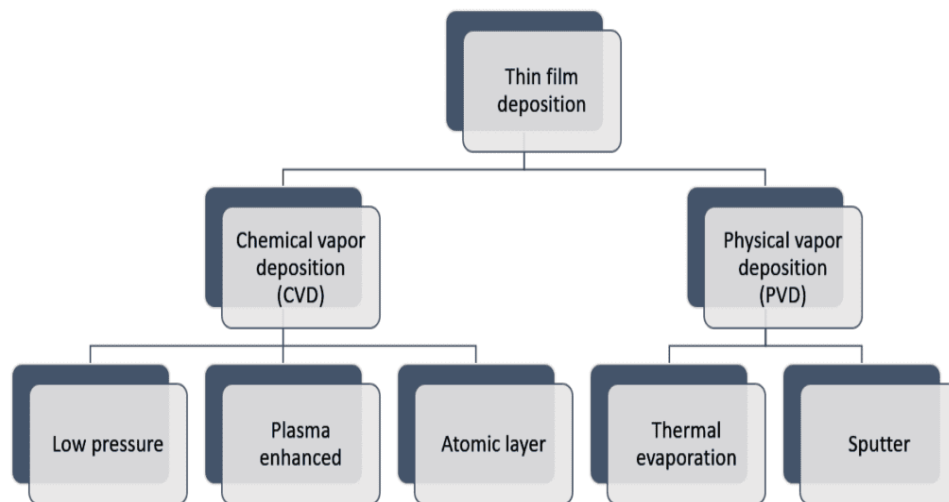


**Figure 2.3** Thin film deposition techniques

Thin film deposition techniques are employed to enhance the surface properties of engineering components by applying coatings that are typically less than 1 micron thick. These surface modifications can significantly influence various material characteristics, including conductivity, wear resistance, fatigue strength, corrosion resistance, hardness, etc., depending on the specific requirements of the application.

### 2.1.7 Deposition Techniques

Several deposition techniques have been used to create thin films of various materials on different substrates with a wide range of structures. These techniques are generally classified into two main categories: chemical methods and physical methods.[4, 9]

#### 2.1.7.1 Chemical Deposition

In chemical deposition, a precursor fluid reacts on the substrate surface, leading to the formation of a thin layer on the solid material. Common chemical deposition techniques include electrodeposition, sol-gel, dip coating, spin coating, chemical vapor deposition (CVD), plasma-enhanced CVD (PECVD), and atomic layer deposition (ALD).

#### 2.1.7.2 Physical Deposition

Physical deposition of thin films is accomplished primarily by depositing material vapor in a low-pressure environment, a process known as physical vapor deposition (PVD). The PVD is widely recognized for its accuracy and uniformity. Common PVD techniques include

sputtering, thermal evaporation, carbon coating, electron beam evaporation, molecular beam epitaxy (MBE), and pulsed laser deposition (PLD).

### 2.1.8 Thin Film Characterization Techniques

#### a) Chemical Composition Determination

The elemental composition of thin films can be analyzed via ion scattering methods such as Rutherford backscattering spectroscopy (RBS) or spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS).

#### b) Morphology and structure

The crystalline structure and microstructure of thin films can be analyzed via techniques such as X-ray diffraction (XRD) and Raman spectroscopy. The morphology of thin films is primarily examined through methods such as field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM).

#### c) Thickness Measurement

The thickness of thin films can be measured both during and after deposition via techniques such as quartz crystal microbalance (QCM) sensors, ellipsometry, profilometry, and interferometry.[10]

#### d) Electrochemical characterization

- **Chronoamperometry:** This technique involves applying a stepped potential to the deposition value and monitoring the resulting current–time response. This study provides insights into the early stages of deposition and helps determine the current density under various conditions.
- **Cyclic voltammetry:** By repeatedly scanning the potential between the cathodic and anodic limits, a cyclic voltammogram is generated, offering valuable information about exchange current densities, Tafel slopes, and other kinetic parameters.
- **Potential Step Methods:** In this approach, the potential is stepped, and the resulting current transients are analyzed under different conditions, enabling the evaluation of specific kinetic parameters, such as the rate constant for the electrodeposition reaction.

- **Electrochemical impedance spectroscopy (EIS):** This technique assesses the impedance of an electrochemical system at various frequencies, providing insights into the charge transfer resistance, double-layer capacitance, and diffusion processes.

### 2.1.9 Thin Film Types and Applications

The advancements in various industries over the past century can be attributed to the development of thin films and their deposition techniques. Key industries that have benefited from these innovations include semiconductor electronics, magnetic recording media, integrated circuits, LEDs, optical coatings (such as antireflective coatings), and hard coatings for tool protection, as well as pharmaceuticals, medicine, and many others.

Thin films have a wide range of applications across different fields. They play a crucial role in the research and development of materials with unique and specialized properties, such as superlattices, which allow for the study of quantum phenomena. Additionally, thin films are important because they alter the surface properties and reactions of materials compared with their bulk counterparts, offering a broad spectrum of characteristics that make them suitable for various applications.[11]

The types of thin films, due to their properties, can be categorized as follows:

- **Optical:** Thin films are used in the creation of reflective coatings, antireflective coatings, solar cells, monitors, waveguides, and optical detector arrays.
- **Electrical/Electronic:** These devices serve in the production of insulators, conductors, semiconductor devices, integrated circuits, and piezoelectric drives.
- **Magnetic:** Thin films are commonly employed in the production of memory disks.
- **Chemicals:** These materials increase the resistance to alloying, catalyze reactions, and protect against diffusion, corrosion, and oxidation. They are also used in gas and liquid sensors.
- **Mechanical properties:** Thin films provide tribological coatings to protect against abrasion, increase hardness and adhesion, and improve micromechanical properties.
- **Thermal:** Thin films are used to create insulation layers and heat sinks for thermal management.

They also have a wide range of industrial and scientific uses, including decorative coatings, biosensors, plasmonic devices, solar cells, batteries, and acoustic wave resonators.

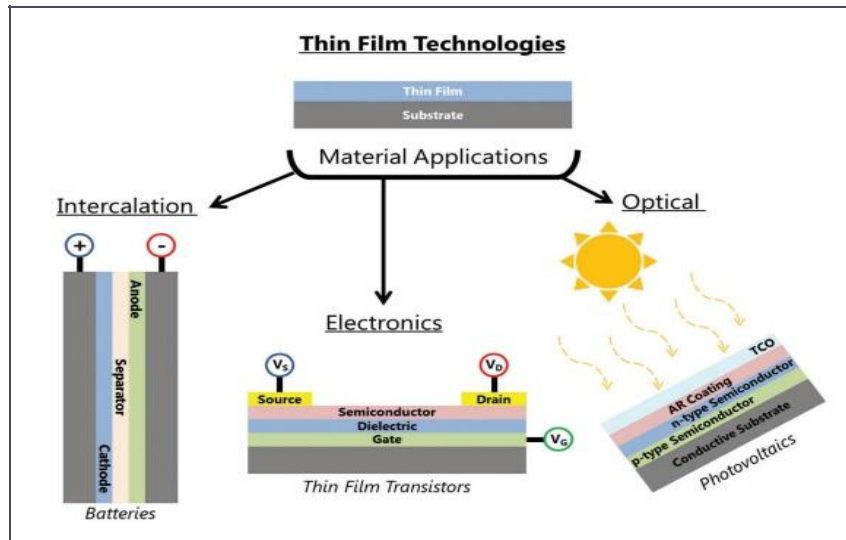


**Figure 2.4** Thin Film Applications

## 2.2 General aspects of electrodeposition

### 2.2.1 Electrodeposition of a metal

In a simple electrochemical system, when a metal  $M$  is immersed in a solution of its  $M^{n+}$  ions, a few atoms from the surface of the metal dissolve in the solution as hydrated ions  $[M(H_2O)_6]^{n+}$ . Moreover, ions from the solution are reduced on the cathode in the form of adatoms. In other words, a pseudo-equilibrium is established at the metal–solution interface according to the following reaction: [12]



The balance between these two opposing reactions is governed by the potential at the interface between the metal and the solution. The potential at which a metal electrode is in equilibrium with its ions is referred to as the equilibrium, reversible, or static potential. This value can be determined via Nernst's equation.[13],[12]

$$E_{eq} = E^0 + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \quad (2.2)$$

where:

$E_{eq}$ : Equilibrium potential (V)

$E^{\circ}$ : Standard potential of the Ox/Red couple (V)

$R$ : Ideal gas constant (8.314 J/K.mol)

$T$ : Temperature at which the reaction occurs (K)

$n$ : Number of electrons involved in the reaction

$F$ : Faraday's constant (96,485.338 C/mol of electrons)

$\frac{a_{ox}}{a_{red}}$ : Activity of the oxidized/reduced species ( $a = \gamma * \text{concentration [mol/l]}$ ), where  $\gamma$  is rarely equal to one. However, their activity and concentration are often confused.

### 2.2.2 Applied Potential:

Applying a potential  $E_i$  different from the equilibrium potential  $E_{eq}$  encourages reaction (2.2) to proceed in either the reduction or oxidation direction on the metal electrode. Notably, when the applied potential is lower than  $E_{eq}$ , the metal ions in the solution are reduced, and the metal is deposited on the electrode.

### 2.2.3 Factors influencing the equilibrium potential:

- **Standard potential ( $E^{\circ}$ ):** The standard potential is an inherent property of the redox couple and indicates the natural tendency of a species to undergo oxidation or reduction. A higher standard potential reflects a stronger inclination for reduction to occur.
- **Temperature ( $T$ ):** An increase in temperature typically results in a more positive equilibrium potential, which promotes the reduction reaction.
- **Number of Electrons ( $n$ ):** The number of electrons involved in the redox reaction influences the magnitude of the logarithmic term in the Nernst equation. A larger value of  $n$  leads to a steeper slope and greater sensitivity to changes in the activity of the species.
- **Activity of Reactants and Products:** The activities of both the oxidized and the reduced species have a direct effect on the equilibrium potential. Higher activities of the reactants (oxidized species) encourage oxidation, whereas higher activities of the products (reduced species) promote reduction.

### 2.2.4 Applications of the Nernst Equation:

- **Predicting the direction of a redox reaction:** By comparing the applied potential ( $E_i$ ) with the equilibrium potential ( $E_{eq}$ ), the direction of the reaction can be determined. If  $E_i$  is less than  $E_{eq}$ , the reaction will proceed spontaneously; if  $E_i$  is greater than  $E_{eq}$ , an external driving force is needed.
- **Calculating the equilibrium concentration of reactants and products:** The Nernst equation allows for the calculation of the equilibrium concentrations of both the oxidized and the reduced species on the basis of the equilibrium potential and the standard potential.
- **Determining the pH dependence of a redox reaction:** The Nernst equation can also be used to assess how the equilibrium potential of a redox reaction is affected by changes in pH, which is crucial in various biological and environmental processes.

The Nernst equation is a key principle in electrochemistry that helps predict and understand the behavior of redox reactions. It is widely used to study a variety of electrochemical processes, ranging from corrosion to battery technology. In particular, the Nernst equation plays a crucial role in understanding the electrodeposition of metal ions, as it defines the relationship between the concentration of ions and the electrode potential. By applying this equation, one can determine the potential at which metal ions are reduced and deposited onto an electrode, helping to control and optimize metal plating processes.

### 2.2.5 Predicting Deposit Formation and Direction:

The Nernst equation helps predict whether a metal ion will deposit or dissolve at the electrode on the basis of the applied potential  $E_{applied}$  and the equilibrium potential  $E_{eq}$  calculated via the Nernst equation.

- **Deposition:**

If  $E_{applied} < E_{eq}$ , the Nernst equation indicates a negative value for the logarithmic term, making the left-hand side of the equation less than zero. This imbalance drives the reaction toward reducing  $M^{(n+)}$  ions to  $M$ , leading to metal deposition.

- **Dissolution:**

Conversely, if  $E_{\text{applied}} > E_{\text{eq}}$ , the logarithmic term becomes positive, causing the left-hand side to be greater than zero. This thermodynamic tendency favors the oxidation of  $M$  to  $M^{(n+)}$  ions, resulting in metal dissolution from the electrode.

### 2.2.6 Optimizing Electrodeposition Conditions:

By manipulating factors in the Nernst equation, one can tailor the deposition conditions for specific metals:

- **Standard potential ( $E^0$ ):** Selecting metals with more positive  $E^0$  values generally requires less negative applied potentials for deposition.
- **Activity of Metal Ions:** Increasing the concentration of metal ions ( $aM^{(n+)}$ ) in the electrolyte shifts the equilibrium potential toward deposition by influencing the logarithmic term.
- **Solution pH:** For reactions involving  $H^+$  ions, changing the  $pH$  alters the activity of  $H^+$  and consequently influences the equilibrium potential. This can be crucial for controlling the deposition of pH sensitive metals.

### 2.2.7 Kinetics of electrodeposition

A schematic diagram of electroplating is shown in **Figure 2.5**. To perform electrodeposition, the substrate is placed at the cathode of an electrolysis cell that contains an electrolyte with the metal ions to be deposited. Generally, the electrolyte consists of a carrier salt, a buffering agent, complexing agents, or additives. The generator allows a current flow between the two electrodes.

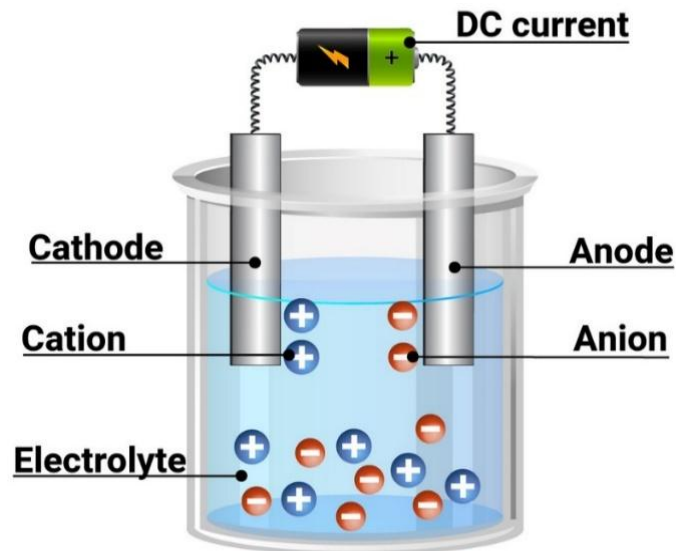


**Figure 2.5** Diagram of the assembly of an electrolysis cell

When a current is applied, the electrode potential deviates from its reversible potential and shifts to a more negative value. This potential is called the deposition (or dynamic) potential, and its difference from the reversible potential is defined by the overpotential  $\eta$ :

$$E = E_{rev} + \eta \quad (2.3)$$

In particular, simultaneous deposition of two metals in a simple solution of their metal salts is only possible when their potentials are substantially close.[14]

### 2.2.7.1 Faraday's law:

#### 1) Determining Deposited Mass (m):

The mass (m) of an element deposited through electrolysis can be calculated via Faraday's law:[15]

$$m = \frac{I \cdot t \cdot M}{n \cdot F} \quad (2.4)$$

where:

**m:** Mass of the deposited element (g)

**I:** Current intensity of the electrolysis (A)

**t:** Time of electrolysis (s)

**M:** Molar mass of the deposited element (g/mol)

***n***: Number of electrons exchanged per atom of the element during the electrodeposition reaction

***F***: Faraday's constant (96,485.338 C/mol)

## 2) Determining Deposit Thickness ( $\varepsilon$ ):

- **Relationship between mass and thickness:**

The mass ( $m$ ) of a deposit is related to its thickness ( $\varepsilon$ ), the density ( $\rho$ ) of the deposited metal, and the surface area ( $S$ ) of the substrate via the following equation:

$$m = \rho \cdot S \cdot \varepsilon \quad (2.5)$$

- **Thickness Formula:**

Combining equations (2.4) and (2.5), we obtain the following expression for the deposit thickness:

$$\varepsilon = \frac{ItM}{n.F.\rho.S} \quad (2.6)$$

**Thickness ( $\varepsilon$ ):** (m)

**Density ( $\rho$ ):** (g/cm<sup>3</sup>)

**Surface area ( $S$ ):** (cm<sup>2</sup>)

## 3) Determining the Deposition Rate ( $V$ ):

The deposition rate ( $V$ ) is defined as the deposit thickness ( $\varepsilon$ ) divided by the electrolysis time ( $T$ ):

$$V = \frac{\varepsilon}{t} = \frac{IM}{n.F.\rho.S} \quad (2.7)$$

**Deposition rate ( $V$ ):** g/cm<sup>2</sup>

### 2.2.7.2 Electrochemical double layer

The electrochemical double layer (EDL) is a nanoscale region at the interface between an electronic conductor (such as a metal electrode) and an ionic conductor (an electrolyte solution). This region is characterized by charge separation resulting from the interaction between the

electrode and the ions in the solution. The electric double layer (EDL) consists of two primary layers: the inner Helmholtz layer (IHP) and the outer Helmholtz layer (OHP). The IHP is mostly composed of solvent molecules that are strongly oriented due to the electric field, and it contains specifically adsorbed, partially solvated ions. The OHP comprises solvated ions that are not directly adsorbed onto the electrode surface. The potential drop in the EDL is linear in the rigid IHP and OHP layers and exponential in the diffuse layer beyond the OHP. The EDL plays a crucial role in electrochemical and heterogeneous catalysis, as it influences charge transfer processes and electrokinetic phenomena. It is also important to understand the behavior of colloids and other surfaces in contact with solutions or solid-state electrolytes. Several models have been proposed to describe the behavior of the electric double layer (EDL), including the Helmholtz model, which assumes that electron transfer reactions do not take place at the electrode, and the Stern model, which considers the movement of ions in the solution and the interaction between the electrode and solvent dipoles. The EDL is a fundamental concept in electrochemistry and is essential for understanding the behavior of electrochemical systems, such as batteries, fuel cells, and electrochemical sensors. [16],[17],[18]

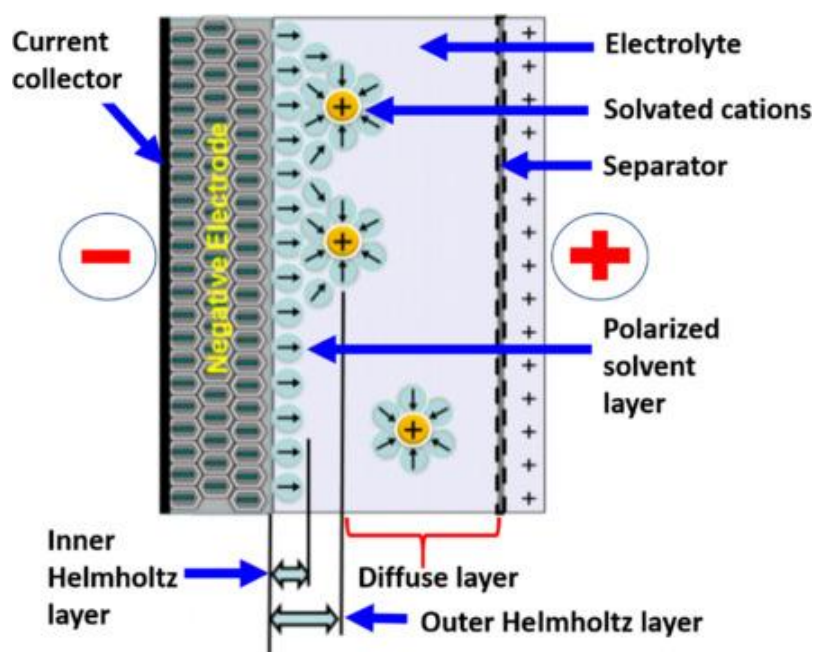


**Figure 2.6** Representation of the electrochemical double layer (EDL) used in electrodeposition. [16]

### 2.2.7.3 Mechanisms of Electrodeposition

Generally, the metal plating process involves three steps [80], which are also shown in **Figure 2.7**.

**a) Mass transfer:** Hydrated or complex metal ions in the electrolyte migrate toward the cathode under the influence of a potential, concentration, and/or convection gradient.

**b) Electron transfer:** Hydrated metal ions penetrate the diffusion layer at the cathode surface. Water molecules with hydrated ions align because of the weak electric field in the diffusion layer. Metal ions are trapped in an electrochemical double layer, where they lose their hydrated layers because of the presence of a higher charge. Individual ions are reduced and adsorb to the cathode surface, resulting in adatom production.

**c) Incorporation:** Adatoms are incorporated into the crystal lattice formed during the germination, growth, and coalescence processes. The competition between these processes determines the shape and microstructure of electrodeposited alloys. The elaboration conditions (pH, temperature, current regime) influence these various processes, which explains why alterations in these variables affect microstructural (such as grain size and crystallographic texture) and morphological characteristics. As previously demonstrated, the refinement of the grain size and the change in crystallographic texture are dependent on the parameters of the applied current regime. [19],[20]

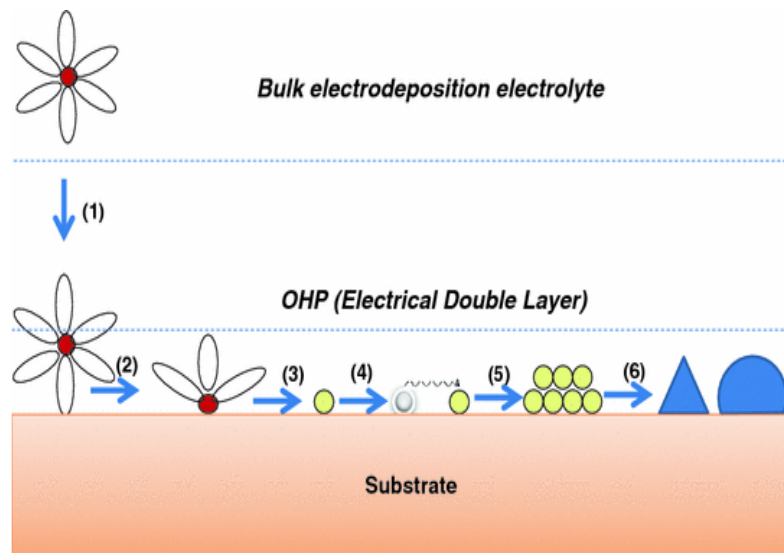


**Figure 2.7** Representation of the mechanisms involved in electrodeposition. [21]

#### 2.2.7.4 Codeposition of metals

In particular, the simultaneous deposition of two metals from a simple solution of their metal salts is possible only when their potentials are quite close. [14] Different tools can be used to approximate the potential of two metals and are discussed in the following paragraph.

##### a) Role of the Reversible Potential

In many binary alloy configurations, the standard potentials of both metals are often very far apart, making their codeposition very difficult. Two methods have been proposed by Brenner [13] to reconcile these potentials. The first approach involves altering the concentration ratio of the two metals, specifically by decreasing the concentration of the more noble metal. The second method involves the use of complexing agents, which results in the formation of more stable bonds. When the complexing anion interacts with the cation of the nobler metal, the potentials of the two metals converge. The adsorption or desorption of specific organic compounds used as complexing agents can impact the coating properties, potentially leading to issues such as cracking, embrittlement, or loss of adhesion.

##### b) Role of the codeposition potential

This potential plays an important role in the process of codeposition of metals. The value of this potential is often modified by increasing the current density, the use of solutions with complex agents, and the use of additives in the bath. Notably, these factors are only effective if

the overpotential of the nobler metal is increased to a greater extent than that of the least noble metal to approximate the deposition potential [13]. Once the appropriate potential and overpotential conditions have been obtained, it will be possible to codeposit two or more metals. As a result of codeposition-related interactions, cathodic polarization curves are often modified. For the two metals to be deposited simultaneously, it is necessary that the polarization curves be close together and have similar kinetics [14]. According to the polarization curves shown in **Figure 2.8**, the codeposition of two metals,  $M_1$  and  $M_2$ , is possible at potential  $E$  with a total current  $j_t = j_1 + j_2$ . Metals  $M_1$  and  $M_2$  are deposited with current fractions of  $j_1/j_t$  and  $j_2/j_t$ , respectively. The deposition potential of the alloy is then given by the following relationship: [82]

$$E_{rev} = E^\circ_{(M_1n+)/ (M_1)} - \frac{RT}{nF} \ln(Q_1) + \eta_{M_1} = E^\circ_{(M_2n+)/ (M_2)} - \frac{RT}{nF} \ln(Q_2) + \eta_{M_2} \quad (2.8)$$

Typically, additional reactions (such as the release of dihydrogen) occur. The following are also involved in the electroplating of metals:



The hydrogen evolution reaction significantly influences electrode polarization and the composition of the deposited alloy. In numerous electrolytic bath formulations, adjusting the concentration ratio of metal ions helps maintain a consistent composition in the deposited alloy.[13]

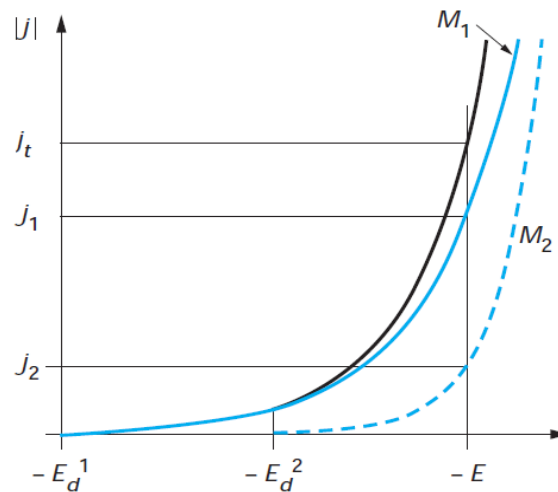


**Figure 2.8** Representation of the codeposition of two metals, M<sub>1</sub> and M<sub>2</sub>, on the basis of cathodic polarization curves with current density  $j_i$  and potential E.

To avoid depletion of the solution into metal cations during codeposition, a soluble anode with a composition similar to that of a bath is often used. For some alloys, the use of insoluble anodes to reduce the presence of impurities in the bath is preferable. However, the disadvantages of using these counter electrodes are as follows: [13]

- 1) decrease in the concentration of metal cations in the bath.
- 2) A decrease in pH occurs as a result of the water oxidation reaction, as follows:



In an alkaline environment, this decrease in pH is less problematic since the metallic ions form complexes with hydroxyl ions. Oxidation of the components of the bath, especially the complexing agents used for the codeposition of metals. This leads to the formation of brittle and loosely adherent deposits.

## 2.2.8 Deposition metal characteristics

### 2.2.8.1 Physicochemical characteristics of nickel (Ni)

**Table 2.1** Fundamental Physicochemical Characteristics of Nickel (Ni)

| Property                                             | Value                     |
|------------------------------------------------------|---------------------------|
| Atomic Number                                        | 28                        |
| Atomic Weight (g/mol)                                | 58.69                     |
| Crystal Structure                                    | Face-centered cubic (FCC) |
| Melting Point (°C)                                   | 1455                      |
| Boiling Point (°C)                                   | 2732                      |
| Density (g/cm <sup>3</sup> )                         | 8.90                      |
| Electrical Resistivity ( $\mu\Omega\cdot\text{cm}$ ) | 68.4                      |
| Thermal Conductivity (W/(m·K))                       | 90.7                      |
| Hardness (Mohs scale)                                | 4.0                       |
| Magnetic Properties                                  | Ferromagnetic             |
| Oxidation State                                      | 0, +2, +3                 |
| Color                                                | Metallic white            |

Nickel stands out for its unique blend of physical and chemical properties. Its face-centered cubic structure endows it with superior ductility and malleability, making it ideal for sheet metal formation and wire drawing. The high melting point (1455°C) reflects its excellent thermal stability, which is crucial for applications such as turbine blades and heat exchangers. While its moderately high electrical resistivity renders it decent for resisting electrical current, its good thermal conductivity facilitates heat dissipation. Nickel's diverse oxidation states (+2, +3) enable it to form various compounds, including corrosion-resistant nickel–chromium alloys in stainless steel. Its ferromagnetic nature allows it to be magnetized, making it vital for permanent magnets, electromagnets, and transformer cores. Additionally, its metallic white appearance has applications in decorative finishes and electroplating. However, understanding the characteristics of nickel extends beyond the table. Its abundance and affordability contribute to its widespread use. Additionally, it readily forms alloys with other metals, further tailoring its properties for specific needs. For example, combining nickel with copper enhances its electrical

conductivity, whereas adding chromium significantly improves its corrosion resistance. In conclusion, the combination of the excellent mechanical properties, good thermal stability, and tunable magnetic behavior of nickel through alloys makes it a versatile and invaluable material across diverse industries. Understanding its key characteristics and exploring its potential in combination with other elements opens doors to even more innovative applications in the future.[22],[23]

### 2.2.8.2 Main Physicochemical Characteristics of Manganese (Mn)

**Table 2.2** Fundamental physicochemical characteristics of manganese (Mn)

| Property                                             | Value                             |
|------------------------------------------------------|-----------------------------------|
| Atomic Number                                        | 25                                |
| Atomic Weight (g/mol)                                | 54.94                             |
| Crystal Structure                                    | Hexagonal close-packed (HCP)      |
| Melting Point (°C)                                   | 1244                              |
| Boiling Point (°C)                                   | 2097                              |
| Density (g/cm <sup>3</sup> )                         | 7.44                              |
| Electrical Resistivity ( $\mu\Omega\cdot\text{cm}$ ) | 1.44                              |
| Thermal Conductivity (W/(m·K))                       | 7.2                               |
| Hardness (Mohs scale)                                | 6.0                               |
| Magnetic Properties                                  | Antiferromagnetic                 |
| Oxidation State                                      | 0, +2, +3, +4, +6, +7             |
| Color                                                | Silvery-gray with a reddish tinge |

Manganese, which is distinct from other transition metals, possesses a unique combination of properties. Its hexagonal close-packed structure provides moderate strength and hardness, making it suitable for applications requiring wear resistance. While the relatively low melting point (1244°C) limits its high-temperature use compared with that of Ni, it simplifies processing. However, the true advantage of manganese lies in its exceptional electrical conductivity (1.44  $\mu\Omega\cdot\text{cm}$ ), which is one of the best among these metals. This property makes it indispensable in batteries and electrical conductors, ensuring efficient current flow. Although the thermal conductivity is lower than that of Ni, it is suitable for various applications. Unlike

Ni, manganese exhibits antiferromagnetic behavior, meaning that its magnetic domains cancel each other out. However, this does not diminish its importance. In fact, manganese plays a crucial role in strengthening and stabilizing ferromagnetic alloys such as steel. Additionally, its diverse oxidation states (+2, +3, +4, +6, +7) enable it to form various compounds, including pigments and oxidizing agents. Furthermore, manganese is readily available and relatively inexpensive, making it a cost-effective choice for numerous applications. It also readily forms alloys with other metals, further tailoring its properties for specific needs. For example, combining manganese with aluminum creates lightweight, high-strength alloys used in aerospace and transportation. In conclusion, while not magnetizable itself, manganese offers exceptional electrical conductivity, moderate strength, and a wide range of oxidation states. Its ability to form alloys with diverse properties and cost-effectiveness positions it as a vital element in modern industries, from batteries and pigments to high-strength alloys.[22],[23]

### 2.2.8.3 Main Physicochemical Characteristics of Cobalt (Co)

**Table 2.3** Fundamental Physicochemical Characteristics of Cobalt (Co)

| Property                       | Value                              |
|--------------------------------|------------------------------------|
| Atomic Number                  | 27                                 |
| Atomic Weight (g/mol)          | 58.93                              |
| Crystal Structure              | Hexagonal close-packed (HCP)       |
| Melting Point (°C)             | 1495                               |
| Boiling Point (°C)             | 3040                               |
| Density (g/cm <sup>3</sup> )   | 8.90                               |
| Electrical Resistivity (μΩ·cm) | 66.2                               |
| Thermal Conductivity (W/(m·K)) | 69.0                               |
| Hardness (Mohs scale)          | 5.0                                |
| Magnetic Properties            | Ferromagnetic                      |
| Oxidation State                | 0, +2, +3                          |
| Color                          | Metallic gray with a reddish tinge |

Like nickel, cobalt has a face-centered cubic structure, leading to good ductility and malleability. Its high melting point (1495°C) signifies excellent thermal stability, making it valuable for high-temperature applications such as jet engines and cutting tools. Additionally, its moderately high electrical resistivity indicates decent resistance to electrical current. The true standout for cobalt lies in its ferromagnetic nature. Like nickel, it can be magnetized, making it essential for permanent magnets, magnetic recording media, and electromagnets. This property has revolutionized data storage and enabled numerous technological advancements. The strength and hardness (Mohs scale of 5.0) of cobalt are comparable to those of nickel, further enhancing its suitability for structural and wear-resistant applications. Like nickel, its ability to form various oxidation states (+2, +3) leads to diverse compounds, including pigments and catalysts. However, the journey of cobalt extends beyond its inherent properties. Its availability and affordability contribute to its widespread use. Furthermore, it readily forms alloys with other metals, allowing for fine-tuning properties for specific needs. Combining cobalt with chromium and tungsten, for example, creates wear-resistant alloys used in cutting tools and prosthetics. In conclusion, the combination of strength, high-temperature resilience, and, most importantly, ferromagnetism make cobalt a vital element in diverse fields. Its ability to form valuable alloys and cost-effectiveness position it as a key player in technological advancements, from data storage to high-performance tools.[22],[23]

### 2.2.8.4 Main Physicochemical Characteristics of Iron (Fe)

**Table 2.4** Fundamental Physicochemical Characteristics of Iron (Fe)

| Property                                             | Value                             |
|------------------------------------------------------|-----------------------------------|
| Atomic Number                                        | 26                                |
| Atomic Weight (g/mol)                                | 55.85                             |
| Crystal Structure                                    | Body-centered cubic (BCC)         |
| Melting Point (°C)                                   | 1538                              |
| Boiling Point (°C)                                   | 3000                              |
| Density (g/cm <sup>3</sup> )                         | 7.87                              |
| Electrical Resistivity ( $\mu\Omega\cdot\text{cm}$ ) | 97.1                              |
| Thermal Conductivity (W/(m·K))                       | 80.2                              |
| Hardness (Mohs scale)                                | 4.0                               |
| Magnetic Properties                                  | Ferromagnetic                     |
| Oxidation State                                      | 0, +2, +3                         |
| Color                                                | Silvery-white with a bluish tinge |

Iron, the backbone of our world, has unique properties that extend far beyond its physical characteristics. Its body-centered cubic structure imparts remarkable strength and toughness, making it ideal for load-bearing applications such as the construction of beams and bridges. The high melting point (1538°C) ensures thermal stability at elevated temperatures, which is crucial for machinery and engines. While iron boasts decent thermal conductivity, its high electrical resistivity signifies its role as a poor conductor, limiting its use in electrical applications. However, this magnetic material exhibits ferromagnetism, readily aligns its domains to become a powerful magnet, drives motors and attracts needles across continents. Despite its vulnerability to rust, the true potential of iron lies in its transformative nature. Bonding with carbon creates a spectrum of steels, each tailored for specific needs. From the towering skyscrapers reaching for the sky to the delicate surgical tools mending our bodies, steel owes its diverse applications and unmatched strength to this partnership. Cast iron, where carbon is in the center stage, is highly brittle but unmatched in terms of machinability and wear resistance, making it perfect for cookware and engine blocks. However, iron's dance card does not end with carbon. Chromium endows stainless steel with resistance to corrosion, whereas

nickel amplifies its magnetic properties in transformers. Molybdenum toughens it to drill deep into the Earth's crust. These partnerships unlock a vast repertoire of properties, making iron a cornerstone of modern civilization. Beyond its utility, iron holds a deeper story. It is the fourth most abundant element on Earth, forged in the fiery hearts of stars and scattered across the cosmos. Every breath we take carries iron atoms, remnants of ancient stars woven into the fabric of life. Therefore, the next time you see a bridge standing tall or feel the comforting weight of a cast iron pan, remember, you're holding a piece of the universe, shaped by time and forever intertwined with our existence. In conclusion, the strength, magnetism, and ability of iron to transform through alloys make it an invaluable material for humans. Understanding its key characteristics and exploring its potential in combination with other elements unlock even more innovative applications in the future.[22],[23]

### 2.2.9 Influence of various parameters on the structure of Deposits

Key Factors Governing Electrodeposition Kinetics:[24],[25],[26],[1]

- **Electrolyte Metal Ion Concentration:** Higher concentrations generally translate to faster deposition due to the increased availability of ions at the cathode surface. However, excessively high concentrations can lead to diffusion limitations or unwanted side reactions.
- **Applied Potential:** The potential difference between the electrodes determines the driving force for the reduction reaction. Adjusting this potential allows control over the deposition rate, the characteristics of the deposited metal (such as morphology and crystal structure), and the overall energy efficiency of the process.
- **Electrolyte temperature:** Elevated temperatures typically increase ionic mobility and reaction rates, potentially accelerating deposition. However, excessively high temperatures might deteriorate deposit quality or trigger side reactions.
- **Electrolyte Composition:** Additional ions can significantly impact deposition kinetics. Certain ions might inhibit or accelerate the process, whereas others can codeposit with the target metal, influencing the final deposit properties.
- **Cathode surface area:** A larger cathode surface area allows for the simultaneous deposition of more metal ions, potentially increasing the overall deposition rate. However, a nonuniform current distribution over the cathode can lead to unevenness in the deposit.

- **Mass Transport:** Efficient delivery of metal ions to the cathode surface is crucial. Diffusion, convection, and migration mechanisms contribute to mass transport, and limitations in any of these mechanisms can hinder the deposition rate.
- **Electrode surface properties:** The surface morphology, roughness, and presence of impurities on the cathode can influence nucleation and growth processes, affecting the texture and adherence of the deposit.
- **Conductivity of the Electrolyte:** The incorporation of neutral electrolytic elements, which do not participate in the electrolytic process but reduce the electrolytic resistance, is often beneficial. This allows the voltage applied to the cell to be reduced, which results in lower energy consumption.
- **Current density:** If the current density is increased, a positive effect can be observed at first: the formation of germs is accelerated without their growth being altered. However, if the current density becomes too high, the growth of the crystals becomes irregular. Beyond a certain threshold, a powdery deposit forms and disintegrates rapidly.
- **Agitation of the Electrolyte:** During electrolysis, the concentration of the electrolyte at the cathode decreases. To achieve a consistent and uniform deposit, maintaining proper agitation is essential, this helps to equalize the concentrations, facilitates the diffusion of ions, and prevents the depletion of the diffusion layer.
- **pH of the Bath:** The pH of the bath is also crucial in the plating process. In nickel plating baths, excessively high pH results in a dull deposit. To prevent these issues, the electrolyte solutions are kept at a stable pH by adding buffer substances.
- **Effect of Deposition Time:** Deposition time is a crucial element in the electrodeposition technique for metals and alloys. The deposition time directly affects the texture of the coating and its ability to adhere firmly to the metallic substrate while considerably influencing its brightness.
- **Additives:** Additives can be of various natures, organic or inorganic. They are commonly added in small quantities to the electrolyte. They alter the electrodeposition mechanism by specifically affecting the speed of the nucleation and/or growth step.

## 2.3 Electrochemistry of water splitting

Electrochemistry explores the relationship between electrical energy and Gibbs free energy and how their interaction drives chemical reactions. These reactions occur at the interface between an electronic conductor (the electrode) and an ionic conductor (the electrolyte). They can be induced by an external current, such as in electrolysis, or by a spontaneous chemical reaction, such as in a battery. Redox reactions, which involve the transfer of electrons, are key examples of electrochemical processes. One such process, water splitting through electrolysis, involves the use of an external voltage to split water into its basic components, hydrogen and oxygen, by facilitating the flow of electrons.

### 2.3.1 Electrochemical cell and reactions

**Figure 2.9** A typical electrolysis cell for water splitting consists of three main components: a cathode, an anode, and an aqueous electrolyte. When a sufficiently high external voltage is applied across the two electrodes, two key reactions occur: the hydrogen evolution reaction (HER) at the cathode (reduction reaction) and the oxygen evolution reaction (OER) at the anode (oxidation reaction). At the cathode, hydrogen gas is produced, whereas at the anode, oxygen gas is released, with both reactions driven by the applied voltage.[27],[28]

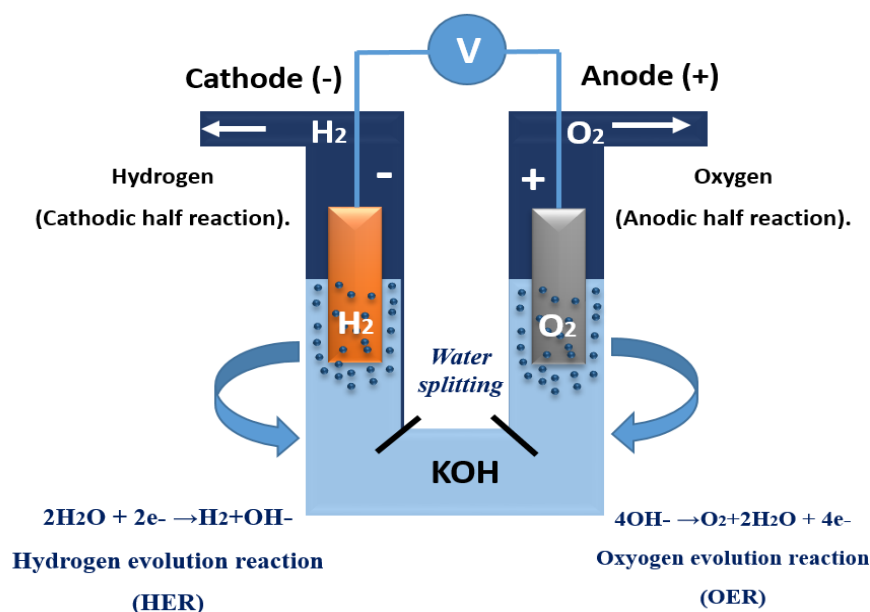
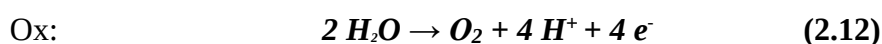
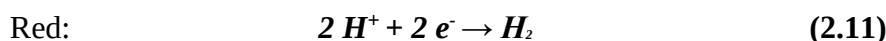


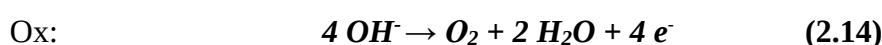
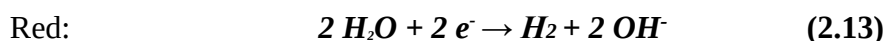
**Figure 2.9** Diagram of an alkaline water electrolyzer.[29]

Depending on the pH of the aqueous electrolyte used for water splitting, the electrochemical half-reaction can typically be represented by the following equations: **(2.11)** to **(2.14)**: [30]

In acidic or neutral solutions:



In alkaline solution:



Adding the two half-reaction pairings results in the same total water splitting reaction. **(2.15)**: [31]



## 2.3.2 Thermodynamic fundamentals

### 2.3.2.1 Cell potential

For a general cell reaction, the Gibbs free energy change of the reaction ( $\Delta_r G$ ) can be written as

$$\Delta_r G = - nFE \quad (2.16)$$

where  $n$  is the number of electrons transferred in the reaction,  $F$  is the Faraday constant (96,485.338 C/mol), and  $E$  is the maximum potential between two electrodes, also known as the zero-current cell potential. This potential is the applied bias potential so that no current flows through the cell. Notably, owing to the minus sign in equation **(2.16)**, all spontaneous reactions (i.e., those with  $\Delta_r G < 0$ ) have a positive equilibrium potential ( $E > 0$ ), and vice versa. If there is a current flowing through an electrochemical cell as a result of a chemical process (i.e. the cell is discharging or behaving as a galvanic cell), then the potential difference between the electrodes, or cell voltage  $E_{\text{galv cell}} < E$ , and if the current flows through an electrolysis cell, then the potential required to drive the cell  $E_{\text{elec cell}} > E$ .

If the reactants and products of the cell reaction are in their standard states at the temperature of the transformation, that is, if the gases are at unit atmospheric pressure and the soluble species are at unit mean activity, equation **(2.17)** can be written as:

$$\Delta_r G_0 = -nFE_0 \quad (2.17)$$

In this case,  $\Delta_r G_0$  is the standard free energy, and the potential is known as the standard cell potential ( $E_0$ ) or the standard potential.

The reaction free energy  $\Delta_r G$  varies with the composition of the reaction mixture as follows:

$$\Delta_r G = \Delta_r G_0 + RT \ln Q \quad (2.18)$$

where  $R$  is the universal gas constant (8.3145 J/mol. K),  $T$  is the absolute temperature, and  $Q$  is the reaction quotient for the cell reaction, which is formulated by writing the activities of the products in the numerator and those of the reactants in the denominator. By combining equations (2.16) and (2.18), the obtained mathematical expression describing the cell potential at equilibrium is known as the Nernst equation:

$$E = E_0 - \frac{RT}{nF} \ln Q \quad (2.19)$$

### 2.3.2.2 Half-cell potential

The following half-cell reaction was considered:



The half-cell electrode potential at equilibrium ( $\mathcal{E}$ ) can be related to the standard electrode potential ( $\mathcal{E}_0$ ) via the Nernst equation (2.21): [32],[33]

$$\mathcal{E} = \mathcal{E}_0 + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Red}} \quad (2.21)$$

The half-cell reaction involves  $n$  transferred electrons, with  $a_{Ox}$  and  $a_{Red}$  representing the activities of the oxidizing and reducing agents, respectively. The activity of species  $i$  ( $a_i$ ) is defined as  $a_i = \gamma_i c_i$ , where  $\gamma_i$  is the activity coefficient and  $c_i$  is the mole fraction. At room temperature (25°C), the Nernst equation is simplified by combining the universal gas constant and the Faraday constant, and it is frequently expressed in terms of the base -10 logarithm, which is written as equation (2.22):

$$\mathcal{E} = \mathcal{E}_0 + \frac{0.059}{n} \lg \frac{a_{Ox}}{a_{Red}} \quad (2.22)$$

Since the particular potential of a half-cell is not directly measurable but rather the difference between two half-cells, the standard hydrogen electrode (SHE) serves as the reference point for all other half-cell reactions. The SHE is made up of a platinized platinum electrode immersed in an aqueous solution with a unit activity of  $H^+$  (aq) that comes into contact with hydrogen gas at one atmosphere of pressure. The potential of the SHE is arbitrarily set to zero at all temperatures. Each half-cell reaction has a unique standard potential, which is determined as the standard cell potential versus the SHE. Common standard potentials for various electrodes (e.g., metal-ion, gas, or redox) are shown in tabular form.[32] The standard electrode potentials for water splitting half-reactions (2.11) to (2.14) are determined to be  $\mathcal{E}_{(H^+/H_2)} = 0$  V,  $\mathcal{E}_{(O_2/H_2O)} = 1.23$  V,  $\mathcal{E}_{(H_2O/H_2)} = -0.83$  V, and  $\mathcal{E}_{(O_2/OH^-)} = 0.40$  V. In an electrochemical cell, the potential difference between the two electrodes is equal to the cell potential.

$$E = \mathcal{E}_{cathode} - \mathcal{E}_{anode} \quad (2.23)$$

Thus, the total potential difference gives the minimum bias potential of 1.23 V required for the water splitting event to occur.

By applying equation (2.22) to the HER and OER half-reactions, the electrode potentials at equilibrium ( $\mathcal{E}$ ) versus the SHE are given by equations (2.24) and (2.25):

$$HER: \mathcal{E} = 0 - 0.059 \text{ pH} \quad (2.24)$$

$$OER: \mathcal{E} = 1.23 - 0.059 \text{ pH} \quad (2.25)$$

Importantly, the potentials required to drive the cell reaction depend on the pH when measured on the standard hydrogen electrode (SHE) scale. However, when evaluating the performance of a catalyst for one of the half-reactions via a potentiostat, the pH of the electrolyte must be considered. In such cases, the potential applies only to the specific half-reaction, and its value varies with pH, as illustrated in **Figure 2.9**. On the reversible hydrogen electrode (RHE) scale, the equilibrium potentials for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) are 0 V and 1.23 V, respectively, and these values remain constant regardless of the pH.

### 2.3.3 Kinetics of electrode reactions

#### 2.3.3.1 Overpotentials

As mentioned earlier, the minimum voltage required to drive the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) for water splitting is 1.23 V under standard conditions. However, additional energy is needed due to internal resistance within the cell system, including solution resistance, contact resistance, and the intrinsic activation barriers of electrochemical reactions. The term "overpotential" ( $\eta$ ) describes the difference between the measured electrode potential ( $E_i$ ) at a specific current ( $i$ ) and the equilibrium potential ( $E_{eq}$ ) when no current flows.

$$\eta = E_i - E_{eq} \quad (2.26)$$

For a water splitting system, the overall operating voltage ( $V_{op}$ ) can be expressed as:

$$V_{op} = 1.23 + \sum \eta + iR \quad (2.27)$$

where  $iR$  represents the ohmic drop occurring due to the internal resistance of the system, which can be minimized by optimizing the cell design;  $\sum \eta$  is the sum over all overpotentials at the anode and cathode electrodes. For an electrode reaction, the overpotential can be considered a sum of different overpotential contributions, including the electron transfer overpotential ( $\eta_{CT}$ ), the mass transport overpotential ( $\eta_{MT}$ ) and the reaction overpotential ( $\eta_R$ ).[32]

At low current densities, the variation in electrode potential with increasing current is influenced primarily by the electron transfer process across the interface between the electronically conducting electrode and the ionically conducting electrolyte. This phenomenon is referred to as the electron transfer overpotential. The rate of electron transfer at a given overpotential depends on the specific reactants involved, as well as the properties of the electrolyte and electrode materials. At higher current densities, electron transfer generally ceases to be the limiting factor. Instead, limitations arise from the slow transport of reactants to the electrode surface or the removal of products away from it. This limitation, governed by ionic transport, is known as the mass transport overpotential. In addition to the effects of electron transfer and mass transport, the rate of an electrochemical reaction can also be constrained by chemical equilibria that occur either before or after the electron transfer step. Such limitations are particularly significant in conditions where electron transfer and mass transport are inherently rapid. Examples include the adsorption or desorption of species

involved in the reaction or chemical transformations preceding or following electron transfer. These processes result in a reaction overpotential.

### 2.3.4 The hydrogen evolution reaction (HER)

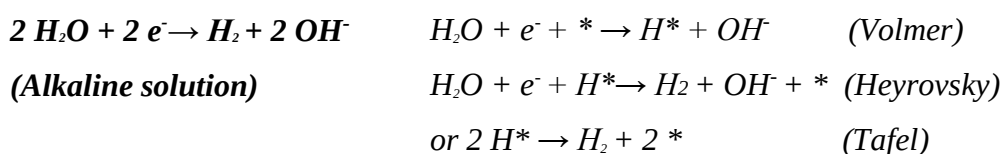
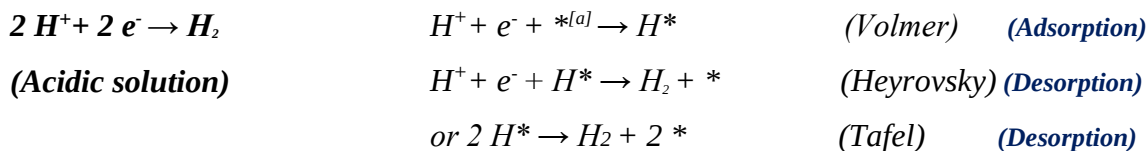
#### 2.3.4.1 Reaction mechanism and kinetics

The hydrogen evolution reaction (HER) represents the cathodic half of the overall water-splitting process, involving the transfer of two electrons to produce one molecule of hydrogen. The reaction proceeds through a single catalytic intermediate,  $H^*$  (where  $*$  denotes an active site on the electrode surface). The HER can occur via two distinct mechanisms: the Volmer–Heyrovsky mechanism or the Volmer–Tafel mechanism.[34][29],[35] The mechanism through which the hydrogen evolution reaction (HER) occurs is heavily influenced by the type of electrolyte, the surface chemistry, and the electronic structure of the catalyst. Typically, the mechanism is identified on the basis of the experimentally measured Tafel slope value.[36],[37] **Table 2.5** provides a summary of the overall equation and the reaction steps involved in the hydrogen evolution reaction (HER). [34],[29]

---

**Overall reaction (Condition)    Reaction pathway**


---



[a] \* represents a binding site at the electrode surface.

The initial step of the hydrogen evolution reaction (HER) in acidic media involves the discharge of protons onto the electrode surface, resulting in the formation of adsorbed hydrogen atoms ( $H^*$ ). This occurs through the interaction of a proton from the electrolyte with an electron supplied via the electrode surface, a process known as the Volmer reaction. The Tafel slope for the Volmer reaction ( $b_{1,v}$ ) is defined as: [38]

$$b_{1,v} = 2.303 \frac{RT}{\alpha F} \quad (2.28)$$

where  $R$  is the ideal gas constant (8.3145 J/mol. K),  $T$  is the absolute temperature,  $\alpha$  is the charge transfer coefficient (typically taken as 0.5), and  $F$  is the Faraday constant (96 485 C/mol). In contrast to acidic environments, where many protons are available to promote the reaction,[39][40] the hydrogen intermediate ( $H^*$ ) in alkaline solutions is formed by an initial water dissociation process in the Volmer reaction. [39] This additional step may increase the energy barrier and affect the overall reaction rate[41]. Depending on the coverage of adsorbed hydrogen ( $H^*$ ), there are two possible steps for the HER to proceed either by electrochemical  $H_2$  desorption, known as the Heyrovsky step, or by chemical desorption of  $H_2$ , known as the Tafel step. [38] If the coverage of  $H^*$  is low and the electrode surface has sufficient active sites near the  $H^*$  sites, the adsorbed  $H$  atoms will preferably bind to a nearby proton, which is simultaneously reduced to  $H$ , to evolve a hydrogen molecule. This is the so-called Heyrovsky step, and its Tafel slope ( $b_{2,H}$ ) can be given by

$$b_{2,H} = 2.303 \frac{RT}{(1+\alpha)F} \quad (2.29)$$

In the case of high  $H^*$  coverage, two adjacent  $H^*$  will chemically bind together and release one hydrogen molecule. This is the Tafel step, and its Tafel slope can be expressed as

$$b_{2,T} = 2.303 \frac{RT}{2F} \quad (2.30)$$

At 25°C (i.e.,  $T = 298.15$  K), the Tafel slopes for the Volmer, Heyrovsky, and Tafel reactions were calculated to be 118, 39, and 29 mV/dec, respectively. Tafel slope values serve as a useful reference for roughly analyzing the reaction pathway and identifying the rate-determining step of a catalyst in a specific electrolyte. These values provide valuable insights into the underlying reaction mechanism and the factors influencing catalytic performance.[39],[36]

### 2.3.5 The oxygen evolution reaction (OER)

#### 2.3.5.1 Reaction mechanism and kinetics

The OER, which is an anodic half-cell reaction, is significantly more complex than the hydrogen evolution reaction. It involves either a direct four-electron ( $4e^-$ ) transfer process or a two-step two-electron ( $2e^-$ ) transfer mechanism. Various research groups have proposed potential reaction pathways for oxygen evolution, depending on whether the process occurs under acidic or alkaline conditions. The generally accepted overall reaction equations for the OER are summarized in **Table 2.6**. [42],[43],[44],[45],[46]. The proposed mechanism for the oxygen evolution reaction (OER) begins with the initial adsorption of water molecules or hydroxide ions onto the catalytically active site (\*) in acidic or alkaline solutions. In the subsequent step, the adsorbed hydroxide ions ( $*OH$ ) are converted into oxygen-containing species ( $*O$ ). From this point, there are two possible pathways to generate molecular oxygen ( $O_2$ ) from  $*O$  intermediates:

1. Direct coupling of two adjacent  $*O$  intermediates results in the formation of  $O_2(g)$ .
2. The formation of a peroxide ( $*OOH$ ) intermediate during the third electron transfer step, which then decomposes during the fourth electron transfer step, releases  $O_2(g)$ .

These pathways highlight the complexity of the OER and its dependence on the reaction environment and catalytic surface.[43],[44],[45]

**Table 2.6** Proposed reaction mechanisms for the OER in acidic and alkaline solutions.

| Overall reaction (Condition)                                                                        | Reaction pathway                                                                                                                                                                                                                                                                                                                                                            |
|-----------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$<br>(Acidic solution)    | $\text{H}_2\text{O} + *^{[a]} \rightarrow *OH + \text{H}^+ + \text{e}^-$ (Adsorption)<br>$*OH \rightarrow *O + \text{H}^+ + \text{e}^-$ (Oxydation)<br>$2 *O \rightarrow 2* + \text{O}_2$ (Desorption)<br>or $*O + \text{H}_2\text{O} \rightarrow *OOH + \text{H}^+ + \text{e}^-$<br>$*OOH \rightarrow *O_2 + \text{H}^+ + \text{e}^-$<br>$*O_2 \rightarrow \text{O}_2 + *$ |
| $4 \text{OH}^- \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^-$<br>(Alkaline solution) | $\text{OH}^- + * \rightarrow *OH + \text{e}^-$<br>$*OH + \text{OH}^- \rightarrow \text{H}_2\text{O} + *O + \text{e}^-$<br>$2 *O \rightarrow 2* + \text{O}_2$<br>or $*O + \text{OH}^- \rightarrow *OOH + \text{e}^-$<br>$*OOH + \text{OH}^- \rightarrow *O_2 + \text{H}_2\text{O} + \text{e}^-$<br>$*O_2 \rightarrow \text{O}_2 + *$                                         |

[a] \* represents a binding site at the electrode surface.

The kinetic barriers related to each elementary step contribute to the overall required activation overpotential. Generally, the overpotential ( $\eta$ ), exchange current density ( $j_0$ ), and Tafel slope ( $b$ ) are the parameters used to evaluate the reaction kinetics of an OER electrocatalyst and are critical for obtaining insightful information on the OER mechanism. [16],[47] Since the OER involves the transfer of four electrons/protons and the possible formation of a range of adsorbed intermediates (e.g.  $*O$ ,  $*OH$ ,  $*OOH$ ), it may give rise to many possible pathways with different rate-determining reaction steps.[48] Moreover, the rate-determining steps for different mechanisms may have similar Tafel slopes. [48] These are the reasons why there is no Tafel slope classification in the literature, which can be used to analyze the reaction route and the rate-determining step for the OER, as has been proposed for the HER [48]. Some of the most typical Tafel slopes for the OER based on metal oxide catalysts are reported to be 120 mV/dec and 60 mV/dec. [49]

### 2.3.6 Nickel

#### 2.3.6.1 History and uses of nickel

Nickel has been used for more than 2000 years, with its origins in China, where it has been utilized in alloys. However, it was not until 1751 that A. F. Cronstedt isolated the metal in Sweden, giving it its name. Nickel constitutes approximately 1.8% of the Earth's total substance, making it the seventh most abundant element, although its mass abundance in the Earth's crust is only 9 ppm. The major producers of nickel include Russia, Canada, and New Caledonia. Nickel has a wide range of applications, from everyday uses to advanced aerospace components. Approximately 1400 tons are produced annually, with 84% used in alloys, 9% in plating processes, and the remainder in smaller applications such as coins, electronics, and batteries. Nickel-based catalysts are considered highly efficient for methane reforming to produce hydrogen owing to their ability to adsorb hydrogen and hydrocarbons. [50],[51] In addition, nickel plays a significant role in alkaline fuel cells (AFCs) and alkaline membrane fuel cells (AMFCs), where it is commonly used as a cathode material. [52],[53] Historically, nickel has been closely associated with NiCd and NiMH batteries, which have been the focus of extensive research in recent decades. However, with the advent of lithium-ion batteries, the use of NiMH batteries has diminished, shifting the focus of research toward fuel cells (FCs).

#### 2.3.6.2 Electrochemical properties of the oxidized nickel and nickel surfaces

The Pourbaix diagram serves as a thermodynamic map that illustrates all possible stable phases of an aqueous electrochemical system, including passivation, corrosion, and metallic phases. **Figure 2.10** presents the Pourbaix diagram for nickel (Ni) [54].

At negative potentials, nickel exists in its metallic form. However, as the potential increases beyond -0.5 V (vs. the standard hydrogen electrode) in an acidic electrolyte,  $\text{Ni}^{2+}$  ions become predominant. In acidic media (up to pH  $\sim 3$ ), corrosion is the dominant process. Between pH 3 and 9,  $\text{Ni}(\text{OH})_3$  can also form at higher potentials. At pH values above 12 and intermediate potentials, NiO transitions into a soluble species,  $\text{H}\text{NiO}_2^-$ . At potentials exceeding 1 V, the  $\text{Ni}^{3+}$  oxide species becomes the prevailing phase. Nickel, with its electronic configuration of  $3d^8 4s^2$ , has oxidation states ranging from 0 to IV. Typically, nickel chemistry is dominated by Ni(II) species, as Ni(III) complexes exhibit low stability in aqueous solutions and are primarily stable in acidic environments.

According to Bode et al. [55], there are two forms of  $\text{Ni(OH)}_2$  and  $\text{NiOOH}$ , and their electrochemical reactions are illustrated in **Figure 2.11**. The  $\alpha\text{-Ni(OH)}_2$  phase features a turbostratic structure with tilted layers and a large volume [55],[56]. The structures of the  $\alpha$  and  $\gamma$  phases are highly influenced by the  $\text{OH}^-$  concentration and the cations present in the solution, as these ions are situated between the layers [57]. During consecutive potential sweeps in alkaline solutions,  $\alpha\text{-Ni(OH)}_2$  transforms into  $\beta\text{-Ni(OH)}_2$ , resulting in a 59% reduction in volume due to a significant decrease in layer spacing. When  $\alpha\text{-Ni(OH)}_2$  is thermodynamically unstable, it becomes positively charged and converts into  $\gamma\text{-NiOOH}$ . During reverse charging, the  $\gamma$  phase may revert to  $\alpha\text{-Ni(OH)}_2$  or directly transform into  $\beta\text{-Ni(OH)}_2$  [58]. After several potential cycles in alkaline solutions, the  $\beta$  phase stabilizes on the electrode surface, and the  $\gamma\text{-NiOOH}$  phase can only reappear through overcharging the system.

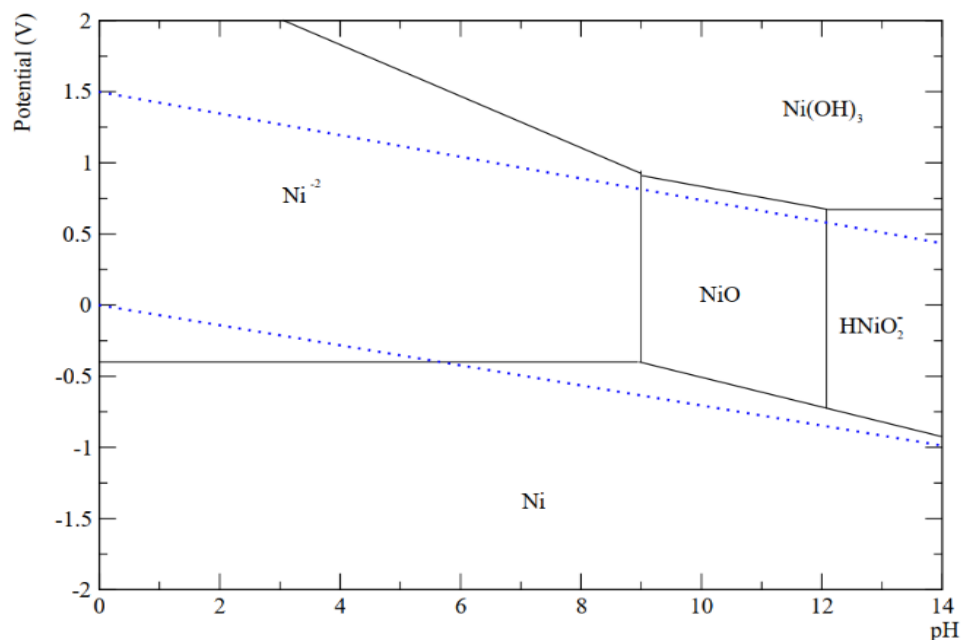


**Figure 2.10** Pourbaix diagram for Ni at 25°C. Adapted from [54]

### 2.3.6.3 Cyclic voltammetry of the Ni electrodes

Cyclic voltammetry (CV) information concerning the formation of oxides and hydroxides on nickel electrodes in alkaline solutions can be obtained, as discussed in **Figure 2.11** and the literature.[59],[60],[61]

Recent studies have revealed that air-oxidized nickel has a bilayer structure. The outer layer at the oxide/solution interface consists of  $\alpha$ -Ni(OH)<sub>2</sub>, whereas the inner layer at the oxide/metal interface is composed of non-stoichiometric NiO<sub>x</sub>. [59], [61]

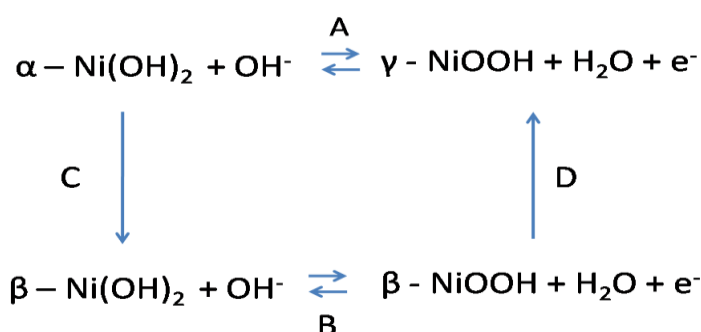


**Figure 2.11** Bode diagram for Ni, A and B are electrochemical reactions, and C and D are chemical reactions. [55]

The  $\alpha$  and  $\gamma$  phases of nickel hydroxides are highly dependent on the concentration of hydroxide ions (OH<sup>-</sup>) and the types of cations present in the solution, as these ions are incorporated into the structure [64-66]. After several potential scans in an alkaline solution,  $\alpha$ -Ni(OH)<sub>2</sub> transitions into  $\beta$ -Ni(OH)<sub>2</sub>, accompanied by a volume reduction due to the removal of water and ions from the interlayer spaces. This transition explains the differences observed between the first and second scans. However, when  $\alpha$ -Ni(OH)<sub>2</sub> becomes thermodynamically unstable, it transforms into  $\gamma$ -NiOOH. During the reverse scan, the  $\gamma$  phase reverts to either  $\alpha$ -Ni(OH)<sub>2</sub> or  $\beta$ -Ni(OH)<sub>2</sub>, as illustrated in **Figure 2.12**.

Since the mid-20th century, the hydrogen evolution reaction (HER) of metallic nickel has been the subject of extensive research. The reaction generally follows the Volmer–Tafel or Volmer–Heyrovsky mechanism [67],[68]. Denavathan et al. [68] studied the HER on nickel via the double-layer charging method to determine surface coverage. At current densities up to 0.5

mA/cm<sup>2</sup>, the Volmer step was identified as the rate-determining step. They suggested that the gradient of  $\log c$  vs.  $\log \theta$  (where  $c$  is the cathodic current density and  $\theta$  is the coverage) indicated a fast Tafel recombination process as the desorption step. Ahn et al. [69] synthesized nickel-based dendrites, particles, and films via controlled electrodeposition via nickel chloride. Their results revealed that the HER activity increased in the following order: dendrite > particle > film > foil. This was attributed to the highly (111)-oriented structures in the nickel dendrites compared with those in the polycrystalline nickel dendrites.

In contrast, Floner et al. [70] demonstrated that the hydrogen oxidation reaction (HOR) is structure sensitive, decreasing in activity in the order of Ni(110) > Ni(100) > Ni(111). Ni(110) was found to be six times more active than polycrystalline nickel. LeRoy et al. [71] reported that hydride formation increased the overpotential during the HER, a finding confirmed by X-ray diffraction and SEM [72]. Hydrides form due to interactions between metallic nickel and dissolved hydrogen, which shifts the reaction pathway to a desorption-limited mechanism, increasing the Tafel slope.

Weininger et al. [74] reported nickel oxidation or hydroxide adsorption at low potentials. Surface hydrogen intermediates may be replaced by hydroxide ions to form water and nickel, reducing the catalytic activity. Nickel, under ambient conditions, oxidizes into a mixed layer of NiO and Ni(OH)<sub>2</sub> [61], [59]. Enhanced activity has been reported for surfaces where metallic nickel coexists with oxidized nickel species such as NiO or  $\beta$ -Ni(OH)<sub>2</sub> [76],[77], likely because synergistic effects improve water dissociation.

The number of oxide–hydroxide interfaces is critical for non-precious metal catalysts. Gong et al. [77] demonstrated that nanoscale NiO/Ni interfaces, created through low-pressure decomposition, significantly improved HER activity compared with NiO/CNT or Ni/CNT.

Oshchepkov et al. [78] reported that the electrocatalytic activity of nickel for the HOR and HER depends on electrode pretreatment. Ambient exposure or controlled chemical conditions increase the activity due to the presence of NiO, as confirmed by ex situ XPS. By reducing the adsorption energy of hydrogen intermediates, partially oxidized nickel surfaces, where metallic nickel and NiO coexist, exhibit high HER and HOR activities, enhancing the Volmer step.

Heterostructure interfaces offer further opportunities to optimize adsorption/desorption energies. Subbaraman et al. [78] created nanosized Ni(OH)<sub>2</sub> clusters on platinum electrodes,

improving the HER activity sevenfold despite reducing the surface area by 35%. This enhancement was attributed to water dissociation and the stabilization of cations, which formed a compact double layer.

Krstajic et al. [67] concluded that the HER mechanism shifts from Volmer-Tafel to Volmer-Heyrovsky at specific potentials, whereas Kreysa et al. [80] identified the Tafel recombination step as the rate-determining process due to slow surface diffusion of adsorbed hydrogen.

Nickel structures with high surface areas are promising catalysts for the HER, but limitations remain owing to the intrinsic activity of metallic nickel. The adsorption energies of H, OH<sup>-</sup>, and H<sub>2</sub>O significantly influence the catalytic performance and can be effectively studied via density functional theory (DFT). Theoretical approaches allow for rapid exploration of new catalysts, saving experimental efforts by providing insights into promising materials. The calculation of hydrogen adsorption energies and reaction activation barriers can guide experimentalists in designing better catalysts.

DFT studies by Fajin et al. [82] demonstrated the importance of step sites and adsorption geometries, whereas Pozzo et al. [84] identified the top site as the most favorable. Modeling current–potential curves for HER/HOR has become a valuable tool, enabling parameter extraction for various electrode materials. Future research combining theoretical modeling and experimental validation will continue to advance the understanding and development of nickel-based HER and HOR catalysts.

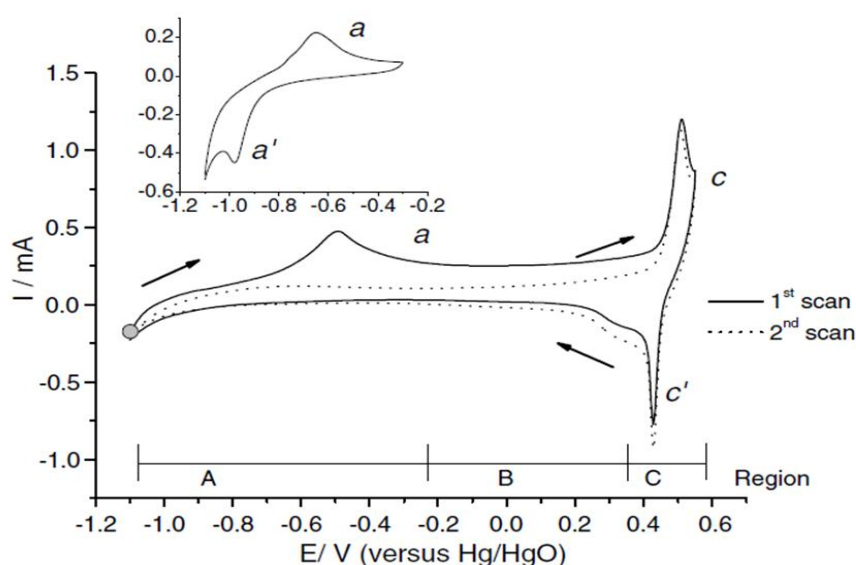


**Figure 2.12** Cyclic voltammograms of Ni in 1 M KOH. Data taken from [61]

## 2.4 Fuel cells

### 2.4.1 Design

Fuel cells (FCs) are devices that directly and spontaneously convert chemical energy into electrical energy through electrochemical reactions. In these reactions, the fuel is oxidized at the anode, whereas oxygen is reduced at the cathode. [86] **Figure 2.2** shows the schematic structure of a fuel cell. FCs are commonly classified into several types on the basis of the electrolyte material used. [87-89] They can also be grouped according to their operating temperature. High-temperature fuel cells include molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs), which function at temperatures above 473 K. In contrast, low-temperature fuel cells, such as phosphoric acid fuel cells (PAFCs), proton exchange membrane fuel cells (PEMFCs), and alkaline fuel cells (AFCs), operate at lower temperatures.

As previously noted, the reactions in a fuel cell occur in distinct sections connected by an external circuit, allowing electrons generated at the anode to flow. The electrolyte, which can be a liquid, solid, or polymer, provides a medium for ion conduction. Each part of the fuel cell has associated challenges. This study focuses on reactions at the anode and examines how its composition influences electrocatalysis.

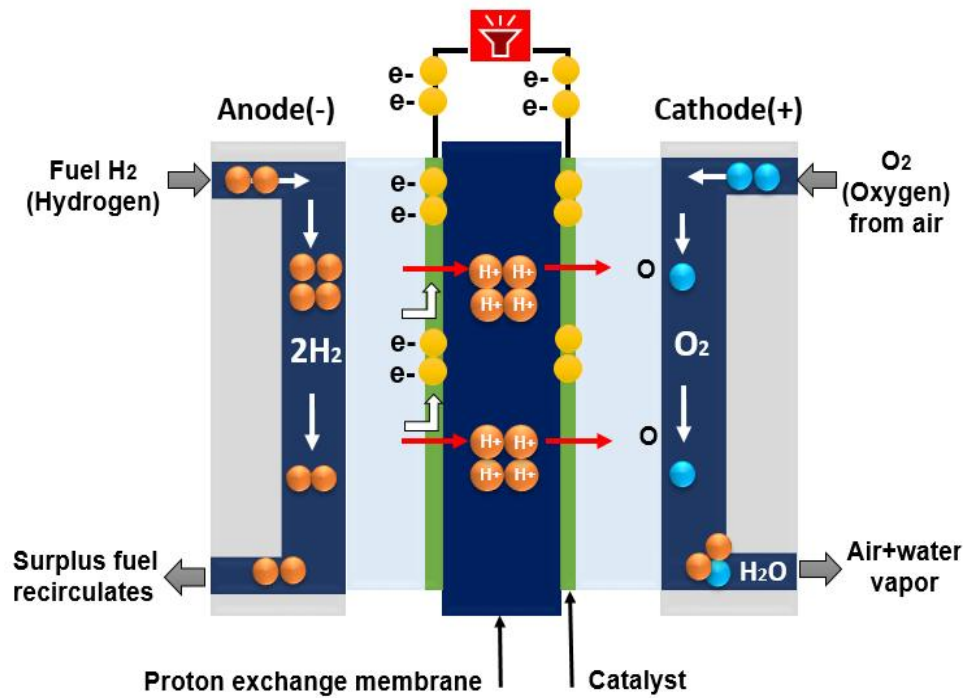


**Figure 2.13** Schematic representation of the fuel cell

### 2.4.2 Types

Fuel cells (FCs) are of various types, each tailored for specific applications and characterized by unique operating temperatures, advantages, and limitations. The key details for each type are summarized in **Table 2.7**.

**Table 2.7** Fuel cell types. Adapted from [26]

| FUEL CELL TYPE                            | COMMON ELECTROLYTE                                                         | OPERATING TEMPERATURE | APPLICATIONS                                                  | ADVANTAGES                                                                      | CHALLENGES                                                                         |
|-------------------------------------------|----------------------------------------------------------------------------|-----------------------|---------------------------------------------------------------|---------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
| <b>Polymer electrolyte membrane (PEM)</b> | Perfluorosulfonic acid                                                     | <120°C                | Backup power<br>Portable power<br>Distributed generation      | Solid electrolyte reduces corrosion and electrolyte management problems.        | Expensive catalysts<br>Sensitive to fuel impurities                                |
| <b>Alkaline (AFC)</b>                     | Aqueous potassium hydroxide                                                | <100°C                | Space<br>Backup power<br>Transportation                       | Wider range of stable materials allows lower cost components<br>Low temperature | Sensitive to CO <sub>2</sub> in fuel and air<br>Electrolyte conductivity (polymer) |
| <b>Phosphoric acid (PAFC)</b>             | Phosphoric acid soaked in a porous matrix or imbibed in a polymer membrane | 150°–200°C            | Distributed generation                                        | Suitable for CHP<br>Increased tolerance to fuel impurities                      | Expensive catalysts<br>Long start-up time                                          |
| <b>Molten carbonate (MCFC)</b>            | Molten lithium, sodium, and/or potassium carbonates                        | 600°–700°C            | Electric utility<br>Distributed generation                    | High efficiency<br>Fuel flexibility<br>Suitable for CHP                         | High temperature corrosion and breakdown of cell components                        |
| <b>Solid oxide (SOFC)</b>                 | Yttria stabilized zirconia                                                 | 500°–1000°C           | Auxiliary power<br>Electric utility<br>Distributed generation | High efficiency<br>Fuel flexibility<br>Solid electrolyte<br>Suitable for CHP    | High temperature corrosion and breakdown of cell components                        |

Phosphoric acid fuel cells (PAFCs) were the first type of fuel cell commercialized by the United Technology Corporation. Currently, approximately 100 units are operational worldwide, with an initial efficiency of 42%. PAFCs offer notable advantages, including high tolerance to carbon monoxide (CO) and the potential for generating heat and electricity. However, they require the use of noble metals for both the anode and cathode, and their performance is significantly influenced by electrode flooding and the adsorption of phosphate anions.

In contrast, high-temperature fuel cells allow the use of nonnoble materials as catalysts. The elevated operating temperatures of these materials increase the reaction kinetics and enable onsite fuel reforming.

Alkaline fuel cells (AFCs) have a long history of use, dating back to the 1950s, during NASA's Apollo program, and continue to be employed in aerospace applications. [90] Recently, interest in AFCs has increased due to their advantages, such as low operating temperatures (23–70°C) and faster reaction kinetics at the cathode under alkaline conditions, which result in higher cell voltages. However, AFCs have limitations related to their potassium hydroxide (KOH) electrolyte, which is highly sensitive to carbon dioxide (CO<sub>2</sub>). [91] If CO<sub>2</sub> is present in the feed gases, it reacts with KOH to form potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), leading to reduced performance due to changes in electrolyte conductivity and the formation of solid deposits. An improper electrolyte volume can also cause issues, such as electrode flooding or drying. While solutions such as electrolyte circulation have been proposed to mitigate carbonate formation, their success has been limited.

Most AFCs rely on noble metal catalysts, making them costly and less viable for large-scale commercialization. Nickel is considered a promising alternative to platinum due to its lower cost. However, pure nickel electrodes demonstrate significantly lower performance for the hydrogen evolution reaction (HER) in alkaline media than palladium or platinum electrodes do, primarily due to strong adsorption of hydrogen intermediates on the nickel catalyst surface. [92]

## 2.4.3 Hydrogen Reactions

### 2.4.3.1 Hydrogen Reactions in Acidic Media

The total HER/HOR reaction can be written as:[93]



Hydrogen electrode reactions were the first electrochemical reactions explored. The many-proposed HER model is as follows:



The reaction mechanism can proceed through two pathways: The Tafel-Volmer mechanism (Tafel step, **eq. 2.33**, followed by the Volmer step, **eq. 2.32**) or the Heyrovsky–Volmer mechanism (Heyrovsky step, **eq. 2.34**, followed by the Volmer step, **eq. 2.32**). In the Tafel–Volmer pathway, molecular hydrogen ( $H_2$ ) dissociates in a chemical step, followed by electron transfer and proton hydration. In contrast, the Heyrovsky–Volmer pathway involves electron transfer in both steps. The choice of mechanism is highly dependent on the electrode material, the composition of the electrolyte, and the electrode potential. Under certain conditions, the Tafel–Volmer mechanism can transition to the Heyrovsky–Volmer pathway or a hybrid of both mechanisms.

For optimal performance, a catalyst must meet specific criteria, including high catalytic activity, chemical and mechanical stability, and cost-effectiveness. References [94] and [95] summarize the key properties of an ideal catalyst: low hydrogen overvoltage in industrial applications, no potential drift, excellent chemical and electrochemical stability, long operational lifespan, no release of harmful byproducts, strong adhesion to the support material, low sensitivity to impurities and current shutdown, minimal safety or environmental risks during manufacturing, and ease of preparation.

In the subsequent sections, the factors influencing the reaction rate are discussed in detail, with a particular focus on the electrode material, heat of adsorption, and pH.

#### 2.4.4 Electrode materials

The exchange current density in the hydrogen evolution reaction (HER) can vary by up to ten orders of magnitude depending on the electrode material. Researchers have extensively studied the correlations between the HER rate and the physical and chemical properties of electrode materials [96]. One such correlation examines the relationship between the exchange current density and the adsorption energy of hydrogen atoms on the electrode surface. This relationship is depicted in the so-called "Volcano plot," named for its characteristic shape. This trend aligns with Sabatier's principle, which states that the interaction between a catalyst and an adsorbed intermediate should be neither too strong nor too weak for optimal activity. A version of this plot, compiled by Trasatti, is illustrated in **Figure 2.14**.

When Trasatti compiled a volcano plot in 1972, hydride formation energy ( $E_{M-H}$ ) was used in place of hydrogen adsorption energy the lack of reliable data on adsorption energies at the time. For low  $E_{M-H}$  values, the Volmer reaction (**eq. 2.32**) is energetically unfavorable. As  $E_{M-H}$  increases, the adsorption energy decreases, making the reaction more favorable. The optimal Gibbs energy for hydrogen adsorption is close to zero. However, if  $E_{M-H}$  becomes excessively high while the Volmer reaction becomes faster, the subsequent Heyrovsky or Tafel steps are hindered by the strong adsorption bonds that must be broken, limiting the rate of these steps.

The descending branch of the volcano plot corresponds to metals with strong hydrogen adsorption. However, many of these metals form an oxide film on their surface, which impedes the reaction. This surface oxidation was not accounted for when the original plot was proposed. When surface oxidation is considered, the evidence for a complete volcano plot weakens, leaving only the ascending branch as clearly observable.

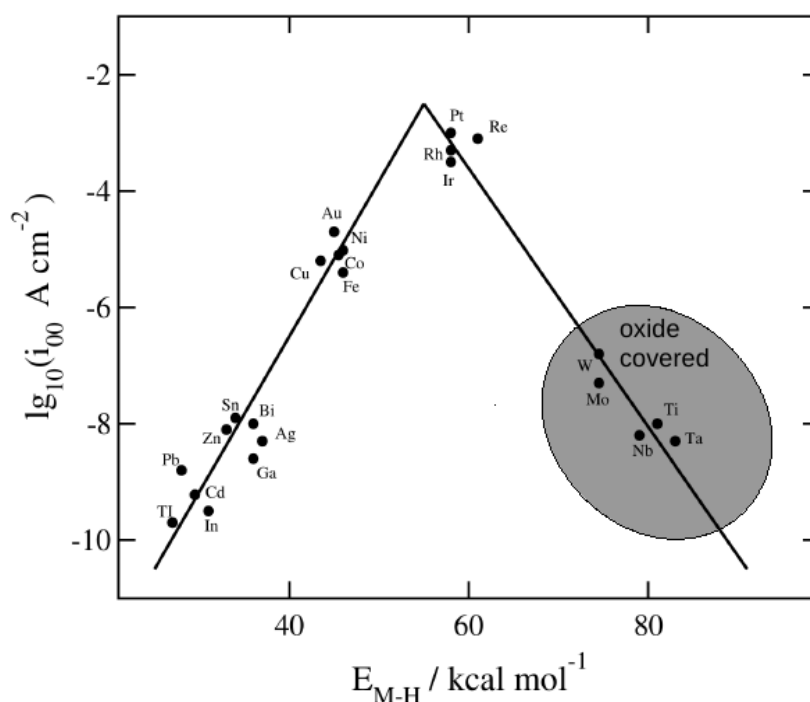


**Figure 2.14** Trasatti version of the volcano plot for HER.  $i_{00}$  is the standard exchange current density of the reaction, and  $E_{M-H}$  is the binding energy between the metal and hydrogen atoms. Data taken from [97].

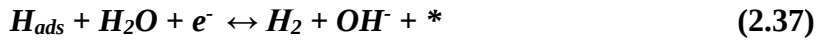
### 2.4.5 pH dependence

Several factors influence the hydrogen evolution reaction (HER), with one of the most critical being the adsorption interactions between the reactants, intermediates, and products and the electrode surface (catalyst) [98],[99],[100]. The pH of the electrolyte solution plays a significant role in this process.

Increasing the pH from 0 to 14 in aqueous electrolytes alters the electrode surface state and affects the adsorption of reactants and intermediates. For example, acid anion adsorption is gradually replaced by hydroxide ( $OH^-$ ) adsorption, which can occur even near the reversible hydrogen electrode potential.

HER mechanisms differ significantly between acidic and alkaline media. In the Volmer step (eq. 2.36), a water molecule, rather than a proton, reacts at the electrode surface in alkaline media. This reaction produces an adsorbed hydrogen atom and a negatively charged hydroxide ion ( $OH^-$ ). The adsorbed hydrogen atom can then follow one of two pathways: it can combine with another adsorbed hydrogen atom to form a hydrogen molecule that desorbs from the

surface (Tafel step, **eq. 2.35**), or it can interact with another water molecule, generating a hydrogen molecule and an additional hydroxide ion (Heyrovsky step, **eq. 2.37**). [93]



The affinity of a metal for  $H^+$  and  $OH^-$  species leads to distinct behaviors in acidic and alkaline media. For example, for platinum in alkaline solutions, the surface coverage with oxygen-containing species increases with increasing pH. As  $OH$  species adsorb onto the surface, the water content in the inner region of the electrical double layer decreases, facilitating the occurrence of a reaction (2.37).[101]



Metals with a high affinity for  $OH$ , such as nickel (Ni), enable efficient hydrogen oxidation only when the surface has a high coverage of  $OH$  species. [70] While the kinetics of adsorbed hydrogen ( $H_{ads}$ ) on metal surfaces have been extensively studied [102, 103], the production of  $OH^-$  from water dissociation and its subsequent adsorption on surfaces during hydrogen oxidation (HOR) and hydrogen evolution reactions (HERs) remain underexplored.

Markovic [104] demonstrated that depositing nickel oxide/hydroxide on an electrode surface enhances the HER rate in alkaline electrolytes. This suggests that an efficient HER requires the optimization of both hydrogen atom adsorption and water molecule adsorption. Markovic proposed that the HER efficiency depends on the density and nature of the sites necessary for water dissociation, the energetics of  $OH^-$  adsorption, and the interaction of adsorbed hydrogen on the metal surface. This optimization involves balancing the transition state energies for water dissociation and the final state energies of  $OH_{ads}$ .

## 2.5 Conclusion

This chapter provides a comprehensive theoretical Structure to support the research conducted in this thesis, encompassing the principles of thin film formation, electrodeposition, water splitting, and fuel cell technology. The discussion of thin films emphasized their structural and functional characteristics, highlighting their critical role in enhancing catalytic performance. The overview of electrodeposition sheds light on the influence of deposition parameters on material properties, underscoring its versatility for synthesizing advanced electrocatalysts.

The detailed exploration of the electrochemistry of water splitting, with a focus on the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), illustrated the thermodynamic and kinetic challenges inherent in these processes. This foundation aids in understanding the design criteria for efficient catalysts. Furthermore, analyses of fuel cell technology and its associated reactions, particularly the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR), have provided insights into the integration of electrocatalysts into sustainable energy systems.

Together, these concepts create a solid theoretical basis for interpreting the experimental results and innovations presented in the subsequent chapters, aligning the fundamental knowledge with practical applications in the fields of renewable energy and advanced material science.

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## Chapter 03: Methods and Experimental Techniques

This chapter outlines the methods and experimental techniques employed in this study to fabricate, analyze, and evaluate thin-layer electrodes for electrocatalytic applications. The section begins with a detailed overview of the chemical products and materials used, emphasizing their purity and suitability for electrochemical processes. The design and functionality of the experimental setup, including the electrochemical cell and potentiostat-galvanostat, are then described to provide insights into the instrumentation facilitating electrodeposition and electrolysis.

To investigate the morphological, structural, and electrochemical properties of the synthesized electrodes, a range of characterization techniques were employed. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to analyze the surface morphology and topology, whereas X-ray diffraction (XRD) provided insights into the crystalline structure. These methods ensure a comprehensive understanding of the material properties.

This chapter also details the electrochemical techniques utilized, including cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS). These methods are critical for evaluating the electrocatalytic performance of the fabricated electrodes, including their activity, stability, and charge transfer properties. A section on current/potential curves further elucidates the relationship between the electrochemical performance and applied potential.

Finally, test procedures are described to ensure reproducibility and reliability in experimental data collection. This chapter serves as the foundation for understanding the experimental workflow and the techniques used to achieve the objectives of this research.

### 3.1 Chemical products and materials

#### 3.1.1. Chemical products

The products used for the preparation of the different treatment baths and their characteristics are summarized in **Table 3.1**

**Table 3.1** Chemical products utilized in the study

| Reactants                                 | Formula                                                                    | Molar mass<br>g/mol |
|-------------------------------------------|----------------------------------------------------------------------------|---------------------|
| Nickel chloride (II) hexahydrate          | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$                                  | 273,71              |
| Manganese (II) Chloride Tetrahydrate      | $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$                                  | 197.90              |
| Cobalt(II) chloride hexahydrate           | $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$                                  | 237.93              |
| Hyptahydrated iron sulfate                | $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$                                  | 287,01              |
| Ammonium chloride                         | $\text{NH}_4\text{Cl}$                                                     | 53,87               |
| Potassium chloride                        | $\text{KCl}$                                                               | 74.55               |
| Ethylenediaminetetraacetic acid dihydrate | $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ | 328.27              |
| Sulfuric acid                             | $\text{H}_2\text{SO}_4$                                                    | 98,079              |
| Potassium hydroxide                       | $\text{KOH}$                                                               | 56,1056             |
| Sodium hydroxide                          | $\text{NaOH}$                                                              | 39.9971             |

#### 3.1.2 Materials

Electrochemical tests are carried out in a conventional three-electrode cell with a working electrode, a counter-electrode, and a reference electrode in a standard 150 ml capacity cell. All of these electrodes were attached to an Autolab potentiostat (PGSTAT302N).

##### 3.1.2.1 Electrochemical cell

The cell consists of a double-walled Pyrex glass with a capacity of 150 mL (**Figure 3.1**) delivered by Metrhom. It is equipped with a cover with five openings, including three for the insertion of the three electrodes and two for the input and output of inert gases for working in an air-free environment.

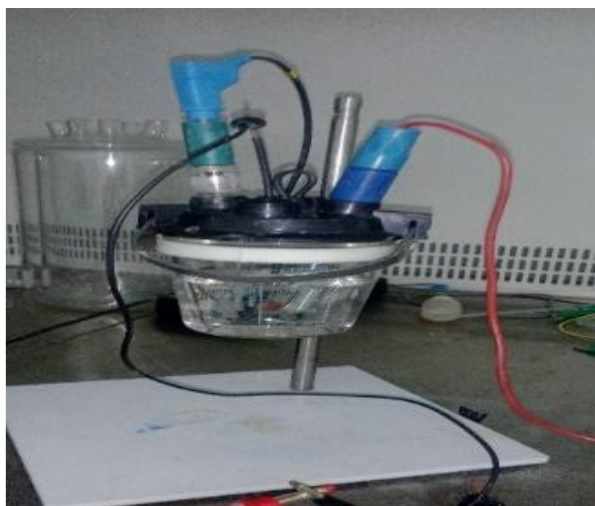


**Figure 3.1** Electrochemical cell for electrodeposition with three electrodes.

### 3.1.2.1.1 Electrodes

It consists of a working electrode, a reference electrode, and an auxiliary electrode.

#### a) Reference electrodes (RE)

In general, the potential of a current-carrying electrode (WE) cannot be determined by measurement of the other current-carrying electrode in the cell (CE) because the measured cell voltage will include contributions from the potential drop due to the electrolyte resistance and the overpotentials of both the WE and the CE. [1] Thus, inserting a third electrode into the cell (the reference electrode) is a critical step in controlling and measuring electrode potentials.

There are many options for the reference electrode. The most commonly used reference electrode is the Ag/AgCl electrode, which consists of a silver wire immersed in an aqueous AgCl solution with a standard potential value determined by the concentration of silver ions in the solution. There are additional mercury-based reference electrodes, such as Hg/HgO, Hg/Hg<sub>2</sub>SO<sub>4</sub>, and calomel (Hg/Hg<sub>2</sub>Cl<sub>2</sub>). **Table 3.2** provides a review of typical reference electrodes and their potentials with respect to the standard hydrogen electrode (SHE) at 25°C. The type of reference electrode used is determined by the specific instance, particularly the electrolyte pH and whether chlorides can interfere with the examined reaction.

In this study, we used a silver electrode (Metrhom Ag/AgCl electrode: 6.0726.100) coated with silver chloride and saturated with a 3.0 M KCl solution. The electrode was 12.5 cm long and could withstand temperatures up to 80°C. With a double junction system and a 10 cm installation length. The standard ground joint 14/15 allows for simple construction, and the flexible ground-joint diaphragm, which is resistant to contamination, can be easily replaced at

any time. The reference electrolyte and bridge electrolyte might be flexibly chosen on the basis of the application and are simple to change. It has a potential of + 0.224 with respect to the standard hydrogen electrode (SHE) at 25°C. The reference electrode is placed as close to the working electrode as possible to reduce measurement mistakes caused by the electrolyte's ohmic drop. Throughout this work, the potentials were measured against this silver chloride electrode.



**Figure 3.2** Ag/AgCl/3.0 M KCl (Mettrom electrode: 6.0726.100)

**Table 3.2** Standard reference electrodes and their potentials relative to the SHE at 25°C.[1],[2]

| Reference electrode                                                       | Condition                                  | Half-cell reaction                                    | Potential (V)           |
|---------------------------------------------------------------------------|--------------------------------------------|-------------------------------------------------------|-------------------------|
| Standard hydrogen electrode (SHE)                                         | $a_{H^+} = 1$                              | $2H^+ + 2e^- \rightleftharpoons H_2$                  | 0.0                     |
| Normal hydrogen electrode (NHE)                                           | $c_{H^+} = 1.0 \text{ M}$                  | $2H^+ + 2e^- \rightleftharpoons H_2$                  | $\approx 0.0$           |
| Reversible hydrogen electrode (RHE)                                       | actual electrolyte                         | $2H^+ + 2e^- \rightleftharpoons H_2$                  | $0 - 0.0591 \text{ pH}$ |
| Silver/silver chloride electrode (Ag/AgCl)<br>KCl ( $c = 3.0 \text{ M}$ ) | $a_{Cl^-} = 1$<br>saturated KCl<br>+ 0.209 | $AgCl + e^- \rightleftharpoons Ag + Cl^-$<br>+ 0.1976 | + 0.224                 |
| Calomel electrode                                                         | $a_{Cl^-} = 1$                             | $Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$      | + 0.2682                |

Each reference electrode was calibrated before use and evaluated for drift on a regular basis via a commercial reversible hydrogen electrode (RHE, an SHE). The potentials experimentally obtained in this study, i.e., potentials measured against the reference electrode (E vs. ref.), are translated into potentials vs. the RHE (E vs. RHE) according to equation (3.1), unless otherwise specified:

$$E_{\text{vs. RHE}} = E_{\text{vs. ref.}} + E_{\text{ref.}}^0 + 0.0591 \text{ pH} \quad (3.1)$$

where  $E_{\text{ref.}}^0$  is the potential of the reference electrode versus the standard hydrogen electrode (SHE).

### b) Counter Electrode (CE)

It is manufactured from chemically inert material. It is connected to the positive end of the current generator and allows the current to circulate by closing the measuring circuit. It is important to position the counter-electrode correctly relative to the working electrode for an optimal distribution of current lines, which ensures uniform deposit. We used nickel as a counter-electrode (2.5cm \* 5cm) for the deposition and a graphite plate electrode (2 cm \* 6 cm) was used for water electrolysis examination.



**Figure 3.3** Counter electrode (a graphite plate electrode measuring 2 cm × 6 cm) utilized for water electrolysis studies.

### c) Working Electrode (WE)

This type of electrode is the seat of an electrochemical reaction and is connected to the negative end of the current generator. It is the seat of electron exchange between electroactive species. In this work, a copper surface was used after special chemical treatments (as detailed below) as the working electrode with the catalyst to be electrodeposited on it. The reason for this selection is that the conductivity of the copper layer should be sufficient so that it does not influence the measurement of the electrocatalytic activity. Thus, this substrate resembles the setup for a complete water-splitting device quite well. Before electrodeposition, the copper surface area ( $A = 1 \text{ cm} \times 1 \text{ cm}$ ) was mechanically sanded with 2500 abrasive SiC sandpaper and then polished with alumina nanoparticles. The electrodes were then immersed in acetone ultrasonically for 15 minutes. The activation was then performed in a 10 wt.% HCl solution at room temperature for 20 s, after which the samples were rinsed with distilled water and instantly immersed in the electrochemical deposition solution (detailed information can be found in Chapter 4, Paragraph 3.2.1).

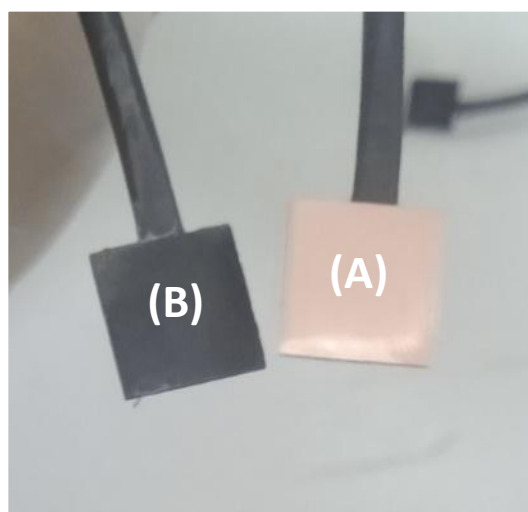


**Figure 3.4** Working Electrode: (A) Substrate Before Electrodeposition (Brown) and (B) Ni-Deposited Layer After Electrodeposition (Black)

#### 3.1.2.2 Potentiostat-Galvanostat

All our electrochemical experiments were conducted via an AUTOLAB potentiostat-galvanostat (PGSTAT302N), which was controlled by a microcomputer equipped with NOVA 2.1 software. It has an electronic circuit that allows it to modify the potential and record the current or vice versa. The electrochemical device used for catalyst preparation and study is shown in **Figure 3.5**.



**Figure 3.5** Electrochemical experimental measurement device

## 3.2 Experimental Setup

### 3.2.1 Electrodeposition of Thin Layers

The preparation of the material required (working electrode) to carry out the deposition of thin layers of Ni, Ni-Mn, Ni-Mn-Co, and Ni-Mn-Co-Fe to ensure good adhesion of the layer and the substrate must be preceded by the process of cleaning.

In this study, copper surfaces were used as substrates to produce electrocatalysts with different compositions. Electrochemical deposition was implemented in a three-electrode cell in which copper substrates served as the working electrode (WE), the reference electrode (Ag/AgCl) was a silver/silver chloride electrode (RE), and the counter electrode (CE) was a high surface area nickel plate to limit  $\text{Ni}^{2+}$  ion loss in the solution. After coating, the samples were rinsed with distilled water, dried, and prepared for further study. All the measurements were taken with natural aeration. To facilitate gas discharge during the experiment, the working electrode was held vertically under natural convection conditions. **Figure 3.6(a)** presents a picture of the three-electrode cell. A schematic illustration of the circuit diagram of the three-electrode arrangement is given in **Figure 3.6(b)**, where the current flow is measured between the WE and the CE, whereas the potential is measured between the WE and the RE.

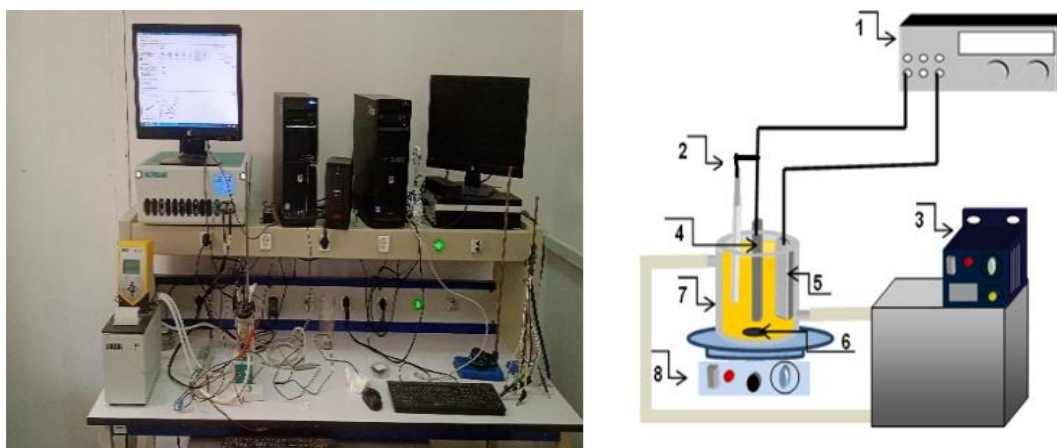


**Figure 3.6 (a)** Photograph of a cell in a three-electrode configuration with a working electrode (WE), a Ag/AgCl a reference electrode (RE), and counter electrode (CE). **(b)** Schematic view of the undivided lab electrolysis cell system: (1) supply source, (2) Ni-Fe-Mo/Cu electrode, (3) thermostatic bath, (4) carbon-felt electrode, (5) electrode, (6) magnet, (7) electrolysis cell, and (8) magnetic stirrer.

All our layers were prepared from aqueous electrolytes. An electrolyte is a solution whose essential role is to provide the species needed for electrochemical reactions. The solutions were obtained by dissolving  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  nickel chloride,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  manganese chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  cobalt chloride,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  iron sulfate, and  $\text{NH}_4\text{Cl}$  ammonium chlorite as supporting electrolytes in 100 ml of distilled water under mechanical agitation via a mechanical stirrer. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and potassium hydroxide ( $\text{NaOH}$ ) were added to control the pH of the bath. The composition and experimental conditions of the bath are presented in **Table 3.3**

**Table 3.3** Composition of the different baths and their operating conditions.

|                                             | Bath1<br>(Ni/Cu)                                                                                                                                                                                                                                                     | Bath2<br>(Ni-Mn/Cu)                                                                                                                                                                                                                                                  | Bath3<br>(Ni-Mn-Co/Cu)                                                                                                                                                                            | Bath4<br>(Ni-Mn-Co-Fe/Cu)                                                                                                                                                                                                                                            |
|---------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Composition                                 | NiCl <sub>2</sub> .6H <sub>2</sub> O<br>NH <sub>4</sub> Cl                                                                                                                                                                                                           | NiCl <sub>2</sub> .6H <sub>2</sub> O<br>MnCl <sub>2</sub> .4H <sub>2</sub> O<br>NH <sub>4</sub> Cl                                                                                                                                                                   | NiCl <sub>2</sub> .6H <sub>2</sub> O<br>MnCl <sub>2</sub> .4H <sub>2</sub> O<br>CoCl <sub>2</sub> .6H <sub>2</sub> O<br>NH <sub>4</sub> Cl                                                        | NiCl <sub>2</sub> .6H <sub>2</sub> O<br>MnCl <sub>2</sub> .4H <sub>2</sub> O<br>CoCl <sub>2</sub> .6H <sub>2</sub> O<br>FeSO <sub>4</sub> .7H <sub>2</sub> O<br>NH <sub>4</sub> Cl                                                                                   |
| Deposition and electrochemical measurements | CV<br>EIS                                                                                                                                                                                                                                                            | CV<br>LSV<br>EIS                                                                                                                                                                                                                                                     | LSV<br>EIS                                                                                                                                                                                        | CV<br>LSV<br>Polarization<br>Fixed potential<br>Two successive fixed potentials<br>EIS                                                                                                                                                                               |
| Stability                                   |                                                                                                                                                                                                                                                                      |                                                                                                                                                                                                                                                                      |                                                                                                                                                                                                   | Chronopotentiometry                                                                                                                                                                                                                                                  |
| Characterisation                            | SEM<br>AFM<br>XRD                                                                                                                                                                                                                                                    | SEM<br>AFM<br>XRD                                                                                                                                                                                                                                                    | SEM<br>AFM<br>XRD                                                                                                                                                                                 | SEM<br>AFM<br>XRD                                                                                                                                                                                                                                                    |
| Study parameters                            | Bath composition<br>Scan rate<br>Temperature<br>pH<br>Supporting electrolyte                                                                                                                                                                                         | Bath composition<br>Scan rate<br>Temperature<br>pH<br>Deposition time<br>Counter electrode type<br>Supporting electrolyte<br>KOH concentration<br>KOH temperature                                                                                                    |                                                                                                                                                                                                   | Bath composition<br>Scan rate<br>Temperature<br>pH<br>KOH concentration<br>KOH temperature                                                                                                                                                                           |
| Fixed conditions for the optimum samples    | Deposition potential by CV :<br>E=[+0.01 to -1.0 V] vs .Ag/AgCl<br>Deposition potential by LSV:<br>E <sub>HER</sub> =[0V to -1.4 V] vs .Ag/AgCl<br>E <sub>OER</sub> =[0V to -1.4 V] vs .Ag/AgCl<br>T=25°C<br>pH=3.5<br>Scan rate=10mV/s<br>T=25°C<br>Agitation=3 min | Deposition potential by CV :<br>E=[+0.01 to -1.0 V] vs .Ag/AgCl<br>Deposition potential by LSV:<br>E <sub>HER</sub> =[0V to -1.4 V] vs .Ag/AgCl<br>E <sub>OER</sub> =[0V to +1.4 V] vs .Ag/AgCl<br>T=25°C<br>pH=3.5<br>Scan rate=10mV/s<br>T=25°C<br>Agitation=3 min | Deposition potential by LSV:<br>E <sub>HER</sub> =[0V to -1.4 V] vs .Ag/AgCl<br>E <sub>OER</sub> =[0V to -1.4 V] vs .Ag/AgCl<br>T=25°C<br>pH=3.5<br>Scan rate=10mV/s<br>T=25°C<br>Agitation=3 min | Deposition potential by CV :<br>E=[+0.01 to -1.0 V] vs .Ag/AgCl<br>Deposition potential by LSV:<br>E <sub>HER</sub> =[0V to -1.4 V] vs .Ag/AgCl<br>E <sub>OER</sub> =[0V to +1.4 V] vs .Ag/AgCl<br>T=25°C<br>pH=3.5<br>Scan rate=10mV/s<br>T=25°C<br>Agitation=3 min |

### 3.2.2 Electrolysis

The evolution reactions of hydrogen and oxygen release from the electrodeposited alloys Ni, Ni-Mn, Ni-Mn-Co, and Ni-Mn-Co-Fe were studied under different conditions (see **Table 3.4**). The experiments were carried out via linear sweep voltammetry (LSV) in a three-electrode electrochemical cell with the studied electrodes as the working electrode, a graphite plate as the counter electrode, and Ag/AgCl as the reference electrode. counter-electrode and Ag/AgCl as a reference electrode. The electrolysis bath is presented in **Figure 3.7**.

**Table 3.4** Electrolysis bath parameters for the Ni, Ni-Mn, Ni-Mn-Co, and Ni-Mn-Co-Fe electrodes.

| Bath          | Electrocatalysts | Parameters                                                                                                                                                                                            |
|---------------|------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Bath 1</b> | Ni/Cu            | <ul style="list-style-type: none"> <li>KOH temperature (23C°)</li> <li>KOH concentration (1.0 M)</li> </ul>                                                                                           |
| <b>Bath 2</b> | Ni-Mn/Cu         | <ul style="list-style-type: none"> <li>KOH temperature (25,50 and 60 C°)</li> <li>KOH concentration (0.25,0.5,0.75,1.0 and 1.5 M)</li> <li>Electrolyte type (1 M KOH,1 M KCl and 1 M NaOH)</li> </ul> |
| <b>Bath 3</b> | Ni-Mn-Co/Cu      | <ul style="list-style-type: none"> <li>KOH temperature (23C°)</li> <li>KOH concentration (1.0 M)</li> </ul>                                                                                           |
| <b>Bath 4</b> | Ni-Mn-Co-Fe/Cu   | <ul style="list-style-type: none"> <li>KOH temperature (25,40,55 and 75C°)</li> <li>KOH concentration (0.25,0.5,0.75,1.0 and 1.5 M)</li> </ul>                                                        |

### 3.3 Characterization Techniques

#### 3.3.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) yields information about the topography, morphology, and composition of the probed samples by scanning the surface with a focused beam of electrons. The interaction between the incident primary electron beam and the sample within a teardrop-shaped volume leads to various signals, which can be detected by specialized detectors, as shown in **Figure 3.7**. The most commonly used SEM mode in this study is the detection of secondary electrons emitted by atoms excited by the electron beam. In secondary electron imaging (SEI), these particles are ejected very close to the sample surface. Consequently, by scanning the sample and collecting the secondary electrons emitted, very high-resolution images displaying the topography of the surface can be produced.[3]

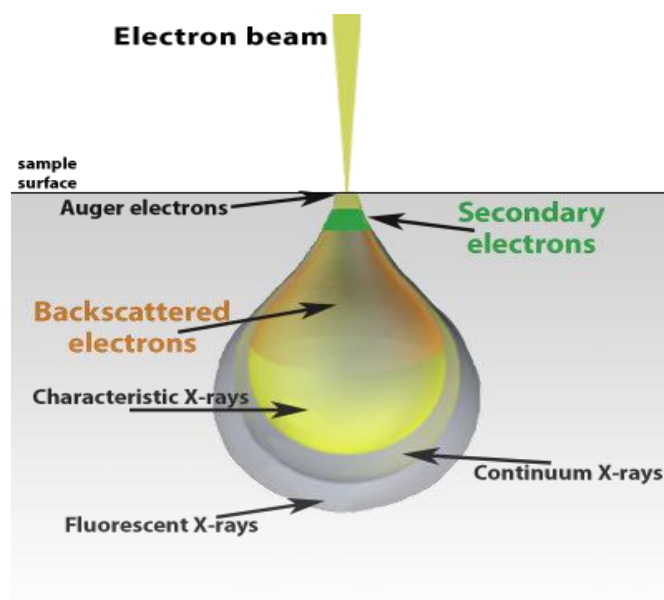


**Figure 3.7** Schematic representation of the interaction between the primary electron beam and the sample within the interaction volume.[4]

In this study, Ni/Cu, Ni-Mn/Cu, Ni-Mn-Co/Cu, and Ni-Mn-Co-Fe/Cu samples were characterized by scanning electron microscopy (SEM, TESCAN MIRA3 INSTRUMENT JSM-6360). The surface morphology of these materials was investigated to determine their catalytic activity.

### 3.3.2 Atomic Force Microscopy (AFM)

AFM is a type of scanning probe microscopy (SPM) that uses a sharp tip to scan across the surface of a sample. The tip interacts with the atoms on the surface, and these interactions are measured to create an image of the surface topography. AFM can image surfaces with incredibly high resolution, down to the level of individual atoms. There are several different modes of AFM, but the basic principle is the same:

- a) **A cantilever:** This is a tiny beam that holds the tip at its end. The cantilever is made of a very stiff material, such as silicon or silicon nitride.
- b) **A laser:** The laser shines a beam onto the back of the cantilever.
- c) **A detector:** The detector measures the deflection of the laser beam.

As the tip scans across the surface of the sample, the forces between the tip and the atoms cause the cantilever to bend. The detector measures the amount of bending, and this information is used to create an image of the surface.[5],[6]

#### 3.3.2.1 Principle of Atomic Force Microscope

Atomic force microscopy works on the principle of measuring intermolecular forces and observing atoms by using probed surfaces of a sample at the nanoscale. Its function is enabled by three of its major working principles: surface sensing, detection, and imaging. [7],[5]

The atomic force microscope (AFM) performs surface sensing by using a cantilever (an element that is made of a rigid block such as a beam or plate that attaches to the end of support, from which it protrudes, making a perpendicularly flat connection that is vertical like a wall). The cantilever has a sharp tip that scans over the sample surface by forming an attractive force between the surface and the tip when it draws closer to the sample surface. When it draws very close contact with the surface of the sample, a repulsive force gradually takes control, causing the cantilever to avert from the surface.

During the deflection of the cantilever away from the sample surface, there is a change in the direction of reflection of the beam, and a laser beam detects the aversion by reflecting off a beam from the flat surface of the cantilever. Using a positive-sensitive photodiode (PSPD, a component that is based on silicon PIN diode technology and is used to measure the position of the integral focus of an incoming light signal), it tracks these changes in deflection and changes in the direction of the reflected beam and records them.

Atomic force microscopy (AFM) takes images of the surface topography of a sample via force by scanning the cantilever over a section of interest. Depending on how raised or how low

the surface of the sample is, the deflection of the beam, which is monitored by a positive-sensitivity photodiode (PSDP), is determined. The microscope has a feedback loop that controls the length of the cantilever tip just above the sample surface; therefore, it maintains the laser position, thus generating an accurate imaging map of the surface of the image. See **Figure 3.8**.

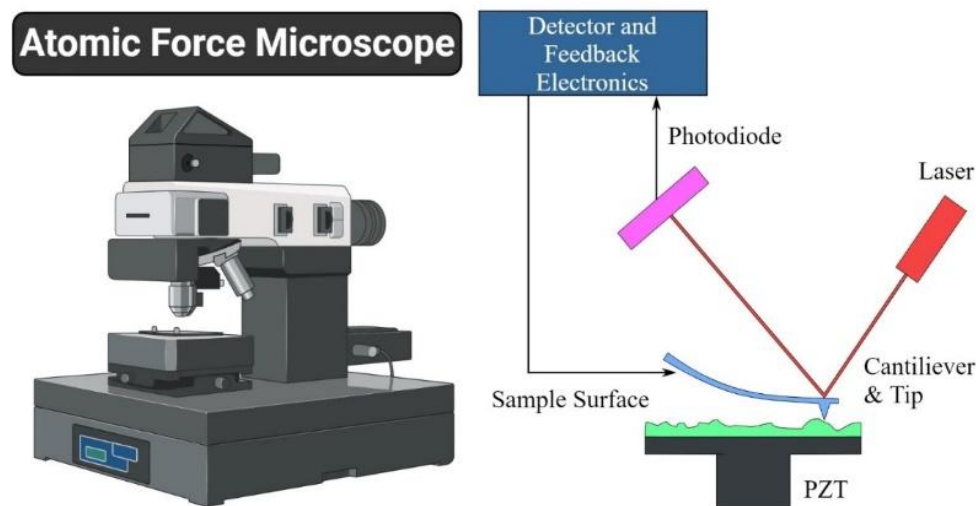


**Figure 3.8** Working principle of the atomic force microscope (AFM).

### 3.3.2.2 Applications

AFM has a wide range of applications in science and technology. Some examples include:

- a) Studying the structure of materials:** AFM can be used to image the surface of any type of material, from biological samples to semiconductors. This information can be used to understand the properties of a material and to develop new materials.
- b) Measuring nanostructures:** AFM can be used to measure the size and shape of nanostructures, such as nanoparticles and nanotubes. This information is important for understanding the behavior of these structures and for developing new nanotechnologies.
- c) Manipulating atoms:** AFM can be used to move atoms one at a time. This has opened a whole new world of possibilities for manipulating matter at the atomic level.

Overall, AFM is a powerful tool that has revolutionized our understanding of the world at the atomic level. It is a key tool in many areas of science and technology, and its applications are only just beginning to be explored.[8]

In this study, the Ni, Ni-Mn, Ni-Mn-Co, and Ni-Mn-Co-Fe samples were characterized using an atomic force microscope (AFM) (Ara A.F.M. Model No.0101/A: Iran) to measure the size and shape of microstructures, as well as a topology surface study, to understand their electrocatalytic behavior.

### 3.3.3 X-ray Diffraction (XRD)

This approach allows for the identification of different phases as well as the extraction of microstructure information. This investigation employed a Philips X'Pert diffractometer. **Figure 3.9 (a)** shows a standard diffractometer graphic. The beam width is determined by the size of the slits utilized to provide the best resolution.

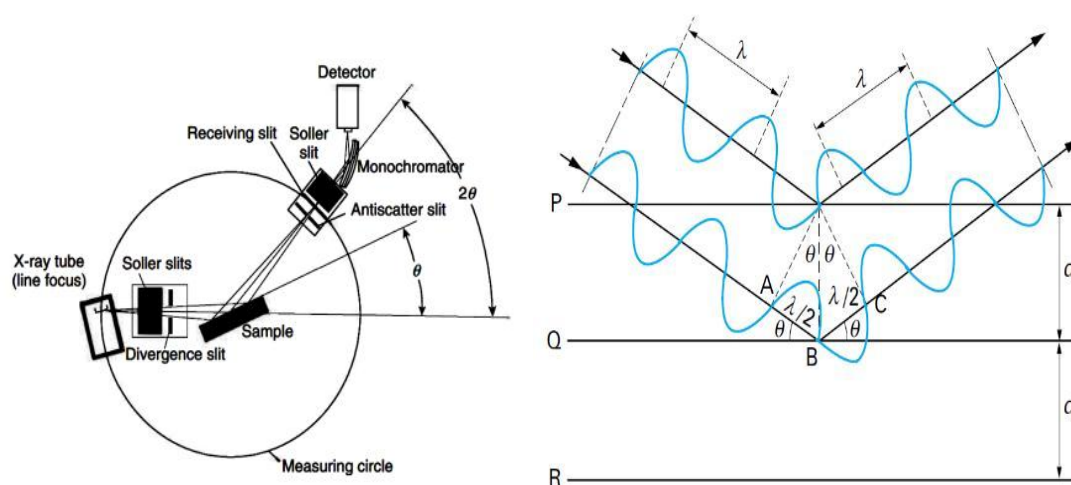


**Figure 3.9 (a)** Diagram of a diffractometer, **(b)** representation of Bragg's law in the case of powder samples of nontextured crystals.

To detect the crystalline planes parallel to the surface of the electrodeposited alloys, the symmetrical analysis mode ( $\theta/2\theta$ ) was used. This technique's diffraction principle is characterized by Bragg's diffraction law (see **Figure 3.9 (b)**), which states that the beam created by the source travels parallel to the sample surface at a Bragg incidence angle  $\theta$ . The beam is reflected at the same angle onto a family of reticular planes  $\{hkl\}$  ( $h$ ,  $k$ , and  $l$  Miller indices) with a reticular distance  $d_{hkl}$ . **Figure 3.9 (b)** shows that  $AB + CB = 2d \sin \theta$  and  $AB + CB = n\lambda$ , which leads to:[9],[10]

$$2d\sin\theta = n\lambda \quad (3.2)$$

where  $d$  = the interticular distance of the family planes  $\{hkl\}$  and where  $\lambda$  = the wavelength of the diffracted beam.

The diffracted beam directions are determined by the size of the crystal lattice. For example, in the case of a cubic system, the interticular distance is represented by the following equation:[11]

$$d = \frac{a}{h^2 + k^2 + l^2} \quad (3.3)$$

From which we can determine the mesh parameter in a cubic system:

$$a = \frac{n\lambda}{2\sin\theta} \times \sqrt{h^2 + k^2 + l^2} \quad (3.4)$$

In this study, the Ni, Ni-Mn, Ni-Mn-Co, and Ni-Mn-Co-Fe samples were characterized via X-ray diffraction (XRD) (using a Philips X'Pert diffractometer) to study the phase structure of the coatings and understand their surface chemical composition.

### 3.4 Electrochemical techniques

In this section, we discuss electrochemical techniques applicable to analyzing the reactive mechanisms involved in the electrodeposition process and the formation of the resulting deposit.

#### 3.4.1 Cyclic Voltammetry

Cyclic voltammetry is one of the most essential and often used electroanalytical methods. Its strength comes from the ease of carrying out and the abundance of qualitative and quantitative data collected during research on oxidation-reduction processes. This method involves varying the potential of the working electrode linearly with time between two terminals in a round-trip scan and measuring the current density passing through the electrical circuit, which includes the working electrode, counter electrode, solution, and Potentiostat. The voltammograms generated depict the variation in current density as a function of the voltage applied to the working electrode. These plots often exhibit one or more peaks, corresponding to reduction or oxidation events occurring at the working electrode. Negative current values are

generally associated with reduction processes, whereas positive currents are indicative of oxidation processes.[12],[13]

The potential of the indicator electrode  $E(t)$  varies linearly with time, whereas the potential scan rate  $v$  is constant.

$$E(t) = E_i \pm vt \quad (3.5)$$

$E_i$ : the initial potential.

The main dimensions of a voltammogram are shown in **Figure 3.10**.

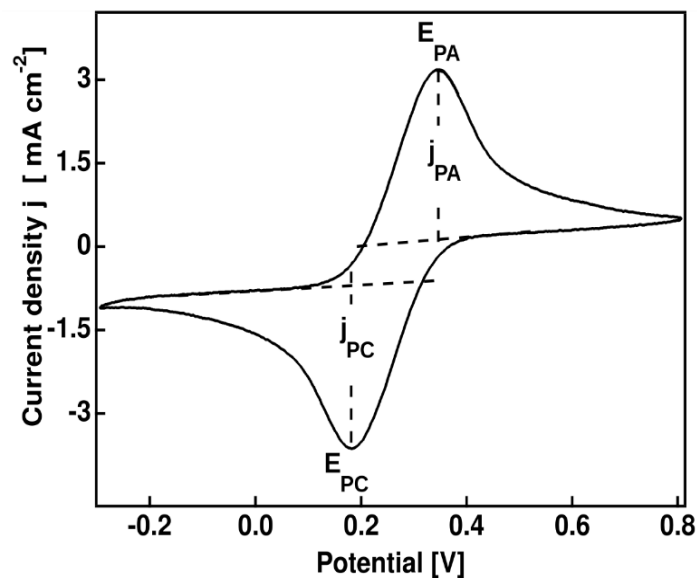


**Figure 3.10** General curve of a voltammogram and its parameters Characteristics.

$I_{Pa}, I_{Pc}$ : Anodic and cathodic current peaks

$E_{Pa}, E_{Pc}$ : Potentials of the anodic and cathodic peaks

Curves of cyclic voltammograms provide information about the distinctive characteristics of the systems under investigation. There are three types of systems to consider: reversible, irreversible, and quasireversible.

#### a- Reversible system

This is the case where charge is transferred very quickly to the electrode surface. The concentrations of oxidant and reductant at the interface confirm Nernst's law, and the relationship between these concentrations is time dependent. This issue was addressed

computationally by Randles and Sevcik and later by Nicholson and Shain. [14] Their work enabled the description of various features of the current-potential curve of the circuit in relation to the system's parameters.

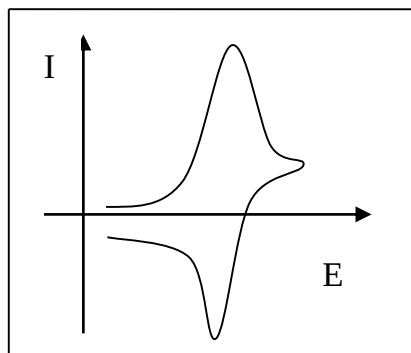


**Figure 3.11** Cyclic voltammogram recorded for a reversible system.

### b- Quasireversible system

Electronic transfer is slow in quasireversible systems, but the reverse reaction is important to consider. The current intensity of such a reaction is no longer directly proportional to the square root of the scanning rate.

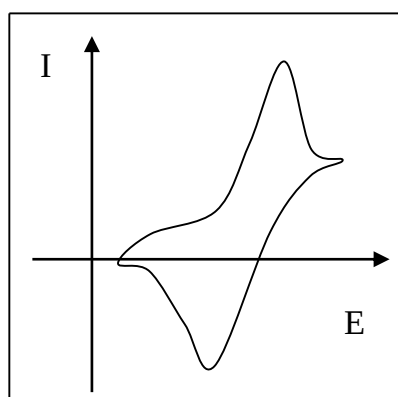


**Figure 3.12** Cyclic voltammogram of a quasireversible system.

### c- Irreversible system

An irreversible system refers to one where the products generated during the forward scan of a cyclic voltammogram cannot participate in the reverse electrochemical half-reaction. In

such cases, the Nernst equation does not apply due to the slow rate of electron transfer. Equation (3.5) specifies the value of the peak current when a single redox species is initially present in solution.

$$I_{pc} = -2.99 \cdot 10^5 n(\beta n_c)^{1/2} S C_{ox}^* \sqrt{D_{ox} v} \quad (3.6)$$

where:

$\beta$ , the cathodic charge transfer coefficient;

$n_c$ , the number of moles of electrons exchanged in the slowest step,

$n$ , the number of moles of electrons exchanged in the overall process,

The voltammogram curve for an irreversible electrochemical system is given in **Figure 3.10**.

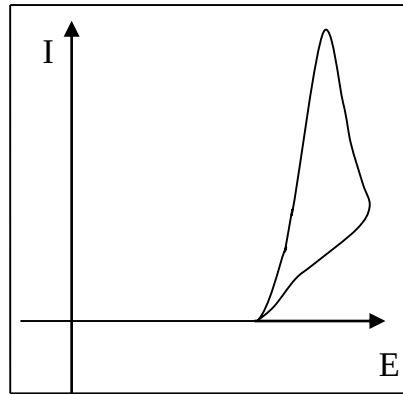


**Figure 3.13** Cyclic voltammogram recorded for an irreversible system.

Unlike a reversible system, an irreversible system's peak potential changes when the potential scan rate increases, according to the Nicholson and Shain equation (3.7).

$$E_p = E^{\circ'} - \frac{RT}{\beta n_c F} \left[ 0.780 + \ln \left( \frac{\sqrt{D_0}}{k^{\circ}} \right) + \ln \left( \sqrt{\frac{\beta n_c F v}{RT}} \right) \right] \quad (3.7)$$

In practice, depending on the scan rate of potential, a system could appear to be reversible, quasireversible, or completely irreversible.

Our work employed the cyclic voltammetry (CV) method to investigate the reduction–oxidation behavior of Ni, Ni-Mn, Ni-Mn-Co, and Ni-Mn-Co-Fe on a Cu substrate at various concentrations. Typical cyclic voltammograms were obtained between +0.01 and -1.0 V vs.

Ag/AgCl at a scan rate of 10 mV/s under various bath conditions, such as various temperatures, scan rates, and pH values. (**Chapter 4** contains the experimental specifics of how we used CV for electrocatalyst deposition).

### 3.4.2 Linear Sweep Voltammetry (LSV)

A method that involves applying a continuous variation in potential in the form of a constant-speed potential ramp between two selected potentials ( $E_1$  and  $E_2$ ) to the working electrode while recording the observed current according to the applied potential. Generally, the initial potential ( $E_1$ ) is chosen such that no reaction occurs (rest potential), and the scanning is carried out in one direction to the final potential ( $E_2$ ) so that the reaction is controlled by material transport [2],[15].

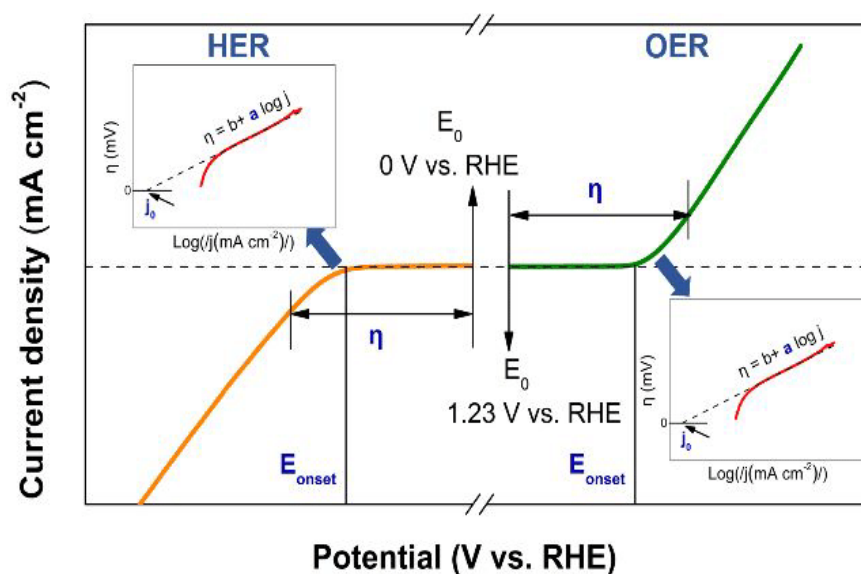


**Figure 3.14** Voltammogram A voltammogram illustrating the relationship between current density and applied potential, obtained via linear sweep voltammetry (LSV).

In this study, linear sweep voltammetry (LSV) was employed to deposit Ni, Ni-Mn, Ni-Mn-Co, and Ni-Mn-Co-Fe films onto a Cu substrate. Furthermore, the electrocatalytic performance of the synthesized materials was analyzed for their hydrogen and oxygen evolution reaction activities.

### 3.4.3 Electrochemical Impedance Spectroscopy (EIS)

Impedance spectroscopy is a powerful method for investigating the electrical characteristics of materials and the interfaces of conductive electrodes. In this study, electrochemical impedance spectroscopy (EIS) was used to correct the electrochemical data for the electrolyte resistance and analyze the reaction kinetics of the catalytic processes across different electrode/electrolyte systems.[16]

#### 3.4.3.1 Basics of EIS

To investigate an electrochemical system, an alternating current (AC) potential is applied, and the resulting AC response is measured. Unlike linear systems, where the output is a direct sum of the individual responses to input signals, electrochemical cells display nonlinear characteristics. To mitigate these nonlinear effects, low-amplitude perturbation signals are used. Under these conditions, the system's pseudolinear behavior can be approximated in a manner similar to linear system impedance, with only slight changes in the electrode state. Generally, electrochemical systems maintain linearity when the signal amplitude is 10 mV or less. The AC potential applied to the electrode is typically represented as a sinusoidal function, as detailed in Equation (3.8). [16]

$$E_t = E_0 \sin(\omega t) \quad (3.8)$$

where  $E_t$  is the potential at time  $t$ ,  $E_0$  is the amplitude of the sinusoidal potential, and  $\omega = 2\pi f$  is the angular frequency. The resulting current response can be described by equation (3.9):

$$I_t = I_0 \sin(\omega t - \phi) \quad (3.9)$$

where  $I_t$  is the current at time  $t$ ,  $I_0$  is the amplitude of the sinusoidal current, and  $\phi$  is the phase difference between the potential and the current. The impedance ( $Z$ ) is generally defined as equation (3.10):

$$Z(\omega) = \frac{E_t}{I_t} = Z_0 e^{j\phi} = Z_0 (\cos \phi + j \sin \phi) \quad (3.10)$$

$$j = (-1)^{1/2} \quad (3.11)$$

The variation in the electrochemical impedance with frequency is often of interest and can be represented graphically in different ways. In a Nyquist plot, the real part of  $Z$  ( $Z_{Re}$ ) is plotted against the imaginary part ( $Z_{Im}$ ) for different values of  $\omega$ . An alternative representation, a Bode plot, displays both  $\log |Z|$  and  $\phi$  versus  $\log \omega$ . Exemplary impedance plots are illustrated in **Figure 3.14**.

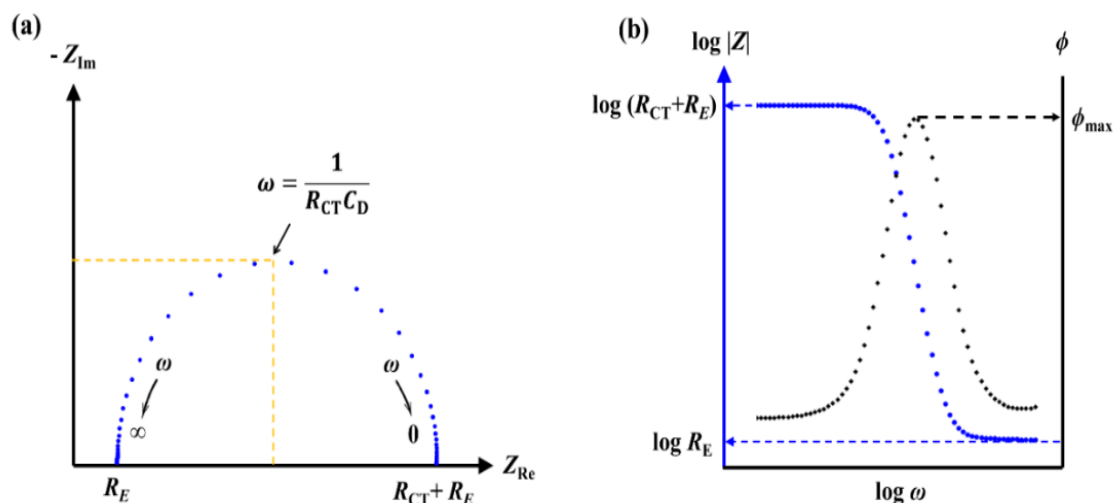


**Figure 3.15** (a) Nyquist plot and (b) Bode plot. [1]

In general, an electrochemical half-cell may be viewed as an impedance for small sinusoidal excitation; hence, its performance can be expressed in terms of an equivalent electrical circuit composed of resistances, capacitances, and inductances. **Figure 3.16** depicts a simple equivalent circuit corresponding to the spectra presented in **Figure 3.15**, considering the electrolyte resistance  $R_E$ , the charge transfer resistance  $R_{CT}$ , and the double layer capacitance  $CD$ . The parallel components are included because the total current flowing across the working interface is the sum of separate contributions from the faradaic process ( $i_f$ ) and double layer charging ( $i_c$ ). Obviously, all current must pass through the solution resistance; thus,  $R_E$  is used as a series component to represent this effect in the equivalent circuit. At high frequencies, the capacitance allows the complete current to flow, with the current being limited only by  $R_E$ . At low frequencies, the current must pass through the  $R_{CT}$ ; hence, the current is defined as the sum of  $R_E$  and  $R_{CT}$ . Notably, the equivalent circuit detailed here uses the most basic electrode method. Many more variables may need to be addressed when investigating more complicated situations, such as electroreactant adsorption, multistep charge transfer, or homogeneous chemistry.

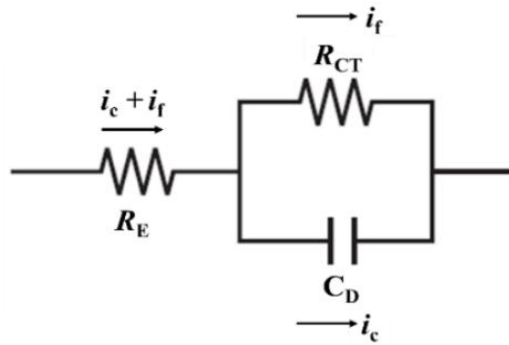


**Figure 3.16** Equivalent circuit (Randell circuit) of an electrochemical half-cell for the impedance plots shown in **Figure 3.15**.

### 3.4.3.2 Correcting for uncompensated series resistance

The flow of electronic and ionic currents in an electrochemical cell leads to an electrostatic potential drop. A significant portion of this drop is associated with the reference electrode (*RE*), which is generally positioned close to the working electrode (*WE*). The potential drop arising from the ionic current flowing through the electrolyte between the *RE* and *WE* remains uncompensated, introducing an additional overpotential for the electrode to achieve the desired current density. Therefore, correction is needed. For a simple, flat electrode with a uniform current distribution, the uncompensated resistance (*R<sub>u</sub>*) can be determined via equation (3.12). [1]

$$R_u = \frac{x}{kA} \quad (3.12)$$

where *x* is the distance between the *WE* and the tip of the *RE*, *A* is the area of the *WE*, and *k* is the solution conductivity. The uncompensated potential is thus given by equation (3.13):

$$E_{uncompensated} = i * R_u \quad (3.13)$$

Here, *E* refers to the applied potential, and *i* represents the current (not the current density) flowing through the electrode. Apart from the previously mentioned factors, the conductivity of the working electrode (*WE*) and any resistive elements in series with the solution, such as bubbles on the electrode surface, can also affect the uncompensated resistance (*R<sub>u</sub>*). [17]

To estimate  $R_u$ , it is compared to the cell impedance ( $RE$  in **Figure 3.12**) at high frequencies, where the phase angle approaches zero, indicating purely resistive circuit behavior.  $R_u$  is determined for each electrode inserted into the electrochemical cell before standard electrochemical characterization studies are initiated. After measuring  $R_u$ , it can be applied to correct the experimental polarization data post-collection using the following equation:

$$E_{\text{compensated}} = E_{\text{measured}} - (i * R_u) \quad (3.14)$$

The equations indicate that the adjustment has a negligible effect on the initial overpotential because the current is minimal at that point. However, as the current increases, the uncompensated potential ( $E_{\text{uncompensated}}$ ) and the shift in the polarization curve become more pronounced. Therefore,  $iR_{\text{compensation}}$  serves as an effective strategy to reduce uncompensated potential drops, allowing for a more precise evaluation of electrocatalyst performance.

In this work, electrochemical impedance spectroscopy (EIS) was used to study the interactions at the catalyst/solution interface under varying electrode potentials. Preliminary data analysis was carried out in 1 M KOH with catalysts consisting of Ni, Ni-Mn, Ni-Mn-Co, and Ni-Mn-Co-Fe. Furthermore, EIS measurements were conducted at three distinct potentials, i.e., -1.3 V, -1.4 V, and -1.5 V versus SCE, to obtain a deeper understanding of the hydrogen evolution reaction (HER) occurring at the electrode–electrolyte interface.

### 3.5 Current/potential curves

Current/potential curves represent the relationship between the current flowing between the working electrode (WE) and the counter electrode (CE) as the potential is incrementally increased with respect to the reference electrode. According to Faraday's law, the electrical current is proportional to the rate of the electrochemical reaction. The shape of these curves provides valuable insights into the specific electrode reactions taking place. For a simple one-electron transfer process, the curve is primarily determined by kinetic factors such as temperature, redox species concentration, and activation energy.

In this study, a range of current/potential curve techniques was employed, including open circuit potential (OCP), cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronopotentiometry (galvanostatic scans), and chronoamperometry (potentiostatic scans):

- ❖ **OCP Measurements:** Monitor the potential changes over time in the absence of current flow.
- ❖ **CV and LSV:** Voltammetric techniques involving the application of a linearly varying potential to the electrode via a potentiostat. These methods measure current as a function of time while the potential changes, typically presenting the results as current versus potential, which defines voltammetry.
- ❖ **Chronopotentiometry:** In this method, a constant current is applied to the electrode, and the corresponding potential changes are recorded over time.
- ❖ **Chronoamperometry:** Conversely, this technique applies a constant potential to the electrode and records the resulting current changes over time.

### 3.6 Test procedures

The electrocatalytic performance of the prepared samples for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) was assessed through a series of standardized test procedures. These included measurements of the open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) conducted over a specified frequency range with a 10 mV modulated signal amplitude near the OCP, cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronopotentiometry scans. Before each test, polarization conditioning was carried out at the initial potentials of the CV and LSV measurements to ensure consistency. A summary of the primary electrochemical test procedures is provided in **Table 3.5**.

**Table 3.5** General electrochemical test procedures.

| Step | Experimental        | Conditions                                 |                                            | Determined value or performance                                                                        |
|------|---------------------|--------------------------------------------|--------------------------------------------|--------------------------------------------------------------------------------------------------------|
|      |                     | HER test                                   | OER test                                   |                                                                                                        |
| 1    | OCP scan            | 10 min                                     | 10 min                                     | Open circuit potential                                                                                 |
| 2    | EIS                 | 0.5 Hz to 100 KHz                          |                                            | Electrolyte resistance                                                                                 |
| 3    | Polarization        | at 0 V vs. RHE                             | at 1.23 V vs. RHE                          | Polarize to start value of step 4                                                                      |
| 4    | CV                  | 10 mV/s, 1 scan, 0.01 V ~ -1 V             |                                            | Overpotential $\eta$ at current density $j$                                                            |
| 5    | Polarization        | at 0 V vs. RHE                             | at 1.23 V vs. RHE                          | Polarize to start value of step 6                                                                      |
| 6    | LSV                 | 10 mV/s, 1 scan, 0 V to -1.4 V vs. Ag/AgCl | 10 mV/s, 1 scan, 0 V to +1.4 V vs. Ag/AgCl | Overpotential $\eta$ at current density $j$ , onset potential, Tafel slop and exchange current density |
| 7    | Chronopotentiometry | at -100 mA/cm                              | at +100 mA/cm                              | Stability                                                                                              |

### 3.7 Conclusion

This chapter presents a comprehensive overview of the materials, methods, and experimental techniques employed in this study. The selection of high-purity chemical products and well-designed electrochemical cells ensures the reliability of the electrodeposition and electrolysis processes. The detailed description of the instrumentation, including the potentiostat-galvanostat, highlights the precision of the experimental setup used to control and monitor the electrochemical reactions.

Characterization techniques such as SEM, AFM, and XRD provided crucial insights into the surface morphology, topology, and crystalline structure of the synthesized thin films, establishing a strong correlation between the material properties and electrocatalytic performance. Furthermore, the use of advanced electrochemical techniques, including CV, LSV, and EIS, enables the thorough evaluation of electrode activity, stability, and kinetic behavior under various conditions.

By detailing the procedures and experimental setups, this chapter lays the groundwork for understanding the subsequent results and discussion. The methodologies described herein ensure reproducibility and provide a robust framework for the development and optimization of electrocatalysts for water splitting and other energy-related applications.

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# Chapter 04

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## Chapter 04: Results and discussion

This chapter presents the results and discussion derived from experimental investigations into the electrodeposition and electrocatalytic performance of nickel-based alloys. The aim is to understand the influence of various deposition parameters, techniques, and bath compositions on the morphology, structure, and catalytic efficiency of synthesized materials.

**Section 4.1** focuses on the electrodeposition of nickel (Ni) and examines the effects of the bath concentration, scan rate, temperature, pH, and support electrolyte concentration. This study provides foundational knowledge of how these parameters affect the quality and characteristics of Ni deposits.

**Sections 4.2 and 4.3** expand the investigation to nickel-manganese (Ni-Mn) alloys. Using different electrodeposition techniques, including cyclic voltammetry and fixed applied current density methods, this section explores the influence of the scan rate, pH, current density, applied potential, deposition time, and bath temperature. The role of supporting electrolytes and electrolysis parameters in enhancing the deposition process is also discussed.

**Section 4.4** highlights the electrodeposition of multicomponent Ni-Mn-Co-Fe catalysts and their performance in the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The effects of the electrochemical deposition method, bath composition, and deposition parameters, such as the scan rate, pH, and temperature, were systematically analyzed. Additionally, the impact of electrolysis conditions, including the KOH concentration and temperature, on the catalytic activity and stability was explored.

This chapter integrates experimental findings with theoretical insights, providing a comprehensive understanding of the key factors influencing the electrodeposition and performance of nickel-based alloys in electrocatalytic applications.

## 4.1 Study of the influence of different parameters on the deposit Ni

### 4.1.1 Electrochemical Study

The process of the electrochemical deposition of nickel (Ni) can be studied via cyclic voltammetry, a technique that enables the analysis of multiple reactions occurring on the surface of the working electrode during deposition. In this method, the potential applied between the working and counter electrodes varies linearly from an initial potential ( $E_i$ ) to a final potential ( $E_f$ ) at a defined scan rate ( $v$ ), which is influenced by the kinetics of the reactions involved. [1] This variation in potential induces changes in current due to the oxidation and reduction of compounds at the interface between the metal and the solution. The current is measured as a function of the potential, generating a plot referred to as a voltammogram. In our study, an Autolab potentiostat was employed to perform forward and reverse scans within the potential range of +0.01 V to -1.0 V versus Ag/AgCl at a scan rate of 10 mV/s.

For Ni electrochemical deposition, we examine the following reactions:



The principal parasitic reaction accompanying the deposition of our alloy is the hydrogen evolution reaction (HER), which is caused by  $\text{H}^+$  proton reduction, as follows:



Notably,  $E_{\text{H}^+/\text{H}_2} = -0,65 \text{ V vs. Ag/AgCl}$

The source of  $\text{H}^+$  ions in the solution also comes from the water dissociation reaction according to the following mechanism:



To understand the reduction–oxidation behavior of the Ni on the Cu substrate at various concentrations, typical cyclic voltammograms were recorded between +0.01 and -1.0 V vs. Ag/AgCl at a scan rate of 10 mV/s (see **Figure 4.1a**). The arrows show the scan directions. The bath compositions were obtained from concentrations A and B (see **Table 4.1**).

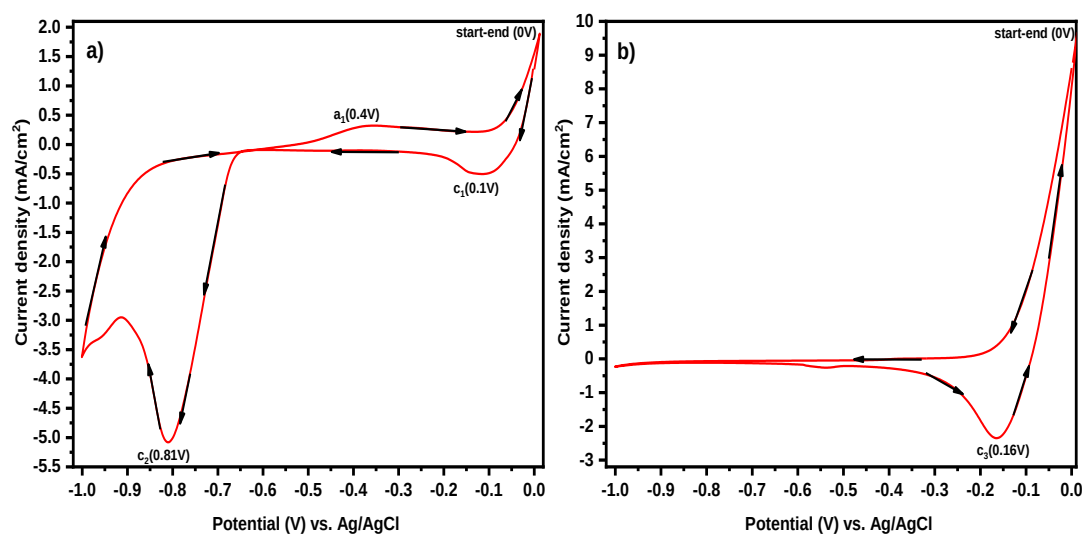


**Figure 4.1 (a)** Cyclic voltammogram of Ni electrodeposition on Cu substrate in an electrolyte containing 25 g/L  $\text{NiCl}_2$  without  $\text{NH}_4\text{Cl}$ ; **(b)** CV of the Cu substrate in an electrolyte containing 50 g/L  $\text{NH}_4\text{Cl}$  without  $\text{NiCl}_2$ . The scan rate was set to 10 mV/s.

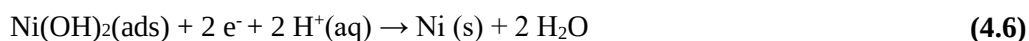
The CV curve has one anodic peak ( $a_1$ ) and two cathodic peaks ( $c_1$  and  $c_2$ ). The anodic peak  $a_1$  observed during the scan from -0.6 V to -0.3 V results from the oxidation of  $\text{Ni}_0$  to nickel oxide species. The cathodic peak  $c_1$  appears at -0.11 V, indicating the electroreduction of  $\text{Ni}^{2+}$  ions into Ni metal (**Figure 4.1(a)**):[2], [3],[4]



At more negative potentials, an exponential increase in current density was observed above -0.65 V, which was related to both  $\text{Ni}^{2+}$  reduction on the substrate and hydrogen evolution on the deposited Ni surface. [2],[5], many publications exist on the electrodeposition of Ni and Ni oxides/hydroxides on different types of substrates, which generally agree that the formation of the Ni hydroxide ( $\text{Ni}(\text{OH})_2$ ) as an important intermediate or as a competing process is the crucial reaction step for Ni deposition. [5], [3],[6],[7],[8] The reduction of  $\text{H}^+$  at the cathode causes a local increase in pH, which then leads to a competing reaction (4.5): [2]



The formed nickel hydroxide ( $\text{Ni}(\text{OH})_2$ ) is then partially reduced to metallic nickel according to the reaction (4.6), which shows a maximum peak  $c_2$  at -0.81 V. The exact position of this peak strongly depends on the scan rate, and it can also depend on the type of anion and the general pH of the solution. The reduction process can also be described as involving singly hydroxylated nickel species adsorbed on the surface. Oriňáková et al. (2006) provide an in-depth analysis of the various stages involved in nickel electroplating, highlighting recent advancements in the electrodeposition of nickel and its alloys.[8]



The anodic peak  $a_1$  at -0.4 V on the CV curve indicates the oxidation of  $\text{Ni}_0$  to nickel oxide species.[2],[3]



#### 4.1.2 Influence of the bath concentration

The concentration of the electrolyte bath plays a crucial role in governing the deposition process and the resulting material properties.

**Table 4.1** Bath composition conditions for different samples, potential scan rate of 10 mV/s,  $T=23^\circ\text{C}$ ,  $\text{pH}=3.5$ .

| Concentration                                   | A   | B   | C    | D   | E   |
|-------------------------------------------------|-----|-----|------|-----|-----|
| $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (g/L) | 25  | 0   | 12.5 | 25  | 75  |
| $\text{NH}_4\text{Cl}$ (g/L)                    | 0   | 50  | 25   | 50  | 150 |
| Temperature ( $^\circ\text{C}$ )                | 23  | 23  | 23   | 23  | 23  |
| pH                                              | 3.5 | 3.5 | 3.5  | 3.5 | 3.5 |

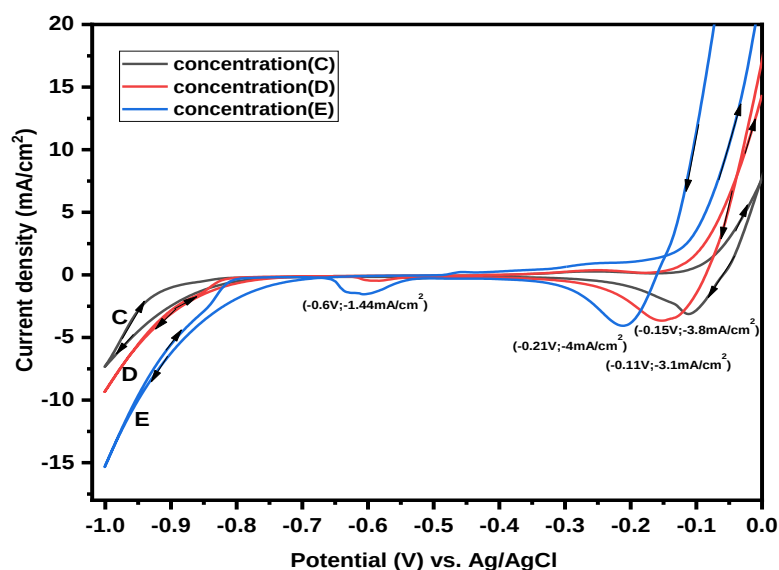


**Figure 4.2** Cyclic voltammograms were obtained for a Ni/Cu electrode in an electrolyte containing concentrations C, D, and E at pH of 3.5, at temperature of 23°C, and a scan rate =10 mV/s.

To study the effects of the bath composition on Ni/Cu electrodeposition and electrocatalytic activity, cyclic voltammetry was performed at various bath concentrations (A, B, C, D, and E) with a scan rate of 10 mV/s in the potential range of +0.01 to -1.2 V vs. Ag/AgCl.

In the absence of  $\text{NH}_4\text{Cl}$  and in the presence of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , an increase in current density to 5.1 mA (in absolute value) at a potential of approximately -0.81 mV vs. Ag/AgCl indicates the reduction of water on the substrate and the reduction of  $\text{Ni}^{+2}$  on the substrate. See **Figure 4.1 (a)**.

**Figure 4.1 (b)** shows that when only  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  is added to the electrolyte, the current density remains at 0 mA/cm<sup>2</sup>, with a negative potential shift to -0.425 V, indicating no reduction in  $\text{Ni}^{2+}$ . As the potential becomes more negative, the current increases, and a reduction peak at -0.81 V (-5.2 mA/cm<sup>2</sup>) is observed, indicating the reduction of  $\text{Ni}^{2+}$  to Ni. A current loop between -0.425 V and -0.825 V formed, indicating nucleation and a nucleation overpotential of -0.4 V. At -0.4 V, a small oxidation peak appeared, suggesting Ni dissolution.

For concentrations C, D, and E, the cyclic voltammetry results indicated that as the bath concentration of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{Cl}$  increased, the reduction peak at -0.81 V weakened and eventually disappeared, suggesting slower deposition. The nucleation potential shifted positively, and the nucleation overpotential decreased, leading to a higher growth rate of the deposited metal. The oxidation peak at -0.4 V decreased with higher concentrations, indicating

less coating dissolution. At the highest concentration (E), the current density reached  $-15.35 \text{ mA/cm}^2$  at  $-1.0 \text{ V}$  vs.  $\text{Ag/AgCl}$ , and the cathodic peak remained prominent but shifted to more negative potentials, indicating an increased overpotential caused by ion saturation effects, which may have impeded mass transfer to the electrode surface. Additionally, excessive ion concentrations can intensify hydrogen evolution, competing with nickel deposition and potentially compromising coating quality. These results highlight that intermediate electrolyte concentrations strike the best balance between ion availability and deposition kinetics, yielding superior efficiency and uniformity in nickel electrodeposition.

#### 4.1.3 Influence of the Scan Rate

The scan rate significantly affects the electrochemical response, providing insight into the kinetics and mechanisms of the redox processes.

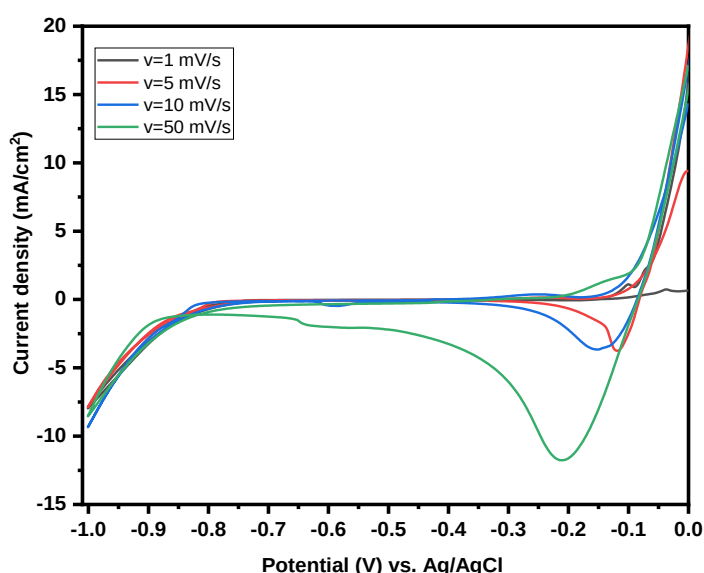


**Figure 4.3** Cyclic voltammetry analysis of the Ni/Cu electrode was carried out in an electrolyte containing  $25 \text{ g/L NiCl}_2$  and  $50 \text{ g/L NH}_4\text{Cl}$  at pH 3.5 and  $25^\circ\text{C}$ , using different scan rates.

Substrates and a series of cyclic voltammograms (**Figure 4.3**) were recorded at scan rates of 1, 5, 10, and  $50 \text{ mV/s}$ . The measurements were conducted in an electrolyte containing  $25 \text{ g/L}$  nickel(II) chloride and  $50 \text{ g/L}$  ammonium chloride, within a potential range of  $+0.01 \text{ V}$  to  $-1.0 \text{ V}$  vs.  $\text{Ag/AgCl}$ , at a temperature of  $25^\circ\text{C}$  and a pH of 3.5. The results reveal that the cathodic peaks associated with the reduction of  $\text{Ni}^{2+}$  to  $\text{Ni}$  are obscured by concurrent hydrogen evolution. The cathodic peaks observed between  $-0.25 \text{ V}$  and  $-0.1 \text{ V}$  vs.  $\text{Ag/AgCl}$  are attributed to the reduction of ammonium chloride ( $\text{NH}_4\text{Cl}$ ). The nickel oxidation peak is identified at  $E_{pc}$

= -0.6 V vs. Ag/AgCl. At an applied potential of -1.0 V vs. Ag/AgCl, the recorded current densities for scan rates of 5, 10, 50, and 100 mV/s were -7.9, -7.91, -9.4, and -8.5 mA/cm<sup>2</sup>, respectively. These findings highlight the interplay between the scan rate and deposition kinetics, with higher scan rates influencing the electrochemical behavior and current response of the system.

#### 4.1.5 Bath temperature influence

The influence of the bath temperature on the electrodeposition of nickel was investigated through cyclic voltammetry (CV) of a Ni/Cu electrode in an electrolyte containing 25 g/L [NiCl<sub>2</sub>] and 50 g/L [NH<sub>4</sub>Cl] under identical conditions of pH 3.5 and a scan rate of 10 mV/s. The CV results obtained at various temperatures provide insights into how thermal variations affect deposition kinetics and overall electrochemical behavior.

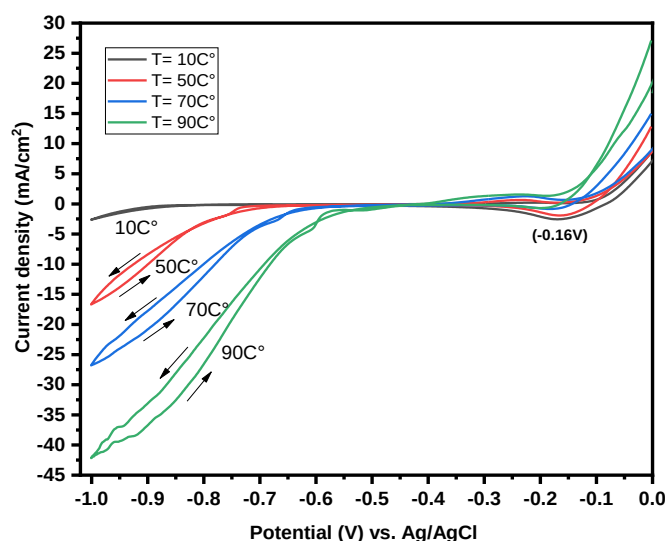


**Figure 4.4** Cyclic voltammetry of the Ni/Cu electrode in an electrolyte with 25 g/L [NiCl<sub>2</sub>] and 50 g/L [NH<sub>4</sub>Cl] at various bath temperatures (pH 3.5, scan rate 10 mV/s).

The cyclic voltammetry results show that the temperature significantly affects nickel deposition. At 10°C, no distinct reduction peak is observed, leading to thin coatings with low nickel contents and poor efficiency due to slow ion movement. As the temperature increases, the reduction peaks become more pronounced, improving the deposition rate and reducing the concentration polarization. However, temperatures above 60°C can cause instability, leading to surface cracks due to accelerated hydrogen evolution. At temperatures of 10°C, 50°C, 70°C,

and 90°C, the current density ranged from -2.64 mA/cm<sup>2</sup> to -42 mA/cm<sup>2</sup>, indicating a marked increase in deposition efficiency with increasing temperature.

#### 4.1.5 Influence of pH

The pH of the electrolyte critically influences the electrochemical behavior, deposition quality, and stability of the formed materials.

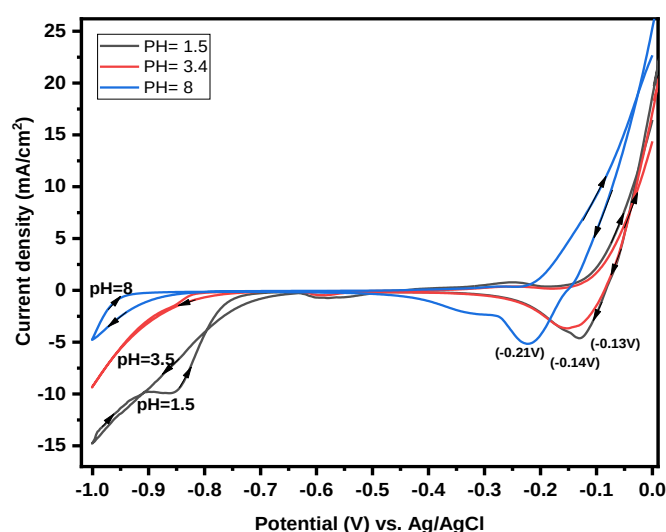


**Figure 4.5** Cyclic voltammetry of the Ni/Cu electrode in electrolytes with 25 g/L [NiCl<sub>2</sub>] and 50 g/L [NH<sub>4</sub>Cl] at various pH values and at 24°C scan rate of 10 mV/s.

The effect of the electrolyte pH on the electrodeposition of nickel was studied via cyclic voltammetry with a Ni/Cu electrode immersed in a solution comprising 25 g/L nickel(II) chloride (NiCl<sub>2</sub>) and 50 g/L ammonium chloride (NH<sub>4</sub>Cl). The investigation was carried out across a range of pH values to assess how variations in acidity or alkalinity influence the electrochemical behavior and deposition efficiency of nickel. **Figure 4.5** illustrates the impact of the electrolyte pH on the cyclic voltammetry results. At pH 8, no distinct reduction or oxidation peaks are observed, although the current density remains relatively high, suggesting a redox reaction on the electrode surface. As the pH decreases to 1.5, the maximum current density is reached, and an oxidation peak appears at -0.3 V, with the NH<sub>4</sub>Cl reduction peak shifting to -0.22 V. Lower pH values increase electrode reaction inhibition, with the equilibrium potential shifting negatively and the nucleation overpotential rising. At -1.0 V vs. Ag/AgCl, the current densities at pH values of 1.5, 3.5, and 8 are -4.71 mA/cm<sup>2</sup>, -9.32 mA/cm<sup>2</sup>, and -14.88 mA/cm<sup>2</sup>, respectively, highlighting the strong influence of pH on the deposition quality.

### 4.1.5 Influence of the electrolyte concentration

The influence of the electrolyte concentration on nickel electrodeposition was investigated via cyclic voltammetry with a Ni/Cu electrode in a solution containing 25 g/L  $\text{NiCl}_2$  and various concentrations of supporting electrolytes ( $\text{NH}_4\text{Cl}$ ,  $\text{KCl}$ , and EDTA ( $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ )) at pH 3.5, a temperature of  $25 \pm 2^\circ\text{C}$ , and a scan rate of 10 mV/s.

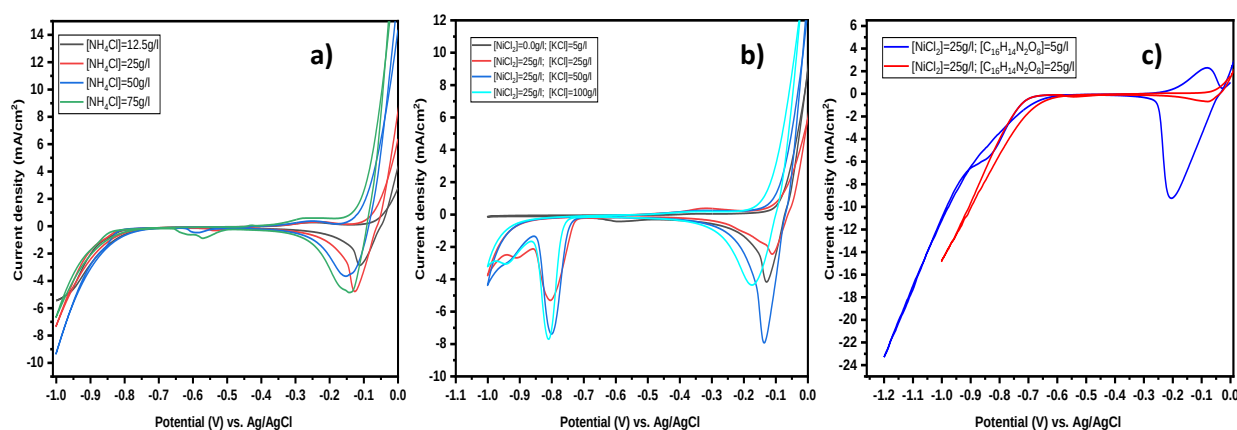


**Figure 4.6** Cyclic voltammetry of a Ni/Cu electrode immersed in an electrolyte under the following conditions: **a)**  $[\text{NiCl}_2] = 25$  g/L and varying ammonium chloride ( $\text{NH}_4\text{Cl}$ ) concentrations; **b)**  $[\text{NiCl}_2] = 25$  g/L with varying potassium chloride ( $\text{KCl}$ ) concentrations; **c)**  $[\text{NiCl}_2] = 25$  g/L with varying  $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$  concentrations; for all cases, pH = 3.5,  $T = 25 \pm 2^\circ\text{C}$ , and a scan rate of 10 mV/s.

**Figure 4.6 a** highlights the impact of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) as a supporting electrolyte, which enhances metallic ion reduction from -0.8 to -1.0 V vs. Ag/AgCl. The optimal performance is observed at 50 g/L  $\text{NH}_4\text{Cl}$ , with a peak current density of  $-9.3 \text{ mA/cm}^2$  and improved water reduction kinetics at -0.6 V.  $\text{NH}_4\text{Cl}$  reduces oxidation on the electrode surface, stabilizes the coatings, shifts the reduction peak to less negative potentials, and affects nucleation. Above 50 g/L, the kinetics are slow, which is consistent with studies showing that  $\text{NH}_4\text{Cl}$  increases the nucleation activation energy.

**Figure 4.6 b** shows the cyclic voltammograms of a Ni/Cu electrode in an electrolyte containing 25 g/L  $\text{NiCl}_2$  with varying  $\text{KCl}$  concentrations. Two cathodic peaks at -0.1 to -0.2 V and -0.75 to -0.85 V correspond to the presence of nickel and  $\text{KCl}$ , indicating metallic ion reduction and enhanced kinetics at 50 g/L  $\text{KCl}$ . The optimal current density of  $-4.4 \text{ mA/cm}^2$  at -1.0 V vs. Ag/AgCl reflects the high electrocatalytic activity at this concentration. The increased

conductivity with increasing KCl concentration aids in electrodeposition and hydrogen evolution. Beyond 50 g/L KCl, the reduced kinetics highlight the concentration-dependent nature of the reaction.

**Figure 4.6 c** shows the cyclic voltammograms of a Ni/Cu electrode in an electrolyte with 25 g/L NiCl<sub>2</sub> and varying concentrations of C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub>·2H<sub>2</sub>O. Increasing concentrations of C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub>·2H<sub>2</sub>O slowed the reaction kinetics, with improved water reduction observed at lower concentrations. At 5 g/L, a high current density of -14.7 mA/cm<sup>2</sup> at -1.0 V vs. Ag/AgCl reflects strong electrocatalytic activity compared with -11.2 mA/cm<sup>2</sup> at 25 g/L. A cathodic peak between -0.25 V and -0.15 V indicates C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub>·2H<sub>2</sub>O reduction, whereas improved conductivity and significant reduction currents near -0.65 V support nickel and H<sup>+</sup> ion deposition on the substrate. At 25 g/L, saturation limits nickel deposition.

As a result, 50 g/L NH<sub>4</sub>Cl is the best supporting electrolyte for enhancing electrocatalytic activity, offering optimal kinetics and improved electrochemical performance across various parameters.

The comparison of NH<sub>4</sub>Cl, KCl, and EDTA as supporting electrolytes in nickel electrodeposition reveals distinct impacts on the deposition efficiency, current density, and coating quality. NH<sub>4</sub>Cl significantly enhances the deposition efficiency by stabilizing the pH near the cathode and improving the solution conductivity, with optimal results observed at concentrations up to 50 g/L, facilitating uniform coatings and high reduction currents. On the other hand, KCl increases the ionic conductivity, reduces electrode polarization and enables fast deposition rates, particularly at concentrations up to 75 g/L; however, excessive KCl does not offer further improvements and may slightly increase the electrolyte resistance. In contrast, EDTA, a chelating agent, controls the release of Ni<sup>2+</sup> ions by forming stable complexes, which enhances coating uniformity at low concentrations (10-20 g/L). However, at higher concentrations (>30 g/L), EDTA significantly reduces the availability of free Ni<sup>2+</sup> ions, lowering the current density and deposition efficiency. Thus, NH<sub>4</sub>Cl and KCl are ideal for high-efficiency deposition, whereas EDTA is suitable for achieving uniform and defect-free coatings when precise control over ion release is needed.

## 4.2 Study of the influence of different techniques on the deposition of Ni-Mn and the catalytic activity for the HER and OER

Nickel-manganese (Ni-Mn) alloys were electrodeposited onto copper (Cu) substrates via two electrochemical techniques: cyclic voltammetry (CV). These methods were employed to

investigate and optimize the deposition process to enhance the structural, morphological, and catalytic properties of the alloy for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The deposition process was systematically studied under various bath parameters, including the bath composition, scan rate, pH, temperature, applied potential, current density, and deposition time. These factors were carefully controlled to achieve uniform and efficient alloy coatings with superior electrochemical performance. The electrolyte consisted of 25 g/L  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 30 g/L  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ , and 50 g/L  $\text{NH}_4\text{Cl}$ .

In the CV technique, the potential was cycled between a set range to promote the codeposition of nickel and manganese, allowing for a detailed analysis of the reduction and oxidation peaks. This comprehensive approach highlights the critical role of the bath composition and electrochemical conditions in achieving high-performance Ni–Mn alloys for water-splitting applications.

#### **4.2.1 Effects of different parameters on the electrodeposition of Ni-Mn alloys via cyclic voltammetry**

The electrodeposition of a Ni-Mn alloy via the cyclic voltammetry (CV) method is significantly influenced by various parameters that affect the nucleation, growth, and overall quality of the deposited alloy. A systematic analysis of these parameters is essential for optimizing the deposition process to achieve uniform, adherent, and catalytically active coatings. The following parameters were evaluated: scan rate, pH, supporting electrolyte effect, and deposition temperature.

##### **4.2.1.1 Influence of the Scan Rate**

The scan rate plays a key role in determining the electrochemical behavior and reaction kinetics during voltammetric analysis.

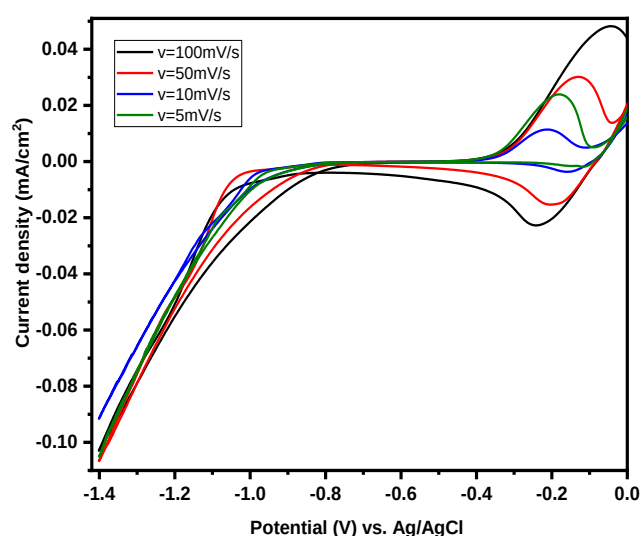


**Figure 4.7** Cyclic voltammetry of the Ni-Mn/Cu electrode in electrolytes with 25 g/L  $[\text{NiCl}_2]$ , 30 g/L  $[\text{MnCl}_2]$  and 50 g/L  $[\text{NH}_4\text{Cl}]$  at various scan rates, pH 3.5 and 25°C.

The effect of the scan rate on the electrochemical behavior of the Ni-Mn/Cu electrode was investigated via cyclic voltammetry (CV) in an electrolyte containing 25 g/L  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 30 g/L  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ , and 50 g/L  $\text{NH}_4\text{Cl}$  at pH 3.5 and 25°C. CVs were recorded at varying scan rates to evaluate their influence on the cathodic reaction kinetics and electrochemical activity. The results demonstrated that both the anodic and cathodic peak currents increased proportionally with higher scan rates, reflecting improved electrochemical activity and faster electron transfer. At lower scan rates (e.g., 5 mV/s), the cathodic reaction was diffusion-controlled, leading to broader and less intense peaks due to limited ion transport to the electrode surface. Conversely, at higher scan rates (e.g., 100 mV/s), the cathodic peak became sharper and more pronounced, indicating enhanced kinetics for the reduction of  $\text{Ni}^{2+}$  and  $\text{Mn}^{2+}$  ions. The anodic peaks also intensified, indicating efficient oxidation during the reverse scan.

The scan rate of 50 mV/s provided an optimal balance between sufficient ion diffusion and reduced mass transport limitations, enabling more uniform and efficient deposition of the Ni-Mn alloy. These findings underscore the critical role of the scan rate in optimizing the deposition conditions and achieving high-quality Ni-Mn coatings for catalytic applications.

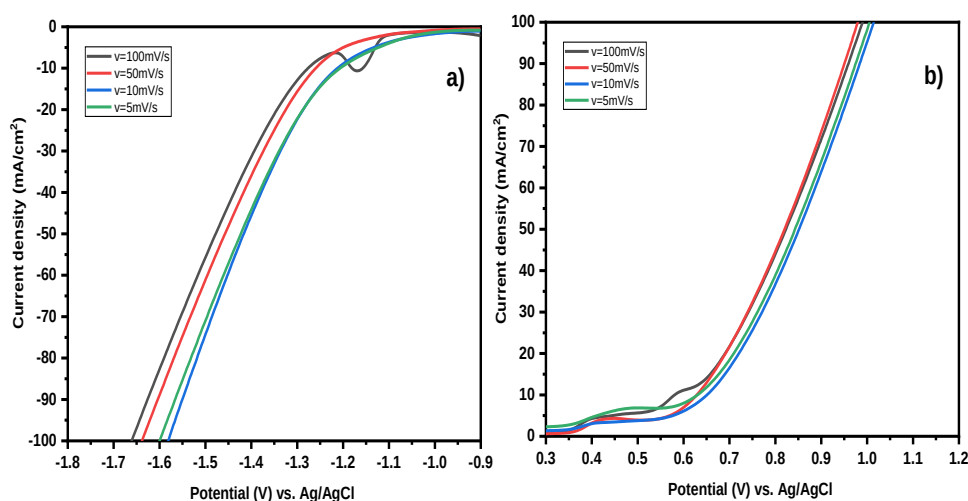


**Figure 4.8** (a) and (b) LSV curves for different scan rates of Ni-Mn-deposited catalysts prepared via the CV method. The experiments were performed in 1 M KOH (pH = 14) at  $T = 23^{\circ}\text{C}$  for the HER and OER at a scan rate of 10 mV/s.

The electrocatalytic performance of Ni-Mn electrocatalysts prepared at various scan rates was systematically studied via linear sweep voltammetry (LSV) in an alkaline electrolyte (1 M KOH) to evaluate their efficiency for the hydrogen evolution reaction (HER). **Figure 4.8(a)** shows the LSV curves for the Ni-Mn-Cu electrodes deposited at scan rates of 5, 10, 50, and 100 mV/s. The corresponding overpotentials ( $\eta_{100}$ ) required to achieve a current density of 100 mA/cm<sup>2</sup> were determined to be 587, 570, 626, and 650 mV.

These results demonstrate that lower deposition scan rates lead to enhanced catalytic performance, potentially due to greater deposition of Ni at these rates. Notably, the Ni-Mn alloy electrode prepared at 10 mV/s exhibited superior electrocatalytic activity, requiring only 570 mV of overpotential to reach 100 mA/cm<sup>2</sup>. Additionally, as the potential increases, the cathodic current density increases substantially. At higher scan rates (50 and 100 mV/s), the overpotentials increased, likely due to less uniform deposition and the formation of thinner layers, reducing the availability of active catalytic sites. Additionally, the LSV curves show a substantial increase in the cathodic current density as the applied potential becomes more negative, indicating the electrode's enhanced ability to facilitate hydrogen evolution at elevated potentials. These findings underscore the importance of optimizing the scan rate during electrodeposition to achieve superior catalytic performance for HER applications.

After the electrocatalytic properties of the electrodes for the hydrogen evolution reaction (HER) were assessed, their performance for the oxygen evolution reaction (OER) was evaluated. Using a three-electrode setup in 1.0 M KOH, the OER activity of Ni-Mn-Cu electrodes synthesized at different scan rates during deposition was analyzed. The deposition scan rates tested included 5, 10, 50, and 100 mV/s. For comparison, linear sweep voltammetry (LSV) curves were recorded and are presented in **Figure 4.8(b)**. Among the tested samples, the Ni-Mn electrode prepared at a scan rate of 50 mV/s exhibited superior performance, achieving a higher current density than the other electrodes. An overpotential of 668 mV was required to deliver a current density of 100 mA/cm<sup>2</sup>, outperforming the electrodes deposited at 5, 10, and 100 mV/s. This finding highlights the critical role of the deposition parameters in optimizing the electrocatalytic performance.

The high electrocatalytic activity of the Ni-Mn electrode results from the synergistic effect between Ni and Mn and its unique 3D structure, increasing the number of oxygen evolution reaction (OER) sites through Ni(III) or Ni(IV) formation. [9],[10] Alloying Ni with Fe and Mn increases the Ni-Ni bond length while decreasing the Ni-Fe and Ni-Mn bond lengths, aligning the d-bonds of Fe and Mn closer to the Fermi level. [11],[12] This adjustment improves the electron conductivity and promotes H<sub>2</sub> formation, with defect engineering at the catalyst surface further enhancing the electrocatalytic performance. [13],[14]

#### 4.2.1.2 pH bath influence

To evaluate the effect of the bath pH on the deposition of Ni-Mn on the copper substrate, the electrolyte composition was prepared with 25 g/L NiCl<sub>2</sub>·6H<sub>2</sub>O, 30 g/L MnCl<sub>2</sub>·6H<sub>2</sub>O, and 50 g/L NH<sub>4</sub>Cl, with the pH values adjusted to 1.5, 2.5, 3.5, and 7.5, respectively. A nickel plate was used as the counter electrode, and the temperature was maintained at room temperature. The scan rate was set to 0.01 V/s, starting from an initial potential of 0 V, with an applied potential range from 0 V at the lower vertex to -1.4 V at the upper vertex.

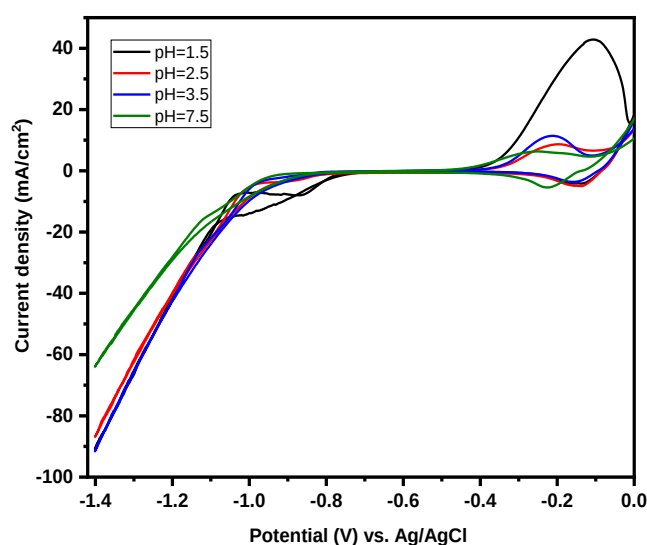


**Figure 4.9** CVs of as-deposited Ni-Mn films collected at different bath pH values at a scan rate of 10 mV/s. The electrode was immersed in an electrolyte containing  $[\text{NiCl}_2] = 25 \text{ g/L}$  and  $[\text{NH}_4\text{Cl}] = 50 \text{ g/L}$  at  $T = 25^\circ\text{C}$ .

**Figure 4.9** illustrates the significant influence of the electrolyte pH on the shape and position of the cyclic voltammetry (CV) curves for the Ni-Mn-Cu electrode. At a low pH of 1.5, the oxidation peak is observed at -0.1 V, accompanied by a high current density, indicating efficient electrochemical activity under strongly acidic conditions. When the pH is increased to 3.5, the oxidation peak shifts to -0.2 V, and the current density increases further, suggesting enhanced electrodeposition kinetics and improved reduction efficiency within this mildly acidic environment. However, as the pH continues to increase to a more neutral level, the reduction peak diminishes and eventually disappears. This is accompanied by a noticeable decrease in current density, indicating that higher pH values suppress electrode reactions. The decline in electrochemical activity at elevated pH values suggests that the deposition process is less favorable under less acidic conditions, likely due to the reduced availability of protons and changes in the electrochemical double layer. These observations underscore that a more acidic electrolyte environment promotes optimal electrodeposition performance, as it enhances ion mobility, facilitates charge transfer, and supports more efficient redox reactions.

The catalytic performance of electrodes prepared in electrolytes with various pH values was evaluated via linear sweep voltammetry (LSV) in a 1.0 M KOH solution for both the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER), as shown in **Figure 4.10**. The measurements were conducted at room temperature, with a scan rate of 10

mV/s. The applied potential ranged from an initial value of 0 V to a final value of -1.6 V, ensuring a comprehensive assessment of the electrocatalytic behavior of the electrodes under these conditions.

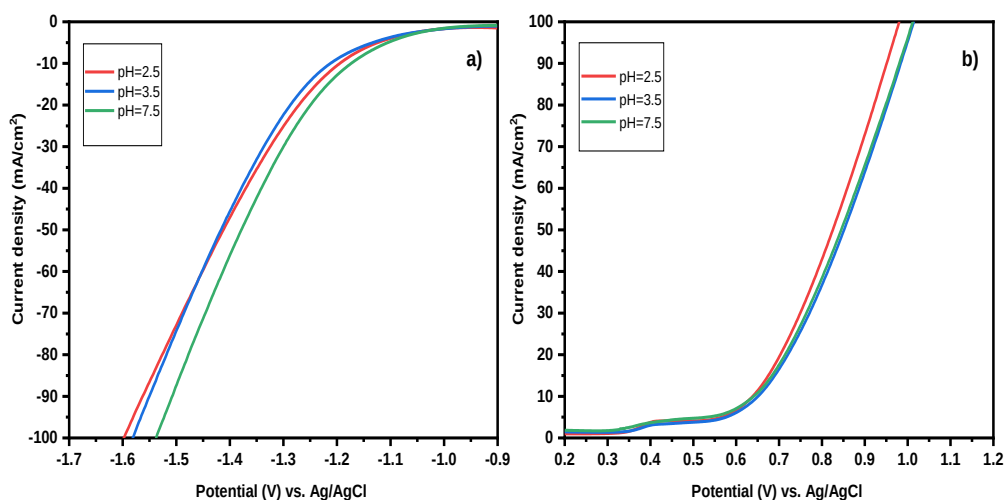


**Figure 4.10** (a) and (b) LSV curves for different bath pH values of Ni-Mn deposited catalysts prepared via the LSV method. The experiments were performed in 1 M KOH (pH = 14) at room temperature and a scan rate of 10 mV/s for the HER and OER.

The electrocatalytic performance of the Ni-Mn electrocatalysts synthesized at different pH values (2.5, 3.5, and 7.5) was evaluated for both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). For the HER, the overpotentials ( $\eta_{100}$ ) required to achieve a current density of 100 mA/cm<sup>2</sup> were measured as 585 mV, 572 mV, and 526 mV. These results demonstrate that the electrocatalyst prepared at a pH of 7.5 has the highest catalytic activity for the HER, potentially because enhanced electrodeposition conditions promote a more active surface structure.

Following the HER analysis, the performance of the Ni-Mn electrocatalysts for the OER was assessed in 1.0 M KOH via linear sweep voltammetry (LSV), and the results are depicted in **Figure 4.10 (b)**. For the OER, the overpotentials required to achieve a current density of 100 mA/cm<sup>2</sup> were 670 mV for the electrocatalyst deposited at pH 2.5 and 705 mV for those deposited at pH 3.5 and 7.5. These findings indicate that the sample prepared in the acidic bath (pH 2.5) displayed superior OER performance compared with the other samples. Additionally, the current density increased rapidly with increasing overpotential. The small preoxidation peaks observed before the onset of oxygen evolution were attributed to the formation of Ni(III) or Ni(IV) species, which serve as active sites for the OER.

The pH of the electrolytic bath significantly affects the nucleation, microstructure, and chemical composition of the coatings produced due to changes in the number of species adsorbed on the cathode as the pH varies. [15],[16, 17] The surface morphology shifts with pH, which is attributed to hydrogen evolution at the cathode, which is particularly effective at low pH, altering the electrochemical conditions. [18] At higher deposition current densities, the local pH at the cathode surface increases due to faster recovery of  $H^+$  ions than in the bulk electrolyte, causing transient local alkalization, hydrogen bubble formation, and rapid  $H^+$  depletion. [19] A lower electrolyte pH, however, favors hydrogen evolution and gradually enhances Mn deposition. [20]

Moreover, the enhanced HER activity at higher pH values is linked to favorable surface modifications that improve the number of catalytic sites and electronic conductivity, whereas the superior OER activity at lower pH values highlights the role of hydrogen evolution and the efficient formation of Mn-rich coatings under acidic conditions. These observations emphasize the importance of pH optimization to tailor the electrocatalytic properties of Ni-Mn alloys for specific applications.

#### 4.2.1.3 Supporting electrolyte effect

The supporting electrolyte influences solution conductivity, ion transport, and overall electrochemical performance during the reaction.

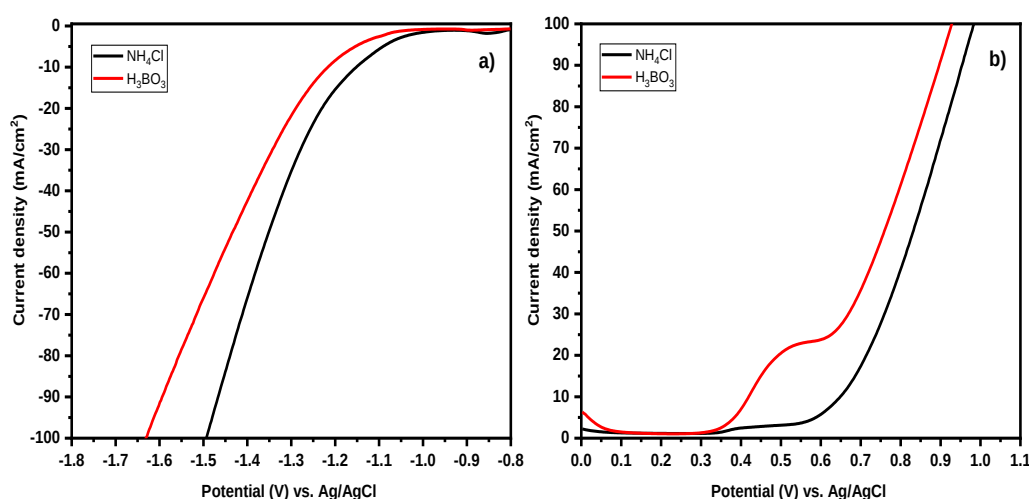


**Figure 4.11** (a) and (b) LSV curves for Ni-Mn-deposited catalysts in  $NH_4Cl$  and  $H_3BO_3$  supporting electrolytes. The experiments were performed in 1 M KOH (pH = 14) at room temperature and a scan rate of 10 mV/s for the HER and OER.

The influence of the supporting electrolyte on the catalytic performance of Ni-Mn coatings deposited on copper substrates was systematically investigated. The catalysts were synthesized

via cyclic voltammetry (CV) in baths containing 25 g/L  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 30 g/L  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ , and either 50 g/L  $\text{NH}_4\text{Cl}$  or 50 g/L  $\text{H}_3\text{BO}_3$  as the supporting electrolyte. The CV deposition process was carried out within a potential range of +0.01 V to -1.0 V versus Ag/AgCl at a scan rate of 10 mV/s.

To evaluate the electrocatalytic performance of the resulting Ni-Mn electrodes, linear sweep voltammetry (LSV) measurements were performed for both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) in a 1.0 M KOH solution. A three-electrode setup was used, with a graphite plate serving as the counter electrode and an Ag/AgCl electrode as the reference. The experiments were conducted at room temperature with a scan rate of 10 mV/s, and the applied potential was varied from 0 V to -1.7 V for the HER and up to +1 V for the OER. The results, presented in **Figures 4.11 (a) and (b)**, reveal distinct effects of the supporting electrolyte on the catalytic activity. For the HER, the Ni-Mn alloy deposited in the  $\text{NH}_4\text{Cl}$  electrolyte exhibited the lowest overpotential, indicating superior catalytic activity for hydrogen evolution. This enhancement can be attributed to the optimized deposition environment provided by  $\text{NH}_4\text{Cl}$ , which likely promotes a more uniform and active surface morphology.

Conversely, for the OER, the Ni-Mn alloy synthesized in the  $\text{H}_3\text{BO}_3$  electrolyte demonstrated the highest catalytic activity, requiring a lower overpotential to achieve a significant current density. This improved performance is potentially due to the stabilizing role of  $\text{H}_3\text{BO}_3$  in the formation of Ni(III) or Ni(IV) species, which are known to act as active sites for oxygen evolution.

These findings underscore the critical role of the supporting electrolyte in tailoring the electrocatalytic properties of Ni-Mn coatings, enabling optimization for specific reactions such as the HER or OER.

#### 4.2.1.4 Deposition temperature effect

Aaboubi et al. highlighted that the superior performance of Ni-Mn-based catalysts for the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and ethanol oxidation reaction (EOR) can be attributed to two key factors. First, the incorporation of manganese (Mn) into nickel (Ni) alloys enhances the intrinsic electrocatalytic activity by optimizing the number of active sites. Second, an increase in the deposition bath temperature above 60°C significantly

increases the effective surface area by increasing the porosity and roughness of the coating, which increases the number of active sites and their accessibility [9]. On the basis of these insights, a deposition bath temperature of 60°C was selected for comparative studies.

This investigation focused on evaluating the effects of the deposition bath temperature on the formation and catalytic properties of Ni-Mn coatings on copper substrates. The catalysts were synthesized via cyclic voltammetry (CV) in an electrolyte containing 25 g/L  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 30 g/L  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ , and 50 g/L  $\text{NH}_4\text{Cl}$ , with the bath temperature systematically varied between 25°C and 60°C. The results revealed significant temperature-dependent changes in the deposition process and the resulting catalyst properties. At a bath temperature of 60°C, the reduction potential was greater than that at 25°C, indicating a more favorable electrochemical environment for the reduction of  $\text{Ni}^{2+}$  and  $\text{Mn}^{2+}$  ions. This increase at elevated temperatures can be attributed to improved ionic mobility, decreased solution viscosity, and increased electrode reaction kinetics.

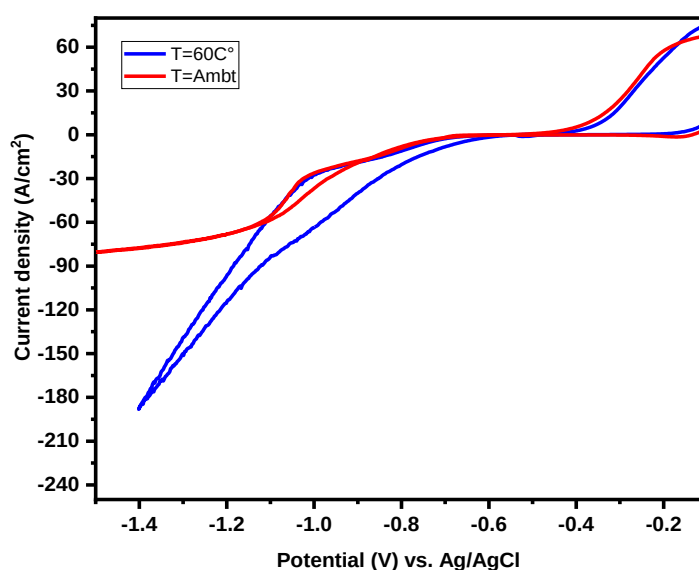


**Figure 4.12** Cyclic voltammetry of Ni-Mn coatings on copper at various bath temperature scan rates of 10 mV/s in electrolytes with 25 g/L  $[\text{NiCl}_2]$ , 30 g/L  $[\text{MnCl}_2]$ , and 50 g/L  $[\text{NH}_4\text{Cl}]$  at pH 3.5.

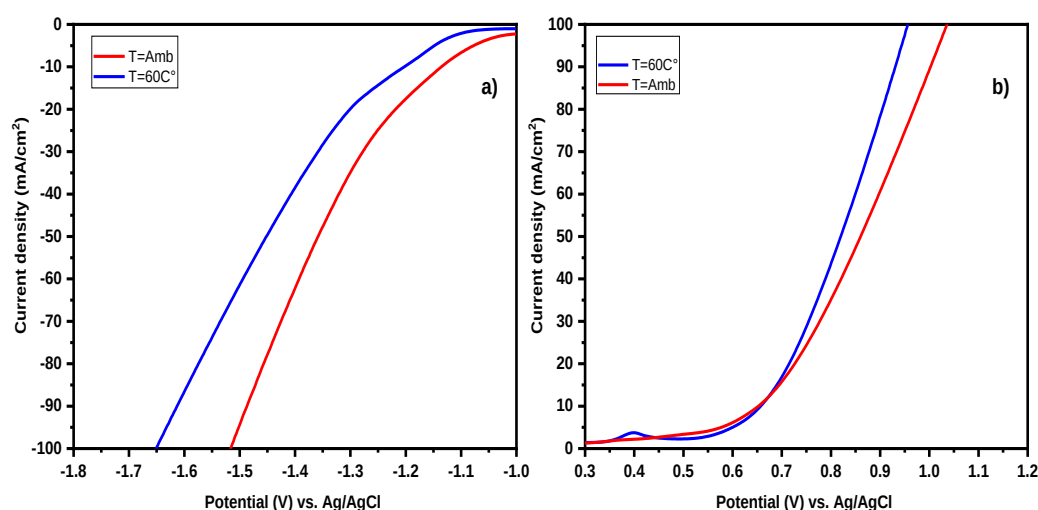


**Figure 4.13** (a) and (b) LSV curves for the Ni-Mn-deposited catalysts at different temperatures (25°C and 60°C). The experiments were performed in 1 M KOH (pH = 14) at pH = 3.5 and a scan rate of 10 mV/s for the HER and OER.

The hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) activities of the Ni-Mn catalysts deposited at 25°C and 60°C were evaluated through water electrolysis via linear sweep voltammetry (LSV) in a 1.0 M KOH solution. The results are shown in **Figures 4.13 (a) and (b)**, highlighting the influence of the deposition temperature on the electrocatalytic performance for both reactions.

For the OER, the Ni-Mn catalyst deposited at 60°C demonstrated superior electrocatalytic activity compared with the catalyst deposited at 25°C. A higher deposition temperature resulted in coatings with greater porosity and roughness, leading to a significant increase in the effective surface area. This morphological improvement promotes a greater number of active sites for oxygen evolution, particularly Ni(III) and Ni(IV) species, which are known to play critical roles in facilitating the OER. The increased electrolyte temperature also enhances ion mobility and reduces viscosity, improving the kinetics of the oxygen evolution reaction. Consequently, the Ni-Mn (60°C) electrode displayed the highest OER activity, outperforming its counterpart prepared at 25°C.

In contrast, for the HER, the Ni-Mn catalyst deposited at 25°C exhibited better catalytic performance than the one deposited at 60°C. At lower deposition temperatures, the HER process benefits from the more compact and uniform structure of the Ni-Mn coating. This denser morphology reduces the charge transfer resistance and facilitates the adsorption of hydrogen intermediates on the active sites, which is critical for the HER mechanism.

Additionally, at lower deposition temperatures, the formation of hydrogen bubbles on the electrode surface is less pronounced, mitigating their blocking effect on the active sites.

The observed differences between the OER and HER performances of the Ni-Mn catalysts at various deposition temperatures can be attributed to the distinct structural and chemical requirements of each reaction. For the OER, high-temperature deposition improves the formation of high-valence Ni species and increases the exposure of active sites due to enhanced surface roughness. However, for the HER, low-temperature deposition favors a compact coating structure and reduces hydrogen bubble interference, leading to superior performance. These findings underline the importance of tailoring the deposition parameters to optimize the catalytic performance of Ni-Mn electrodes for specific electrochemical processes. High deposition temperatures are recommended for applications prioritizing the OER, whereas lower temperatures are more suitable for efficient HER performance.

#### **4.2.2 Electrodeposition of a Ni-Mn alloy on copper via the fixed applied current/potential method**

In this study, all samples were synthesized using a fixed applied current density. The plating bath, which was maintained at a pH of 3.5, consisted of 25 g/L  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 30 g/L  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ , and 50 g/L  $\text{NH}_4\text{Cl}$ . A nickel plate served as the counter electrode during deposition, with experiments conducted at ambient temperature and a scan rate of 10 mV/s.

The performance of the Ni-Mn catalysts was evaluated in a 1 M KOH solution using a graphite plate as the counter electrode. The hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) activities were analyzed through water electrolysis via linear sweep voltammetry (LSV). Key parameters such as current density, applied potential, deposition time, and bath temperature were systematically investigated to assess their impact on the catalytic performance of the electrodes prepared under these conditions.

##### **4.2.2.1 Current density influence**

The current density plays a crucial role in the electrodeposition process and significantly influences the performance of synthesized catalysts. While the behavior of conventional alloy systems can often be explained via diffusion theory, the complexities associated with induced codeposition systems, particularly in relation to current density, remain less understood. To examine the impact of current density on the catalytic performance of the Ni-Mn catalysts, the

electrodes were synthesized at current densities of 50, 150, 310, and 500 A/cm<sup>2</sup>, with a deposition time of 2 minutes. The electrocatalytic activities of these electrodes for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) were evaluated through water electrolysis. Linear sweep voltammetry (LSV) curves illustrating the performance of the Ni-Mn catalysts deposited under these conditions are shown in **Figure 4.14**.

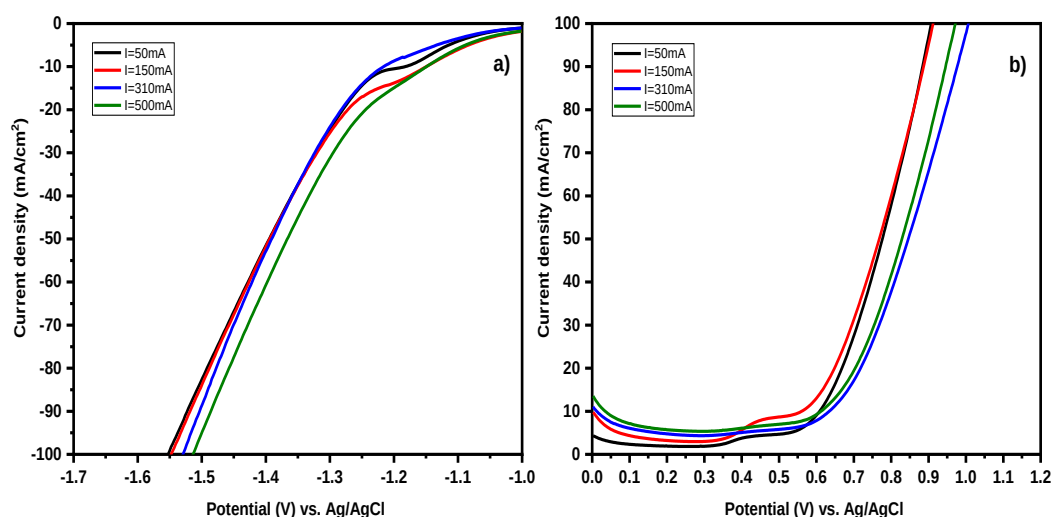


**Figure 4.14 (a) and (b)** LSV curves for Ni-Mn-deposited catalysts prepared at different current densities for 2 min at pH = 3.6 and T = 27°C. The electrode was immersed in 1 M KOH (pH = 14) at a scan rate of 10 mV/s for the HER and OER tests.

**Figures 4.14 (a) and (b)** demonstrate the dependence of the catalytic activity on the current density, indicating that higher current densities enhance the performance of the cathode. The deposition process yielded optimal coatings within a specific current density range. The optimal current density was 500 mA/cm<sup>2</sup> for the hydrogen evolution reaction (HER) and 150 mA/cm<sup>2</sup> for the oxygen evolution reaction (OER). Below these values, the deposits were dark, likely due to the presence of partially reduced Ni and Mn oxides. Conversely, excessively high current densities compromised the deposit quality, leading to defects such as poor adhesion and inconsistent surface morphology.

The current density significantly influences the composition and properties of an alloy. Higher current densities, such as 500 mA/cm<sup>2</sup>, promoted Ni deposition, enhancing the HER activity. Lower current densities, such as 150 mA/cm<sup>2</sup>, were more favorable for OER activity, as they facilitated a balanced Ni-Mn composition. [9, 21]

In addition to the current density, the pH of the electrolyte played a crucial role in shaping the microstructure and chemical state of the alloy. Both parameters influence the balance between the metallic and oxide phases, which directly affects the catalytic performance. [22] These findings highlight the need for careful optimization of the current density and pH during synthesis to produce high-performance Ni–Mn coatings with tailored properties for HER and OER applications.

#### 4.2.2.2 Applied potential influence

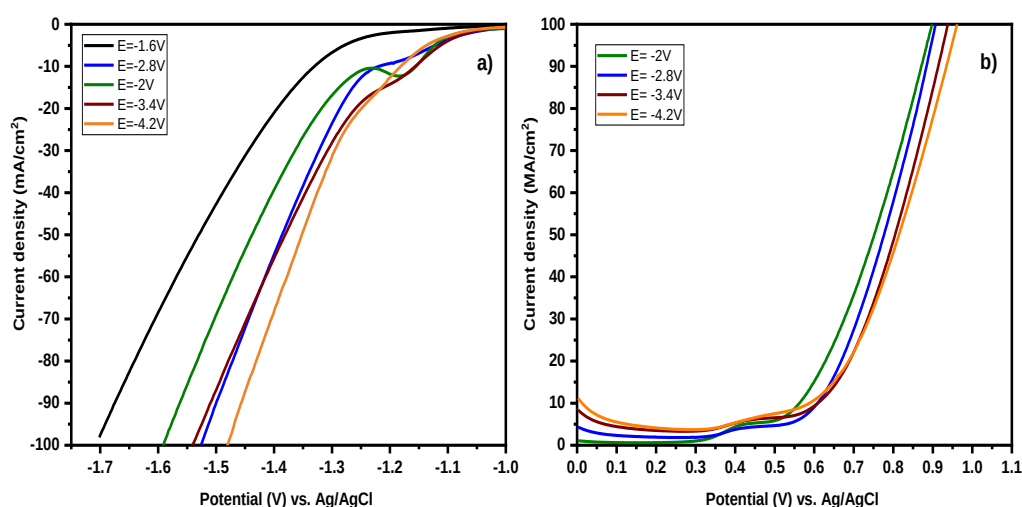


**Figure 4.15 (a) and (b)** LSV curves for Ni-Mn-deposited catalysts prepared at different applied potentials for 2 min at pH = 3.6 and T = 27°C. The electrode was immersed in 1 M KOH (pH = 14) at a scan rate of 10 mV/s for the HER and OER tests.

The influence of the applied reduction potential on the electrodeposition process and catalytic performance of the Ni-Mn samples was thoroughly investigated. **Figure 4.15 (a)** presents linear sweep voltammetry (LSV) curves for the hydrogen evolution reaction (HER) of the Ni-Mn catalysts deposited at various reduction potentials. The applied potential was adjusted from -2.0 V to -4.2 V, with a deposition time of 2 minutes at room temperature. As the reduction potential became more negative, the catalytic activity improved significantly. This enhancement was attributed to the morphological refinement of the coating and the increased electroactive surface area, which collectively increased the catalytic efficiency for the HER.

Similarly, the effect of the reduction potential on the oxygen evolution reaction (OER) performance of the Ni-Mn electrodes was evaluated, as shown in **Figure 4.15 (b)**. The samples exhibited distinct catalytic behaviors based on the potential applied during electrodeposition. Interestingly, an applied potential of -2.0 V resulted in superior OER performance compared with more negative potentials. This outcome highlights the intricate balance required in

electrodeposition: excessively negative potentials can lead to defects such as hydrogen evolution-induced porosity or uneven surface morphology, which degrade the catalytic activity of the OER.

#### 4.2.2.3 Deposition time influence

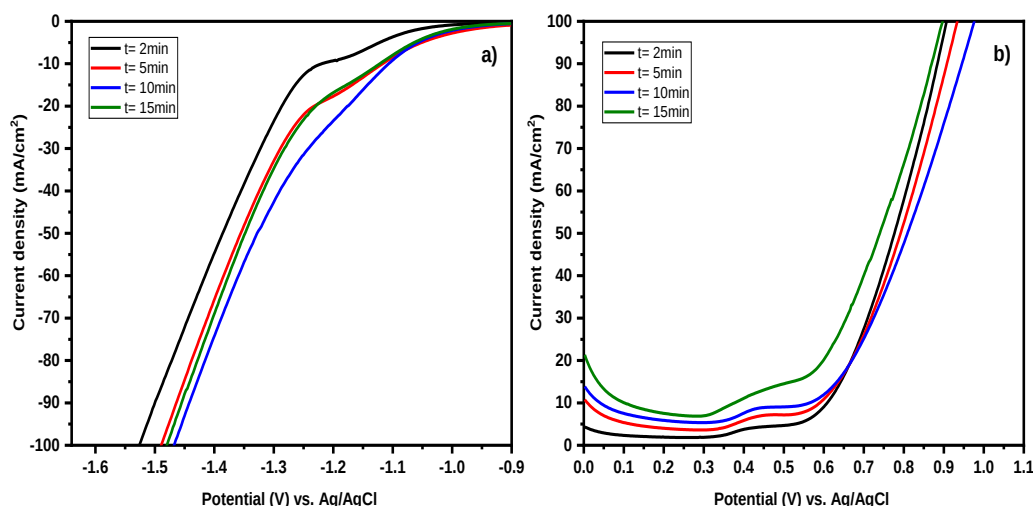


**Figure 4.16** (a) and (b) LSV curves for Ni–Mn-deposited catalysts prepared at different deposition times and a fixed applied potential of  $E = -2.8$  V,  $\text{pH} = 3.6$ , and  $T = 27^\circ\text{C}$ . The electrode was immersed in 1 M KOH ( $\text{pH} = 14$ ) at a scan rate of 10 mV/s for the HER and OER tests.

The effects of the deposition time on the electrocatalytic performance of the Ni-Mn catalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) were thoroughly examined. The catalysts were synthesized with deposition times of 2, 5, 10, and 15 minutes at a fixed potential of  $-2.8$  V. The HER performance improved significantly with increasing deposition time, as indicated by a decrease in the overpotential at  $100 \text{ mA/cm}^2$  ( $\eta_{100}$ ) to 460 mV for the sample deposited for 10 minutes. This increase is attributed to the formation of denser coatings with more active sites. For the OER, increasing the deposition time led to improved catalytic activity, with  $\eta_{100}$  reaching 448 mV for the 15-minute sample, due to increased surface area and active nickel oxidation states. These results demonstrate the critical role of deposition time in optimizing Ni-Mn coatings for specific electrochemical reactions.

The sharp increase in current density with increasing potential suggests improved activity. Additionally, anodic peaks appearing near 1.3 V, just before the onset of the OER, indicate a change in the oxidation state of nickel, likely serving as active sites for improved OER catalytic performance [23].

#### 4.2.2.4 Bath temperature influence

The effects of the bath temperature during deposition on the performance of the Ni-Mn catalysts were investigated. For each sample, a potential of  $E = -2.8$  V was applied for 2 minutes in a deposition bath maintained at three different temperatures: 25°C, 50°C, and 60°C. The Ni-Mn catalysts were then examined in a 1 M KOH solution.

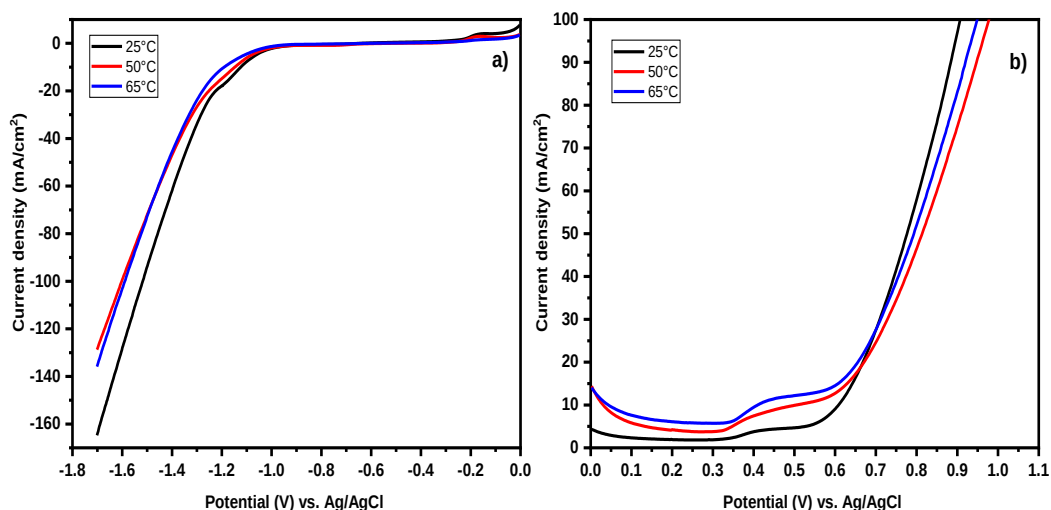


**Figure 4.17** (a) and (b) LSV curves for Ni-Mn-deposited catalysts prepared at different bath temperatures, with a fixed applied potential of  $E = -2.8$  V for 2 min and a scan rate of 10 mV/s. The electrode was immersed in 1 M KOH (pH = 14) for the HER and OER tests.

The catalytic performance of the Ni-Mn electrodes prepared at different electrodeposition bath temperatures was evaluated for both HER and OER activities. **Figure 4.17 (a)** shows the LSV curves for the HER activity of the Ni-Mn coatings deposited at 25°C, 50°C, and 65°C. Among these samples, the NiMn25°C coating exhibited the highest HER activity, outperforming the NiMn/50°C and NiMn/65°C samples. The superior catalytic activity of the NiMn/25°C coating can be attributed to the favorable surface morphology and electrochemical characteristics achieved at ambient temperature, which promote efficient hydrogen evolution. Similarly, **Figure 4.17 (b)** shows the LSV curves for the OER activity of the Ni-Mn coatings deposited at the same temperatures. Compared with the NiMn/50°C and NiMn/65°C coatings, the NiMn/25°C coating also demonstrated superior OER activity. These results indicate that electrodeposition at ambient temperature optimizes the catalytic performance of Ni-Mn coatings for both the HER and OER, likely due to enhanced structural integrity and active site availability.

Furthermore, the NiMn/25°C coating may possess a favorable oxidation state distribution for the OER. The ambient deposition conditions likely create a Ni-Mn alloy surface with a balanced mix of  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  species, which are known to serve as active sites for the OER. This balance enhances the catalytic efficiency by facilitating the oxidation of hydroxide ions to oxygen gas.

In contrast, higher deposition temperatures (50°C and 65°C) may cause more pronounced side reactions, such as hydrogen evolution during deposition, which can compromise the uniformity and compactness of the coating.

### **4.3 Influence of electrolysis bath parameters on the catalytic performance for the HER and OER**

In this study, Ni-Mn catalysts were synthesized under a fixed applied current density via an electroplating bath containing 25 g/L  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 30 g/L  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ , and 50 g/L  $\text{NH}_4\text{Cl}$ , with the bath pH maintained at 3.5. The deposition process employed a nickel plate as the counter electrode and was conducted at ambient temperature.

Both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) activities were assessed via linear sweep voltammetry (LSV). This study systematically examined the influence of key parameters, including the KOH concentration, electrolyte type, and bath temperature, on the electrochemical performance of Ni-Mn catalysts.

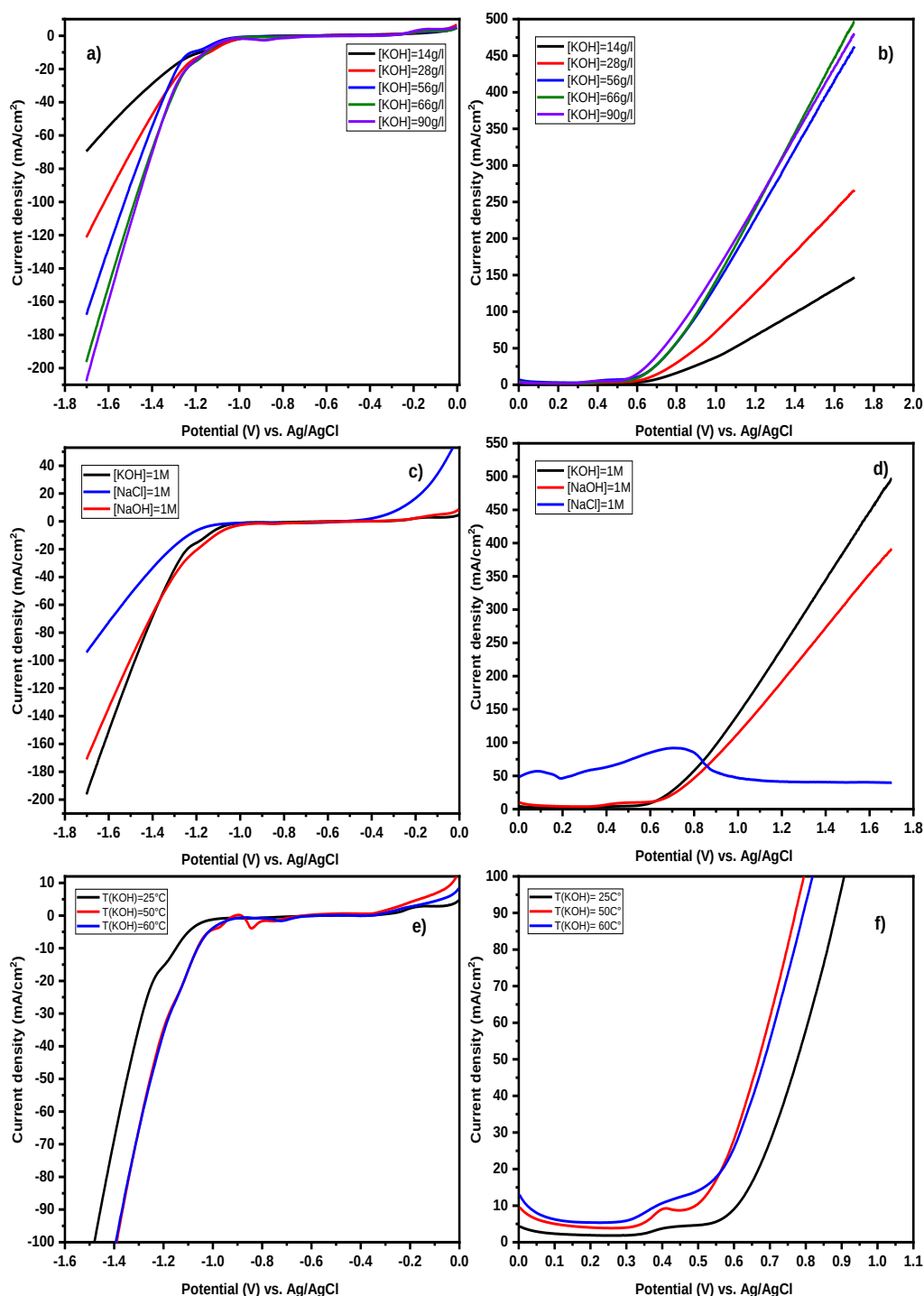


**Figure 4.18** (a) and (b) LSV curves for Ni-Mn-deposited catalysts at different KOH concentrations. (c) and (d) LSV curves for different electrolytes containing 1 M KOH, NaCl, and NaOH. (e) and (f) LSV curves for KOH at different temperatures. All electrodes were prepared at a fixed applied potential of  $E = -2.8$  V for 2 minutes,  $\text{pH} = 3.5$ , and  $T = 25^\circ\text{C}$ , with a scan rate of 10 mV/s for the HER and OER tests.

### 4.3.1 Effect of the KOH concentration:

The performance of the Ni-Mn catalyst was evaluated at KOH concentrations of 14, 28, 56, 66, and 90 g/L via water electrolysis to assess both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) activities. The corresponding LSV curves are shown in **Figure 4.18 (a) and (b)**. **Figure 4.18 (a)** illustrates the effect of the KOH concentration on the HER activity. Higher KOH concentrations enhanced the catalytic performance, primarily due to improved solution conductivity. Similarly, as shown in **Figure 4.18 (b)**, increasing the KOH concentration also improved the OER activity, which was attributed to the same effect of increased conductivity. These findings are consistent with the observations of Muhammad Aqeel Ashraf [17], where higher KOH concentrations significantly increased the catalytic performance by increasing the conductivity of the electrolyte solution.

### 4.3.2 Electrolyte type influence:

The catalytic performance of the Ni-Mn catalysts was evaluated with three electrolytes (KOH, NaOH, and NaCl) for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) activities. The LSV curves for these experiments are shown in **Figures 4.18 (c) and (d)**. **Figures 4.18 (c) and (d)** show that 1 M KOH significantly outperformed 1 M NaOH and 1 M NaCl. The superior performance of KOH is attributed to its higher ionic conductivity and better transport of hydroxide ions ( $\text{OH}^-$ ), which increase the reaction kinetics and minimize energy losses. Additionally, the smaller potassium ions of KOH improve charge transport, whereas NaCl introduces competing reactions, such as chlorine evolution, reducing efficiency. Thus, 1 M KOH proves to be the most effective electrolyte for optimizing HER and OER activities.

### 4.3.3 Effect of the electrolyte temperature:

For the HER, **Figure 4.18 (e)** shows that increasing the electrolyte temperature enhanced the catalytic activity. This improvement is attributed to the increased ionic mobility and reduced solution viscosity at elevated temperatures, which improve charge transfer and reduce the overpotential. At higher temperatures, the faster diffusion of reactants and products also facilitates better reaction kinetics.

For the OER, **Figure 4.18 (f)** illustrates a similar trend, with the catalytic activity increasing as the temperature increased, reaching optimal performance at 50°C. The enhanced OER activity at this temperature is likely due to improved surface reactions and the activation of additional catalytic sites. However, at 60°C, slight performance degradation was observed, possibly due to gas bubble accumulation on the electrode surface or decreased stability of the catalyst layer.

## 4.4 Electrodeposition of Ni-Mn-Co-Fe catalysts for the HER and OER

The catalytic performance of Ni-Mn-Co-Fe catalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is strongly influenced by the electrodeposition bath parameters and bath electrolysis conditions. Key factors such as electrochemical methods for electrodeposition, the bath composition, the scan rate, the pH, and the temperature of the bath play significant roles in determining the alloy composition, phase distribution, and surface morphology. Proper adjustment of these parameters ensures the formation of a uniform, well-alloyed catalyst with an optimal balance of active sites for both reactions. Similarly, electrolysis conditions such as the KOH concentration and bath temperature directly affect the catalyst's structural and catalytic performance.

In this study, a series of experiments was conducted to examine how deposition parameters influence the surface morphology and chemical composition of Ni-Mn-Co-Fe/Cu catalysts, as these factors critically impact their HER and OER catalytic activities (refer to **Tables 2, 3, and 4**). Additionally, the effects of water electrolysis bath parameters, including the KOH temperature and concentration, were investigated (see **Table 4.4**). This study evaluated the catalytic activity and stability of these catalysts under alkaline conditions for the HER and OER.

#### 4.4.1 Effect of electrodeposition bath parameters

The Ni-Mn-Co-Fe catalysts were electrodeposited onto Cu substrates via electrochemical techniques such as fixed potential, LSV, linear polarization, and two sequential potentials. The deposition bath comprised  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and  $\text{NH}_4\text{Cl}$ . Parameters such as the electrochemical method for electrodeposition, bath composition, scan rate, pH, temperature, and deposition duration were optimized to study their effects on the electrodeposition process and enhance the catalytic properties of the Ni-Mn-Co-Fe electrodes.

##### 4.4.1.1 Different electrochemical methods for electrodeposition

This study assesses the impact of various electrochemical techniques on the electrodeposition of a Ni-Mn-Co-Fe coating onto a copper substrate. The catalysts were fabricated via four different techniques: (1) a fixed potential of -2.8 V held for two minutes, (2) LSV from an initial value of -0.5 V to a final value of -1.6 V, (3) linear polarization from -0.5 V to -1.6 V, and (4) two sequential potentials, starting at -0.8 V for one minute, followed by -1.2 V for an equal duration. The coating solution contained 25 g/L  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 30 g/L  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ , 10 g/L  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 10 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and 50 g/L  $\text{NH}_4\text{Cl}$ , with the pH adjusted to 3.5 at room temperature. For HER and OER testing, a graphite plate was used as the counter electrode, and the Ni-Mn-Co-Fe catalysts were assessed in a 1 M KOH solution (pH 14) at room temperature with a scan rate of 10 mV/s. The HER and OER characteristics were evaluated through water electrolysis, and the LSV curves of the Ni-Mn-Co-Fe-deposited catalysts prepared by various techniques are shown in **Figure 4.19**.

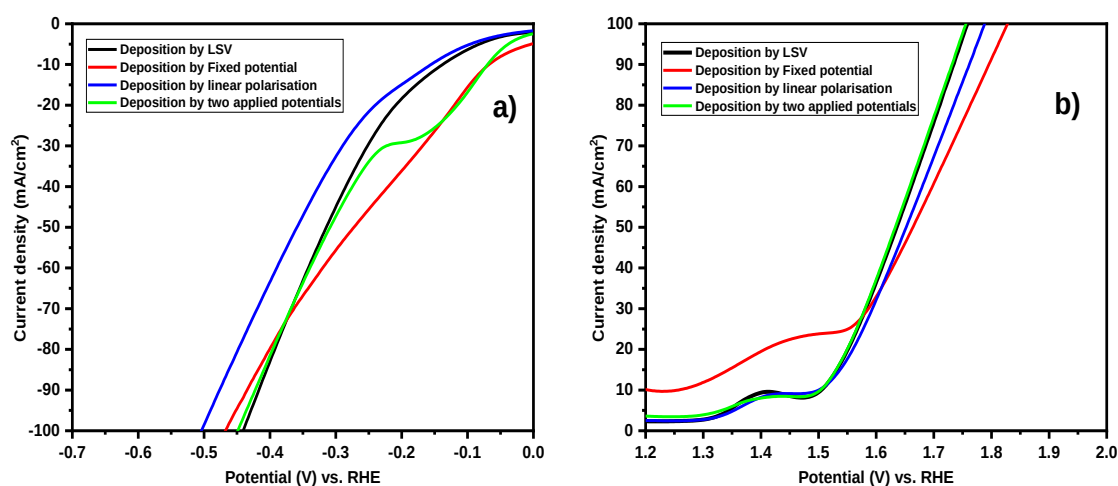


**Figure 4.19** (a) and (b) LSV curves for Ni-Mn-Co-Fe-deposited catalysts prepared via different electrochemical methods for the HER and OER. The experiments were performed in 1 M KOH (pH = 14) at a potential scan rate of 10 mV/s and  $T = 23^{\circ}\text{C}$ .

The electrocatalytic activity of the Ni-Mn-Co-Fe catalysts for the hydrogen evolution reaction (HER) was assessed by measuring the overpotentials necessary to reach a current density of  $100 \text{ mA/cm}^2$ . The LSV curves showing the HER performance of the catalysts deposited via various methods are presented in **Figure 4.19 (a)**. The overpotentials for catalysts deposited via linear polarization, fixed potential, two-step variable potentials, and LSV were -510 mV, -460 mV, -450 mV, and -440 mV, respectively. These results highlight the superior HER activity of the Ni-Mn-Co-Fe catalyst prepared via the LSV method, which exhibited the lowest overpotential. This enhanced performance can be attributed to the uniform distribution of active sites and the optimized surface morphology achieved through the LSV deposition process. The cathodic current density also increased with the applied potential, reflecting the catalyst's capacity to sustain efficient hydrogen evolution under higher driving forces.

The oxygen evolution reaction (OER) performance of the catalysts was also assessed, as shown in the LSV curves in **Figure 4.19(b)**. The Ni-Mn-Co-Fe catalyst deposited via LSV demonstrated the highest OER activity, achieving a current density of  $100 \text{ mA/cm}^2$  at a potential of 1.74 V vs. RHE. This performance surpasses that of catalysts prepared via two-step variable potentials (1.75 V vs. RHE), fixed potentials (1.77 V vs. RHE), and linear polarizations (1.81 V vs. RHE). The enhanced OER performance of the LSV-deposited catalyst is likely due to a more favorable alloy composition and increased availability of electrochemically active sites resulting from the precise control of the deposition parameters in the LSV process.

The small peaks observed before the onset of oxygen evolution were attributed to the formation of Ni(III) or Ni(IV) species, which serve as active sites for the OER [10]. The enhanced electrocatalytic performance of the Ni-Mn-Co-Fe catalysts can also be attributed to alloying with Co and Fe, which are known for their intrinsic catalytic activity. These elements, when incorporated into nanostructures, improve the overall electrocatalytic activity by increasing the availability of active sites [24, 25].

#### 4.4.1.2 Bath Composition Effect

This research investigated how the bath composition influences the catalytic performance of a Ni-Mn-Co-Fe coating on copper. The catalysts were synthesized via the LSV process, with the bath concentrations detailed in **Table 5**. A nickel plate served as the counter electrode, the temperature was maintained at room temperature, the scan rate was set at 10 mV/s, and the applied voltage ranged from -0.5 to -1.4 V. The HER and OER activities of the catalysts were assessed in 1 M KOH through water electrolysis.

**Table 4.2** Bath composition conditions for different samples and their corresponding overpotential values for the HER and OER. Experiments were conducted with a potential scan rate of 10 mV/s at  $T = 23^{\circ}\text{C}$  and  $\text{pH} = 3.5$ .

| Concentration | NH <sub>4</sub> Cl<br>(g/L) | NiCl <sub>2</sub> ·6H <sub>2</sub> O<br>(g/L) | MnCl <sub>2</sub> ·6H <sub>2</sub> O<br>(g/L) | CoCl <sub>2</sub> ·6H <sub>2</sub> O<br>(g/L) | FeSO <sub>4</sub> ·7H <sub>2</sub> O<br>(g/L) | Overpotential<br>(mV)<br>At -100 mA<br>for<br>(HER) | Overpotential<br>(mV)<br>At 100 mA<br>for (OER) | Tafel<br>slope<br>(mV/dec)<br>for<br>(HER) | Tafel<br>slope<br>(mV/dec)<br>for<br>(OER) |
|---------------|-----------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------------|-------------------------------------------------|--------------------------------------------|--------------------------------------------|
| <b>A</b>      | 25                          | 12.5                                          | 15                                            | 2.5                                           | 2.5                                           | -494                                                | 606                                             | 100                                        | 180                                        |
| <b>B</b>      | 25                          | 12.5                                          | 15                                            | 5                                             | 5                                             | -578                                                | 544                                             | 173                                        | 120                                        |
| <b>C</b>      | 25                          | 12.5                                          | 15                                            | 10                                            | 10                                            | -551                                                | 590                                             | 149                                        | 150                                        |
| <b>D</b>      | 50                          | 25                                            | 30                                            | 5                                             | 5                                             | -463                                                | 482                                             | 95                                         | 110                                        |
| <b>E</b>      | 50                          | 25                                            | 30                                            | 10                                            | 10                                            | -436                                                | 447                                             | 92                                         | 90                                         |
| <b>F</b>      | 50                          | 25                                            | 30                                            | 20                                            | 20                                            | -494                                                | 511                                             | 102                                        | 140                                        |

The results presented in **Table 4.2** and **Figure 4.20** highlight the influence of the bath composition on the electrocatalytic performance of the Ni-Mn-Co-Fe alloys for both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). Sample E, which featured the highest concentrations of active metal species (Ni, Mn, Co, and Fe), demonstrated superior performance, with the lowest overpotentials of -436 mV for the HER and 447 mV for the OER at a current density of 100 mA/cm<sup>2</sup>. Additionally, this sample exhibited the smallest Tafel slopes for the HER (92 mV/dec) and OER (90 mV/dec), indicating excellent reaction

kinetics. In contrast, Sample B, which has the lowest metal concentrations, shows the poorest catalytic activity, with the highest overpotentials (-578 mV for the HER and 544 mV for the OER) and the largest Tafel slopes (173 mV/dec for the HER and 120 mV/dec for the OER), reflecting slower reaction kinetics. These results suggest that increasing the concentration of active metals in the bath enhances both the catalytic efficiency and reaction kinetics, with Sample E achieving optimal performance because of its well-balanced composition. This aligns with studies showing that Mn, Co, and Fe enhance the OER performance of Ni in such alloys. [9, 26, 27]

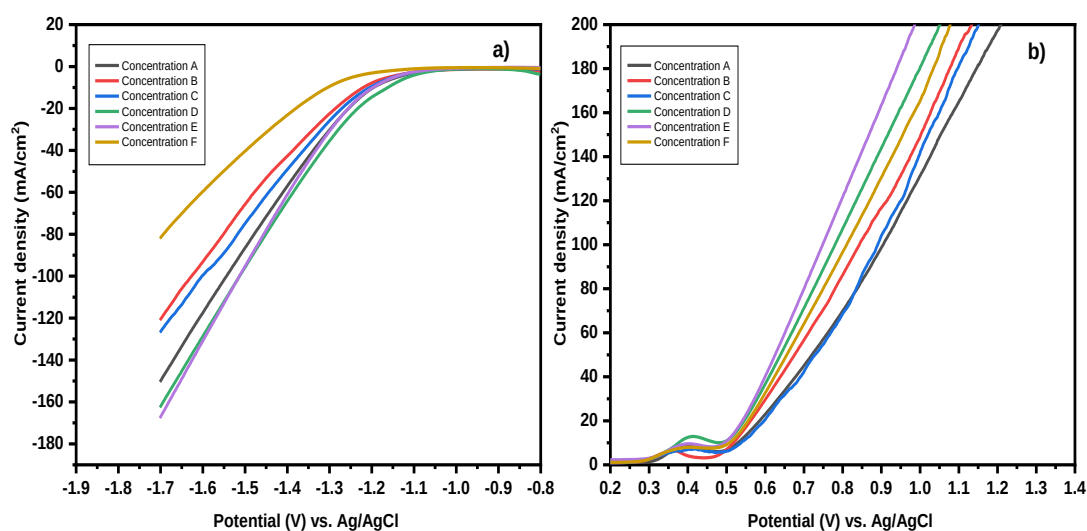


**Figure 4.20** (a) and (b) LSV curves for the Ni-Mn-Co-Fe deposited catalysts at different bath concentrations. The experiments were performed in 1 M KOH (pH = 14) at a potential scan rate of 10 mV/s and  $T = 22^{\circ}\text{C}$  for the HER and OER.

#### 4.4.1.3 Effects of Bath Electrodeposition Parameters: Scan Rate, pH, and Temperature

The performance of Ni-Mn-Co-Fe catalysts is significantly influenced by the electrodeposition parameters, including the scan rate, bath pH, and temperature, which play critical roles in determining the catalyst morphology, composition, and catalytic activity. The scan rate affects the deposition dynamics by influencing the uniformity and distribution of the alloy on the substrate. A higher scan rate promotes rapid deposition but may lead to uneven surface morphology, whereas a lower scan rate favors controlled deposition, enhancing uniformity and active site availability. The bath pH impacts the electrochemical behavior of metal ions during deposition. An optimal pH range ensures proper ionic interaction and electrodeposition efficiency. Deviations from this range can result in incomplete alloy

formation or altered catalyst composition, negatively affecting catalytic performance. The bath temperature is another crucial parameter, as it governs the kinetics of the electrodeposition process and influences the diffusion of ions in the electrolyte. Elevated temperatures improve ion mobility and deposition rates but may also lead to changes in surface morphology or alloy phase distribution. Conversely, lower temperatures can reduce the deposition efficiency, resulting in a less active catalyst. Optimizing these parameters ensures the formation of a well-alloyed, morphologically favorable catalyst with enhanced electrocatalytic properties for both the HER and OER. The relationships among the scan rate, pH, and temperature were systematically evaluated in this study to identify the conditions that maximize the catalytic performance of the Ni-Mn-Co-Fe alloys (**Table 4.3** and **Figure 4.21**).

**Table 4.3** Bath electrodeposition parameters for different samples and their corresponding overpotential values for the HER and OER. The bath composition included  $[\text{NiCl}_2 \cdot 6\text{H}_2\text{O}] = 25$  g/L,  $[\text{MnCl}_2 \cdot 6\text{H}_2\text{O}] = 30$  g/L,  $[\text{CoCl}_2 \cdot 6\text{H}_2\text{O}] = 10$  g/L,  $[\text{FeSO}_4 \cdot 7\text{H}_2\text{O}] = 10$  g/L, and  $[\text{NH}_4\text{Cl}] = 50$  g/L.

| Parameters                                                |                              | HER | OER | Overpotential<br>(mV)<br>At -100mA for<br>(HER) | Overpotential<br>(mV)<br>At 100mA for<br>(OER) | Tafel<br>slope<br>(mV/dec)<br>for<br>(HER) | Tafel<br>slope<br>(mV/dec)<br>for<br>(OER) |
|-----------------------------------------------------------|------------------------------|-----|-----|-------------------------------------------------|------------------------------------------------|--------------------------------------------|--------------------------------------------|
| <b>pH = 3.5 and<br/>Temperature =<br/>25°C</b>            | Scan rate<br>mV/s            | 05  | 05  | -508                                            | 450                                            | 110                                        | 120                                        |
|                                                           |                              | 10  | 10  | -436                                            | 547                                            | 92                                         | 90                                         |
|                                                           |                              | 50  | 50  | -615                                            | 590                                            | 115                                        | 145                                        |
| <b>pH = 3.5 and<br/>Scan<br/>rate = 10 mV/s</b>           | Bath<br>temperatur<br>e (°C) | 25  | 25  | -436                                            | 547                                            | 92                                         | 90                                         |
|                                                           |                              | 50  | 50  | -530                                            | 640                                            | 124                                        | 140                                        |
|                                                           |                              | 65  | 65  | -540                                            | 660                                            | 125                                        | 140                                        |
| <b>Temperature =<br/>25°C and Scan<br/>rate = 10 mV/s</b> | pH bath                      | 1.5 | 1.5 | -582                                            | 586                                            | 117                                        | 140                                        |
|                                                           |                              | 3.5 | 3.5 | -436                                            | 447                                            | 92                                         | 90                                         |
|                                                           |                              | 7.5 | 7.5 | -659                                            | 482                                            | 158                                        | 110                                        |

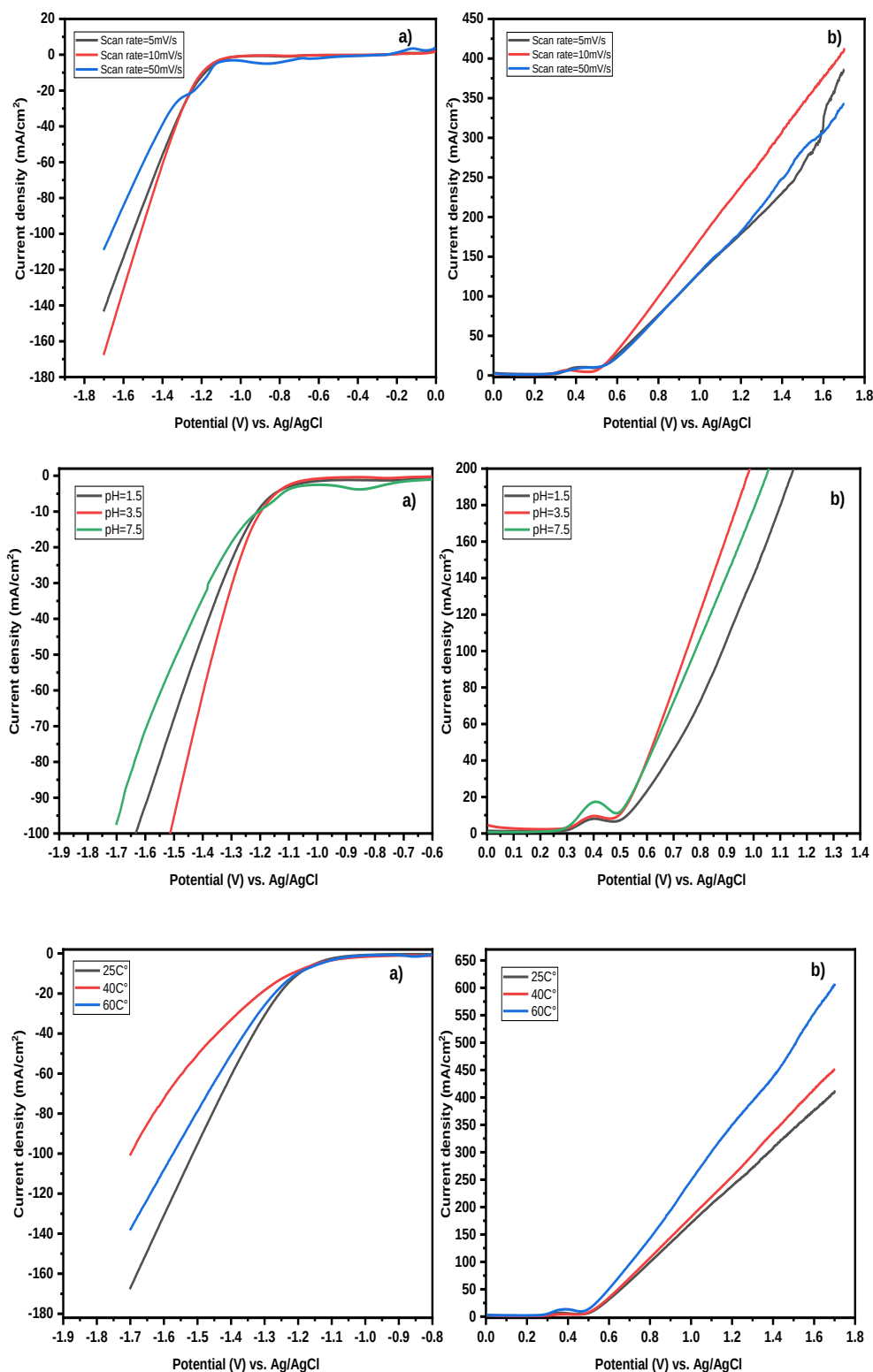


**Figure 4.21** LSV curves for Ni-Mn-Co-Fe-deposited catalysts prepared at different scan rates, pH values and bath temperatures via the LSV method. The experiments were performed in 1 M KOH (pH = 14) at a scan rate of 10 mV/s for the HER and OER.

The electrocatalytic performance of the Ni-Mn-Co-Fe catalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) was investigated via water electrolysis via linear sweep voltammetry (LSV) in a 1 M KOH solution (**Figure 4.21**). The applied potential ranged from 0 V to -1.7 V for the HER tests and 0 to +1.7 V for the OER, with the electrodeposition conditions and corresponding overpotentials summarized in **Table 4.3**.

#### a) Effect of the Scan Rate on the Electrocatalytic Activity

The impact of the scan rate on the electrocatalytic performance of the Ni-Mn-Co-Fe coatings deposited on copper was analyzed at scan rates of 5, 10, and 50 mV/s. All the experiments were conducted at room temperature, with the solution pH adjusted to 3.5. **Figure 4.21 (a)** shows the  $P_{100}$  values (potentials required to achieve a current density of 100 mA/cm<sup>2</sup>) for the various electrodes. The results demonstrate that the Ni-Mn-Co-Fe catalyst prepared at a scan rate of 10 mV/s exhibited the best electrocatalytic performance, achieving a  $P_{100}$  value of -1.50 V. In contrast, the  $P_{100}$  values for the electrodes synthesized at scan rates of 5 mV/s and 50 mV/s were -1.56 V and -1.67 V, respectively. This improved performance at 10 mV/s is attributed to a balance between kinetic and capacitive behavior, allowing for enhanced charge transfer and better utilization of active sites. Furthermore, increasing the applied potential led to a proportional increase in the cathodic current density, highlighting the robust catalytic activity of the Ni-Mn-Co-Fe alloy.

#### b) Influence of Bath pH on Catalytic Performance

The effect of the bath pH on the electrocatalytic activity of the Ni-Mn-Co-Fe catalysts was investigated by synthesizing electrodes at pH values of 1.5, 3.5, and 7.5 while maintaining a room temperature bath and a scan rate of 10 mV/s. **Figure 4.21** presents the  $P_{100}$  values obtained under these conditions. The catalyst prepared at pH 3.5 demonstrated superior performance, with a  $P_{100}$  value of -1.51 V, compared with -1.72 V at pH 7.5, -1.62 V at pH 5.5, and -1.615 V at pH 1.5. The enhanced activity at pH 3.5 is attributed to favorable proton exchange dynamics and optimal modification of the catalyst surface charge, which facilitates increased reaction kinetics. These findings underscore the critical role of pH in modulating the surface chemistry and catalytic efficiency of the Ni-Mn-Co-Fe alloy.

### c) Effect of Bath Temperature on Electrocatalytic Activity

The influence of the bath temperature on the catalytic performance of the Ni-Mn-Co-Fe electrodes was examined by preparing catalysts at 25°C, 40°C, and 60°C, with the bath pH set to 3.5 and the scan rate maintained at 10 mV/s. **Figure 4.21** depicts the current densities achieved at an applied potential of 1.7 V. The catalysts exhibited current densities of 400 mA/cm<sup>2</sup>, 430 mA/cm<sup>2</sup>, and 600 mA/cm<sup>2</sup> at 25°C, 40°C, and 60°C, respectively. A clear increase in catalytic activity was observed with increasing temperature for the OER, with the highest performance achieved at 60°C. This improvement is likely due to accelerated reaction kinetics and improved mass transport at elevated temperatures, which facilitate greater utilization of active sites. Additionally, the small peaks observed prior to the onset of oxygen evolution are attributed to the formation of Ni(III) or Ni(IV) species, which act as active intermediates for the OER.

The electrocatalytic performance of Ni-Mn-Co-Fe catalysts is strongly influenced by the scan rate, bath pH, and temperature. A scan rate of 10 mV/s optimizes the balance between kinetic and capacitive processes, reducing overpotentials and Tafel slopes, which correspond to improved catalytic activity. Similarly, a bath pH of 3.5 enhances proton exchange dynamics and modifies the surface charge, significantly lowering the  $P_{100}$  value, whereas an acidic environment and ambient temperature further improve catalyst performance. Increasing the bath temperature to 60°C markedly increased the activity, particularly for the OER, by accelerating the reaction kinetics and promoting the formation of active Ni(III) or Ni(IV) species. The lowest Tafel slopes observed for both the HER and OER highlight optimal catalytic conditions, attributed to an increased electrochemical surface area (ECSA) and favorable intrinsic interactions among Ni, Mn, Co, and Fe, underscoring the potential of Ni-Mn-Co-Fe alloys as efficient bifunctional electrocatalysts for water splitting applications.

#### 4.4.2 Effects of bath electrolysis

This study aims to investigate the influence of the KOH concentration and temperature on the electrocatalytic activity of Ni-Mn-Co-Fe in the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The catalysts were synthesized via linear sweep voltammetry (LSV) at various concentrations of KOH (0.25, 0.50, 0.75, 1.00, and 1.5 M) and different temperatures (25, 40, 55, and 75°C) with a scan rate of 10 mV/s (**Figure 4.22**). The pH was maintained at 14.

**Table 4.4** presents the overpotentials for the Ni-Mn-Co-Fe-deposited catalysts across different electrolytes. These results highlight the significant impact of the KOH concentration and temperature on the electrocatalytic performance of the Ni-Mn-Co-Fe electrode for the HER and OER. Increasing the KOH concentration from 0.25 to 1.50 mol/L substantially reduces the overpotential to achieve a current density of  $-50 \text{ mA/cm}^2$  for the HER (from  $-533 \text{ mV}$  to  $-314 \text{ mV}$ ) and OER (from  $566 \text{ mV}$  to  $324 \text{ mV}$ ) to achieve a current density of  $50 \text{ mA/cm}^2$ . Similarly, increasing the bath temperature from  $25^\circ\text{C}$  to  $75^\circ\text{C}$  decreases the overpotential for the HER (from  $-315 \text{ mV}$  to  $-199 \text{ mV}$ ) and OER (from  $365 \text{ mV}$  to  $247 \text{ mV}$ ), reflecting the beneficial effects of elevated temperatures on the reaction kinetics and active site formation.

**Table 4.4.** Bath electrolysis parameters for different samples and their overpotential values for the HER and OER at  $\text{pH} = 14$ , with a potential scan rate of  $10 \text{ mV/s}$ .

| Parameters                              | HER conditions | OER conditions | Overpotential (mV)<br>At $-50 \text{ mA}$<br>for<br>(HER) | Overpotential (mV)<br>At $50 \text{ mA}$ for<br>(OER) |
|-----------------------------------------|----------------|----------------|-----------------------------------------------------------|-------------------------------------------------------|
| KOH concentration<br>mol/L              | 0.25           | 0.25           | -533                                                      | 566                                                   |
|                                         | 0.50           | 0.50           | -432                                                      | 409                                                   |
|                                         | 0.75           | 0.75           | -320                                                      | 409                                                   |
|                                         | 1.00           | 1.00           | -314                                                      | 358                                                   |
|                                         | 1.50           | 1.50           | -314                                                      | 324                                                   |
| KOH temperature<br>( $^\circ\text{C}$ ) | 25             | 25             | -315                                                      | 365                                                   |
|                                         | 40             | 40             | -388                                                      | 303                                                   |
|                                         | 55             | 55             | -314                                                      | 275                                                   |
|                                         | 75             | 75             | -199                                                      | 247                                                   |

#### a) For the KOH concentration:

The performance of the Ni-Mn-Co-Fe catalysts in alkaline media for both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) improved significantly with increasing KOH concentration. A KOH concentration of  $1.5 \text{ M}$  resulted in the highest catalytic activity for the HER, achieving a current density of  $180 \text{ mA/cm}^2$  at  $-1.7 \text{ V}$  vs.  $\text{Ag/AgCl}$ . This improvement is attributed to the increased ionic conductivity and increased availability of hydroxide ions ( $\text{OH}^-$ ), which facilitate faster charge transport and reduce overpotentials. Similarly, for the OER, the current density increased with increasing KOH concentration, reaching a peak of  $530 \text{ mA/cm}^2$  at  $1.7 \text{ V}$  vs.  $\text{Ag/AgCl}$  in  $1.5 \text{ M}$  KOH. The higher  $\text{OH}^-$

availability at elevated concentrations promotes oxygen intermediate formation and improves the reaction kinetics, further lowering the overpotential. These findings confirm that the optimized KOH concentration (1.5 M) maximizes the electrocatalytic efficiency of the Ni-Mn-Co-Fe electrodes, making them highly effective for water-splitting applications.

**b) For temperature:**

The electrocatalytic activity of the Ni-Mn-Co-Fe electrodes was assessed via LSV in 1.0 M KOH, and the effects of the solution temperature on the HER and OER performance were examined. For the HER, the current density at -1.7 V vs. Ag/AgCl was used as an indicator of activity, with higher KOH temperatures significantly enhancing the catalytic performance. At 75°C, the Ni-Mn-Co-Fe electrode achieved a maximum current density of 190 mA/cm<sup>2</sup>, which was attributed to improved ionic conductivity and reaction kinetics at elevated temperatures. For the OER, the electrocatalytic performance peaked at 55°C, where the electrode reached 600 mA/cm<sup>2</sup> at 1.7 V vs. Ag/AgCl. Beyond this temperature, the performance slightly decreased to 550 mA/cm<sup>2</sup> at 75°C, potentially due to increased gas bubble formation, mass transport limitations, or electrode stability issues. These results highlight the temperature-dependent nature of the HER and OER, demonstrating the potential of the Ni-Mn-Co-Fe electrode as a robust bifunctional electrocatalyst for water splitting under optimized conditions.

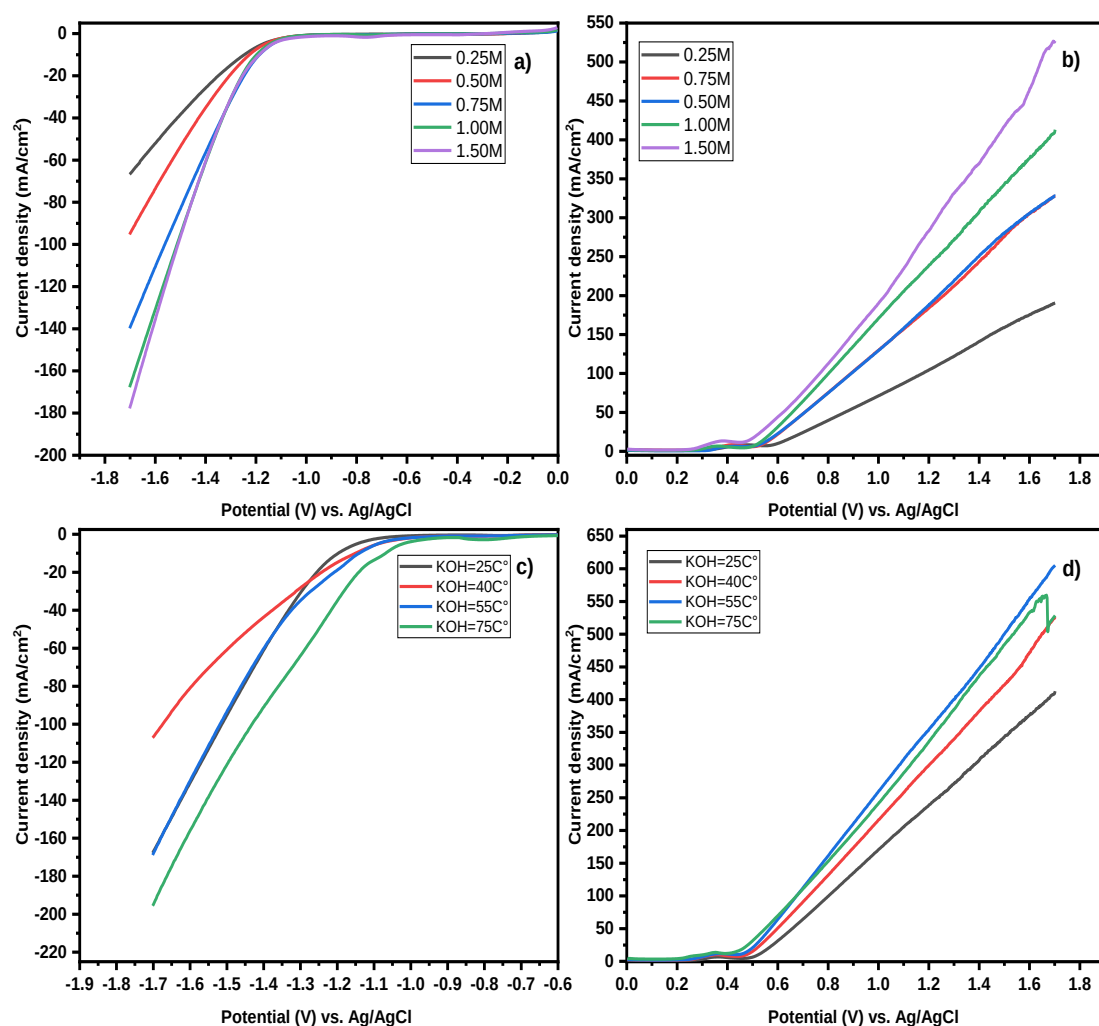


**Figure 4.22** (a) and (b) LSV curves for Ni-Mn-Co-Fe-deposited catalysts at different KOH concentrations obtained via the LSV method. (c) and (d) LSV curves for Ni-Mn-Co-Fe-deposited catalysts at different KOH temperatures obtained via the LSV method for the HER and OER, respectively.

## 4.5 Conclusion

In this chapter, the electrodeposition and electrocatalytic performance of Ni, Ni-Mn, and Ni-Mn-Co-Fe alloys for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) were systematically studied. For Ni deposition on copper substrates, various bath parameters, such as composition, scan rate, temperature, pH, and supporting electrolytes, were optimized, revealing that higher concentrations of nickel chloride and ammonium chloride, moderate scan rates, and elevated temperatures significantly enhanced the coating quality and catalytic activity. For the Ni-Mn alloys, both cyclic voltammetry (CV) and fixed potential were employed, which demonstrated that an acidic deposition pH, lower scan rates, and optimized current density positively influence the HER activity, whereas neutral to alkaline conditions are favorable for the OER performance. The addition of supporting electrolytes, such as  $\text{NH}_4\text{Cl}$ , and increased deposition times further improved the catalytic properties. Finally, for the Ni-Mn-Co-Fe alloys, LSV proved to be the most effective deposition method, and the optimized bath composition, scan rate, pH, temperature, and KOH concentration collectively resulted in superior electrocatalytic activity. These findings highlight the critical role of deposition parameters in tailoring the properties of these alloys, establishing their potential as efficient catalysts for water splitting applications.

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# Chapter 05

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## Chapter 5: Catalysts comparison

This chapter provides an in-depth comparison of catalysts, focusing on their synthesis, characterization, and electrocatalytic performance for the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and overall water splitting. The discussion begins with the electrodeposition of various nickel-based alloys, detailing their structural and morphological characterization via advanced techniques, followed by an analysis of their electrochemical measurements. The results and discussion include surface morphology studies, XRD analysis to investigate the crystal structure and phase composition, and a comparative evaluation of the electrocatalytic performance of the alloys in the HER and OER. The chapter then delves into the electrochemical impedance spectroscopy (EIS) and stability of the Ni-Mn-Co-Fe alloy, highlighting its charge transfer properties, capacitive behavior, and long-term durability. The dual functionality of the catalysts in overall water splitting was explored, emphasizing their potential in integrated water-splitting systems. Finally, a detailed comparison of the electrocatalytic hydrogen evolution capabilities of the developed catalysts is presented, benchmarking their performance against existing systems and highlighting their advantages. This chapter underscores the critical role of material properties in enhancing electrocatalytic performance and provides valuable insights for designing advanced catalysts for renewable energy applications.

## 5.1 Electrodeposition of different nickel-based alloys

**Table 5.1** presents the chemical compositions of the bath solutions used for the five samples: Ni, Ni-Mn, Ni-Co, Ni-Mn-Co, and Ni-Mn-Co-Fe.

**Table 5.1** provides the chemical composition, pH, and temperature values of the bath used for deposition.

|                                            | Ni  | Ni-Mn | Ni-Co | Ni-Mn-Co | Ni-Mn-Co-Fe |
|--------------------------------------------|-----|-------|-------|----------|-------------|
| NiCl <sub>2</sub> .6H <sub>2</sub> O (g/l) | 25  | 25    | 25    | 25       | 25          |
| MnCl <sub>2</sub> .4H <sub>2</sub> O (g/l) | 0   | 30    | 0     | 30       | 30          |
| CoCl <sub>2</sub> .6H <sub>2</sub> O (g/l) | 0   | 0     | 10    | 20       | 10          |
| FeSO <sub>4</sub> .7H <sub>2</sub> O (g/l) | 0   | 0     | 0     | 0        | 10          |
| NH <sub>4</sub> Cl (g/l)                   | 50  | 50    | 50    | 50       | 50          |
| pH                                         | 3.5 | 3.5   | 3.5   | 3.5      | 3.5         |
| Temperature (C°)                           | 23  | 23    | 23    | 23       | 23          |

### 5.1.1 Characterization

After the electrodeposition process and electrochemical evaluation, the coating electrodes were analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). SEM (TESCAN MIRA3 INSTRUMENT JSM-6360) was utilized to investigate the microstructure, surface morphology, and chemical composition of the optimized catalyst. The surface roughness and topography were further examined via AFM (Ara-A.F.M., Model No. 0101/A, Iran). To study the phase structure of the coatings, X-ray diffraction (XRD) analysis was performed via a Philips X'Pert diffractometer. Additional details regarding the characterization methods and parameters are provided in Chapter 3.

### 5.1.2 Electrochemical measurements

Electrochemical measurements were performed at room temperature following the methodology outlined in Chapter 3. A copper substrate served as the working electrode, whereas a nickel plate was used as the counter electrode. For tests in 0.1 M KOH, an Ag/AgCl reference electrode (3 M KCl, 0.209 V vs. SHE) was employed, and for 1 M KOH, a Hg/HgO reference electrode (1 M NaOH, 0.11 V vs. SHE) was used. Electrochemical impedance spectroscopy (EIS) was conducted to determine the electrolyte resistance over a frequency range of 0.5 Hz to 100 kHz with a signal amplitude of 10 mV near the open circuit potential (OCP). Linear sweep voltammetry (LSV) was utilized to assess the catalytic activity for the

hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) across a potential range of 0.0 to -1.4 V versus Ag/AgCl at a scan rate of 10 mV/s. Stability tests were conducted under constant current densities of -100 and +100 mA/cm<sup>2</sup> for up to 20 hours in 1 M KOH. Additional methods, including long-term chronopotentiometric measurements and cyclic voltammetry (CV), were used to investigate the electrocatalytic stability. Potentials measured against reference electrodes (E vs. ref) were converted to the reversible hydrogen electrode scale (E vs. RHE) via the following formula:

$$E_{(RHE)} = E^0_{(Ag/AgCl)} + 0.059 \text{ pH} + 0.204 \dots\dots\dots(5.1)$$

The values were corrected for electrolyte resistance on the basis of the EIS data, and the current density was normalized to a geometrical surface area of 1 cm<sup>2</sup>. To evaluate the capability of the bifunctional electrode for overall water splitting, a two-electrode system was used, where the synthesized electrode acted as both the anode and cathode. All the electrochemical analyses were carried out with an Autolab PGSTAT302N in a three-electrode cell configuration.

Compared with the hydrogen evolution reaction (HER), the oxygen evolution reaction (OER) is more challenging both thermodynamically and kinetically. Ideally, in an efficient electrocatalytic system, the anodic and cathodic reactions should proceed simultaneously within the electrolyte, which implies that HER and OER catalysts need to be stable under similar conditions. Using the same electrocatalyst for both the HER and OER is advantageous, as it simplifies the system and reduces overall costs. Consequently, developing catalysts capable of promoting both the OER and HER is essential to streamline electrolysis and achieve cost-effectiveness. Despite significant progress, only a few catalysts have been found that can effectively facilitate both the HER and OER in the same environment.[1, 2] Furthermore, most of the described electrocatalysts are in powder form and require assembly before being used in water electrolysis on a conductive surface. Binder polymers are commonly utilized in combination with these powders, reducing contact between the catalyst and electrolyte and thereby limiting the electrocatalytic activity. [3]

### 5.1.3 Results and Discussion

#### 5.1.3.1 Surface morphology

Surface morphology provides critical insight into the texture, structure, and uniformity of electrodeposited materials.

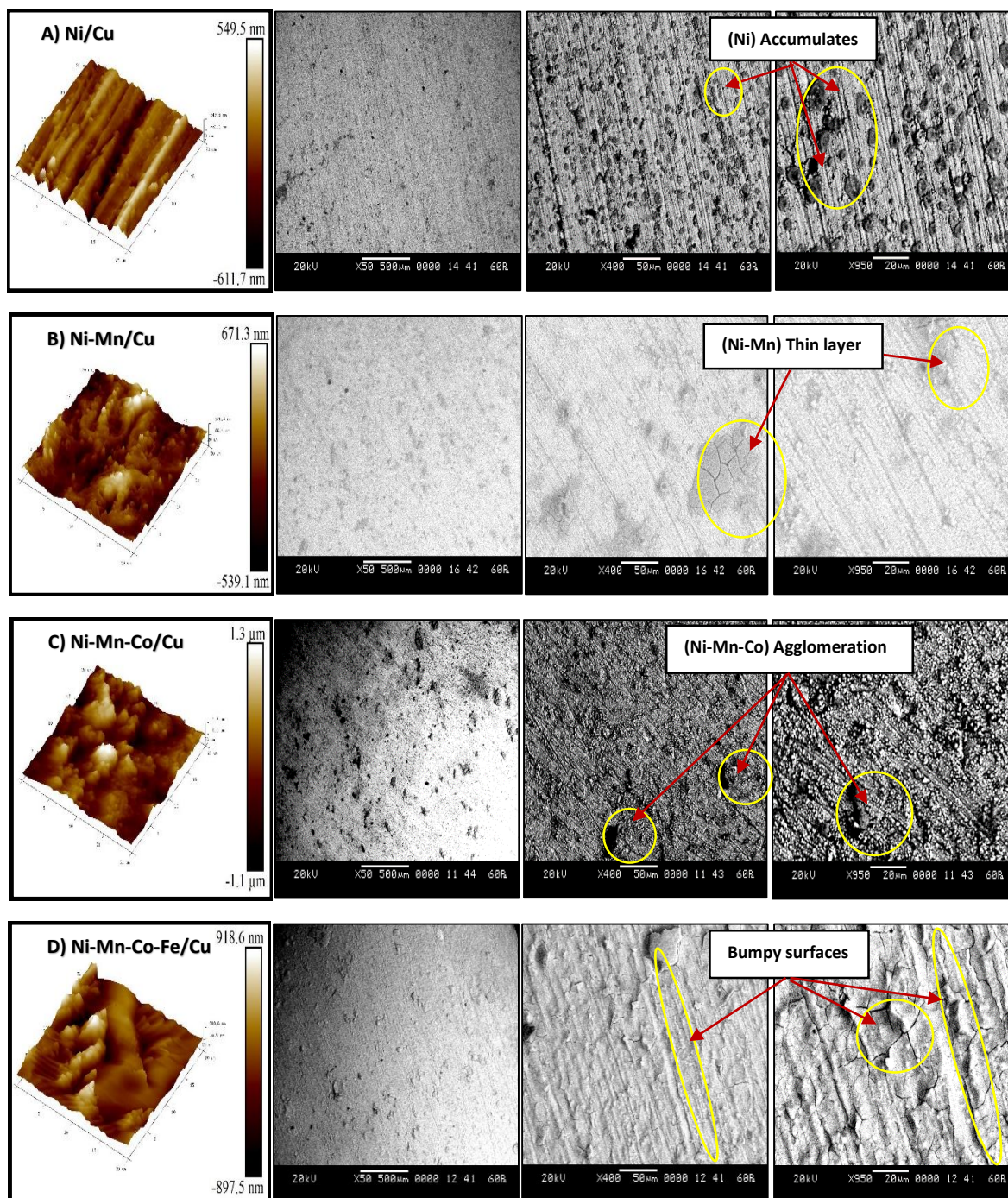


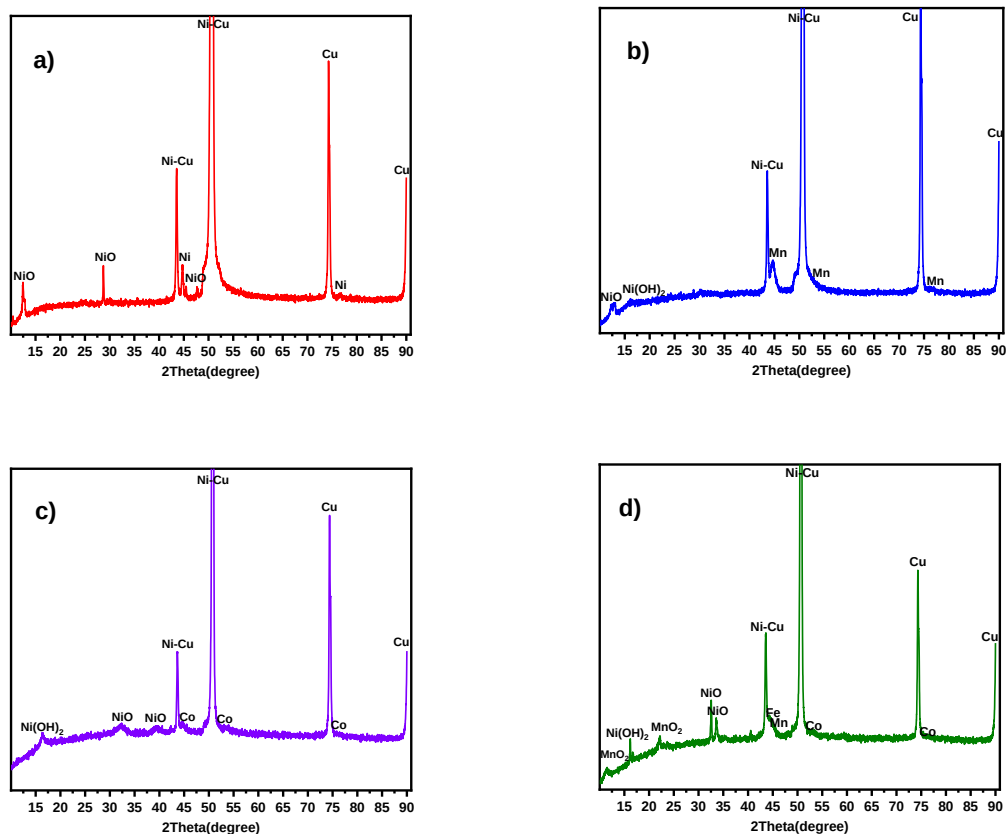
**Figure 5.1** SEM images and 3D AFM surface scanning images of (a) Ni, (b) Ni-Mn, (c) Ni-Mn-Co, and (d) Ni-Mn-Co-Fe alloys.

**Figure 5.1** displays SEM images depicting the morphology of the prepared electrodes and 3D AFM analyses highlighting the surface texture of each electrode. High-magnification ( $\times 950$ ) SEM image of electrode (a), where Ni is deposited on the Cu substrate, demonstrating that Ni forms distinct spherical structures on the surface of the substrate. This phenomenon is known as aggregation. The 3D AFM image shows a deep valley, indicating high roughness. The roughness parameters, presented in **Table 5.1** for electrode (a), give Ra (the mean height) as 107 nm and Rq (root mean square) as 146 nm. The ratio Rq/Ra is 1.36, which is a very high value. The ratio of 1.25~1.31 for the Gaussian distribution means that the statistical relationship for this surface is not applicable. It can be concluded that the measurements mainly represent the substrate surface roughness rather than the Ni surface roughness. In the SEM images of electrode (b), a thin layer covers the substrate, and some cracks are visible at a magnification of  $\times 400$ . The presence of Mn ensures that the surface is fully covered despite the presence of Ni metal. The 3D AFM image reveals a highly rough surface, with roughness parameters (Ra and Rq) of 131 nm and 168 nm, respectively (see Table 1 for the (b) electrode). The ratio of Rq/Ra is 1.28. The kurtosis value (Rku) of 3.83 suggests a spiky surface, with many peaks (125) and valleys (120). In areas where Ni-Mn-Co is deposited on the electrode (c), the surface is rough and has agglomerations with high heights, as shown in the SEM images. The 3D AFM image indicates the formation of a very high peak (1.3  $\mu\text{m}$ ) and deep valley (-1.1  $\mu\text{m}$ ), resulting in a distance between the highest and lowest points (Rt) of 2400 nm and a ten-point average roughness (Rz) of 284 nm, which is twice as high as those of electrodes (a) and (b). The surface texture parameter Ra is 259 nm, which is also twice as high as that of electrodes (a) and (b), and Rq is 331 nm. The ratio of Rq to Ra is approximately 1.27. The surface texture Rku is 3.72 lower than that of sample (b), but it still has a spiky surface. The skewness of the line (Rsk) value for electrode (c) of 0.52 is much lower than that of electrode (d). An examination of electrode (d), specifically the (Ni-Mn-Co-Fe) SEM image at high magnification ( $\times 950$ ), revealed a bumpy surface with cracks. The 3D AFM images revealed a lower height than that of sample (c), with roughness parameters of Ra = 327 nm and Rq = 432 nm. The resulting Rq/Ra ratio of 1.32 is slightly high but still acceptable. The Rku value is 3.65, indicating a bumpier surface than the samples (b-c). The Rsk value is 0.50 lower than that of previous samples; however, the Ra value is the highest, indicating that this thin film has more cracks. For more information, please refer to **Table 5.2**.

**Table 5.2** AFM properties of (a) Ni, (b) Ni-Mn, (c) Ni-Mn-Co, and (d) Ni-Mn-Co-Fe alloys.

| Proprieties    | (a) Ni | (b) Ni-Mn | (c) Ni-Mn-Co | (d) Ni-Mn-Co-Fe |
|----------------|--------|-----------|--------------|-----------------|
| <b>Ra (nm)</b> | 107    | 131       | 259          | 327             |
| <b>Rq (nm)</b> | 146    | 168       | 331          | 432             |
| <b>Rq/Ra</b>   | 1.36   | 1.28      | 1.27         | 1.32            |
| <b>RKu</b>     | 4.17   | 3.83      | 3.72         | 3.65            |
| <b>RSk</b>     | -0.37  | 0.58      | 0.52         | 0.50            |
| <b>Rz (nm)</b> | 120    | 103       | 284          | 459             |
| <b>Rt (nm)</b> | 1161.2 | 1210.4    | 2400         | 1816.1          |
| <b>Peaks</b>   | 98     | 125       | 70           | 30              |
| <b>Valley</b>  | 67     | 120       | 45           | 20              |

### 5.1.3.2 XRD analysis

**Figure 5.2** XRD patterns of the electrodes: A (Ni on the Cu substrate), B (Ni then Mn on the Cu substrate), C (Ni, Mn, and Co on the Cu substrate), and D (Ni, Mn, Co, and Fe on the Cu substrate).

XRD analyses were conducted in a powder configuration with a high substrate effect. For electrode A, where Ni was deposited on a Cu substrate, we identified eight peaks at  $2\theta$  ( $12.49^\circ$ ,  $28.74^\circ$ ,  $43.56^\circ$ ,  $44.75^\circ$ , with large peaks at  $50.13^\circ$ ,  $51.12^\circ$ ,  $74.32^\circ$ , and  $90.00^\circ$ ), as shown in

**Figure 5.2 a.** The first two peaks correspond to nickel oxide (NiO) [4, 5]. However, the third peak at  $43.56^\circ$  is likely a signature of copper, whereas the fourth peak at  $44.75^\circ$  appears to be a nickel signature. The large peak between  $50.13^\circ$  and  $51.12^\circ$  could be attributed to both the Cu and Ni materials. The last two peaks are attributed mainly to the Cu material. We observed similar XRD patterns with the same peak positions for electrodes B, C, and D, indicating that the deposited metals have more amorphous phases. Additionally, these metals have closely positioned  $2\theta$  values. The peaks appearing before  $2\theta = 35^\circ$  in Figure 2d correspond to nickel oxides (NiO), manganese dioxide ( $\text{MnO}_2$ ), and nickel hydroxide ( $\text{Ni}(\text{OH})_2$ ). These phases are characterized by their distinct diffraction patterns in the low-angle region.[6-9]

|           | <b><math>2\theta</math></b>                                                                                                                                                                     |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Cu</b> | 43.298/50.434/74.133/89.934/95.143/116.923/136.514/144.723/                                                                                                                                     |
| <b>Ni</b> | 44.508/51.847/76.372/92.947/98.449/121.936/144.679/155.666/                                                                                                                                     |
| <b>Mn</b> | 19.900/31.670/34.785/40.397/42.952/45.378/47.728/52.201/54.330/60.428/62.381/64.288<br>/66.149/68.001/69.838/73.462/75.199/76.978/78.721/82.173/83.874/90.740/92.451/94.17<br>0/95.858/97.609 3 |
| <b>Co</b> | 44.217/51.524/75.855/92.227/97.660/                                                                                                                                                             |
| <b>Fe</b> | 44.674/65.023/82.335/98.949/116.390/137.144/                                                                                                                                                    |

### 5.1.3.3 Electrocatalytic performance of different catalysts

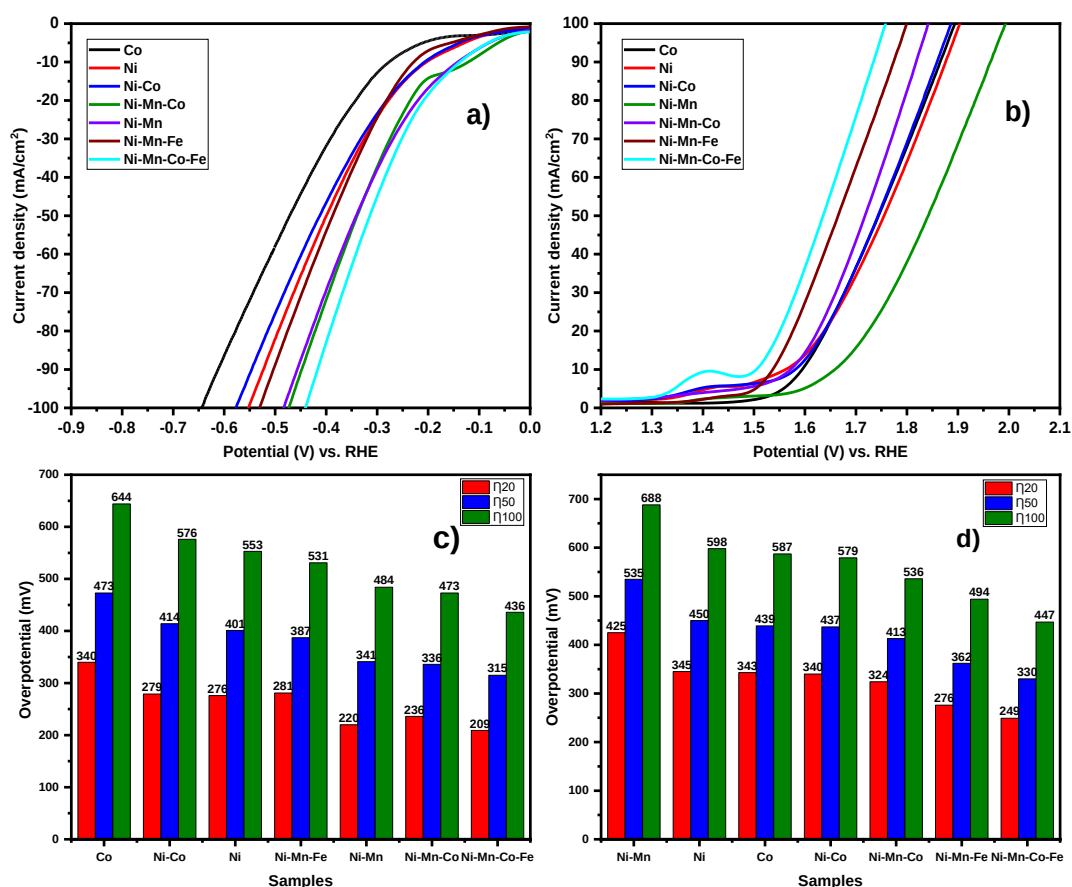


**Figure 5.3** (a) and (b) displays the LSV curves for various electrocatalysts, including Ni, Co, Ni-Mn, Ni-Fe, Ni-Co, Ni-Mn-Co, Ni-Mn-Fe, and Ni-Mn-Co-Fe, in a 1.0 M KOH solution at a scan rate of 10 mV/s. These curves were used to analyze the electrocatalytic activities for the HER and OER, respectively.

#### a) HER catalytic activity performance

The HER catalytic properties were tested in a three-electrode configuration system using our seven as-prepared electrocatalysts (Ni, Co, Ni-Fe, Ni-Co, Ni-Mn-Co, Ni-Mn-Fe, and Ni-Mn-Co-Fe) as the working electrode, a graphite plate counter electrode, a saturated Ag/AgCl reference electrode, and a 1.0 M KOH electrolyte solution. First, the HER linear sweep voltammetry (LSV) curves of the electrocatalysts are shown in **Figure 5.3a**. Generally, the overpotentials required to achieve current densities of 10, 20, and 100 mA/cm<sup>2</sup> in the LSV curves indicate electrocatalytic activity. Among the tested electrodes, the Ni-Mn-Co-Fe electrode demonstrated the best electrocatalytic activity, requiring overpotentials of only 139 and 209 mV to generate current densities of 10 and 20 mA/cm<sup>2</sup>, respectively. Additionally, as the overpotential increases, the current density also increases, with an overpotential of 436 mV

needed to generate a current density of 100 mA/cm<sup>2</sup>. The overpotentials required to achieve current densities of 20, 50, and 100 mA/cm<sup>2</sup> are presented in **Figure 5.3c**. The overpotential at 100 mA/cm<sup>2</sup> decreased as Mn, Co, and Fe were added, with values of 553 mV for Ni, 484 mV for Ni-Mn, 473 mV for Ni-Mn-Co, and 436 mV for Ni-Mn-Co-Fe. These results indicate that the Ni-Mn-Co-Fe electrode is an efficient electrocatalyst for hydrogen generation from water. In addition, the overpotentials required to achieve a current density of 100 mA/cm<sup>2</sup> for various electrodes are detailed in **Table 5.3**.

Tafel curves were employed to further examine the kinetics and mechanisms of the hydrogen evolution reaction (HER). These curves serve as valuable tools for understanding the kinetics, processes, and rate-determining steps involved in the HER. The Tafel slope values for various samples, derived from the linear region of the LSV curves via the Tafel equation ( $n = b \log j + a$ ), are summarized in **Table 5.3**. Here,  $b$  represents the Tafel slope, and  $j$  denotes the current density. [10]. In alkaline environments, it is generally accepted that the HER mechanism can take one of two paths: Volmer–Heyrovsky or Volmer–Tafel. The possible steps are as follows [11, 12]:



where  $M_{cat}$  represents the catalyst surface for the adsorption of atomic hydrogen and where  $M_{cat}H^*$  represents the amount of atomic hydrogen adsorbed on the catalyst surface. In both mechanisms,  $H^+$  must first be adsorbed onto the electrode surface (Volmer step), after which the evolution of a hydrogen molecule can occur via either the Heyrovsky or Tafel steps. The Tafel slope is widely used to determine the main mechanism of the HER, which can follow either the Volmer-Heyrovsky or Volmer-Tafel pathways in alkaline solution. According to classical theory, if the Volmer step is the rate-determining step, the slope of the Tafel curve should be 120 mV/dec; if the Heyrovsky and Tafel reactions are rate-determining steps, the slopes should be 40 and 30 mV/dec, respectively. The mechanism of the electrochemical HER in an alkaline environment for the Ni-Mn-Co-Fe electrocatalyst is illustrated in **Figure 5.4**.

As presented in **Table 5.3**, the Tafel slopes decrease from 125 mV/dec for pure Ni to 107 mV/dec for Ni-Mn and 106 mV/dec for the Ni-Mn-Co electrodes, demonstrating that alloying significantly improves the HER kinetics. The decrease in Tafel slopes due to alloying

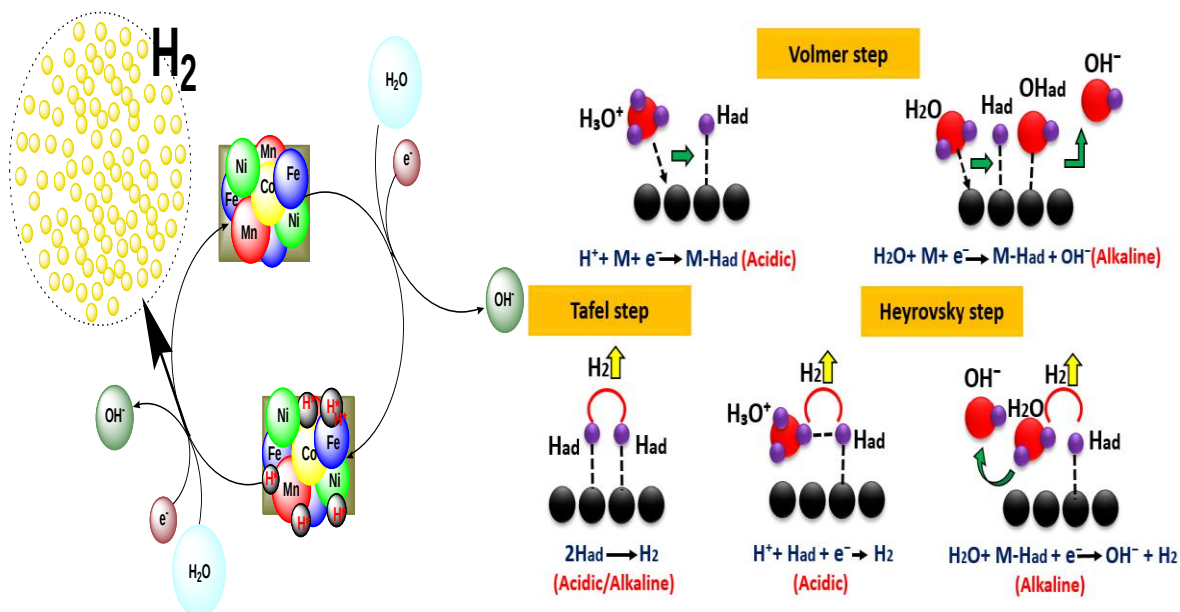
demonstrates that the presence of Co and Mn in the Ni matrix improves catalytic activity, likely by modifying the electronic properties of the catalyst surface, optimizing adsorption energies, and enhancing charge transfer processes.[12-14]

Additionally, the Ni-Mn-Co-Fe sample exhibited a Tafel slope of 92 mV/dec, reflecting the most efficient HER kinetics among all the samples. This suggests that the synergistic effects of these elements create a highly active surface for the HER, lowering the energy barrier for the reaction and improving the overall efficiency.

These results are consistent with previously reported values for nickel-based electrodes, suggesting that the Volmer step predominantly governs the overall reaction kinetics. The slight deviations from the expected values may arise from the formation of thin oxide layers on the electrode surfaces. Furthermore, the lower Tafel slopes observed indicate enhanced HER kinetics, allowing the catalyst to promote hydrogen evolution at reduced overpotentials. This ultimately translates to higher efficiency in converting electrical energy into chemical energy ( $H_2$ ). The Ni-Mn-Co-Fe alloy, with a Tafel slope of 92 mV/dec, which is controlled by the Volmer-Heyrovsky step (**Figure 5.4**), has the highest HER kinetic efficiency, highlighting the beneficial synergistic effects of the alloying elements. The Tafel slopes required for various electrodes are detailed in **Table 5.3** [14]. Furthermore, we recognize the importance of comparing our Ni-Mn-Co-Fe catalyst with standard catalysts such as *Pt* for the HER. While *Pt* demonstrates superior intrinsic performance, our Ni-Mn-Co-Fe alloy presents a competitive balance of cost and efficiency, positioning it as a viable alternative for large-scale applications. These comparisons are detailed in **Table 5.3** [12].

**Table 5.3** Comparison of the electrocatalytic performance of different prepared electrodes (Ni, Ni-Mn, Ni-Co, Ni-Mn-Co, and Ni-Mn-Co-Fe).

| Electrocatalysts      | Overpotential (mV)<br>At -100 mA<br>for<br>(HER) | Overpotential<br>(mV)<br>At 100 mA<br>for<br>(OER) | Tafel slope<br>(mV/dec) for<br>(HER) | Tafel<br>slope<br>(mV/dec)<br>for (OER) |
|-----------------------|--------------------------------------------------|----------------------------------------------------|--------------------------------------|-----------------------------------------|
| Ni                    | -553                                             | 598                                                | 125                                  | 134                                     |
| Co                    | -644                                             | 587                                                | 141                                  | 115                                     |
| Ni-Co                 | -576                                             | 579                                                | 136                                  | 110                                     |
| Ni-Mn-Co              | -473                                             | 536                                                | 106                                  | 110                                     |
| Ni-Mn                 | -484                                             | 688                                                | 107                                  | 145                                     |
| Ni-Mn-Fe              | -531                                             | 494                                                | 117                                  | 100                                     |
| Ni-Mn-Co-Fe           | -436                                             | 447                                                | 92                                   | 90                                      |
| Pt[12]                | -                                                | -                                                  | 39                                   | 79                                      |
| RuO <sub>2</sub> [15] | -                                                | -                                                  | -                                    | 88.6                                    |
| IrO <sub>2</sub> [16] | -                                                | -                                                  | -                                    | 66                                      |

**Figure 5.4** Mechanism of the electrochemical HER in an alkaline environment for the Ni-Mn-Co-Fe electrocatalyst.

The electrocatalytic characteristics of electrodes depend on both the material and surface morphology; key qualities for industrial electrolysis include a high active surface area, high stability, high conductivity, low overpotential, high activity, and corrosion resistance. [17] NNCs form nickel films with large active areas, which enhance their electrocatalytic activity,

whereas trapped hydrogen bubbles can reduce the active area and increase the overpotential due to a bubble resistance barrier. [18], [19] The composition and microstructure, such as nanocrystalline structures, further increase the activity by increasing the number of surface defects. [20, 21], [22-24], [24, 25] The synergistic effects of metals such as Ni, Mn, Co, and Fe provide optimal hydrogen adsorption and desorption energy states, enhancing intrinsic activity. [20, 26], [27]

## B) OER catalytic activity performance

The OER catalytic properties were tested in a three-electrode configuration system using our seven as-prepared electrocatalysts (Ni, Co, Ni-Fe, Ni-Co, Ni-Mn-Co, Ni-Mn-Fe, and Ni-Mn-Co-Fe) in a 1.0 M KOH electrolyte solution. First, the OER linear sweep voltammetry (LSV) curves of the electrocatalysts are shown in **Figure 5.3b**. Owing to its complexity, the OER is generally a slower process than the HER. As a result, with a significant thermodynamic potential of 1.23 V vs. RHE, the OER is often considered the primary barrier in the overall water-splitting process. Like the HER process, alloying has a substantial effect on the electrocatalytic activity of the OER. The Ni electrode exhibited an overpotential ( $\eta_{10}$ ) of 251 mV. Alloying with Mn, Co, and Fe reduces the  $\eta_{10}$  value, with the Ni-Mn-Co-Fe alloy achieving a reduction to 194 mV. As a result, this sample demonstrates the highest electrocatalytic activity for the OER. At high current densities, the current density increases significantly with rising potential, requiring an overpotential of only 447 mV to achieve a current density of 100 mA/cm<sup>2</sup>. **Figure 5.3d** illustrates the overpotentials required to reach current densities of 20, 50, and 100 mA/cm<sup>2</sup>.

Compared with the electrodes shown in this study and previous studies, the excellent electrocatalytic activity of the Ni-Mn-Co-Fe electrode can be attributed to the synergistic effects of the four elements Ni-Mn-Fe, Mn-Fe, Co-Fe, and iron, as well as its specific three-dimensional structure [12, 14]. The small peaks observed before the onset of oxygen evolution are related to the formation of Ni(III) or Ni(IV), which act as active sites for the OER [14].

The oxygen evolution reaction in alkaline solutions can be divided into the following four steps [28]:



The asterisk (\*) represents the active site, and the four steps mentioned above are known as rate-determining steps, which can be inferred from the Tafel slope value [29]:

- **120 mV/dec:** This suggests that the initial electron transfer step is the rate-determining step, which is often associated with the formation of surface-bound hydroxyl species ( $\text{OH}^*$ ).
- **60 mV/dec:** This indicates that the rate-determining step may involve the transfer of the second electron, which is typically related to the formation of surface-bound oxyhydroxide species ( $\text{O}^*$ ).
- **40 mV/dec:** This may indicate that the rate-determining step involves subsequent electron transfer or desorption processes, which are often linked to the evolution of oxygen molecules ( $\text{O}_2$ ).

The mechanism of the electrochemical OER in an alkaline environment for the Ni-Mn-Co-Fe electrocatalyst is illustrated in **Figure 5.5**. The kinetics of the oxygen evolution reaction (OER) were assessed through Tafel curves, which exhibited a linear relationship even at high current densities, indicating efficient electron and mass transfer between the catalyst and electrolyte. The Tafel slope for the Ni-Mn electrode was 145 mV/dec, whereas the slope for the Ni-Mn-Co electrode was 110 mV/dec. The Tafel slope for the Ni-Mn-Fe electrode was 100 mV/dec, and the Ni-Mn-Co-Fe electrode had the lowest value at 90 mV/dec. The decrease in the Tafel slope reflects enhanced electron and mass transfer kinetics, with the Ni-Mn-Co-Fe electrode exhibiting the best performance. These findings suggest that Ni-Mn-Co-Fe electrodes could serve as highly efficient catalysts for the OER (**Figure 5.5**). Additionally, we acknowledge the importance of comparing our Ni-Mn-Co-Fe catalyst with standard catalysts such as  $\text{RuO}_2/\text{IrO}_2$  for the OER. Although  $\text{RuO}_2/\text{IrO}_2$  exhibits superior intrinsic performance, the Ni-Mn-Co-Fe alloy offers a strong balance between cost and efficiency, making it a promising alternative for large-scale applications. A detailed comparison can be found in **Table 5.3** [15, 16].

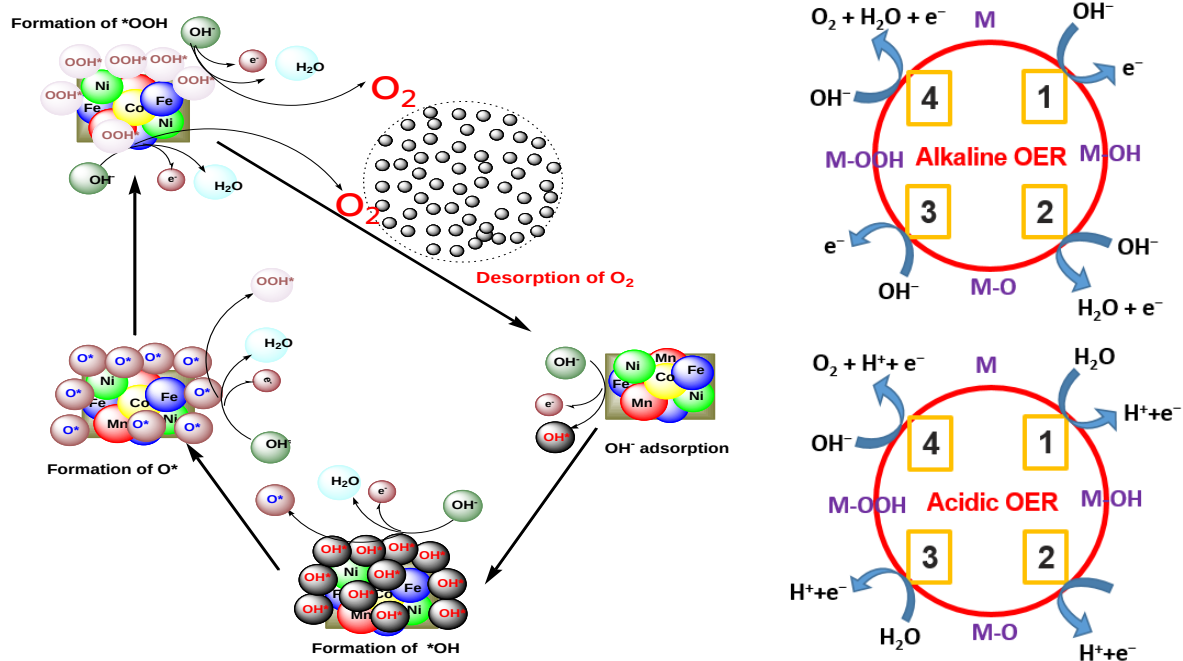


**Figure 5.5** Mechanism of the electrochemical OER in an alkaline environment for the Ni-Mn-Co-Fe electrocatalyst.

## 5.2 Ni-Mn-Co-Fe electrochemical impedance spectroscopy and stability

### 5.2.1 Electrochemical impedance spectroscopy (EIS)

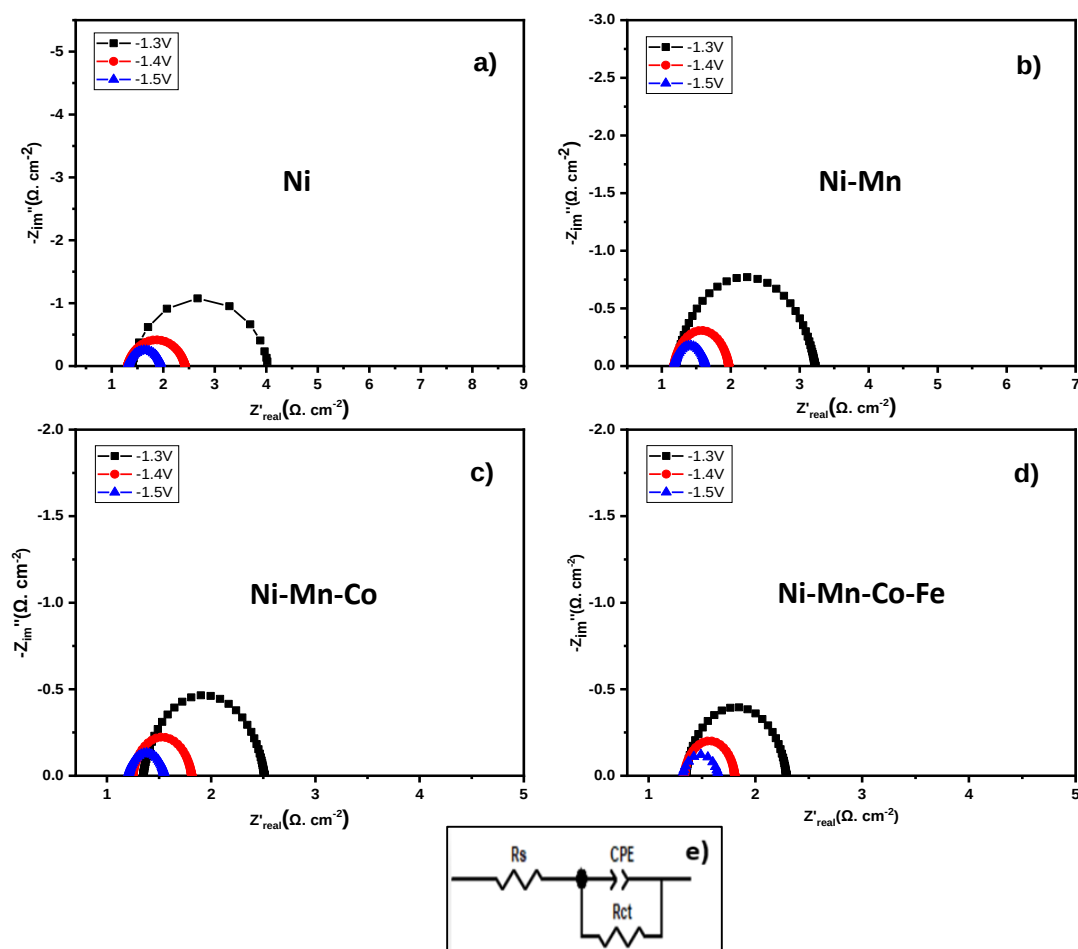


**Figure 5.6** Nyquist plots for HER on (a) Ni, (b) Ni-Mn, (c) Ni-Mn-Co, and (d) Ni-Mn-Co-Fe electrodes, along with (e) the equivalent electrical circuit (EEC). Conditions:  $[\text{KOH}] = 1 \text{ M}$ ,  $T_{\text{bath}} = 24^\circ\text{C}$ . Nyquist curves are shown for different potentials: (black)  $E = -1.30 \text{ V vs. SCE}$ , (red)  $E = -1.40 \text{ V vs. SCE}$ , and (blue)  $E = -1.50 \text{ V vs. SCE}$ .

Electrochemical impedance spectroscopy (EIS) measurements were carried out to investigate the processes that occur at the catalyst/solution interface when the electrode potential is changed. We provide a preliminary analysis of experimental data obtained in 1 M KOH using Ni, Ni-Mn, Ni-Mn-Co, and Ni-Mn-Co-Fe catalysts. Additionally, an EIS test was conducted at three potentials of -1.3 V, -1.4 V, and -1.5 V vs. SCE to gain a more comprehensive understanding of the HER process at the electrode-electrolyte interface. The Nyquist plots for the different electrodes are presented in **Figures 5.6 a-d**. All the Nyquist curves are comparable to one another, indicating that all the samples have the same charge transfer process and electrochemical mechanism. The Nyquist curves are composed of one semicircle. The radius of the semicircle decreased as the applied potential increased. This

suggests an improvement in the kinetics of hydrogen production. Nyquist curves must be fitted by an appropriate electrical equivalent circuit (EEC) for more precise and numerical analysis. This EEC is made up of one parallel unit of resistance and capacitance and another unit of resistance ( $R_s$ ).  $R_s$  is the solution's uncompensated resistance, which was taken into consideration when changing the LSV curves. The HER kinetics are related to the time constant parameters ( $R_{ct}$  and CPE). The  $R_{ct}$  value decreases substantially with increasing applied potential (**Table 5.4**), which implies that at high potentials, the HER kinetics of the catalysts are accelerated. Furthermore, when the Nyquist curves (**Figure 5.6**) and  $R_{ct}$  values of the Ni-Mn-Co-Fe electrode are compared with those of the Ni, Ni-Mn, and Ni-Mn-Co electrodes (**Table 5.4**), it is clear that the Ni-Mn-Co-Fe alloy has a much lower  $R_{ct}$  than the other electrodes at all applied potentials. The  $R_{ct}$  value of the Ni sample at -1.5 V potential is  $0.63 \Omega/\text{cm}^2$ , which is decreased by alloying to  $0.45 \Omega/\text{cm}^2$  and  $0.35 \Omega/\text{cm}^2$  for the Ni-Mn and Ni-Mn-Co electrodes, respectively. This involves increasing electrochemical charge transfer and, as a result, improving electrocatalytic activity. Furthermore, the Ni-Mn-Co-Fe sample has the lowest charge transfer resistance of  $0.33 \Omega/\text{cm}^2$ , suggesting that this electrode has the highest electrochemical and kinetic charge transfer HER.

After deposition, EIS measurements were conducted to investigate the processes occurring at the catalyst/solution interface when the electrode potential varied. A preliminary analysis of experimental data obtained in 1 M KOH using Ni, Ni-Mn, Ni-Mn-Co, and Ni-Mn-Co-Fe catalysts is presented. The EIS test was performed at three potentials, namely, -1.3, -1.4, and -1.5 V vs. SCE, to gain deeper insight into the HER process at the electrode–electrolyte interface. The Nyquist plots for the various electrodes are shown in **Figures 5.6 a-d**. All the Nyquist curves were comparable, indicating that all the samples exhibited the same charge transfer process and electrochemical mechanism. The Nyquist plots consisted of a single semicircle, and the radius of the semicircle decreased as the applied potential increased. This suggests an increase in the kinetics of hydrogen production. For a more precise and quantitative analysis, the Nyquist plots were fitted via an appropriate electrical equivalent circuit (EEC) (**Figure 5.6e**). The EEC comprises one parallel unit of capacitance (CPE), a charge transfer or polarization resistance ( $R_{ct}$ ), and another unit of resistance ( $R_s$ ), which represents the solution's uncompensated resistance. This resistance was considered when adjusting the LSV curves. The kinetics are associated with the time-constant parameters  $R_{ct}$  and CPE. The  $R_{ct}$  value decreases significantly with increasing applied potential (**Table 5.4**), indicating that at higher potentials, the kinetics of the catalysts are accelerated. Moreover, when the Nyquist plots (**Figure 5.6**) and

$R_{ct}$  values of the Ni-Mn-Co-Fe electrode are compared with those of the Ni, Ni-Mn, and Ni-Mn-Co electrodes (**Table 5.4**), it is evident that the Ni-Mn-Co-Fe alloy has a much lower  $R_{ct}$  than the other electrodes at all applied potentials. The  $R_{ct}$  value for the Ni sample at -1.5 V is  $0.63 \Omega \cdot \text{cm}^{-2}$ , which decreases to  $0.45 \Omega \cdot \text{cm}^{-2}$  and  $0.35 \Omega \cdot \text{cm}^{-2}$  for the Ni-Mn and Ni-Mn-Co electrodes, respectively, due to alloying. This reduction suggests increased electrochemical charge transfer, leading to improved electrocatalytic activity. The charge transfer resistance ( $R_{ct}$ ) is directly related to the exchange current density ( $j_0$ ), with lower  $R_{ct}$  values indicating higher  $j_0$  values, which reflects enhanced catalytic activity at the catalyst surface. Furthermore, the Ni-Mn-Co-Fe sample has the lowest charge transfer resistance of  $0.33 \Omega \cdot \text{cm}^{-2}$ , which indicates that the electrode has the highest electrochemical and kinetic charge transfer efficiency for the HER.

The improvement in the electrocatalytic properties of the microstructure developed in this study, in comparison with other nickel-based electrocatalysts reported in the literature, can be attributed to its distinctive surface structure. Electrocatalytic performance is typically believed to be influenced by both the active surface area and the intrinsic electrocatalytic capabilities of the material. To evaluate the enhancements in the electrocatalytic properties of the Ni-Mn-Co-Fe electrodes compared with those of the other electrodes, the electrochemically active surface area (ECSA) and inherent electrocatalytic properties of these electrodes were investigated via EIS. The ECSA is directly related to the CPE and inversely related to the charge transfer resistance ( $R_{ct}$ ) [30]. An increase in the CPE and  $C_{dl}$  indicates a higher ECSA, as more surface area is available for electrochemical reactions. Through alloying, the CPE increased, and  $R_{ct}$  decreased, indicating an increased ECSA (**Table 5.4**). The increase in the ratio of  $CPE/R_{ct}$  suggests a more accessible and active surface area. Additionally, since  $C_{dl}$  is proportional to the ECSA, the observed increase in the CPE corresponds to a greater  $C_{dl}$ , confirming the increase in the ECSA. These findings confirm that alloying significantly improves the electrochemical performance by increasing the active surface area.

**Table 5.4** Parameters obtained by fitting the EIS experimental spectra via the EEC models presented in **Figure 5.6e**.

| Electrode   | Applied potential<br>(V vs. SCE) | $R_s$<br>( $\Omega \cdot \text{cm}^{-2}$ ) | CPE<br>( $\text{F.s}^{n-1}/\text{cm}^2$ ) | $n$  | $R_{ct}$<br>( $\Omega \cdot \text{cm}^{-2}$ ) | $\text{CPE}/R_{ct}$<br>$\cdot 10^{-3}$<br>( $\text{F.s}^{n-1} \cdot \Omega^{-1}$ ) |
|-------------|----------------------------------|--------------------------------------------|-------------------------------------------|------|-----------------------------------------------|------------------------------------------------------------------------------------|
| Ni          | -1.3                             | 1.395                                      | 0.00265                                   | 0.86 | 2.64                                          | 1.00                                                                               |
|             | -1.4                             | 1.308                                      | 0.00212                                   | 0.82 | 1.11                                          | 1.90                                                                               |
|             | -1.5                             | 1.321                                      | 0.00177                                   | 0.85 | 0.63                                          | 2.81                                                                               |
| Ni-Mn       | -1.3                             | 1.204                                      | 0.00405                                   | 0.83 | 2.02                                          | 2.00                                                                               |
|             | -1.4                             | 1.178                                      | 0.00356                                   | 0.84 | 0.79                                          | 4.51                                                                               |
|             | -1.5                             | 1.182                                      | 0.00326                                   | 0.85 | 0.45                                          | 7.25                                                                               |
| Ni-Mn-Co    | -1.3                             | 1.348                                      | 0.00438                                   | 0.86 | 1.16                                          | 3.77                                                                               |
|             | -1.4                             | 1.247                                      | 0.00438                                   | 0.85 | 0.56                                          | 7.82                                                                               |
|             | -1.5                             | 1.205                                      | 0.00546                                   | 0.82 | 0.35                                          | 15.6                                                                               |
| Ni-Mn-Co-Fe | -1.3                             | 1.349                                      | 0.00259                                   | 0.89 | 0.94                                          | 2.75                                                                               |
|             | -1.4                             | 1.335                                      | 0.00382                                   | 0.89 | 0.47                                          | 8.12                                                                               |
|             | -1.5                             | 1.317                                      | 0.00823                                   | 0.80 | 0.33                                          | 24.9                                                                               |

### 5.2.2 Electrocatalytic stability

#### A/ Electrocatalytic stability for the HER

Electrocatalytic stability is a key parameter for evaluating the long-term performance and durability of catalysts during the hydrogen evolution reaction (HER).

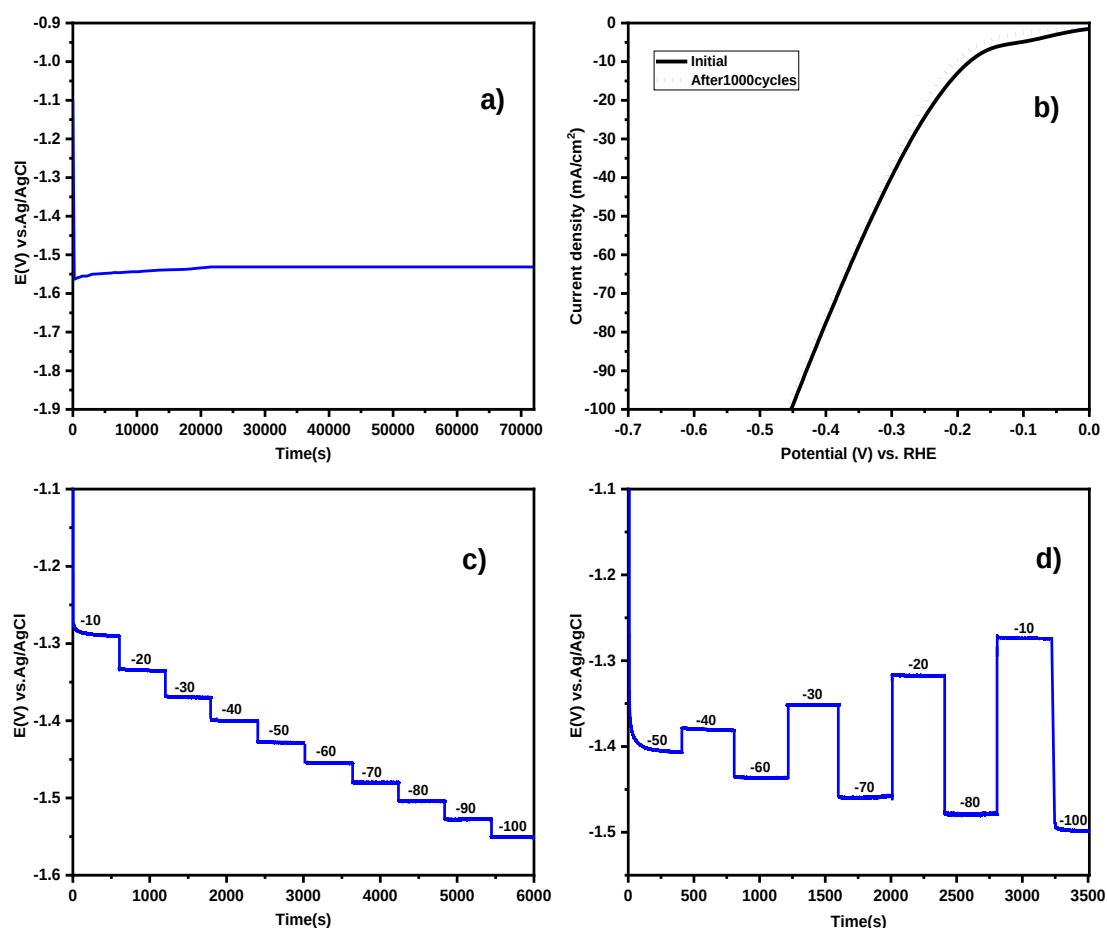


**Figure 5.7** (a) Chronopotentiometry test for the HER at a current density of  $-100 \text{ mA/cm}^2$ , (b) LSV curves before and after CV curves for analyzing the catalytic stability, and (c), (d) multistep chronopotentiometry with current densities varying from  $-10$  to  $-100 \text{ mA/cm}^2$ .

The stability of electrocatalysts in long-term water electrolysis is one of the most important criteria for industrial use. Multiple methods have been used to assess the electrochemical stability of the optimal Ni-Mn-Co-Fe/Cu electrode. After 20 hours of chronopotentiometry analysis at a current density of  $-100 \text{ mA/cm}^2$  in a  $0.1 \text{ M KOH}$  electrolyte solution, with the temperature maintained at  $25^\circ\text{C}$  and a scan rate of  $10 \text{ mV/s}$ , the catalyst exhibited a small potential increase of approximately 4% (**Figure 5.7a**), indicating its exceptional durability. Additionally, no significant degradation was observed during the tests, although minor changes in surface morphology may have occurred due to prolonged electrochemical cycling. The

primary degradation mechanisms observed during long-term stability tests include catalyst dissolution, surface oxidation, and loss of active sites. These effects can be mitigated by optimizing the alloy composition, improving surface coatings to enhance stability, and incorporating protective layers that reduce oxidation and degradation (**Figure 5.7 (a)**). [31] The change in the HER polarization curve after 1000 voltammetry cycles is the second method utilized to study the stability of Ni-Mn-Mo-Fe/Cu (**Figure 5.47 (b)**). After the CVs, the LSV curve moves slightly toward higher overpotentials, suggesting favorable catalyst stability for cyclic use. Additionally, the multistep chronopotentiometry method was used with current densities varying from -10 to -100 mA/cm<sup>2</sup> (**Figure 5.7 (c)**). The constant potential curves at every phase confirm the electrode's notable durability. The potential remains constant at each current density and then rapidly changes when the current density varies, suggesting that the electrolytic stability is excellent, as are the good mass transfer properties and mechanical robustness. [32] Altering the current density clearly causes the potential to shift immediately, indicating that the electrode has high conductivity and easy mass transfer. Moreover, the electrocatalytic stability was studied by varying the current density at lower and higher levels (**Figure 5.7 (d)**). The current density was first -50 mA/cm<sup>2</sup>, followed by an increase to -40 mA/cm<sup>2</sup> after 600 s, and then decreased to -60 mA/cm<sup>2</sup> after another 600 s. The findings of this test also show that the electrode above is electrocatalytically stable.

The constant potential curves at each stage further demonstrate the electrode's remarkable durability. It is also clear that the potential can be altered instantly by adjusting the current density; this finding supports good conductivity, fast mass transfer, and mechanical robustness of the electrode.

## B/ Electrocatalytic stability for the OER

Electrocatalytic stability is essential for assessing the durability and efficiency of catalysts under prolonged oxygen evolution reaction (OER) conditions.

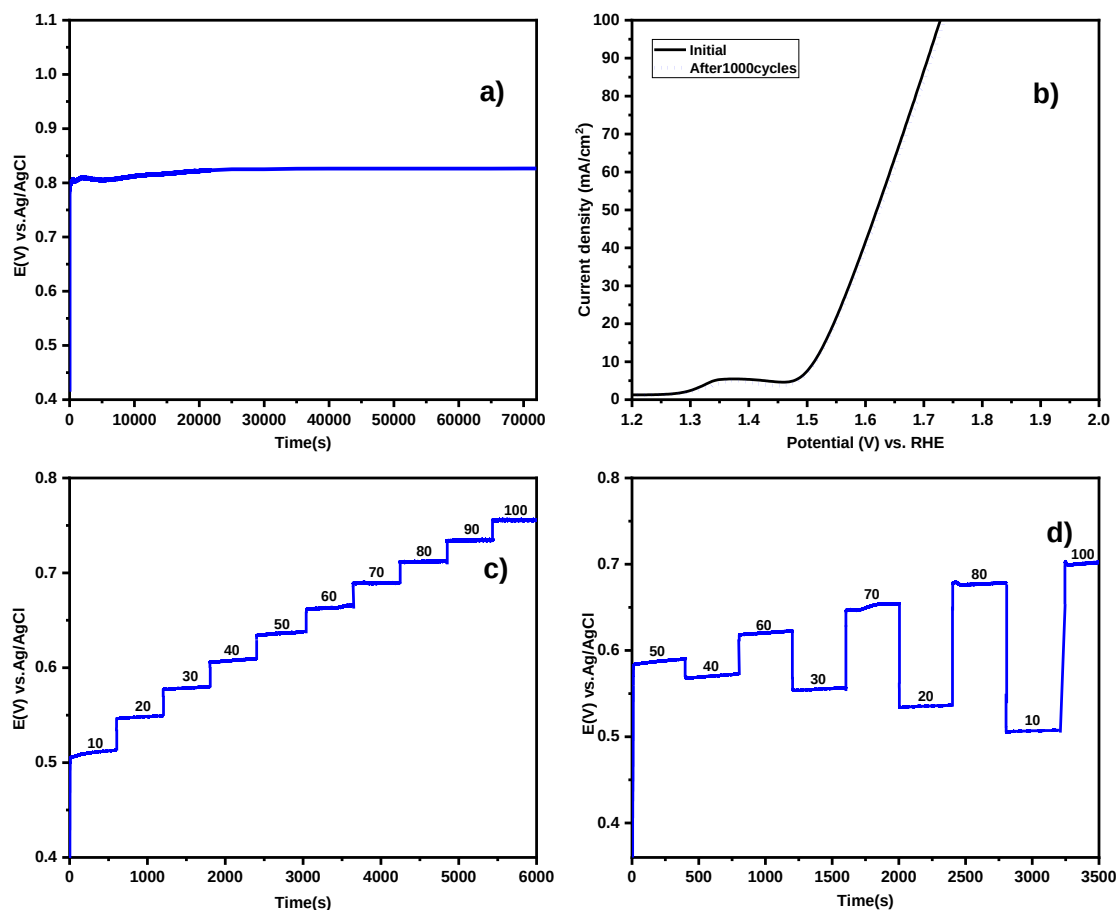


**Figure 5.8** (a) Chronopotentiometry test for the OER at a current density of 100 mA/cm<sup>2</sup>, (b) LSV curves before and after CV curves for analyzing the catalytic stability, and (c), (d) multistep chronopotentiometry with current densities varying from 10 to 100 mA/cm<sup>2</sup>.

Chronopotentiometry and multiple CV scanning experiments were conducted to assess the electrocatalytic stability of the OER (**Figure 5.8 a, b**). The results revealed that after 20 hours of chronopotentiometry testing at a current density of 100 mA/cm<sup>2</sup> in a 0.1 M KOH electrolyte solution, with the temperature held at 25°C and a scan rate of 10 mV/s, the catalyst showed a slight potential increase of approximately 4% (**Figure 5.8a**), demonstrating its remarkable durability. Moreover, no significant degradation was detected during the experiments. However, minor changes in surface morphology might occur due to extended electrochemical cycling, and the change in the LSV curve after 1000 cycles in the CV test is negligible. The multistep chronopotentiometry method was employed with current densities varying from 10 to 100 mA/cm<sup>2</sup> (**Figure 5.8c, d**). The consistent potential curves at each phase confirm the

electrode's notable durability. It is also evident that altering the current density causes an immediate potential shift, indicating that the electrode possesses high conductivity and enables efficient mass transfer. The improved electrocatalytic activity and stability of the electrode for the OER can be attributed to several key factors. The primary contributors to this enhanced performance are the increased surface area and the synergistic interactions between the various elements within the electrode.

### 5.3 Overall water splitting

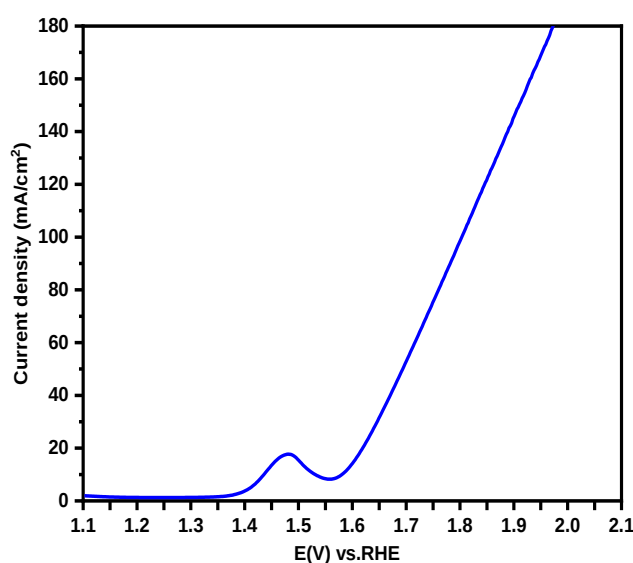


**Figure 5.9** Overall water splitting curve for the Ni-Mn-Co-Fe catalyst. The concentrations used were  $[\text{NiCl}_2 \cdot 6\text{H}_2\text{O}] = 25 \text{ g/L}$ ,  $[\text{MnCl}_2 \cdot 6\text{H}_2\text{O}] = 30 \text{ g/L}$ ,  $[\text{CoCl}_2 \cdot 6\text{H}_2\text{O}] = 10 \text{ g/L}$ ,  $[\text{FeSO}_4 \cdot 7\text{H}_2\text{O}] = 10 \text{ g/L}$ , and  $[\text{NH}_4\text{Cl}] = 50 \text{ g/L}$ . The experiments were conducted in 1 M KOH at a pH of 14, with a potential scan rate of 10 mV/s and a temperature of 23°C.

Electrochemical water splitting provides an environmentally friendly method for producing high-purity hydrogen. [33, 34] In this process, hydrogen is generated at the cathode, whereas oxygen is released at the anode. For an efficient water-splitting process, it is essential to use high-efficiency, active, corrosion-resistant, and stable electrocatalysts that enable the simultaneous occurrence of the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode, both at high rates. [35, 36]

Water electrolysis is a flexible and sustainable way to produce highly pure hydrogen, which includes the anodic oxygen evolution reaction (OER,  $2\text{H}_2\text{O} (\text{l}) = 4\text{H}^+ (\text{aq}) + \text{O}_2 (\text{g}) + 4\text{e}^-$  in alkaline solutions) and the cathodic hydrogen evolution reaction (HER,  $2\text{H}^+ (\text{aq}) + 2\text{e}^- = \text{H}_2 (\text{g})$  in alkaline solutions) occurring at separate electrodes [37, 38]. Compared with the HER, the

OER process has intrinsically slow kinetics and requires a large overpotential because of its multistep proton-coupled electron transfer mechanism. [39, 40] Currently, noble metal-based electrocatalysts such as IrO<sub>2</sub> or RuO<sub>2</sub> have been identified as the best candidates for the OER due to their optimal binding with essential intermediates. Unfortunately, their low stability, high cost, and restricted resource availability significantly limit their large-scale applicability in commercialized water electrolyzers. [41, 42]. Therefore, the design of alternative efficient and inexpensive electrocatalysts for the OER is urgently needed.

The experimental results indicated that the Ni-Mn-Co-Fe catalyst was prepared in a coating solution comprising 25 g/L NiCl<sub>2</sub>·6H<sub>2</sub>O, 30 g/L MnCl<sub>2</sub>·6H<sub>2</sub>O, 10 g/L CoCl<sub>2</sub>·6H<sub>2</sub>O, 10 g/L FeSO<sub>4</sub>·7H<sub>2</sub>O, and 50 g/L NH<sub>4</sub>Cl, with the pH adjusted to 3.5, the ambient temperature prevailed, and the scan rate was 10 mV/s. had excellent electrocatalytic activity and stability for both the HER and OER processes in alkaline environments. Notably, the development of electrocatalysts for water splitting under alkaline conditions appears to be more attractive due to the lower corrosion rate, higher durability of the electrodes, and absence of acidic fog. [43]. However, in contrast to acidic solutions, the HER in alkaline media includes an extra water dissociation phase, which lowers the kinetics of the production of hydrogen. [43, 44]. Therefore, designing effective electrocatalysts for the HER under alkaline conditions is a satisfying task.

As a result, a water electrolysis system was developed in which the Ni-Mn-Co-Fe electrode works as both an anode and a cathode at the same time. As a consequence, the dual functionality of the Ni-Mn-Co-Fe electrode was exploited. In addition, for full water splitting, the potential-current density curve for the Ni-Mn-Co-Fe catalyst is shown in **Figure 5.9**. To generate a current density of 10 mA/cm<sup>2</sup>, this electrode requires only a 1.57 V vs. RHE cell voltage. Its electrolytic performance in full water splitting is consistent with the findings from half-reaction tests for both the HER and OER, indicating that the electrode synthesized in this study demonstrates excellent integration. This electrode functions efficiently as a bifunctional electrode in a water-splitting system.

## 5.4 Comparison of Electrochemical Catalytic Hydrogen Evolution for Various Noble Ni-based Electrodes

**Table 5.5** summarizes the electrocatalytic activities of various Ni-based HER catalysts in alkaline solutions. Among the catalysts listed, the Ni-Mn-Co-Fe/Cu electrocatalyst demonstrated the lowest overpotential, achieving a 10 mA/cm<sup>2</sup> current density at just 139 mV vs. RHE in 1 M KOH. This performance surpasses that of other nickel-based catalysts, highlighting its superior efficiency for hydrogen evolution under alkaline conditions.

**Table 5.5** Summary of the electrocatalytic activity of representative Ni-based HER catalysts in an alkaline solution.

| Electrocatalyst                    | Electrolyte                            | Current density<br>(mA/cm <sup>2</sup> ) | Overpotential<br>(mV vs.RHE) | Ref.       |
|------------------------------------|----------------------------------------|------------------------------------------|------------------------------|------------|
| Ni-Mn-Co-Fe/Cu                     | KOH (1.0 M)                            | 10                                       | 139                          | This study |
| Ni-Mn-Fe/Cu                        | KOH (1.0 M)                            | 10                                       | 226                          | This study |
| Ni-Mn/Cu                           | KOH (1.0 M)                            | 10                                       | 143                          | This study |
| Ni/Cu                              | KOH (1.0 M)                            | 10                                       | 197                          | This study |
| Ni nanoparticles                   | NaOH (1.0 M)                           | 10                                       | 180                          | [45]       |
| 3DOM/m Ni                          | NaOH (1.0 M)                           | 10                                       | 171                          | [46]       |
| Ni dendrites                       | KOH (6.0 M)                            | 10                                       | 300                          | [47]       |
| NiFe LDH-NS@DG[a]                  | KOH (1.0 M)                            | 10                                       | 300                          | [48]       |
| Ni <sub>3</sub> N                  | PBS[b] (1.0 M)                         | 10                                       | 234                          | [49]       |
| Ni <sub>3</sub> N                  | H <sub>2</sub> SO <sub>4</sub> (0.5 M) | 10                                       | 145                          | [49]       |
| Ni <sub>5</sub> P <sub>4</sub> /Ni | KOH (1.0 M)                            | 10                                       | 150                          | [50]       |
| Ni <sub>5</sub> P <sub>4</sub> /Ni | H <sub>2</sub> SO <sub>4</sub> (0.5 M) | 10                                       | 140                          | [50]       |
| NiSe <sub>2</sub> /Ni              | H <sub>2</sub> SO <sub>4</sub> (0.5 M) | 10                                       | 143                          | [51]       |
| Ni                                 | KOH (1.0 M)                            | 10                                       | 400                          | [52]       |
| Ni wire                            | NaOH (1.0 M)                           | 10                                       | 350                          | [53]       |
| Ni/C NFs                           | KOH (2.0 M)                            | 10                                       | 290                          | [54]       |
| NiCoP/rGO                          | KOH (1.0 M)                            | 10                                       | 209                          | [55]       |
| Ni <sub>2</sub> P nanoparticles    | KOH (1.0 M)                            | 10                                       | 255                          | [56]       |
| Ni-P                               | KOH (1.0 M)                            | 10                                       | 350                          | [57]       |
| Ni <sub>3</sub> Se <sub>2</sub>    | KOH (1.0 M)                            | 10                                       | 203                          | [58]       |
| nanoforest/Ni                      |                                        |                                          |                              |            |
| Mesoporous Ni-Co alloys            | NaOH (1.0 M)                           | 10                                       | 162                          | [59]       |
| Ni-Cu                              | NaOH (1.0 M)                           | 10                                       | 180                          | [60]       |
| Nickel-Cobalt-Titanium             |                                        | 10                                       | 150                          | [61]       |

## 5.5 Conclusion

In conclusion, this chapter presents a comprehensive comparative study of electrocatalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), with a focus on the development of a cost-effective Ni-Mn-Co-Fe alloy via electrodeposition. By optimizing key operational parameters, including the bath composition, scan rate, pH, and temperature, the Ni-Mn-Co-Fe catalyst demonstrated remarkable electrocatalytic performance, requiring overpotentials of 436 mV for the HER and 447 mV for the OER to achieve a current density of 100 mA/cm<sup>2</sup>. Additionally, it exhibited the lowest charge transfer resistance (0.33  $\Omega \cdot \text{cm}^2$ ), superior electrochemical kinetics, and excellent long-term stability with minimal overpotential degradation over 20 hours of continuous operation. Comparative analysis highlighted the superiority of the quaternary alloy over its monometallic, binary, and ternary counterparts, as well as commercial noble metal catalysts, underscoring its potential as a highly efficient and durable catalyst for water splitting applications.

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# **General Conclusion**

This chapter provides a comprehensive synthesis of the findings from the four main sections of this study, encompassing the general conclusion, key innovations, future perspectives, and scientific production.

The general conclusion consolidates the outcomes of the investigation into Ni, Ni-Mn, Ni-Co, Ni-Mn-Co, and Ni-Mn-Co-Fe alloy electrodes, showcasing their enhanced electrocatalytic performance for hydrogen (HER) and oxygen evolution reactions (OER) under optimized deposition conditions. The Ni-Mn-Co-Fe alloy emerged as the most effective catalyst, with superior activity, stability, and efficiency, demonstrating its potential for water splitting and industrial applications.

The key innovations of this study include the development of a scalable and additive-free electrodeposition process, the successful alloying of multiple metals to enhance catalytic performance, and the identification of the synergistic effects of Ni, Mn, Co, and Fe in reducing charge transfer resistance and improving reaction kinetics. These advancements contribute significantly to the field of electrochemical catalysis.

Future perspectives highlight the need for scaling up the electrodeposition process, optimizing alloy compositions through doping with additional elements, evaluating long-term durability under industrial conditions, and conducting a detailed cost analysis to assess economic feasibility compared to noble metal-based catalysts. Additionally, the potential application of these alloys as electrodes for fuel cells presents a promising avenue for further exploration.

Finally, the scientific production resulting from this research has contributed to the advancement of knowledge in electrocatalysis, with key findings disseminated through publications, conference presentations, and collaborative initiatives, reinforcing the relevance and impact of this work in the scientific community.

### **6.1. Part 1: Electrodeposition of Ni/Cu**

Nickel was electrodeposited onto copper (Cu) substrates via cyclic voltammetry (CV) under various bath conditions, including various bath compositions, scan rates, pH values, temperatures, supporting electrolyte concentrations, and electrolyte types. The key findings are summarized below:

- **Bath Composition:** Increasing the concentrations of nickel chloride ( $[\text{NiCl}_2] = 75 \text{ g/L}$ ) and ammonium chloride ( $[\text{NH}_4\text{Cl}] = 150 \text{ g/L}$ ) significantly improved the deposition kinetics and electrocatalytic activity for  $\text{H}^+$  ion reduction.
- **Scan Rate:** Cyclic voltammograms recorded at scan rates of 5, 10, 50, and 100 mV/s revealed that the reduction peak current for  $\text{NH}_4\text{Cl}$  increased with increasing scan rate, peaking at 10 mV/s ( $E_{\text{pc}} = -0.21 \text{ V}$ ,  $I_{\text{pa}} = 11.7 \text{ mA}$ ). In addition, the current density slightly decreased.
- **Temperature:** Bath temperature ( $10^\circ\text{C}$  to  $90^\circ\text{C}$ ) influenced the electrodeposition efficiency. The reduction peaks became more pronounced at higher temperatures, with  $60^\circ\text{C}$  yielding the optimal coating quality and catalytic activity.
- **pH:** A lower pH increased the  $\text{Ni}^{2+}$  reduction rate and cathodic reduction current density. A relatively high pH hindered the dissolution of plated Ni, reducing the anodic peak current density.
- **Supporting Electrolytes:** Increasing the  $\text{NH}_4\text{Cl}$  concentration to 50 g/L improved the coating durability and inhibited dissolution.  $\text{NH}_4\text{Cl}$  exhibited better performance than KCl and EDTA.

In conclusion, optimizing the bath composition, scan rate, temperature, pH, and supporting electrolyte significantly enhanced the electrodeposition of Ni on the Cu substrates, resulting in improved coating quality and catalytic activity for  $\text{H}^+$  reduction.

## 6.2. Part 2: Electrodeposition of Ni–Mn on copper for the HER and OER

Ni-Mn films were electrodeposited on Cu substrates via cyclic voltammetry (CV) and fixed applied potential under various bath conditions. The performance of the films in the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) was studied as follows:

- **Scan Rate:** Lower deposition scan rates improved the catalytic activity for both the HER and OER, with Ni-Mn deposited at 50 mV/s resulting in the highest current density.
- **pH:** Optimal HER performance was observed at a deposition pH of 7.5. For the OER, a higher electrolyte pH decreased the reaction rate.
- **Supporting Electrolytes:**  $\text{NH}_4\text{Cl}$  in the deposition bath reduced the overpotential for the HER in 1 M KOH compared with  $\text{H}_3\text{BO}_3$ , enhancing the catalytic activity.

- **Deposition pH:** Acidic deposition environments (pH 3.5) enhanced the cathodic reaction kinetics, suggesting a preference for acidic conditions.
- **Current density:** Increasing the deposition current density from 50 to 500 mA/cm<sup>2</sup> improved the HER activity. For the OER, the catalytic activity increased to 150 mA/cm<sup>2</sup> but decreased beyond this value.
- **Reduction potential:** Higher applied potentials during deposition (-1.6 V to -4.2 V) enhanced the HER activity, with 2 V being optimal for the OER.
- **Deposition time:** A 10-minute deposition optimized the HER catalytic properties, whereas 15 minutes yielded the best OER kinetics.
- **KOH concentration:** Increasing the KOH concentration (14-90 g/L) increased the catalytic activity for both the HER and OER due to improved solution conductivity.
- **Electrolyte Type:** 1 M KOH produced the best performance for the HER, outperforming NaOH and KCl.
- **Temperature of KOH:** Increasing the KOH temperature (25°C to 60°C) improved the OER activity, with 50°C being optimal.

In conclusion, controlling the bath parameters, such as pH, scan rate, electrolyte composition, and deposition conditions, is critical for optimizing the catalytic performance of Ni-Mn electrocatalysts for the HER and OER. These findings underscore the potential of Ni-Mn films as effective electrocatalysts for water splitting applications.

### 6.3. Part 3: Electrodeposition of Ni-Mn-Co-Fe on copper for the HER and OER

- **Electrodeposition of Ni-Mn-Co-Fe Films:** Ni-Mn-Co-Fe alloy films were deposited on copper substrates via linear sweep voltammetry (LSV) under various bath parameters, including composition, scan rate, pH, temperature, and deposition duration. The bath solution consisted of 25 g/L NiCl<sub>2</sub>·6H<sub>2</sub>O, 30 g/L MnCl<sub>2</sub>·6H<sub>2</sub>O, 10 g/L CoCl<sub>2</sub>·6H<sub>2</sub>O, 10 g/L FeSO<sub>4</sub>·7H<sub>2</sub>O and 50 g/L NH<sub>4</sub>Cl.
- **Influence of Electrochemical Method:** The efficiency of deposition and electrocatalytic performance vary depending on the electrochemical method applied:
  - **Fixed potential:** -2.8 V for 2 minutes.
  - **LSV:** Scanning potential from -0.5 V to -1.6 V.
  - **Linear Polarization:** Potential range from -0.5 V to -1.6 V.

- **Dual potential:** -0.8 V for 1 min followed by -1.2 V for 1 min. The LSV technique demonstrated the highest electrocatalytic activity with the lowest overpotential, as increasing the applied potential increased the cathodic current density in both the HER and OER.
- **Effect of Bath Composition:** Under optimized conditions (10 mV/s scan rate, room temperature, and a potential range from -0.5 V to -1.4 V), a bath composition of 25 g/L  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 30 g/L  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ , 10 g/L  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 10 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and 50 g/L  $\text{NH}_4\text{Cl}$  exhibited maximum catalytic activity for the HER and OER.
- **Influence of the Scan Rate:** A scan rate of 10 mV/s was found to significantly enhance the electrocatalytic activity for both the HER and OER.
- **Effect of the bath pH:** LSV experiments revealed that the cathodic reaction kinetics improved at lower pH values. The optimal reduction potential for the HER and OER was achieved at pH 3.5.
- **Effects of Bath Temperature:** Bath temperatures of 25°C, 40°C, and 60°C were tested. The results showed that the HER and OER activity peaked at 25°C, highlighting the temperature dependency of the catalyst performance.
- **Influence of the KOH concentration and temperature:** The electrocatalytic activity of Ni-Mn-Co-Fe was tested at KOH concentrations ranging from 0.25 M to 1.5 M at room temperature with a scan rate of 10 mV/s. With 1.5 M KOH, the catalyst achieved the highest electrocatalytic activity, with a current density of 180 mA/cm<sup>2</sup> at -1.7 V vs. Ag/AgCl for the HER.
- **Effect of the KOH temperature:** In an alkaline environment (pH 14) with a scan rate of 10 mV/s, the impact of the bath temperature (25°C, 40°C, 55°C, or 75°C) was evaluated. The catalyst displayed the highest HER activity at 75°C. However, for the OER, the catalytic efficiency decreased at higher temperatures, with 55°C showing optimal results relative to the HER.

These findings provide valuable insights into the optimal conditions for the electrodeposition and performance enhancement of Ni-Mn-Co-Fe alloy films, demonstrating their viability for efficient HER and OER.

#### 6.4. Part 4: Comparative Study of Catalysts

This study successfully developed a cost-effective Ni-Mn-Co-Fe alloy electrocatalyst for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) via electrodeposition. The key operational parameters, including the bath composition, scan rates (5, 10, and 50 mV/s), pH values (1.5, 3.5, and 7.5), and temperatures (25°C, 40°C, and 60°C), were optimized.

The Performance Highlights in:

- The Ni-Mn-Co-Fe catalyst achieved remarkable electrocatalytic activity, requiring overpotentials of 436 mV for the HER and 447 mV for the OER to generate a current density of 100 mA/cm<sup>2</sup>.
- The catalyst exhibited the lowest charge transfer resistance of 0.33  $\Omega \cdot \text{cm}^2$ , indicating excellent electrochemical kinetics and high efficiency.
- Long-term stability tests revealed minimal overpotential degradation (less than 4%) after 20 hours of continuous electrolysis, confirming its durability.

The performance of the Ni-Mn-Co-Fe catalyst was benchmarked against the following:

- Monometallic catalysts (Ni, Co)
- Binary alloys (Ni-Fe, Ni-Co)
- Ternary alloys (Ni-Mn-Co, Ni-Mn-Fe)
- Commercial noble metal catalysts (Pt/C for HER and RuO<sub>2</sub>/IrO<sub>2</sub> for OER)

The results revealed that the quaternary Ni-Mn-Co-Fe alloy outperformed the other catalysts, offering superior efficiency and stability for water splitting.

## 6.5. Conclusion

The electrochemical deposition method successfully produced a range of electrodes, including Ni, Ni-Mn, Ni-Co, Ni-Mn-Co, and Ni-Mn-Co-Fe alloys, with their electrocatalytic activities for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) thoroughly evaluated. The study demonstrated that optimized deposition conditions, without the need for additives, facilitated the formation of microstructured surfaces, significantly enhancing the catalytic performance. Alloying notably improved the HER and OER efficiencies, with the Ni-Mn-Co-Fe electrode exhibiting overpotentials of 19 mV and 194 mV to reach current densities of 10 mA/cm<sup>2</sup> for the HER and OER, respectively, and 436 mV and 447 mV for 100 mA/cm<sup>2</sup>.

The Ni-Mn-Co-Fe electrode exhibited the most efficient reaction kinetics among the tested samples, with Tafel slopes of 92 mV/dec for the HER and 90 mV/dec for the OER, indicating that synergistic interactions among Ni, Mn, Co, and Fe reduced the energy barriers for both reactions. Electrochemical impedance spectroscopy (EIS) analysis revealed a low charge transfer resistance ( $R_{ct}$ ) of 0.33  $\Omega \cdot \text{cm}^2$ , underscoring its excellent electrochemical performance. This low  $R_{ct}$ , coupled with a significant capacitance (CPE) component, reflected rapid charge transfer and enhanced kinetics at the catalyst surface, which are critical for high activity.

Long-term stability tests demonstrated minimal cell voltage variation over 20 hours, confirming outstanding electrocatalytic durability. The superior performance was attributed to an increased electrochemically active surface area, synergistic effects of the alloy components, optimized electrode-electrolyte interactions, and increased availability of reaction sites. In a bifunctional water-splitting system, the Ni-Mn-Co-Fe electrode required a cell voltage of only 1.57 V vs. RHE to achieve a current density of 10 mA/cm<sup>2</sup>.

The effects of the bath composition, scan rate, pH, and temperature on the deposition process were systematically investigated for the Ni-Mn-Co-Fe electrodes, along with the influences of the KOH concentration and operating temperature on the electrocatalytic performance. The combination of a simple and scalable fabrication process, exceptional catalytic activity, and excellent durability make the Ni-Mn-Co-Fe electrode a promising and cost-effective candidate for industrial water electrolysis applications.

### 6.6. Key innovations:

- **Surface Nanostructuring:** Electrodeposited Ni-Mn-Co-Fe alloys achieved high electrocatalytic activity due to enhanced surface area and improved electronic interactions between transition metals.
- **Synergistic effects:** The combination of Ni, Mn, Co, and Fe led to optimized electronic configurations and active site availability, increasing HER and OER kinetics.
- **Electrodeposition Techniques:** This study systematically explored cyclic voltammetry, linear sweep voltammetry, and dual-potential approaches to achieve optimal catalyst deposition.

### 6.7. Future perspectives:

- **Industrial scaling:** Further studies should focus on scaling up the electrodeposition process for large-area electrodes and assessing catalyst performance in industrial alkaline electrolyzers.
- **Durability Testing:** Long-term stability and performance under continuous operation must be evaluated to confirm industrial viability.
- **Alloy Optimization:** Exploring the effects of doping with additional elements (e.g., Mo, W) and fine-tuning the Ni-Mn-Co-Fe composition may further improve the catalytic activity and efficiency.
- **Cost Analysis:** A detailed cost-benefit analysis is necessary to assess the economic feasibility of noble metal-based systems compared with noble metal-based systems.
- **Application in fuel cells:** The potential of these electrodes for use in fuel cells should be explored, with a focus on their electrocatalytic performance and durability under fuel cell operating conditions.

## 7. Scientific Production

### 7.1. International publication

Belhani, I., et al., *Enhanced Electrocatalytic Activity of Ni-Mn-Co-Fe Alloys for Efficient Hydrogen and Oxygen Evolution Reactions: A Study on the Effects of Electrodeposition Parameters*. Renewable Energy, 2024: p. 121688 . [49]  
<https://doi.org/10.1016/j.renene.2024.121688>

### 7.2. International Conferences

Belhani, I., et al, **International Conference on the Environment Technologies and Sustainable Energy (ICETSE'2023)** held on October 17-18, 2023, in Algiers, Algeria. The presentation was titled *"Influence of bath parameters on the electrodeposition of Ni-Mn alloys as effective electrocatalysts for both hydrogen and oxygen evolution reactions."*

Belhani, I., et al ,**The 2nd International Conference on Science, Engineering, and Advanced Technology (ICSEAT-2023)** in Morocco. The presentation was titled *"Electrodeposition of affordable and efficient electrocatalysts for both hydrogen and oxygen evolution reactions."*

### 7.3. National Conferences

Belhani, I., et al, **The Seventh Students Symposium on Engineering Application of Mechanics (SSEAM'7)** on April 29-30, 2024, at Pole 1, Khenchela University. The presentation will be on *"Catalysts for hydrogen production."*

Belhani, I., et al., also attended the **1st Doctoral Symposium on Numerical Simulation in the Applied Sciences (Doctoral'2023)** held on December 18-19, 2023, at the Faculty of Exact Sciences and Informatics, Hassiba Benbouali University of Chlef, Algeria.

Belhani, I., et al , **The Second Doctoral Symposium on Technology: Process, Mechanical and Electrical Engineering (DST'02-2022)** on October 26-27, 2022, at the Faculty of Technology, Hassiba Benbouali University of Chlef, Algeria.