

**AMMONIA ELECTROOXIDATION REACTION USING
TRANSITION METAL BASED CATALYSTS
TOWARDS HYDROGEN PRODUCTION: AN
EXPERIMENTAL AND COMPUTATIONAL
APPROACH**

BY

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In

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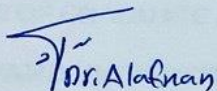
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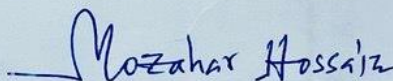
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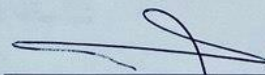
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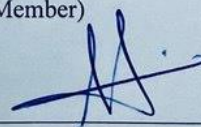
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Dedication

I dedicate this work to my family

ACKNOWLEDGMENT

I express my deep and sincere gratitude to the Almighty for granting me the wisdom and strength to undertake this thesis project. I am also grateful to my parents and siblings, whose love, support, advice, and prayers have kept me going throughout.

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LIST OF ABBREVIATIONS

Density Functional Theory	DFT
Nickel Foam	NF
Computational Hydrogen Electrode	CHE
Grand Canonical Density Functional Theory	GC-DFT
Potential-Adjusted Grand Free Energy	PAGE
Beyond-DFT Electrochemistry with Accelerated and Solvated Techniques Database	BEAST DB
Joint Density Functional Theory	JDFTx
Ammonia Oxidation Reaction	AOR
Nitrogen Reduction Reaction	NRR
Hydrogen Evolution Reaction	HER
Proton Exchange Membrane	PEM
Low Temperature Electrolysis	LTE
High Temperature Solid Oxide Electrolysis Cells	HTSOEC
Potential of Zero Charge	PZC
Proton-Coupled Electron Transfer	PCET
X-ray Diffraction	XRD
Face-Centered Cubic	FCC
Silver Chloride Electrode	Ag/AgCl
Brønsted–Evans–Polanyi	BEP
Cyclic Voltammetry	CV
Linear Sweep Voltammetry	LSV
X-ray Photoelectron Spectroscopy	XPS
Gas Chromatograph	GC
Thermal Conductivity Detector	TCD
Flame Ionization Detector	FID
Atomic Force Microscopy	AFM
Scanning Electron Microscopy	SEM
Energy Dispersive Spectroscopy	EDX
Electrochemical Surface Area	ECSA
Electrochemical Impedance Spectroscopy	EIS
Oxygen Evolution Reaction	OER

ABSTRACT

Full Name : Umar Musa Jafar
Thesis Title : Ammonia Electrooxidation Reaction using Transition Metal based Catalysts Towards Hydrogen Production: An Experimental and Computational Approach

Major Field : Chemical Engineering

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Hydrogen, a clean and sustainable energy alternative, faces significant challenges in storage and transportation. Ammonia offers a promising solution as a hydrogen carrier due to its ease of storage, transport, and efficient electrochemical decomposition. In this study, Ni and Co catalysts were investigated for the ammonia oxidation reaction (AOR) to produce hydrogen. To gain mechanistic insights, previously reported Grand Canonical Density Functional Theory (GC-DFT) data were utilized and adjusted using a Potential-Adjusted Grand Free Energy (PAGE) approach to account for potential-dependent reaction energetics. The results indicate that ammonia adsorption is thermodynamically more favorable on Ni surfaces, while nitrogen desorption is more efficient on Co surfaces, highlighting their distinct roles in facilitating AOR. Additionally, Ni and Co nanostructures were synthesized on nickel foam (NF) via a hydrothermal method to assess their catalytic properties for ammonia decomposition. The synthesis induced significant morphological and chemical modifications, as confirmed by comprehensive characterization techniques. The electrochemical performance of Ni/NF and Co/NF electrodes was evaluated in an alkaline electrolysis cell under ambient conditions. Compared to bare NF, both modified electrodes exhibited superior catalytic activity, demonstrated by lower onset potentials, higher current densities, and reduced charge transfer resistance. Consistent with DFT predictions, Co/NF outperformed Ni/NF, achieving higher ammonia conversion, greater hydrogen production rates, and improved energy efficiency. Overall, this study demonstrates the potential of nanostructured metal-modified NF electrodes to enhance ammonia oxidation catalysis, offering a promising route for efficient and sustainable hydrogen production. These findings reinforce ammonia's role as a viable hydrogen carrier in the transition toward a clean energy future.

ملخص الرسالة

الاسم الكامل : عمر موسى جعفر

عنوان الرسالة : تفاعل الأكسدة الكهروكيميائية للأمونيا باستخدام محفزات قائمة على المعادن الانتقالية لإنتاج الهيدروجين: منهج تجريبي وحسابي

التخصص : الهندسة الكيميائية

تاريخ الدرجة العلمية : أبريل 2025

الهيدروجين، باعتباره بديلاً خالياً من الانبعاثات الملوثة ومصدراً مستداماً للطاقة، يواجه تحديات كبيرة في مجالي التخزين والنقل، وتُعد الأمونيا حلاً واعدًا لحمل الهيدروجين بفضل سهولة تخزينها ونقلها، إضافةً إلى تحللها الكهروكيميائي الفعال، وفي بهدف إنتاج (AOR) لتفاعل أكسدة الأمونيا (Co) والكوبالت (Ni) هذه الدراسة، تم دراسة المحفزات المعتمدة على النيكل الهيدروجين، وللحصول على فهم آلي للتفاعل، تم الاستفادة من بيانات سابقة تم حسابها باستخدام نظرية دالة الكثافة في النظام (PAGE) ، وتم تعديل هذه البيانات باستخدام نهج طاقة جيبس الحرة المعدلة حسب الجهد الكهربائي (GC-DFT) الكبير لأخذ تأثير الجهد في الاعتبار على طاقة التفاعل، وأظهرت النتائج إلى أن ادمصاص الأمونيا يكون أكثر تفضيلاً من الناحية الديناميكية الحرارية على أسطح النيكل، بينما يكون انفصال النيتروجين أكثر كفاءة على أسطح الكوبالت، مما يبرز الأدوار على رغوة Ni وCo المختلفة لكلا المعدنين في تسهيل تفاعل أكسدة الأمونيا، وعلاوة على ذلك، تم تصنيع تراكيب نانوية من باستخدام طريقة التحلل المائي الحراري لدراسة خواصها التحفيزية لتحلل الأمونيا، وأدى هذا التصنيع إلى (NF) النيكل تعبيرات كبيرة في البنية الشكلية والتركيب الكيميائي، كما أكدت تقنيات التحليل الشامل، وقد تم تقييم الأداء الكهروكيميائي في خلية تحليل كهربائي تحت ظروف قلوية، فبالمقارنةً برغوة النيكل غير المعدلة، أظهرت Co/NF و Ni/NF لأقطاب الأقطاب المعدلة أداءً تحفيزياً متفوقاً تمثل في انخفاض جهود البدء، وزيادة كثافة التيار، وانخفاض مقاومة نقل الشحنة، وتماشياً من حيث تحويل الأمونيا، ومعدلات إنتاج الهيدروجين، وكفاءة الطاقة، Co/NF على Ni/NF ، تفوقت DFT مع تنبؤات وبشكل عام، تُبرز هذه الدراسة إمكانيات أقطاب رغوة النيكل المعدلة بالمعادن النانوية في تحسين تحفيز أكسدة الأمونيا، مما يوفر مساراً واعدًا لإنتاج الهيدروجين بكفاءة واستدامة، وتدعم هذه النتائج دور الأمونيا كناقل فعال للهيدروجين في التحول نحو مستقبل طاقة نظيفة.

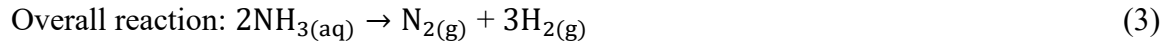
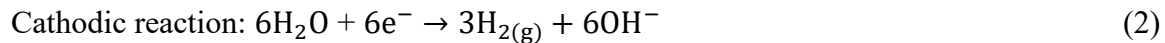
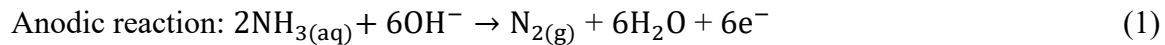
CHAPTER 1 INTRODUCTION

1.1 Background of the Study

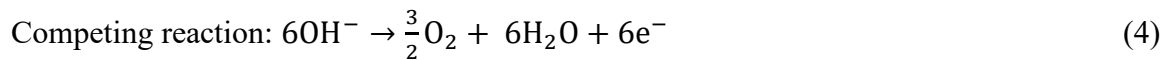
The continuous reliance on fossil fuels has significantly contributed to CO₂ emission, driving climate change and global warming [1]. Coupled with increasing global energy demands due to population growth, the urgent need for sustainable and clean energy alternatives has become evident. Among potential solutions, hydrogen has emerged as a promising fuel due to its clean combustion and high energy density. [2, 3] However, the high costs, energy-intensive processes, and safety risks associated with hydrogen production, storage, and transportation remain significant barriers to its widespread adoption [4, 5]. Nitrogen-based compounds, including ammonia, urea, and hydrazine, have garnered attention as alternative hydrogen carriers owing to their advantageous properties. [6-9] Among these, ammonia stands out with a hydrogen mass fraction of 17.7%, surpassing that of urea (6.6%) and hydrazine (12.5%). Additionally, ammonia decomposition does not produce CO₂ emissions, unlike urea, and offers safer handling compared to hydrazine. As urea and hydrazine are derivatives of ammonia, using ammonia directly also provides economic benefits. [10] With a high volumetric density of 121 kg/m³ and its existence as a liquid under ambient conditions, ammonia is particularly well-suited for transportation and storage. [11-15] Furthermore, the electrochemical decomposition of ammonia into hydrogen has attracted considerable attention due to its lower energy requirements and compatibility with renewable power sources, offering a sustainable pathway for clean energy production. [16-18]

Ammonia decomposition offers a thermodynamically favorable alternative to conventional hydrogen production methods, such as water electrolysis. Although both

processes involve water splitting as a source of hydrogen, they differ in their energy requirements. In traditional water electrolysis, the anodic oxygen evolution reaction (OER) requires a high overpotential, leading to a theoretical voltage requirement of 1.23 V_{SHE} . In contrast, replacing OER with the ammonia oxidation reaction (AOR) significantly reduces this energy demand, as AOR requires only 0.06 V_{SHE} . By circumventing the high-energy OER step, AOR presents a significantly more energy-efficient route for hydrogen production. [19-21] Additionally, the risk of O_2 - H_2 explosion is minimized when AOR is employed in place of OER. The electrochemical decomposition of ammonia reverses the Haber–Bosch process [22-24], wherein ammonia is oxidized at the anode to produce nitrogen (Equation 1), while water is reduced at the cathode to generate hydrogen gas (Equation 2). This combination of AOR and the hydrogen evolution reaction (HER) results in the overall reaction (Equation 3). However, at higher applied potentials, the competing OER side reaction (Equation 4) may occur, reducing efficiency.



$$E_{\text{overall}} = 0.06 \text{ V vs. SHE}$$



Electrocatalysts play a crucial role in facilitating the electrolysis process. While noble metals such as Pt, Ir, and Ru have been investigated as active components for AOR [25-

29], their practical application is hindered by surface poisoning from adsorbed nitrogen atoms (*N), competing OER at higher potentials, and poor selectivity, which leads to NO_x formation. [30, 31] These challenges have driven research toward non-noble metal-based electrocatalysts [10], with Ni emerging as a promising candidate due to its abundance, low cost, and favorable electrochemical properties in alkaline media. Various studies have explored Ni in different forms, pure, alloyed, oxidized, hydroxidized, or incorporated into composite materials to enhance catalytic activity. [32-36] However, the underlying mechanism of AOR on Ni-based electrocatalysts remains poorly understood.

Recent advances in computational studies, particularly DFT, have provided valuable insights into the AOR mechanism at catalyst surfaces, accelerating the discovery of new electrocatalysts. [37-41] Typical DFT studies model electrochemical reactions using vacuum or continuum electrolyte models to approximate solvent effects and either neglect the applied potential or employ the CHE approach to estimate its impact on reaction energetics. [41-44] However, CHE has inherent limitations in accuracy, as it does not explicitly incorporate the applied potential within the quantum mechanical framework. In contrast, Grand Canonical DFT (GC-DFT) provides a more accurate representation of electrified interfaces by self-consistently varying the number of electrons to maintain equilibrium with the applied potential. Additionally, GC-DFT also accounts for solvent effects through polarizable continuum models or explicit solvent molecules, enabling more precise predictions of reaction energetics and adsorbate geometries. [45, 46] However, the computational cost associated with GC-DFT makes it less attractive, particularly for qualitative comparisons.

1.2 Aim and Objectives of the Study

This project aims to conduct a comprehensive study of ammonia decomposition for hydrogen production using nickel (Ni) and cobalt (Co) catalysts via the electrochemical method. This is designed to be achieved via the following objectives:

- DFT investigations into the reaction mechanism and to optimize the electrolysis environment
- Catalyst design and electrode preparation
- Physical characterizations of prepared electrodes to investigate the catalysts' structure
- Electrochemical characterizations and activity tests to investigate the catalytic activity of the Ni and Co electrodes
- Electrochemical performance tests to investigate hydrogen production in an electrolysis cell
- Energetic span, ammonia adsorption, and reaction kinetic investigations to validate how the catalysts' structure and properties affect the performance.

Overall, by isolating and comparing the catalytic efficiencies of each metal, this project provides a novel perspective on the activities of Ni and Co in ammonia decomposition and hydrogen production.

1.3 Structure of the Study

The project is structured into chapters to ensure a systematic approach in achieving the overall aim of the study. The chapters are organized in an orderly manner to present specific aspects, as illustrated in Figure 1.

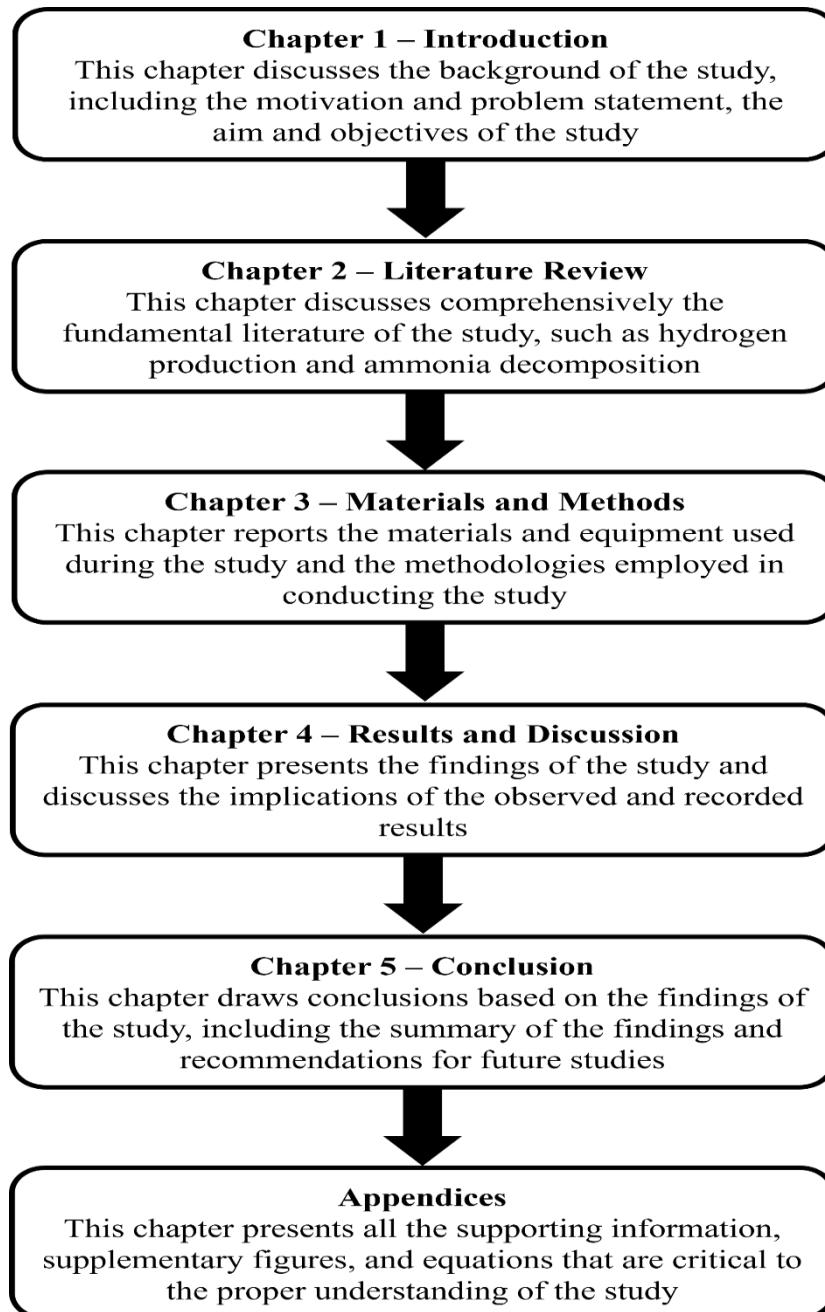


Figure 1: Structure of the study

CHAPTER 2 LITERATURE REVIEW

2.1 Hydrogen Production Methods

Hydrogen can be generated using several different technologies, such as thermochemical, photochemical, electrochemical, biochemical and radiochemical methods, as well as integrated systems such as electro-thermo-chemical processes. A summary of these methods, along with their respective advantages and disadvantages, is provided in Table 1. [47, 48] The primary sources of hydrogen for commercial production are natural gas, petroleum reforming, coal gasification, and electrolysis coupled with renewable energy sources. [49, 50] Thermochemical methods are the predominant approach for commercial hydrogen production, involving high temperature processes such as reforming and pyrolysis. However, to achieve high purity hydrogen, additional units for separation and purification are required. [49, 51] Hydrogen can also be produced as a byproduct in various hydrocarbon processes. This method has the potential to generate approximately 3.5 million metric tons of hydrogen annually. Nevertheless, most hydrogen production processes exhibit low energy efficiency, high costs, and the need for integrating carbon capture technologies. [49, 52]

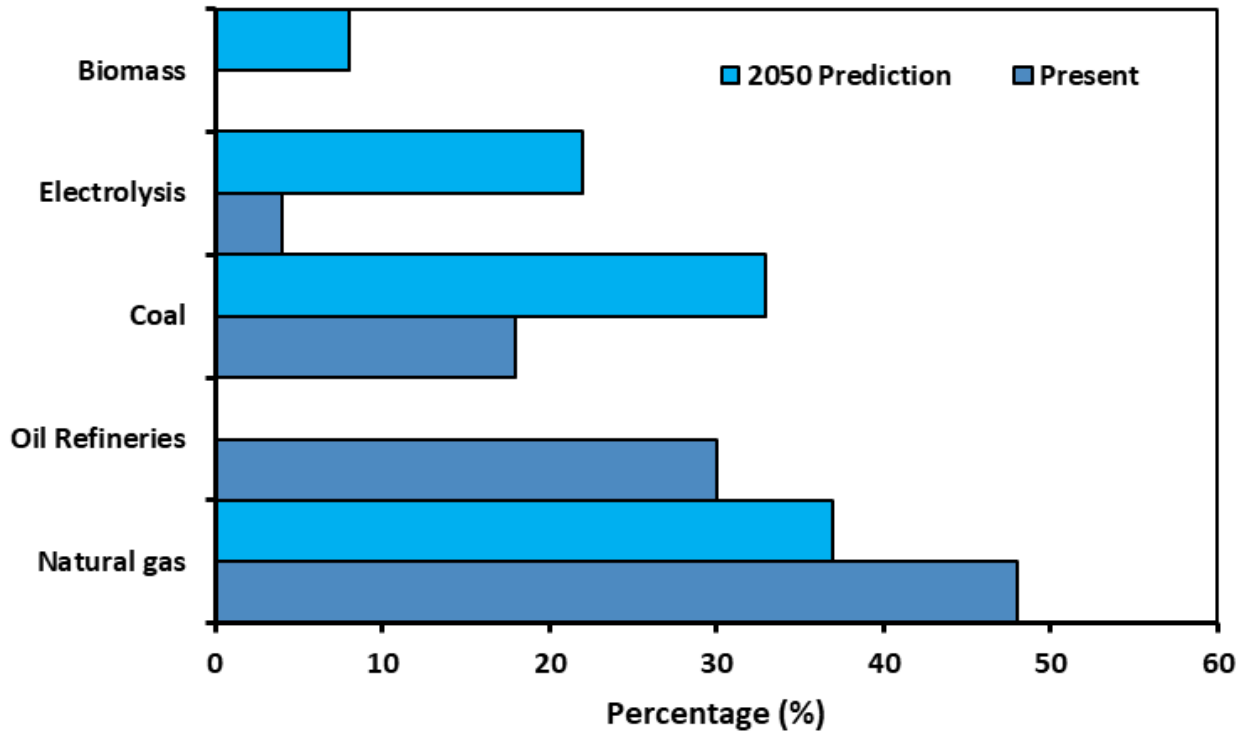


Figure 2: Overview of Hydrogen Production from Various Sources. It is predicted to reduce by 2050, while hydrogen production from electrolysis and biomass sources are expected to increase. [49]

Despite the widespread use of thermochemical methods for hydrogen production, both the prediction shown in Figure 2 and current research trends highlight the potential of the electrochemical method, primarily via electrolysis. The electrochemical method utilizes electricity to produce pure hydrogen at ambient conditions, eliminating the need for an additional hydrogen purification system. Common feedstocks for hydrogen production through electrolysis include water and ammonia, both of which exhibit high conversion efficiencies and produce exceptionally pure hydrogen, which is a key factor for establishing a sustainable and environmentally friendly hydrogen production process. [49] However, the electrochemical hydrogen production technology is still in the early

stages of development, with unresolved challenges related to material costs and practical implementation. [53]

Established technologies, such as alkaline electrolysis, proton exchange membranes (PEM) electrolysis, and low-temperature electrolysis (LTE), can produce high-purity hydrogen as a by-product through electrochemical processes. These methods can be implemented on a large scale using renewable electricity. High-temperature electrolysis, particularly with solid oxide electrolysis cells (HTSOEC), offers higher electrical energy efficiency compared to LTE, as HTSOEC utilizes heat in addition to electricity to derive the process. Furthermore, hydrogen production using renewable energy sources is gradually transitioning from traditional alkaline electrolysis to the more adaptable PEM electrolysis, with this transition occurring on an increasing scale in several countries. However, it is important to note that PEM electrolysis currently exhibits lower energy efficiency compared to other electrolysis technologies. [49, 51]

The simultaneous production of hydrogen, electricity, ammonia, and thermal energy can be achieved by integrating solar cell electrolysis, a solar-steam cycle, and wind-powered electrolysis. Large towns in China and India have reported generating 10 MW of power. The maximum energy efficiency achieved in these processes is 50%. [53] This technology results in zero carbon emissions. Additionally, hydrogen production using nuclear power generates no carbon emissions; however, it raises significant environmental, health, and safety concerns, often surpassing those associated with conventional fossil fuels. [54] Another promising approach for hydrogen production is photochemical methods, which involve the decomposition of substances using radiation energy at ambient temperatures. These methods include photo-electrolysis,

photocatalysis, and photo-biological processes. [55] Renewable biomass sources can be effectively utilized for large-scale hydrogen production, yielding a clean energy output. However, these techniques are still in need of further refinement, as their conversion efficiencies remain relatively low. [56]

Table 1: Different production methods and their associated advantages and disadvantages [49, 51-54, 56]

Production method	Benefits	Drawbacks
Electrochemical	• Temperature and pressure close to room conditions • High purity hydrogen, no need for a purification system • Excellent conversion efficiencies • Selective production • Integration with renewable energy	• Currently at the phase of advancement • Issues regarding material and practical challenges remain unresolved • Complexity of electrodes
Thermochemical	• High yield, with potential of around 3.5 million metric tons of hydrogen per year • High catalyst efficiency • Scalability • Simplicity	• High energy and temperature requirement • Lower level of hydrogen purity • High equipment cost • CO₂ emissions
Photochemical	• Renewable energy source • Low operational costs • Room temperature operation	• Low efficiency • Intermittent energy source • Complexity and cost

Biochemical	• Renewable biomass source	• Requires further refinement utilization
	• Environmentally friendly	• Scalability issues
	• High level of cleanliness and green chemistry	• Stability issues
Radiochemical/nuclear		• Slow reaction rate with low conversion efficiencies
	• High energy density	• Safety concerns
	• Unique reaction pathways	• High cost
	• Non-thermal process	• Limited availability

2.2 Fundamentals of Ammonia Decomposition

2.2.1 Thermodynamics of Ammonia Decomposition

Thermodynamics determines the process feasibility and sets constraints on the maximum achievable yield and conversion. Gibbs free energy (ΔG) is a key function that encompasses various properties, including enthalpy (ΔH), associated with the process. [57] It evaluates a thermodynamic system's capacity to undergo changes under standard conditions. Ammonia decomposition, which is the reverse of its synthesis reaction [58] and is essential for hydrogen production [59], is a typical endothermic process represented by the reaction:



In practice, the choice of catalyst and the reaction temperature significantly influence the reaction kinetics and equilibrium position, which can result in thermodynamic limitations and barriers. [58] Despite the limited number of detailed systematic thermodynamic studies on ammonia decomposition in the literature, a maximum NH_3 conversion of over

99% has been reported at temperatures exceeding 400°C under ambient pressure. [60-63] Subsequently, the reaction reached a point of irreversibility and became less influenced by temperature.

Sun et al. [59] examined the effects of pressure and temperature on the ammonia decomposition process, finding that under isothermal conditions, ammonia conversion decreases as pressure increases. However, this effect is more pronounced at lower temperatures compared to those above 400 °C. As shown in Figure 3(a), these findings indicate that pressure has a minimal impact on ammonia conversion during decomposition at higher temperatures. Another study by Ojelade and Zaman [57], which utilized the minimization of the Gibbs free energy objective function using MATLAB's 'fmincon' function by applying a constrained optimization algorithm, also demonstrated a similar trend (Figure 3(b)). Thus, it can be concluded that ammonia can thermodynamically decompose into hydrogen at temperatures of 400 °C. However, the rate of the decomposition reaction and the potential for catalyst utilization to enhance NH_3 conversion at temperatures below 400 °C can only be assessed by examining the reaction kinetics and mechanisms.

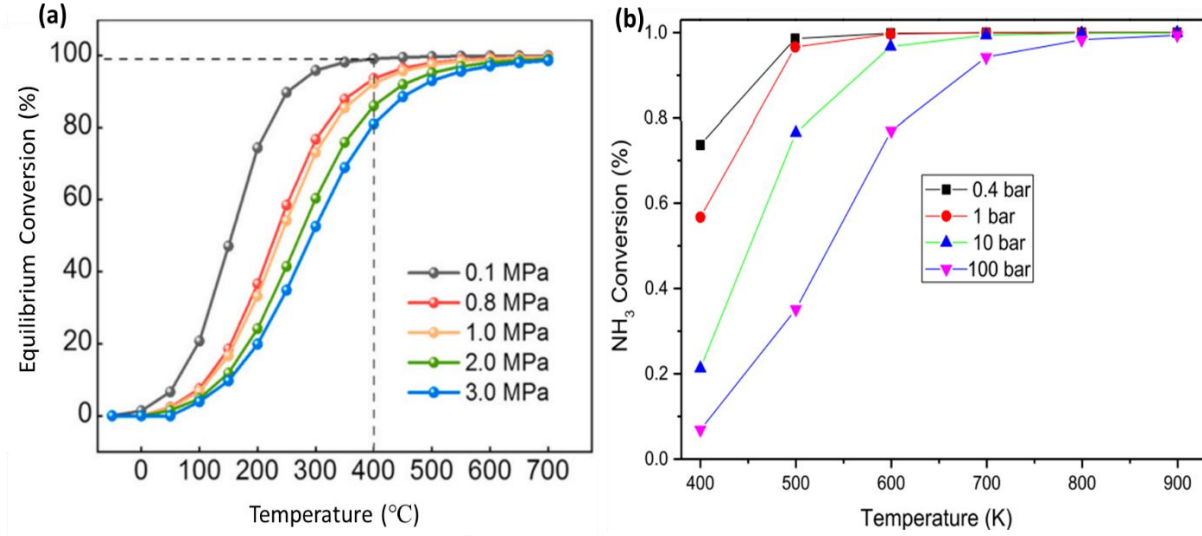


Figure 3: (a and b) Equilibrium conversion of NH₃ to H₂ under varying temperatures and pressures. The effect of pressure on the conversion is observed to be more pronounced at lower temperatures. However, the conversion becomes less pressure-dependent at higher temperatures. [57, 59]

2.2.2 Reaction Kinetics

Recently, there have been numerous studies and investigations into ammonia decomposition kinetics. The main objective of these studies has been to derive a mathematical expression for the reaction rate and to deepen the understanding of the mechanisms behind the decomposition process. [64] The following equation clarifies the empirical rate expression for the decomposition of ammonia. [65]

$$r_{\text{NH}_3} = k \times c^\alpha(\text{NH}_3) \times c^\beta(\text{H}_2) \times c^\gamma(\text{N}_2) \quad (6)$$

where r_{NH_3} is the rate of reaction. The reaction order α is always greater than 0, while β and γ are less than 0. As a result, the rate expression favors decomposition when the NH₃ concentration is higher and H₂ and N₂ concentrations are lower. It is also preferable for

ammonia decomposition to have a large value of k [59, 65], which can be estimated using the Arrhenius equation:

$$k = Ae^{\frac{-E_a}{RT}} \quad (7)$$

where A is the pre-exponential factor, E_a is the activation energy of the decomposition reaction, R is the molar gas constant, and T is the temperature of the system.

From the presented equations, it can be inferred that increasing the reaction temperature is an effective method to enhance NH_3 decomposition, which in turn facilitate H_2 generation. However, this approach would substantially raise the energy requirements. The most effective strategy is to decrease the activation energy (E_a), which can be accomplished through rational catalyst design. [59, 65] Consequently, it is crucial to develop catalysts with exceptional efficiency for energy conservation and to enhance hydrogen production, while also gaining a comprehensive understanding of the reaction mechanism.

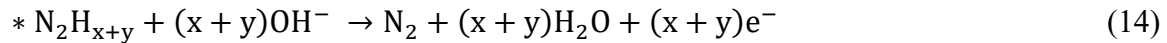
2.2.3 Reaction Mechanism

Studying the ammonia decomposition reaction mechanism is essential, as it provides a foundational understanding of the effect of catalysts and their formulations. Furthermore, establishing the correlation between catalyst modifications and the reaction mechanism provides crucial insights that can inform the future development and optimization of catalytic materials. [66] Numerous review articles have documented common mechanisms of ammonia decomposition. [67-69] For example, Temkin proposed that the mechanism for this reaction is the reverse of that considered in ammonia synthesis. In general, there are two distinct reaction routes for ammonia decomposition through AOR.

In 1963, Oswin and Salomon described a persistent dehydrogenation mechanism known as the O-S mechanism. In this process, adsorbed NH_3 molecules on the catalyst undergo sequential dehydrogenation by OH^- ions, resulting in the formation of Ni atoms. These nitrogen atoms subsequently combine to form N_2 . The mechanism can be described as follows:



Gerischer and Mauerer further advanced the O-S process, revealing that AOR encompasses not only dehydrogenation by OH^- ions but also the recombination of $*\text{N}_x\text{H}_y$ species, a process referred to as the G-M mechanism. [69] The G-M mechanism occurs sequentially after the equations (8) and (9) as the follows:



where x and y can each be either 1 or 2.

The $*\text{NH}_x$ and $*\text{NH}_y$ adsorbed species combine to form N_2H_{x+y} , which then undergoes further dehydrogenation to produce N_2 . Most studies such as [30, 70-72] reported the G-M mechanism for the recombination of intermediates in AOR.

Unlike the synthesis of NH_3 in which the dissociation of N_2 is the well-known rate-limiting step [73], the identification of the rate-limiting step for the decomposition of NH_3 remains uncertain due to the reaction's high sensitivity to the type of catalyst used. [74] Additionally, other factors including the reaction temperature and pressure alter the limiting step. [64] The cleavage of *N-H bonds or the coupling of *N species is commonly considered a potential rate-limiting step in NH_3 decomposition. Depending on the catalyst composition and the design of the active sites, the cleavage of the *N-H bond has been proposed as the rate-limiting step for noble metals, while the recombination of *N species is proposed as the rate-limiting step for non-noble metals. [75, 76]

In summary, understanding ammonia decomposition requires a thorough examination of reaction thermodynamics, kinetics, and mechanisms. Thermodynamic analyses suggest that complete ammonia decomposition is feasible at low temperatures. However, kinetic studies and mechanistic investigations indicate that the high activation energy required for N-H bond cleavage, coupled with the subsequent recombination of adsorbed nitrogen species, leads to slower reaction rates and incomplete conversion. [77] To gain a deeper understanding of the process, the reaction mechanism should be investigated in conjunction with DFT studies on various catalysts, as this knowledge is crucial for the development of highly active catalysts that can enhance the reaction rate and facilitate large-scale hydrogen production through ammonia decomposition.

2.3 Catalysts for Electrochemical Ammonia Decomposition to Hydrogen

Electrochemical ammonia decomposition to hydrogen involves the simultaneous occurrence of the AOR and the HER. During AOR at the anode, N_2 is produced, releasing protons in the process, while H_2 is generated at the cathode through HER, driven by the

reduction of protons from the anode. As a result, H_2 production is primarily dependent on the AOR. In the absence of catalysts, the rate of AOR can be significantly reduced. Electrocatalysts are commonly employed to accelerate these reactions and lower the excess energy required for the electrochemical AOR. [78] This highlights that, with an effective catalyst, the AOR can occur at lower applied potentials, improving energy efficiency and reducing process costs. This section reviews the history and advancements in electrocatalysts, their design principles, and their common synthesis and fabrication methods used for AOR applications.

2.3.1 History and Advances in Electrocatalysts and AOR

In the 1890s, Elbs and Schonherr discovered that nitrogen is produced during the electrolysis of ammonium sulfate, a breakthrough that paved the way for research into AOR. Since then, researchers have focused on the gradual decomposition of ammonia through oxidation reactions. Significant advancements have been made in the study of AOR electrocatalysts, and the chronological development of these discoveries is illustrated in Figure 4. Inspired by the work of Elbs and Schonherr, Muller and Spitzer conducted a study in 1905 and found that the oxidation process and the resulting products are influenced by the material used for the anode. They were the first to propose that Pt electrodes could produce N_2 through AOR at high applied potentials in alkaline solutions. [70] In 1963, Katan and Galiotto studied the effect of Pt black as a catalyst in the anode reaction, revealing an average current efficiency of approximately 99.7%. Another important study by Despić et al. in 1966 investigated the kinetics of AOR on Pt-plated and Raney nickel anodes in an alkaline solution using the galvanostatic method. Their findings demonstrate that Raney nickel lacks catalytic activity for AOR, providing early

evidence that non-noble metals are inactive in the reaction. [79] In 1969, McKee et al. explored noble metal alloying as an anode material for ammonia fuel cells and discovered that a platinum-iridium (Pt-Ir) alloy exhibited significantly greater catalytic activity than a Pt anode alone. [80]

For the past 50 years, research on AOR catalysts has primarily focused on the stability of Pt-based catalysts, along with their reaction mechanisms and the intermediate products formed during the reaction. [81, 82] Thus, alloys of these Pt with other noble and non-noble metals have also been explored. In 2004, Takashi Miura et al. conducted a study that compared the effectiveness of Pt-Ir and Pt-Cu binary alloys as electrocatalysts for ammonia oxidation. [83] The results showed that the oxidation activity varied, with Pt-Ir demonstrating the highest activity, followed by Pt, and then Pt-Cu. Nevertheless, research into non-noble metal catalysts for ammonia oxidation remains a critical area of study due to the high costs associated with precious metal catalysts. In 2008, Yao and Cheng [84] examined the performance of a nickel catalyst in AOR. Their findings indicated that the catalytic activity of nickel, a non-noble metal, was minimal. However, by exploring the behavior of non-noble metal compounds, there is potential for significant improvements in catalytic activity. Building on this idea, Kapalka et al. [32] developed the Ni/Ni(OH)₂ electrode in 2010 and investigated its electrochemical performance in AOR. Notably, this electrode remained active and stable even at high ammonia concentrations during the AOR process. Their findings marked a significant step forward in the development of ammonia oxidation catalysts, shifting the focus from noble metals to more affordable alternatives. In 2019, Habibzadeh et al. [85] reported that ruthenium polypyridyl complexes can effectively accelerate the oxidation of ammonia at ambient temperature

and pressure. This research introduced a novel molecular catalyst for electrochemical AOR. Scientists are expected to continue enhancing catalyst systems in the future through ongoing research.

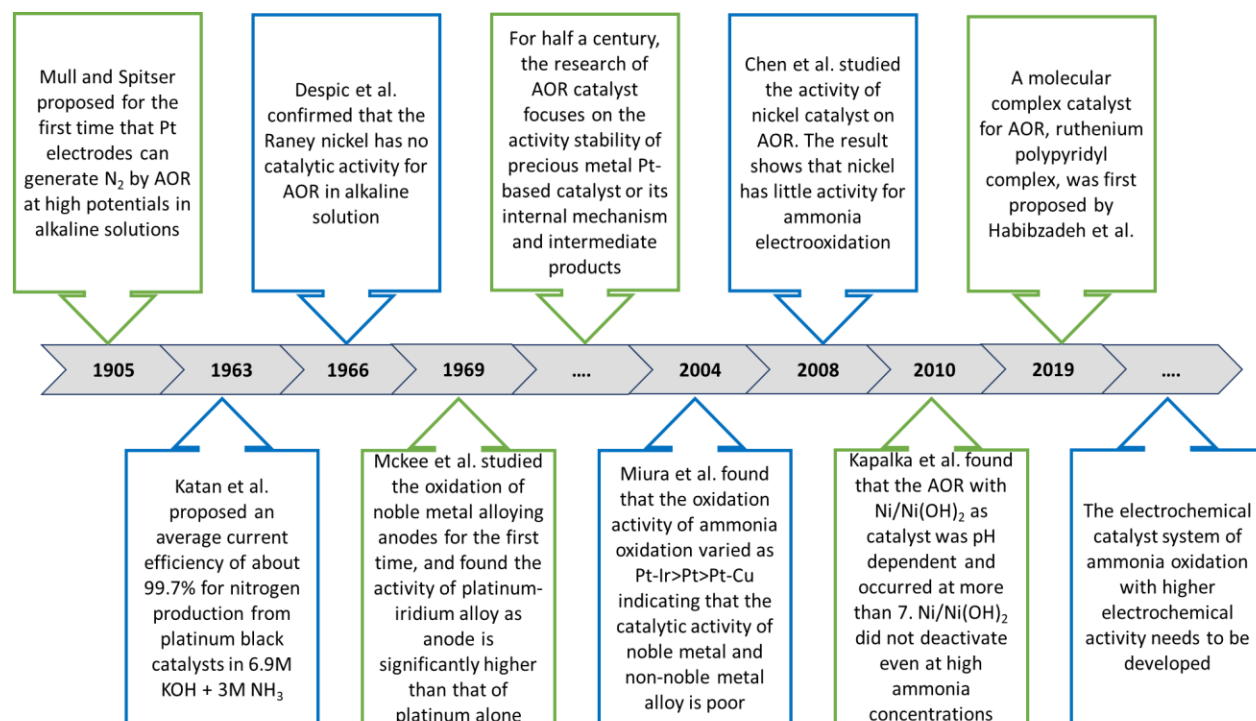


Figure 4: The progress of the AOR system. The catalytic activity of noble metals, such as Pt, was reported prior to that of non-noble metals, such as Ni, which were previously unrecognized for their activity in AOR. [70]

2.3.2 Catalyst Design

2.3.2.1 Active component

The active components of electrocatalysts used in ammonia decomposition typically consist of single metals, metal alloys, or their compounds, which can include both noble and non-noble metals. Noble metals such as Pt, Ru, Ir, Rh, and Pd, along with non-noble metals like Ni, Fe, Co, and Cu, have been extensively studied as catalysts for the AOR. [21, 60, 86-92] Alloy electrocatalysts offer several advantages over pure metal

electrocatalysts, including enhanced activity, selectivity, durability, and reduced reliance on precious metals. By tailoring the alloy composition, the reaction rate can be significantly improved. [78]

2.3.2.2 Common supports

Supporting materials may not directly participate in the decomposition of NH_3 , but they play a crucial role in enhancing catalytic performance. They improve dispersion, increase specific surface area, modify surface acidity or alkalinity, and enhance the conductivity and stability of the active components by altering the size distribution, morphology, and electronic state of the catalysts. [66, 77, 93] Additionally, an effective support can induce a strong metal–support interaction (SMSI), which further enhances catalyst performance. [59] In designing catalysts for the AOR, a variety of materials, including carbon-based compounds, metal oxides, transition metal oxides, and rare earth metal oxides, are commonly used as supports. [29, 53, 87, 92, 94-97] Recently, materials such as MOFs, MXenes, electrides, and industrial wastes have also been explored as potential supports. [59, 74, 77, 98]

2.3.2.3 Common promoters

Promoters that enhance the catalyst's activity, selectivity, and longevity during the AOR can significantly improve ammonia decomposition.[99] Common types of these materials include alkali, alkaline earth, and rare earth metal oxides. [21, 77, 90, 99-101] Each promoter functions differently depending on specific requirements. Alkali metals are typically used as electron promoters to facilitate the transfer of electrons from the supports to the active metal surface, thereby improving the electrical environment. Rare

earth metals act as structural promoters, enhancing the catalyst's thermal stability, while alkaline earth metals serve a dual role as both electronic and structural promoters. [77]

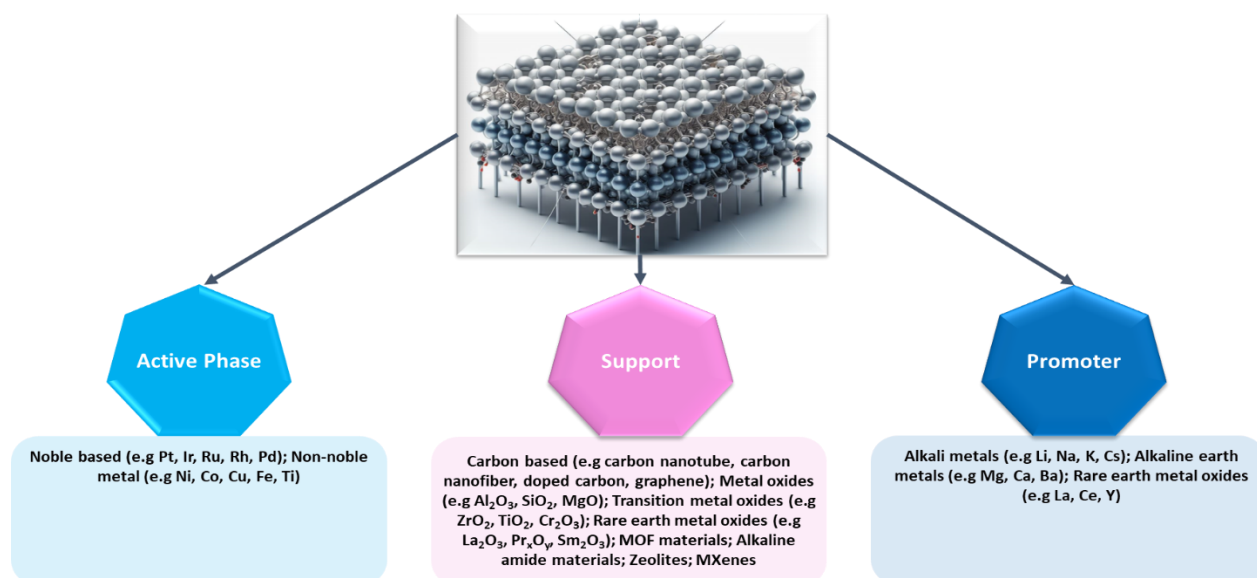


Figure 5: Common materials employed in designing catalysts. These involved various elements and compounds used as active sites, supports, and promoters in the catalysts.

CHAPTER 3 MATERIALS AND METHODS

3.1 DFT Calculations

The computational data reported in this study were adapted from the Beyond-DFT Electrochemistry with Accelerated and Solvated Techniques Database (BEAST DB) [102] and subsequently adjusted to incorporate the effects of the applied potential. All GC-DFT calculations were originally performed using the joint density functional theory (JDFTx) code [103]. BEAST DB is specifically designed to explore reaction pathways for electrochemical processes.

Since AOR is the reverse of NRR, its reaction coordinate diagram was derived by inverting the NRR reaction energetics obtained from BEAST DB. In addition to reversing the pathway, adjustments were made to account for the alkaline reaction environment in AOR. Unlike NRR, where protons facilitate nitrogen formation by interacting with adsorbed species, AOR occurs in an alkaline medium, where hydroxide ions react with hydrogen-containing intermediates, extracting hydrogen atoms and forming water molecules. Furthermore, because BEAST DB considers negative applied potentials for NRR, an additional adjustment was required to account for the positive applied potentials relevant to AOR. This adjustment employs a straightforward approach to modifying reaction energetics as a function of the applied potential. Instead of relying on canonical DFT calculations, like the CHE approach, which are performed at the potential of zero charge (PZC) for each reaction state, our method utilizes the Helmholtz free energy and the exact number of electrons evaluated at 0 V_{SHE} through grand canonical calculations. This approach is particularly effective for qualitative analyses, especially in systems

where the geometries of reaction intermediates remain largely unchanged as the applied potential varies. [46]

The modification of reaction energetics as a function of the applied potential is governed by the equation:

$$\Delta G = \Delta F(0 V_{SHE}) - \mu \Delta N \quad (15)$$

Where ΔG is the adjusted free energy, $\Delta F(0 V_{SHE})$ is the Helmholtz free energy evaluated at 0 V_{SHE} using grand canonical calculations, μ is the chemical potential of the electrons, which is related to the applied potential, and ΔN represents the exact number of electrons transferred in each elementary step of the reaction coordinate diagram, relative to the reference state (the initial reactants in this study) at 0 V_{SHE} . Thus, Equation (15) follows directly from the definition of the grand free energy, where the Helmholtz free energy is corrected by the chemical potential of the electrons, weighted by the exact number of electrons transferred. This formulation inherently assumes that the applied potential does not significantly alter the electron difference between states. By explicitly considering ΔN instead of approximating it as an integer (typically one electron per proton-coupled electron transfer (PCET) step), this approach provides a more accurate representation of potential-dependent free energy changes than the conventional CHE approach.

To validate the accuracy of this method, reaction coordinate diagrams for NRR on both Ni(111) and Co(111) surfaces were developed and compared with those obtained from actual GC-DFT calculations. The (111) facet was chosen because it has the lowest energy and is therefore the most abundant. The results, presented in **Figures A1 and A2** show that GC-DFT calculations at self-consistent -0.25 V_{SHE} and -0.50 V_{SHE} closely align with

the reaction coordinate diagrams obtained using this method, demonstrating remarkable accuracy in capturing potential-dependent free energy changes. Given its strong agreement with GC-DFT, this approach serves as a reliable and computationally efficient alternative for investigating AOR reaction pathways on both Co(111) and Ni(111) surfaces. This method, which we refer to as the Potential-Adjusted Grand Free Energy (PAGE) approach, provides a more precise representation of electrochemical reaction energetics than conventional approximations. The detailed equations used to generate the reaction coordinate diagrams are provided in the Appendices.

3.2 Preparation of NF, Ni/NF, and Co/NF electrodes

A schematic illustration of the electrode preparation process is presented in **Figure 6**. The procedure began with a pretreatment of NF to remove surface impurities and oxide layers. This involved immersing the NF in 3 M HCl and subjecting it to ultrasonication for 30 minutes. The treated NF was then rinsed three times with deionized (DI) water and ethanol to ensure thorough cleaning. Depending on its intended use, the NF was either employed directly in synthesis or dried in a vacuum oven to serve as a reference material (bare NF). Metal precursor solutions were prepared by dissolving 145.5 mg of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 30 mL of DI water, yielding solutions containing 0.5 mmol of Ni or Co, respectively. To these solutions, 75 mg of urea was added, and the mixtures were stirred at 500 rpm for 10 minutes under ambient conditions. The deposition of metal nanostructures onto the NF framework was achieved via a hydrothermal process. The precursor solution, along with the cleaned NF, was placed into a Teflon-lined stainless-steel autoclave, which was then sealed and heated at 150 °C for 6 hours. After completion, the autoclave was allowed to cool naturally to room

temperature. The obtained Ni/NF or Co/NF electrodes were subjected to ultrasonication in DI water and ethanol for 10 minutes each to remove residual impurities. Finally, the electrodes were rinsed thoroughly and dried in a vacuum oven at 80 °C for 24 hours, completing the preparation process.

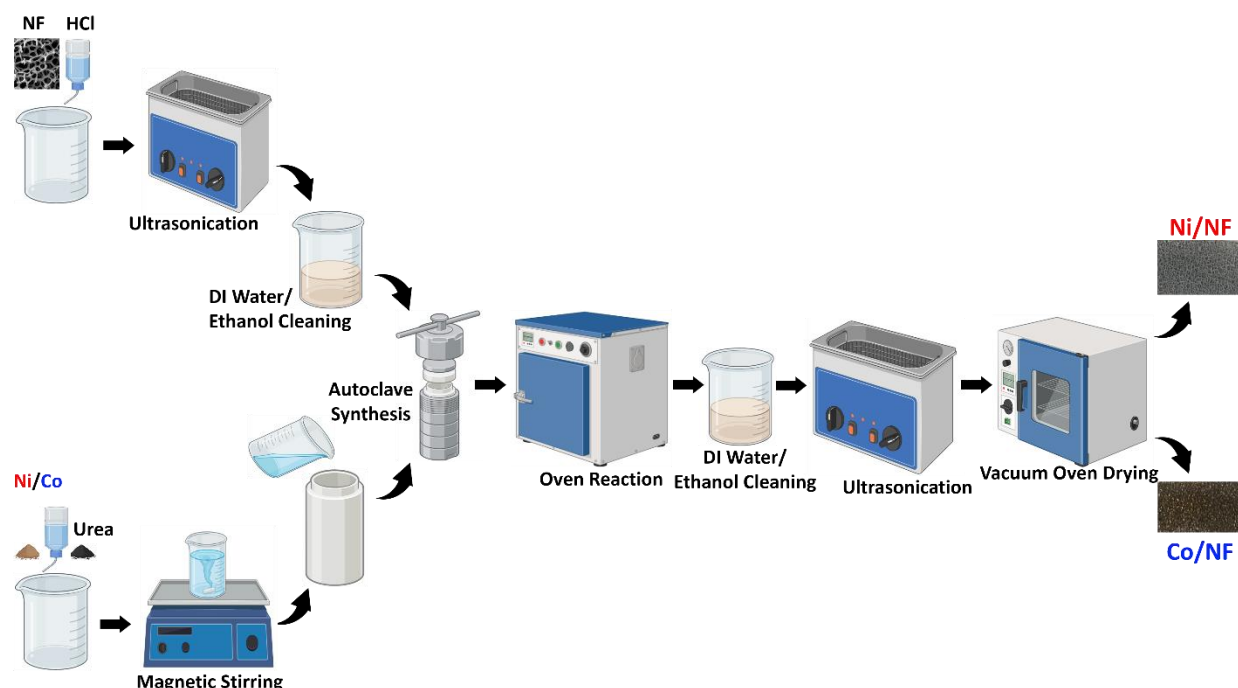


Figure 6: Schematic diagram illustrating the hydrothermal synthesis and fabrication method of Ni/NF and Co/NF electrodes. The process begins with pretreatment of NF using 3 M HCl and ultrasonication to remove surface impurities. Metal precursor solutions containing Ni or Co, along with urea, are prepared and introduced to the NF within a Teflon-lined stainless-steel autoclave. The sealed system is heated, allowing for the formation of Ni/NF or Co/NF electrodes. Following synthesis, the electrodes undergo cleaning to remove residual impurities, then are thoroughly rinsed and dried in a vacuum oven.

3.3 Physical Characterization

The surface morphology and structure of the prepared electrodes were examined using scanning electron microscopy (SEM) (Zeiss Crossbeam550), operating at 15 kV and a scan speed of 5 pps. The SEM system was equipped with an energy-dispersive X-ray spectroscopy (EDX) detector for atomic composition analysis and electron mapping. X-ray diffraction (XRD) patterns were recorded using a Rigaku Ultima IV X-ray diffractometer, operating with Cu K- α radiation at 40 kV and 20 mA. The analysis covered a 2θ range of 10–90°, with a total scan time of 16 minutes and a scan speed of 5° per minute. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a PHI 5000 Versa Probe II spectroscope from ULVAC-PHI Inc. to analyze the chemical composition and oxidation state of surface elements. The surface roughness of the electrodes was characterized using an Agilent 5500 Atomic Force Microscope (AFM) in contact mode, with a scan area ranging from 5 to 10 μm .

3.4 Electrochemical Tests

Electrochemical measurements were conducted using a three-electrode setup connected to a Gamry electrochemical workstation in a single-compartment electrolytic cell under ambient conditions. The prepared electrode (Ni/NF or Co/NF), a saturated Ag/AgCl (KCl) electrode, and a Pt wire were used as the working, reference, and counter electrodes, respectively. A 40 mL Ar-saturated electrolyte solution containing 1 M KOH and 0.5 M NH_4OH was used as both the electrolyte and ammonia feed. Before each experiment, the counter and reference electrodes were thoroughly rinsed with DI water. The working electrode was electrochemically activated by performing 10 CV scans within a potential range of 0.0–1.0 V vs. Ag/AgCl, at a scan rate of 20 mV/s. Electrolysis

experiments were conducted using both CV and LSV over the same potential range. All equations relevant to additional electrochemical characterizations are provided in the Appendices.

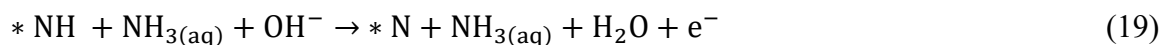
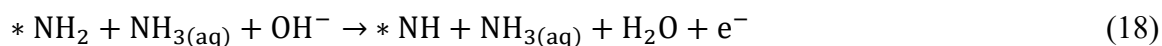
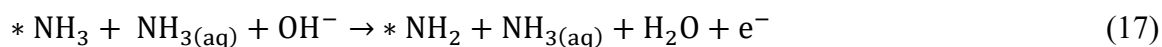
3.5 Performance Tests

Hydrogen generated during electrolysis was analyzed in real-time using a Clarus 580 gas chromatograph (GC, PerkinElmer). Argon gas was used as the carrier gas, and the GC system featured a 1 mL sample loop for analysis. To ensure system integrity, argon purging was conducted to remove residual contaminants from the GC lines, and a water trap was installed upstream of the GC instrument to eliminate moisture interference. In-operando analysis was performed to determine hydrogen volume and flow rate. Although electrolysis was carried out under continuous conditions, GC analysis was conducted in discrete sampling intervals rather than consecutive real-time measurements. Additionally, electrolysis data were used to compute energy consumption and cell efficiency, with all relevant equations detailed in the Appendices.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 DFT Study

The AOR reaction mechanism at the working electrode consists of nine elementary steps, as described in Equation (16) - (24). Meanwhile, at the counter electrode, hydrogen gas is produced through the reduction of water molecules generated during the reaction of the working electrode. The counter electrode reaction, in which six water molecules are reduced to form three molecules of hydrogen gas, is given in Equation (25). At the working electrode, protons originating from adsorbed reaction intermediates react with oxidizing hydroxyl group (OH^-) during the elementary steps of AOR, leading to the formation of water molecules. Meanwhile, at the cathode, alkaline HER generates OH^- , completing the overall electrochemical process.





At the working electrode, the catalytic process begins with ammonia adsorption, followed by sequential dehydrogenation steps mediated via oxidative proton-coupled electron transfer (PCET) where water is generated in the presence of OH^- . Here, hydrogen atoms from the adsorbed intermediates react with hydroxide ions, forming water molecules, while electrons are transferred to the external circuit. This process continues until nitrogen dimerization and desorption as $\text{N}_{2(\text{g})}$ occur. The released water molecules then migrate to the counter electrode, where they participate in the alkaline HER and are reduced to hydrogen gas.

To determine the reaction energetics at the working electrode, it is critical to identify the active sites of the catalysts. The (111) facet was identified as the most thermodynamically stable surface for both Ni and Co. [104] Therefore, all theoretical calculations for ammonia adsorption and reaction pathway energetics were conducted on the (111) facets of Ni and Co. Among the possible adsorption sites, the hollow site on the (111) facet was selected as the active reaction site in BEAST DB, as it provides a favorable coordination environment for stabilizing reaction intermediates. Furthermore, the adsorption energies of nitrogen-containing species were found to be lower at the hollow site, making it the most energetically preferred site for facilitating AOR. [102] It is important to note that DFT studies focus on atomic-scale interactions and do not explicitly consider the catalyst support. As a result, these calculations assume pure metallic Ni and Co surfaces, rather than accounting for any interactions between the catalyst and the electrode substrate. These calculations are particularly important in giving insight into the catalytic activity of the reactive sites directly involved in the AOR.

To compute the reaction coordinate diagram for AOR on the Ni and Co surfaces, Equation 15 was applied. The AOR reaction pathway is illustrated in **Figure 7(a)**. The reaction coordinate diagrams (**Figure 7(b)**) were computed using $\text{NH}_{3(\text{aq})}$ and a pristine surface as the initial reference state. The resulting thermodynamic energy profiles predict a superior AOR activity of the Co surface. The thermodynamic energy differences show that $\text{NH}_{3(\text{g})}$ adsorption is exergonic on both Ni and Co surfaces, with a greater driving force observed on Ni. In contrast, N_2 desorption is endergonic on Ni but becomes exergonic on Co, indicating that the Co surface more efficiently facilitates nitrogen release, thereby enhancing its overall AOR efficiency.

To investigate the influence of applied potential, reaction coordinate diagrams were computed at various oxidative potentials of 0.6 V vs. Ag/AgCl, 0.8 V vs. Ag/AgCl, and 1.0 V vs. Ag/AgCl (**Figure 7(b)**). At 0.6 V vs. Ag/AgCl, the dimerization and coupling of NN to N_2 emerged as the most thermodynamically demanding step on the Ni surface, potentially limiting the overall reaction efficiency. According to the Brønsted–Evans–Polanyi (BEP) relationship, a higher reaction energy is often correlated with a higher activation barrier. [105] As the applied potential becomes more oxidizing, the intermediate steps become increasingly favorable, rendering the overall reaction more thermodynamically favorable at 0.8 V vs. Ag/AgCl. On the Ni surface, the dimerization and coupling of *NN to N_2 remained endergonic; however, the associated energy cost decreased by approximately 27% as the potential increased from 0.6 V to 0.8 V vs. Ag/AgCl. Although this step is non-Faradaic, and thus traditionally assumed by the CHE approach to be unaffected by the applied potential, the PAGE approach used in our calculations accounts for the electron differences along the reaction coordinate. As a

result, it captures the potential-dependent behavior of the dimerization and coupling of *NN to N₂. The calculations indicate that the AOR energetics on both surfaces become increasingly favorable as the applied potential becomes more oxidizing. However, at 1.0 V vs. Ag/AgCl, the likelihood of interference from OER increases, despite the enhanced thermodynamic favorability of AOR, due to the higher tendency for water oxidation at elevated potentials. Therefore, it is important to identify an optimal applied potential that enhances AOR activity while minimizing the onset of competing OER, thereby improving overall catalytic efficiency.

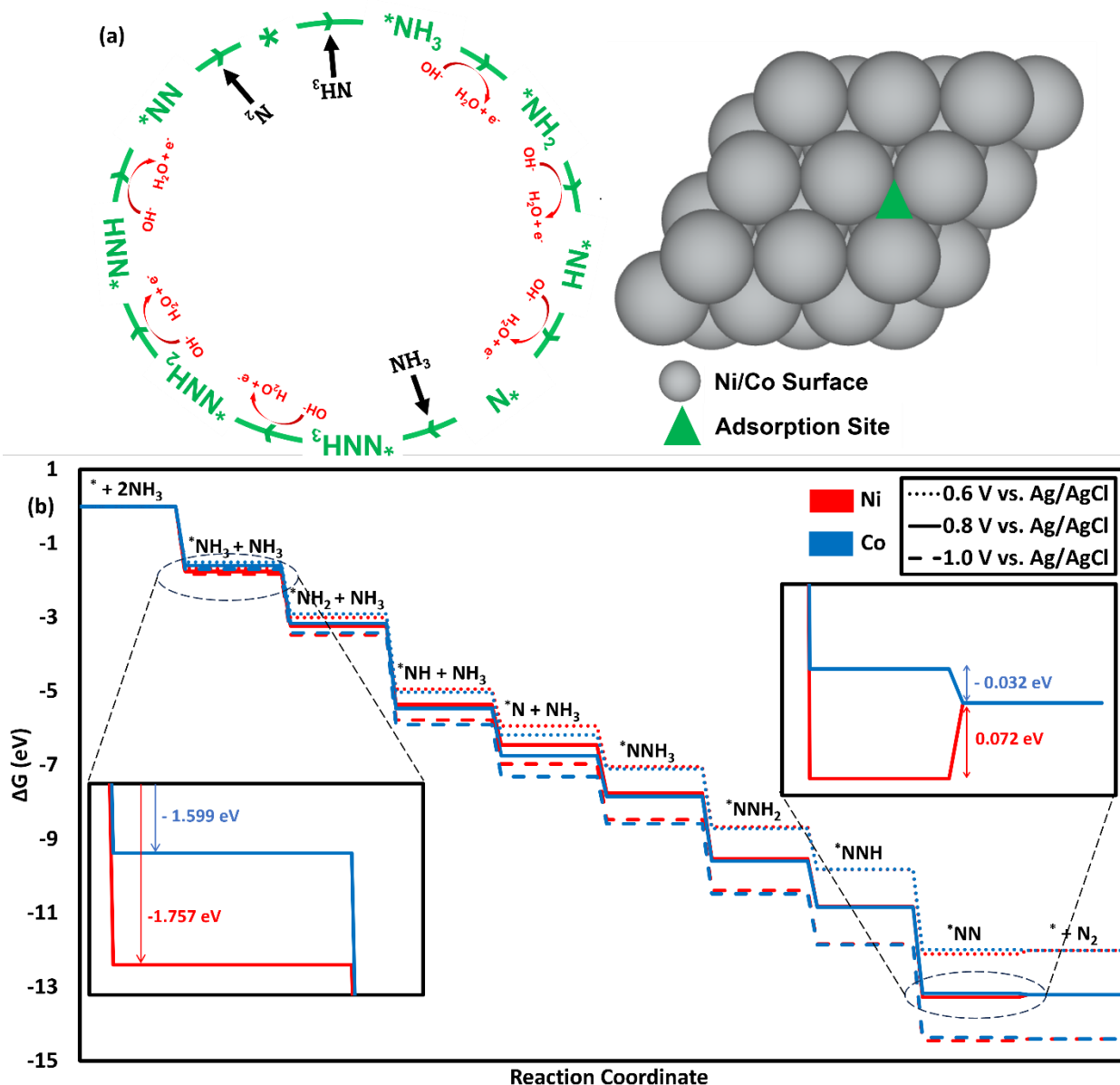


Figure 7: (a) Electrochemical reaction pathway of AOR on Ni or Co surfaces, where each step involves oxidative dehydrogenation of the intermediate species, releasing H_2O from the catalyst surface. The panel also includes a top view of the (111) facet, highlighting the hollow site selected as the active reaction site. (b) Reaction coordinate diagrams for AOR on Ni(111) and Co(111) surfaces using the PAGES method at different applied potentials. At 0.8 V vs. Ag/AgCl, $\text{NH}_3(\text{g})$ adsorption is more favorable on Ni, while $\text{N}_2(\text{g})$

desorption is more favorable on Co. The comparison of diagrams at 0.6, 0.8, and 1.0 V vs. Ag/AgCl illustrates how intermediate steps become increasingly exergonic with more oxidizing potentials.

4.2 Electrodes Characterization

The crystal structure and phase composition of the bare NF, Ni/NF, and Co/NF electrodes were analyzed using XRD, and the corresponding patterns are presented in **Figure 8(a)**. The three primary diffraction peaks of NF, observed at $2\theta = 44.2^\circ$ (111), 51.6° (200), and 76.3° (220), were attributed to metallic nickel, consistent with the NF substrate and in agreement with previous studies [33, 34, 86, 106, 107]. These peaks remained visible after the deposition of Ni or Co nanoparticles, indicating that the structural integrity of the NF was preserved. The formation of metallic, oxide, and hydroxide phases of Ni and Co on NF was confirmed after deposition. The Ni/NF XRD pattern exhibited diffraction peaks characteristic of NiO and Ni(OH)₂ at 37.5° , 43.7° , 63.9° , 77.3° , and 81.2° [86, 106, 108], while the Co/NF pattern displayed peaks associated with CoO, Co(OH)₂, and metallic Co at 37.5° , 44.2° , 76.4° , and 77.3° [106, 109-111]. This phase transformation is attributed to surface reconstruction during the hydrothermal synthesis process, which generates and exposes new active phases while forming a fresh surface layer. Additionally, changes in NF peak intensity after deposition suggest the successful formation of new active layers, which reduced the prominence of previously exposed facets. The XRD characterization confirmed the dominance of the (111) facet on both surfaces, as evidenced by its strongest diffraction peak, thereby supporting its selection for the DFT calculations.

The morphologies of the bare NF, Ni/NF, and Co/NF electrodes were examined using SEM, as illustrated in **Figure 8(b-d)**. The bare NF exhibited a porous architecture with interconnected struts forming an open framework. Initially, its surface appeared smooth (**Figure 8(b)**), providing an ideal template for the deposition of Ni and Co nanoparticles. Following synthesis, the smooth NF surface underwent a significant transformation, developing a rough texture covered with uniformly distributed nanoparticles, as shown in **Figures 8(c) and 8(d)**. These structural modifications, attributed to the hydrothermal synthesis process, successfully facilitated the growth of Ni and Co nanoparticles on the NF framework, increasing the density of exposed active sites for electrochemical reactions. Additionally, SEM-EDX elemental mapping confirmed a uniform spatial distribution of elements across the surfaces of bare NF, Ni/NF, and Co/NF electrodes, indicating comprehensive and even coverage of reaction sites. To further assess surface characteristics, AFM analysis was conducted, revealing significant changes in surface roughness (R_a) and topography after modification. The R_a value increased from 0.796 nm for bare NF to 28.5 nm for Ni/NF and 12.6 nm for Co/NF. Similarly, topographical heights increased from 40.8 nm for bare NF to 711 nm for Ni/NF and 222 nm for Co/NF, as shown in **Figure 8(e)**. These observations highlight the formation of abundant active sites on the modified electrodes, emphasizing the distinct morphological changes induced by the synthesis process.

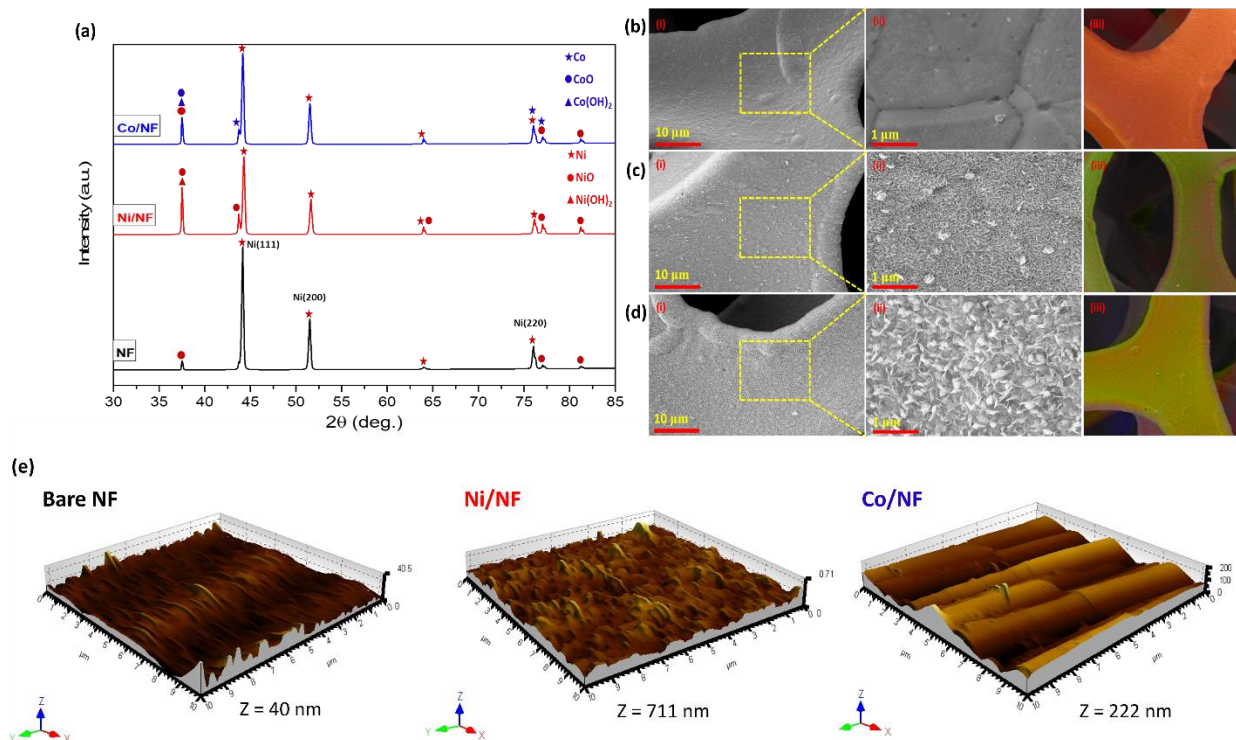


Figure 8: Structural and morphological characterization of bare NF, Ni/NF, and Co/NF electrodes (a) XRD patterns of bare NF, Ni/NF, and Co/NF, showing the characteristic peaks of metallic Ni at $2\theta = 44.2^\circ$ (111), 51.6° (200), and 76.3° (220). The presence of NiO and Ni(OH)₂ in Ni/NF at 37.5° , 43.7° , 63.9° , 77.3° , and 81.2° and CoO, Co(OH)₂, and metallic Co in Co/NF at 37.5° , 44.2° , 76.4° , and 77.3° confirms the formation of new phases following hydrothermal synthesis. Changes in peak intensity indicate successful deposition of Ni and Co, modifying the electrode surfaces. (b-d) SEM images at (i) 10 μm and (ii) 1 μm magnifications, depicting the morphological evolution of the electrodes. (b) Bare NF exhibits a smooth, porous structure with interconnected struts forming an open framework. (c) Ni/NF after synthesis shows a significant surface transformation, where Ni nanoparticles form a rough, textured layer uniformly distributed across the NF framework. (d) Co/NF exhibits a similar transformation, with Co nanoparticles covering the NF surface, enhancing surface roughness and increasing the density of exposed active

sites. (e) AFM surface roughness analysis, demonstrating increased R_a values from 0.796 nm (bare NF) to 28.5 nm (Ni/NF) and 12.6 nm (Co/NF). Similarly, topographical height rises from 40.8 nm (bare NF) to 711 nm (Ni/NF) and 222 nm (Co/NF), confirming the significant morphological modifications induced by hydrothermal deposition.

XPS analysis was carried out to identify the chemical composition and oxidation states of the electrodes, as illustrated in **Figure 9**. In the Ni 2p spectrum of bare NF, Ni/NF, and Co/NF electrodes, two prominent peaks at 854.4 eV and 872.0 eV were assigned to metallic Ni (Ni^0), while additional peaks at 855.4 eV, 857.3 eV, 873.4 eV, and 875.0 eV corresponded to Ni^{2+} species. [34, 35, 106, 108] Similarly, the Co 2p spectrum of the Co/NF electrode exhibited a peak at 772.7 eV, characteristic of metallic Co (Co^0), along with additional peaks at 781.3 eV, 785.5 eV, and 798.4 eV which were attributed to Co^{2+} species. [34, 106, 112] The increased presence of higher valence states suggests the formation of Ni and Co oxides and hydroxides, which are active species generated during the hydrothermal synthesis process. Furthermore, the O 1s spectrum revealed peaks at 530.8 eV, corresponding to metal oxides, and 531.3 eV, attributed to metal hydroxides. On the modified Ni/NF and Co/NF electrodes, an additional peak at 533.5 eV was observed, corresponding to adsorbed water molecules [86], as detailed in **Figure A3**. These findings are consistent with the XRD analysis (**Figure 8(a)**), further validating the chemical states of the active phases and confirming the successful modification of the electrodes with Ni and Co species.

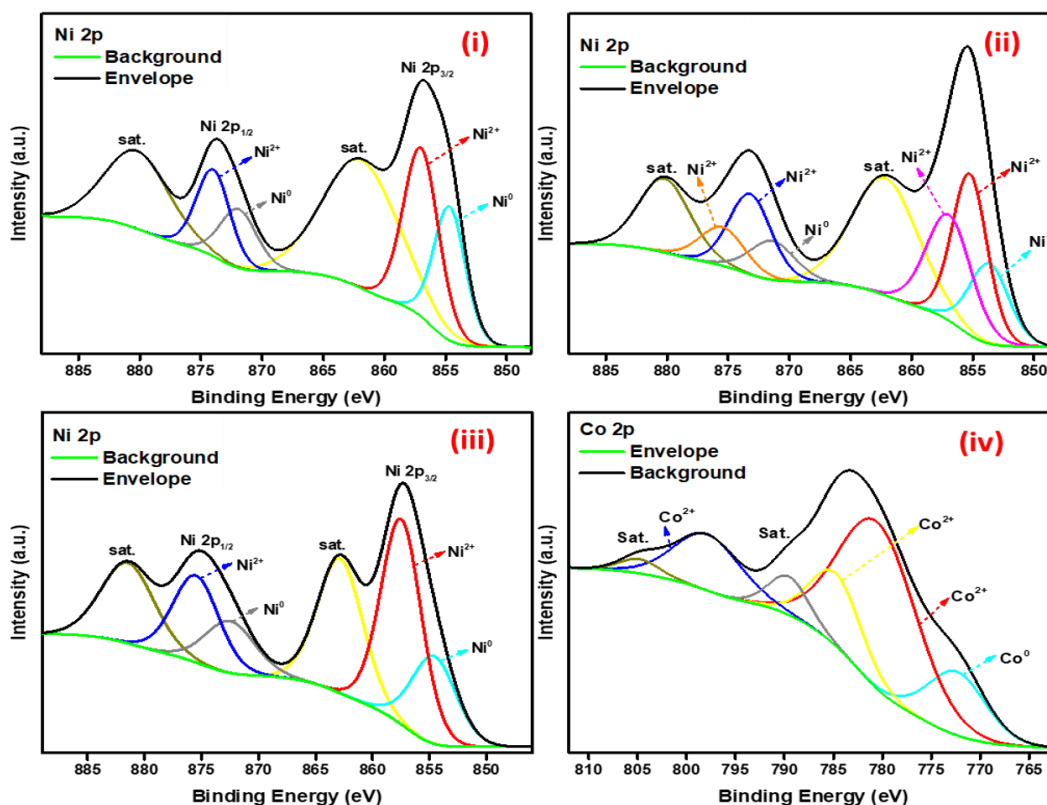


Figure 9: XPS analysis of the chemical states of Ni and Co in the electrodes. (i–iii) Ni 2p spectra of bare NF, Ni/NF, and Co/NF, showing peaks at 854.4 eV and 872.0 eV, corresponding to metallic Ni (Ni⁰), and additional peaks at 855.4 eV, 857.3 eV, 873.4 eV, and 875.0 eV, associated with Ni²⁺ species, indicating the formation of Ni oxides and hydroxides. (iv) Co 2p spectrum of Co/NF, displaying a peak at 772.7 eV, assigned to metallic Co (Co⁰), alongside peaks at 781.3 eV, 785.5 eV, and 798.4 eV, corresponding to Co²⁺ species, confirming the presence of Co oxides and hydroxides. The increased presence of higher valence states suggests the formation of Ni and Co oxides/hydroxides during the hydrothermal synthesis process.

4.3 Electrochemical Tests

The electrochemical activity of the bare NF, Ni/NF, and Co/NF electrodes was evaluated using LSV and CV measurements in an alkaline solution containing ammonia (1 M KOH and 0.5 M NH_4OH), with the results presented in **Figures 10(a)** and **10(b)**. All electrodes exhibited redox peaks within the potential range of 0.0 V to 0.9 V vs. Ag/AgCl. The bare NF (black curve) demonstrated moderate ammonia oxidation activity, which was significantly enhanced upon the incorporation of Ni (red curve) or Co (blue curve) onto the electrode surface. Both Ni/NF and Co/NF exhibited higher current densities, more pronounced redox peaks, and reduced onset potential compared to the bare NF. Specifically, while the bare NF achieved an anodic current density of approximately 308 mA cm^{-2} , the Ni/NF electrode produced a maximum current density of 522 mA cm^{-2} , and the Co/NF electrode exhibited an even higher value of 819 mA cm^{-2} , as shown in the CV curve in **Figure 10(b)**. Additionally, both electrodes exhibited lower onset potentials, with Ni/NF reducing the onset potential from 0.38 V vs. Ag/AgCl to 0.31 V vs. Ag/AgCl and Co/NF from 0.38 V vs. Ag/AgCl to 0.32 V vs. Ag/AgCl, further highlighting their superior catalytic activity for ammonia oxidation compared to the bare NF. This enhanced electrochemical performance is attributed to the increased density of active sites on the modified electrode surfaces, which facilitate rapid ion diffusion and significantly improve AOR activity.

To investigate the effect of ammonia diffusion on the electrodes and optimize electrolysis conditions, CV measurements were performed at varying ammonia concentrations, as shown in **Figures 10(c)** and **10(d)**. The CV curves for Ni/NF and Co/NF electrodes were recorded in 1 M KOH with different NH_4OH concentrations. In general, the maximum

anodic current density for the AOR increased as ammonia concentration was raised. For the Ni/NF electrode, the anodic current density progressively increased from 0 M NH_4OH to 0.5 M NH_4OH (**Figure 10(c)**). However, upon further increasing the concentration to 1 M NH_4OH , a decline in current density was observed. A similar trend was observed for the Co/NF electrode, where the anodic current density increased with rising NH_4OH concentration, reaching a maximum at 0.5 M NH_4OH before declining at 1 M NH_4OH (**Figure 10(d)**). This behavior underscores the influence of ammonia diffusion and system saturation. At low concentrations, the reaction is diffusion-controlled, meaning ammonia transport to the electrode surface limits the overall reaction rate. However, at higher concentrations, oversaturation of ammonia within the system leads to performance degradation. This can result in undesirable reaction kinetics, reduced yields of the expected products, and potential surface poisoning by intermediates such as *N . [86] Additionally, at elevated ammonia concentrations, reduced catalytic activity may arise due to the formation of metal oxynitrides resulting from metal oxidation, which inhibits AOR performance. [16] Further investigations into adsorption mechanisms and reaction kinetics are necessary to better understand ammonia diffusion dynamics and optimize electrolysis efficiency.

Similarly, the influence of OH^- concentration on the performance of Ni/NF and Co/NF electrodes was investigated using CV in a 0.5 M NH_4OH solution with varying KOH concentrations, as shown in **Figures 10(e) and 10(f)**. The KOH concentration was varied from 0 M to 1 M. In the absence of KOH (0 M), no redox peaks or catalytic activity for AOR were observed, as the system lacked a supporting electrolyte to facilitate ion transfer. However, as the OH^- concentration increased, the anodic current density

improved, and the onset potential of AOR shifted towards lower values. This enhancement is attributed to the higher OH^- concentration, which accelerates reaction kinetics and lowers the thermodynamic potential required for AOR. Despite these benefits, higher OH^- concentrations may introduce potential drawbacks, including electrode leaching and degradation. Additionally, an excess of OH^- can promote the competing OER, leading to O_2 generation, which adversely affects AOR efficiency and should be minimized. [113-116] Based on these findings, the effects of both ammonia and electrolyte concentrations were optimized for AOR. For both Ni/NF and Co/NF electrodes, the optimal conditions were determined to be 0.5 M NH_4OH and 1 M KOH under ambient conditions. All subsequent electrochemical tests and performance evaluations were conducted under these optimized conditions.

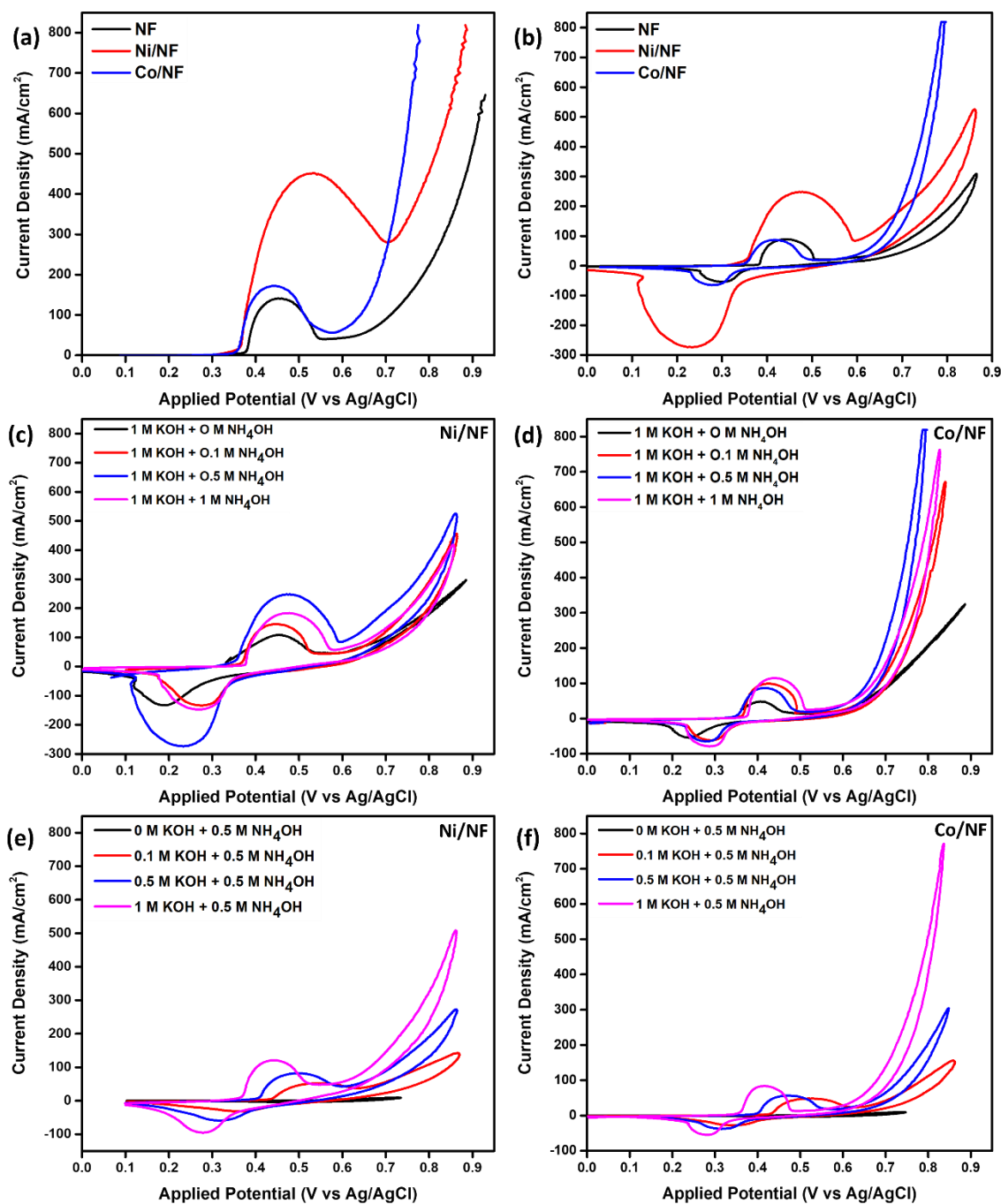


Figure 10: Electrochemical characterization of bare NF, Ni/NF, and Co/NF electrodes for AOR, recorded at a scan rate of 20 mV/s. (a) LSV curves and (b) CV curves of bare NF, Ni/NF and Co/NF in 0.5 M NH_4OH and 1 M KOH, demonstrating enhanced catalytic activity upon Ni or Co incorporation. (c) CV curves of Ni/NF and (d) CV curves of

Co/NF recorded in 1 M KOH with varying NH_4OH concentrations, showing an initial increase in anodic current density up to 0.5 M NH_4OH , followed by a decline at 1 M NH_4OH due to ammonia oversaturation effects. (e) CV curves of Ni/NF and (f) CV curves of Co/NF in 0.5 M NH_4OH with varying KOH concentration, illustrating the impact of OH^- concentration on AOR kinetics, where increasing OH^- concentrations enhance catalytic activity. All measurements were conducted at 25°C under ambient conditions.

To further assess electrocatalytic activity, the effect of electrooxidation cycles on the AOR performance of bare NF, Ni/NF, and Co/NF electrodes was evaluated by recording CV measurements over 5, 10, 20, 40, 60, 80, and 100 cycles, as shown in **Figure A4**. In general, the observed redox peaks correspond to redox pseudocapacitance, a Faradaic process occurring on the electrode surface that reflects the apparent activity of the electrodes. For the bare NF electrode, the redox peak intensity initially increased with the number of cycles, reaching a maximum at 10 cycles (**Figure A4(a)**). However, beyond 10 cycles, the redox peak intensity declined, indicating a reduction in AOR performance due to the depletion of surface-active sites and limited active substance conversion. In contrast, the Ni/NF and Co/NF electrodes exhibited consistent redox peak intensities across all tested cycles (**Figures A4(b)** and **A4(c)**), with no significant decline even after 100 cycles. The larger and stable redox peaks observed for these electrodes suggest the presence of abundant and stable redox-active materials, which facilitate charge transfer and contribute to sustained catalytic activity for AOR. [86] Similarly, the effect of scan rate on electrode performance in the Faradaic region was investigated, as shown in **Figure A5**. As the scan rate increased from 20 mV/s to 100 mV/s, the redox peak

intensity increased, indicating an expansion in the active redox area. The observed trend in active redox area followed the order: Co/NF > Ni/NF > bare NF, suggesting that the Co/NF electrode may exhibit superior AOR performance due to its higher redox activity and greater availability of active sites. These findings highlight the critical role of electrode modification in enhancing both stability and catalytic activity during prolonged electrochemical processes.

The electrochemical surface area (ECSA) of the electrodes was determined using the double-layer capacitance (C_{dl}) method to assess their intrinsic activity. CV curves were recorded at varying scan rates (20 mV/s to 100 mV/s) in the non-Faradaic region between -0.1 to 0.1 V vs. Ag/AgCl, as illustrated in **Figure A6**. A linear correlation between the current response at intermediate potentials and the scan rate was observed, with the slope representing the C_{dl} value (**Figure 11(a)**). The calculated C_{dl} values for bare NF, Ni/NF, and Co/NF were 1.01 mF/cm², 1.87 mF/cm², and 1.61 mF/cm², respectively. Using Equation S2, the ECSA was derived, showing that the modified electrodes (Ni/NF and Co/NF) had a higher ECSA, indicating a greater number of active sites for AOR activity. This increased ECSA improves the reactant accessibility to active sites, enhancing the intrinsic catalytic activity for AOR. To further explore the AOR kinetics, Tafel plot analysis and electrochemical impedance spectroscopy (EIS) were conducted. The Tafel slope, which reflects the electron transfer rate, indicates that a lower slope corresponds to faster electron transfer. [86, 117] As shown in **Figure 11(b)**, the Tafel slopes for bare NF, Ni/NF, and Co/NF were 34.43 mV/dec, 25.25 mV/dec, and 23.82 mV/dec, respectively. The Co/NF electrode exhibited the lowest slope, suggesting the most efficient electron transfer and superior AOR performance. This implies that the Co/NF electrode facilitates

faster electron transfer, thereby reducing the energy barrier for the reaction and improving catalytic efficiency. EIS measurements were used to investigate charge transfer kinetics, with the Nyquist plots (**Figure 11(c)**) revealing solution resistance (R_s) at the x-intercept and the charge transfer resistance (R_{ct}) from the semicircle diameter. Lower R_s and R_{ct} values correspond to improved reaction kinetics. The Co/NF electrode exhibited the lowest R_s of 2.36 Ω and R_{ct} of 0.67 Ω outperforming Ni/NF, which had an R_s of 2.51 Ω and an R_{ct} of 1.65 Ω . Although the bare NF electrode had a slightly lower R_s than Ni/NF (2.36 Ω), it exhibited a significantly larger R_{ct} (1.80 Ω), confirming its inferior charge transfer efficiency compared to the modified electrodes. The lower R_s and R_{ct} values observed for Co/NF highlight its ability to facilitate rapid ion and electron transport, enabling faster charge transfer and superior AOR kinetics. Despite its slightly higher ECSA, the higher electron and charge transfer resistances of Ni/NF limited its overall electrocatalytic performance compared to Co/NF. Overall, the Co/NF electrode exhibited superior electron and ion transport, along with faster charge transfer at the electrode-electrolyte interface, making it the most effective catalyst, followed by Ni/NF and bare NF. These findings highlight the critical role of enhanced ECSA, faster electron transfer rates (Tafel analysis), and lower charge transfer resistance (EIS analysis) in achieving superior AOR performance, positioning Co/NF as the optimal choice for AOR applications.

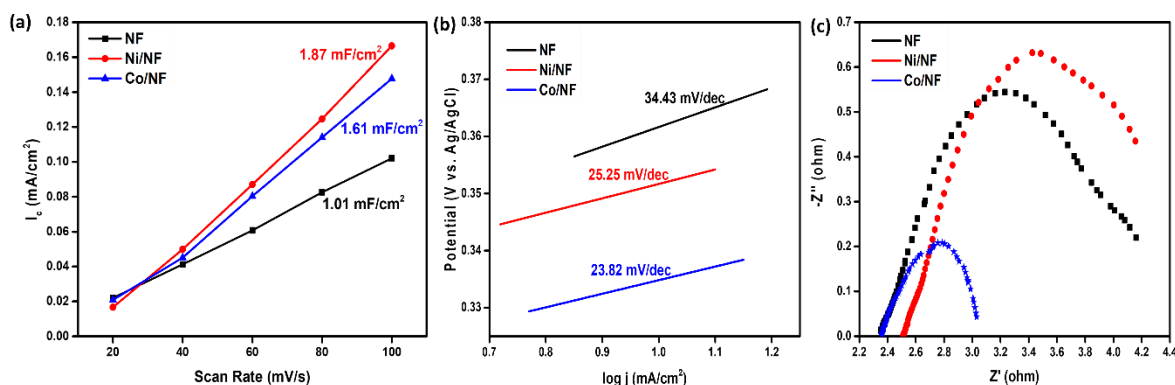


Figure 11: Electrochemical characterization of bare NF, Ni/NF, and Co/NF electrodes for AOR performance. (a) C_{dl} plots derived from CV scans in the non-Faradaic region at varying scan rates, used to estimate ECSA and compare the electrochemically active surface areas of the electrodes. The calculated C_{dl} values indicate increased active sites on Ni/NF and Co/NF, enhancing catalytic activity. (b) Tafel slopes, representing the electron transfer kinetics during AOR, where lower slopes indicate faster electron transfer. The Co/NF electrode exhibited the lowest Tafel slope, followed by Ni/NF and bare NF, confirming the superior reaction kinetics of Co/NF. (c) EIS Nyquist plots, used to analyze R_{ct} and R_s . The Co/NF electrode exhibited the lowest R_s and R_{ct} , demonstrating superior ion and electron transport capabilities, which contribute to enhanced AOR performance.

4.4 Performance Tests

Controlled potential coulometry was conducted over a potential window of 0.4 V to 0.9 V vs. Ag/AgCl for each electrode, as shown in **Figures 12(a)** and **12(b)**. The current density increased with the applied potential, leading to a corresponding rise in hydrogen peak intensity. To compare the activity of the modified electrodes with bare NF, controlled potential coulometry was performed at a constant potential of 0.8 V, which was identified as the optimal potential, where a reasonable hydrogen peak intensity was recorded

(Figure 13(a)). After 100 minutes, the measured ammonia conversion reached 573.3 ppm for Co/NF, 464.1 ppm for Ni/NF, and 313.9 ppm for bare NF. During this period, the hydrogen flow rate and total hydrogen volume were monitored via in-operando GC analysis at 20-minute intervals **(Figure 13(c) and 13(d))**. The modified electrodes exhibited superior performance compared to bare NF, which showed a decline in hydrogen flow rate within the first hour. The enhanced activity of Co/NF and Ni/NF is attributed to their higher current density and improved reaction kinetics, facilitated by the abundant presence of newly formed active nanostructures. This result is in line with the predicted performance from the DFT reaction coordinate at 0.8 V vs. Ag/AgCl, where the intermediate energetic steps were found to be thermodynamically favorable for AOR.

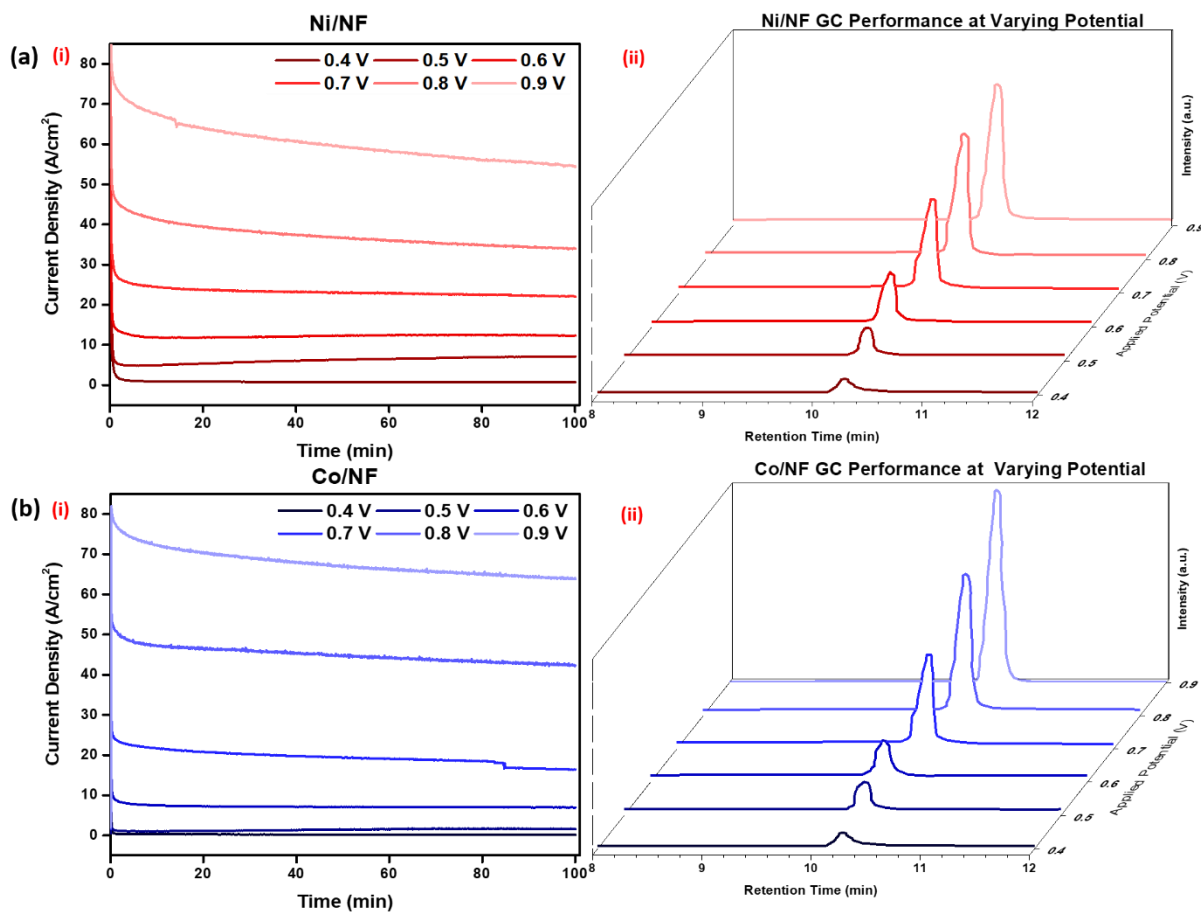


Figure 12: Electrochemical performance evaluation of Ni/NF and Co/NF electrodes for ammonia oxidation and hydrogen production. (i) Controlled potential coulometry recorded at varying applied potentials (0.4-0.9 V vs. Ag/AgCl) in 1 M KOH and 0.5 M NH₄OH, showing the relationship between current density and applied potential for (a) Ni/NF and (b) Co/NF. The increasing current density at higher potentials correlates with enhanced ammonia oxidation activity and hydrogen generation. (ii) H₂ GC peaks, confirming the formation of hydrogen as a reaction product, with peak intensity increasing with applied potential, indicating higher hydrogen evolution efficiency.

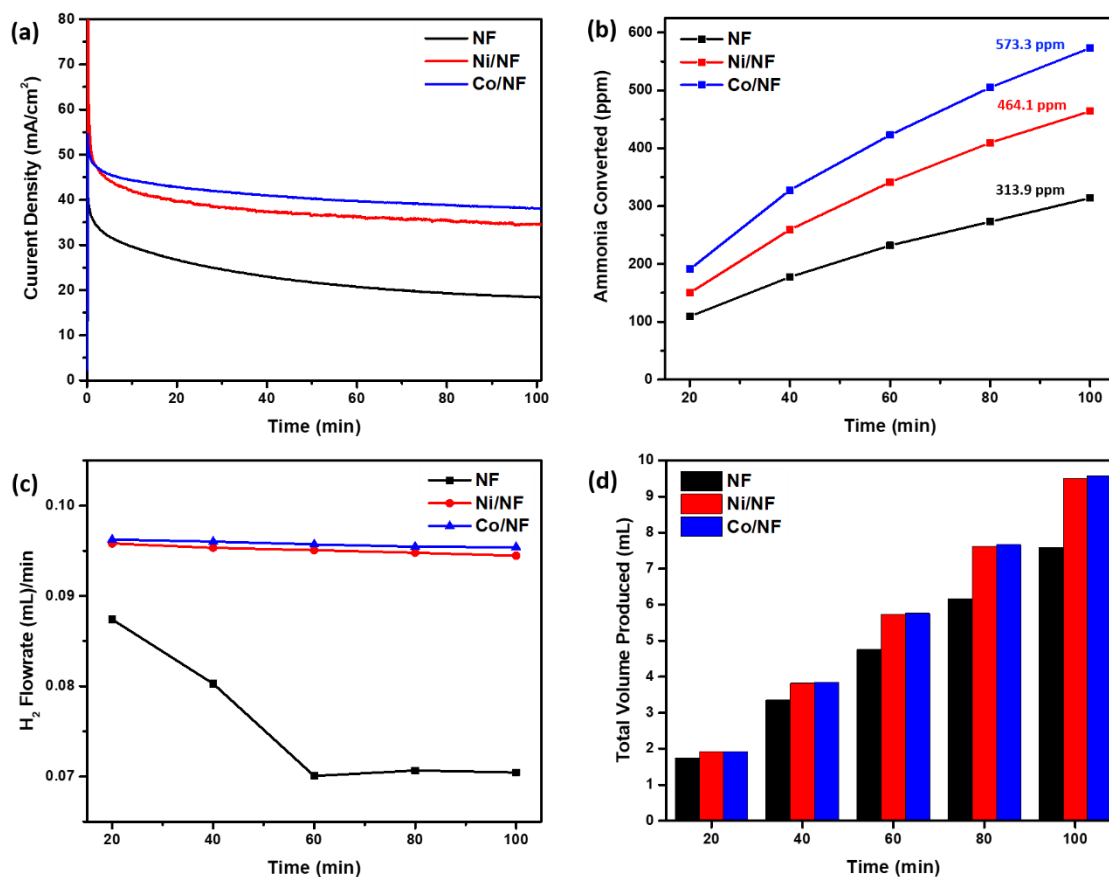


Figure 13: Comparative electrochemical performance of bare NF, Ni/NF, and Co/NF electrodes for ammonia oxidation and hydrogen production at 0.8 V vs. Ag/AgCl. (a) Controlled Potential Coulometry, showing the current response of each electrode over time in 1 M KOH and 0.5 M NH₄OH, demonstrating higher and more stable current densities for the modified electrodes compared to bare NF. (b) ammonia conversion (ppm) after 100 minutes, highlighting the superior catalytic efficiency of Co/NF and Ni/NF compared to bare NF. (c) H₂ generation rate (mL/min) monitored via in-operando GC analysis, showing higher and sustained H₂ production for Co/NF and Ni/NF, while bare NF exhibited a declining trend within the first hour. (d) Total H₂ volume (mL) collected at 20, 60, 80, and 100 minutes, confirming that Co/NF exhibited the highest H₂

yield, followed by Ni/NF and bare NF, further supporting the enhanced catalytic performance of the modified electrodes.

To assess the influence of electrode properties on performance, chronopotentiometry measurements were conducted at a constant current density of 50 mA cm^{-2} , as shown in **Figure 14(a)**. This current density was selected based on the initial current response of the modified electrodes in the previous controlled potential coulometry experiment. After 100 minutes, the Co/NF, Ni/NF, and bare NF electrodes required potentials of 0.83 V, 0.89 V, and 1.0 V, respectively, to sustain the fixed current density. Hydrogen flow rates, recorded every 20 minutes during the chronopotentiometry test, remained consistently lower for bare NF compared to the modified electrodes (**Figure 14(b)**). Despite requiring a higher potential, the bare NF electrode exhibited inferior performance, generating less hydrogen than Co/NF and Ni/NF. As shown in **Figure 14(c)**, energy consumption was measured to be $4.89 \text{ mWhg}^{-1}\text{NH}_3$ after 100 minutes for bare NF, compared to $4.38 \text{ mWhg}^{-1}\text{NH}_3$ for Ni/NF and $4.08 \text{ mWhg}^{-1}\text{NH}_3$ for Co/NF, demonstrating the lower energy requirements of the modified electrodes. Similarly, the cell efficiencies of Co/NF (64.8%) and Ni/NF (62.9%) surpassed that of bare NF (59.7%), further confirming the enhanced catalytic efficiency of the modified electrodes. The higher resistance values associated with bare NF, arising from solution resistance, charge transfer resistance, and electron transfer resistance, contributed to its lower efficiency and hydrogen production. These findings underscore the advantages of Co/NF and Ni/NF electrodes in achieving efficient ammonia decomposition and low-energy hydrogen production, reinforcing their potential for practical applications.

To evaluate long-term operational stability, controlled potential coulometry was performed at the optimal potential of 0.8 V for 24 hours. As depicted in **Figure 14(d)**, the modified electrodes exhibited excellent stability, maintaining their performance with only minor deactivation in the first 4 hours, highlighting their suitability for prolonged electrochemical applications.

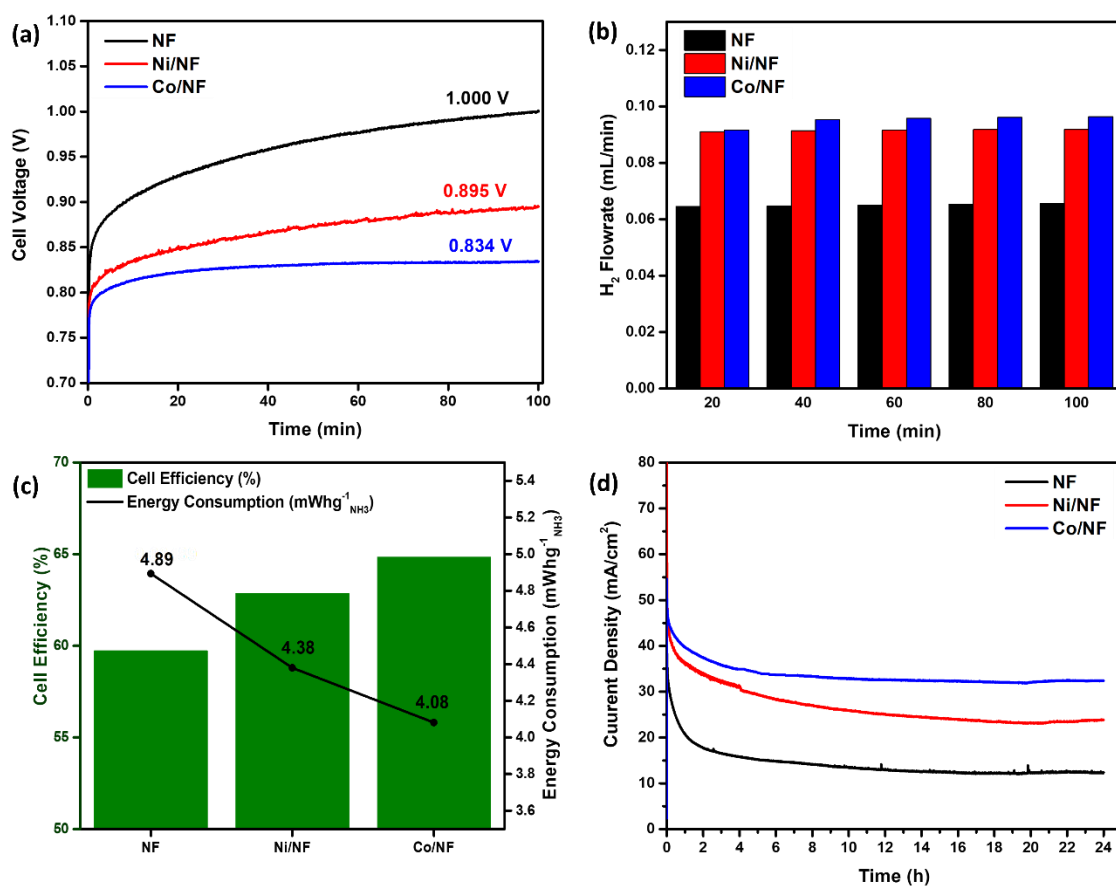


Figure 14: Electrochemical performance and long-term stability of bare NF, Ni/NF, and Co/NF electrodes for ammonia oxidation and hydrogen production. (a) Chronopotentiometry measurements conducted at a constant current density of 50 mAcm⁻² in 1 M KOH and 0.5 M NH₄OH, showing the potential required to sustain the fixed current for each electrode. The Co/NF electrode exhibited the lowest potential, followed

by Ni/NF and bare NF, indicating the superior energy efficiency of the modified electrodes. (b) H₂ generation rate (mL/min) monitored every 20 minutes, demonstrating sustained and higher H₂ production for Ni/NF and Co/NF, while bare NF exhibited a declining trend over time. (c) Energy consumption and cell efficiency after 100 minutes, revealing lower energy consumption for Co/NF and Ni/NF compared to bare NF. Correspondingly, Co/NF achieved the highest cell efficiency, followed by Ni/NF and bare NF, highlighting the enhanced electrochemical performance of the modified electrodes. (d) Long-term stability test (i-t curve) recorded over 24 hours at 0.8 V vs. Ag/AgCl, demonstrating excellent stability of the modified electrodes with minor deactivation, reinforcing their suitability for prolonged operation.

4.5 Energetic Span, Ammonia Adsorption and Reaction Kinetics Study

To further understand the catalytic activity of each surface in the AOR, the energetic span analysis was performed based on the computed ΔG of the reaction intermediates at an applied potential of 0.8 V vs. Ag/AgCl. The energetic span serves as a key descriptor for evaluating catalytic performance by quantifying the free energy difference between the highest energy transition state and the lowest-energy intermediate within the catalytic cycle. [118, 119] However, a simplified energetic span approach, following the work of Exner, approximates the highest-energy transition state as the highest-energy intermediate, thus avoiding the computational expense of optimizing transition state structures. [120] Exner referred to this approximation as $G_{\max}$ representing the maximum Gibbs free energy difference. [119, 121] In this work, we adopted this simplified energetic span, formulated as:

$$G_{\max} = \begin{cases} E_{\max}^k - E_{\min}^j & \text{if } k > j \\ E_{\max}^k - E_{\min}^j + \Delta G_{\text{rxn}} & \text{if } k \leq j \end{cases} \quad (26)$$

Where $E_{\max}^k$ and $E_{\min}^j$ are the free energies of states k and j on the reaction pathway, representing the highest- and lowest-energy states, respectively, while ΔG_{rxn} is the free energy of the reaction. As observed from the reaction coordinate diagram (**Figure 15(a)**), the highest-energy intermediate ($E_{\max}^k$) appears before the lowest-energy intermediate ($E_{\min}^j$) (i.e., $k < j$) on both Ni and Co surfaces. Therefore, ΔG_{rxn} was determined to be 13.213 eV and must be subtracted from the free energy difference between these intermediates due to the cyclic nature of the catalytic process. In our calculations, the initial reference state was assigned an energy of 0 eV, making it the highest-energy state in the reaction cycle. The values of $E_{\min}^j$ were identified as -13.284 eV for Ni and -13.213 eV for Co. Using Equation 16, the calculated $G_{\max}$ values were found to be 0.072 eV on Ni and 0 eV on Co. The energetic span serves as a descriptor of catalytic efficiency, providing insight into the thermodynamic driving force for AOR. A lower energetic span corresponds to a reduced overall energy cost, facilitating a more favorable reaction pathway. The results revealed a substantial difference between the two surfaces, with the Co surface exhibiting superior catalytic performance. This distinction aligns well with the experimental findings, highlighting the effectiveness of Co modification enhancing AOR kinetics and reducing energy barriers compared to Ni.

To further elucidate how electrode surface properties influence AOR performance, ammonia adsorption behavior was analyzed using isotherm models derived from the CV data in **Figure 10(c)** and **10(d)**. Common adsorption models, including Langmuir, Freundlich, and Temkin, were evaluated to assess the relationship between ammonia

adsorption, electrochemical reaction kinetics, and diffusion. Among these, the Freundlich isotherm provided the best fit for the modified electrodes (**Figure 15(b)**), indicating that adsorption occurs on a heterogeneous surface with multiple active sites rather than a uniform monolayer. Both Ni/NF and Co/NF electrodes exhibited linear ammonia adsorption behavior (with Freundlich exponent $n = 1$), consistent with multilayer adsorption on energetically diverse sites. Notably, $\text{NH}_{3(\text{g})}$ adsorption was more favorable on the Ni/NF electrode, which exhibited a higher adsorption capacity of 1.32, compared to 1.09 on the Co/NF electrode. This enhanced adsorption capacity is attributed to the higher ECSA and increased surface roughness of Ni/NF, allowing for greater ammonia uptake under identical conditions. These findings align with DFT results, which indicate that ammonia adsorption is thermodynamically more favorable on Ni surface than on Co, further supporting experimental observations.

The apparent reaction kinetics, specifically the reaction rate constant (k), were analyzed using ammonia conversion data from **Figure 13(b)**. To determine the reaction order, zero, first, and second-order models were tested, with the best fit observed for second-order kinetics on both modified electrodes (**Figure 15(c)**). This indicates that the reaction rate is significantly influenced by not only ammonia concentration, but also by the concentration of KOH in the electrolytic cell. Using the slope of the fitted second-order kinetic model, the rate constants (k) for AOR on Ni/NF and Co/NF electrodes were determined to be $5.1 \text{ mmol}^{-1}\text{min}^{-1}$ and $6.0 \text{ mmol}^{-1}\text{min}^{-1}$, respectively. The higher k value for the Co/NF electrode reflects its superior catalytic activity, allowing for faster AOR completion and greater H_2 production under identical conditions. These findings align with the controlled potential coulometry results, which demonstrated higher hydrogen

generation on the Co/NF electrode, as well as with DFT calculations, which revealed 0 eV energetic span for the Co surface.

While numerous studies have investigated AOR for hydrogen production, none have provided the comprehensive scope of this work. In addition to demonstrating superior activity and performance compared to previous studies, this work introduces novel insights by integrating adsorption and kinetic investigations, aspects that are often overlooked in the literature. A comparative analysis with prior research, summarized in **Table A3**, highlights the advancements and unique contributions of this study, reinforcing its significance in the field of electrochemical ammonia oxidation.

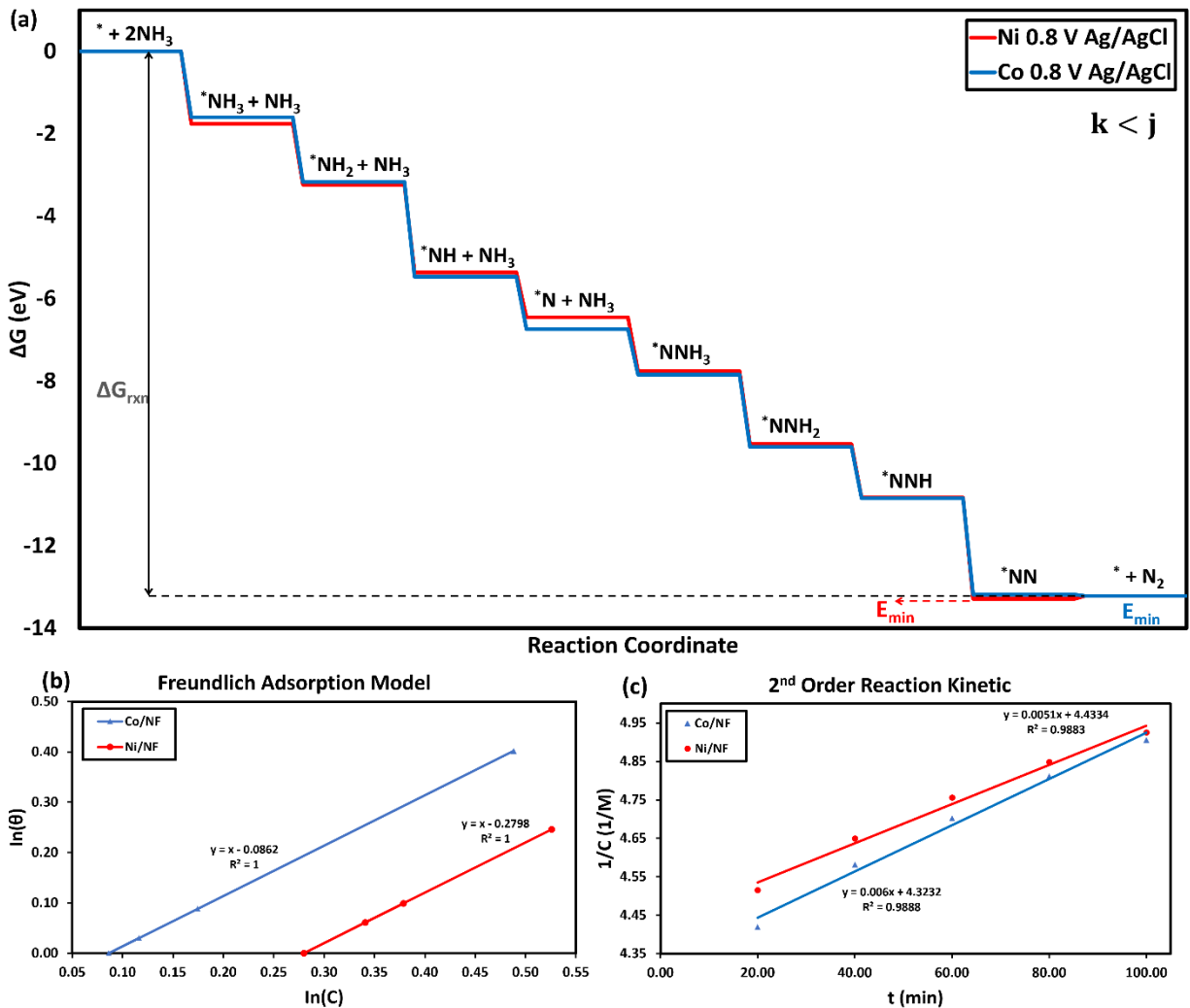


Figure 15: Energetic span analysis, Freundlich ammonia adsorption fitting, and second order reaction fitting. (a) AOR reaction coordinate diagram on Ni(111) and Co(111) using PAGE method showing the thermodynamic energy steps of the intermediates at the experimental potential of 0.8 V vs. Ag/AgCl. The highest energy level (k) appeared before the lowest energy level (j). Based on the coordinate diagram, the energetic span was found to be 0.072 eV on the Ni surface and 0 eV on the Co surface; (b) Freundlich Adsorption Isotherm for Ni/NF and Co/NF. The fitting parameters indicate a higher adsorption capacity of $\text{NH}_3(\text{g})$ on the Ni surface than on the Co surface; (c) The second order reaction kinetics fitting. The results indicate a faster reaction rate on the Co/NF electrode due to a higher reaction constant calculated from the slope of the fit line

CHAPTER 5 CONCLUSION

5.1 Conclusion

This study provides a comprehensive investigation into the electrochemical AOR as a pathway for sustainable hydrogen production. Starting with DFT calculations, the catalytic activity of Ni and Co surfaces for AOR was explored to elucidate the reaction mechanism. The DFT energies revealed that the energetic span for AOR is significantly lower on Co, indicating a more favorable catalytic pathway compared to Ni. While ammonia adsorption was exergonic on both surfaces, N₂ desorption was identified as an endergonic step on Ni but exergonic on Co, reducing the thermodynamic bottleneck for nitrogen evolution on the Co surface. This mechanistic understanding paved the way for experimental investigations into the catalytic activity of these surfaces for ammonia decomposition.

By utilizing nanostructured metal catalysts of these surfaces (Ni/NF and Co/NF) synthesized via hydrothermal deposition on NF, we demonstrated significant improvements in catalytic performance compared to bare NF. Structural and electrochemical characterization revealed that both Ni/NF and Co/NF exhibited enhanced catalytic activity, characterized by lower onset potentials, higher current densities, and reduced charge transfer resistance. Among the two, Co/NF showed superior performance, achieving higher ammonia conversion, greater hydrogen production rates, and improved energy efficiency, making it the more efficient catalyst for AOR.

Additionally, adsorption and kinetic studies provided further insight into the role of surface properties in influencing AOR efficiency. The Freundlich adsorption isotherm model confirmed a higher ammonia adsorption capacity for Ni/NF, while kinetic analysis

revealed that Co/NF exhibited a higher rate constant, consistent with faster AOR kinetics and increased hydrogen production. These results highlight the distinct roles of Ni and Co in facilitating AOR and reinforce the importance of surface structure in catalytic performance.

By establishing a comprehensive baseline between Ni/NF and Co/NF, this work lays the foundation for further advancements in bimetallic catalysts, alloying strategies, and synergistic modifications to further improve AOR kinetics and hydrogen production efficiency. These insights contribute to the ongoing development of efficient and sustainable electrochemical systems for hydrogen generation.

APPENDICES

A.1 Materials and Chemicals

Nickel(II)nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 98\%$) was supplied by Sigma-Aldrich, while Cobalt(II)nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 98\%$) was obtained from Fluka Analytical. Urea Crystals (NH_2CONH_2 , Baker Analyzed Reagent) were supplied by J.T. Baker Chemical Co. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, $\geq 99.8\%$) was obtained from Riedel-de-Haën Honeywell, and hydrochloric acid (HCl , $\geq 37\%$) was supplied by Fluka Honeywell. Nickel foam purchased from DekResearch. High-purity deionized (DI) water was produced using a Thermo Scientific Barnstead Nanopure water purification system. No further purification or treatment was applied to the chemicals.

A.2 Supplementary Figures

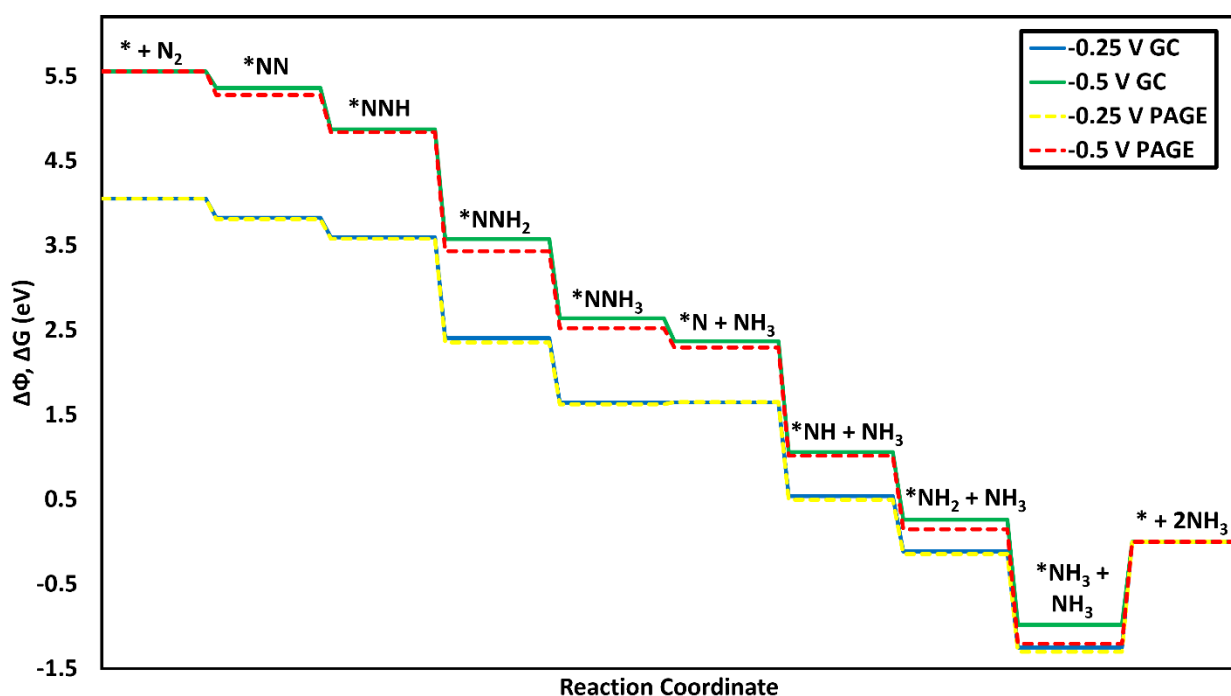


Figure A1: Reaction coordinate diagram of NRR for comparison of GC-DFT and the Potential-Adjusted Grand Free Energy (PAGE) method on Ni(111) surface at different

applied potentials. The PAGE approach approximates to the GC-DFT with sufficient accuracy at both -0.25 V and -0.5 V applied potentials.

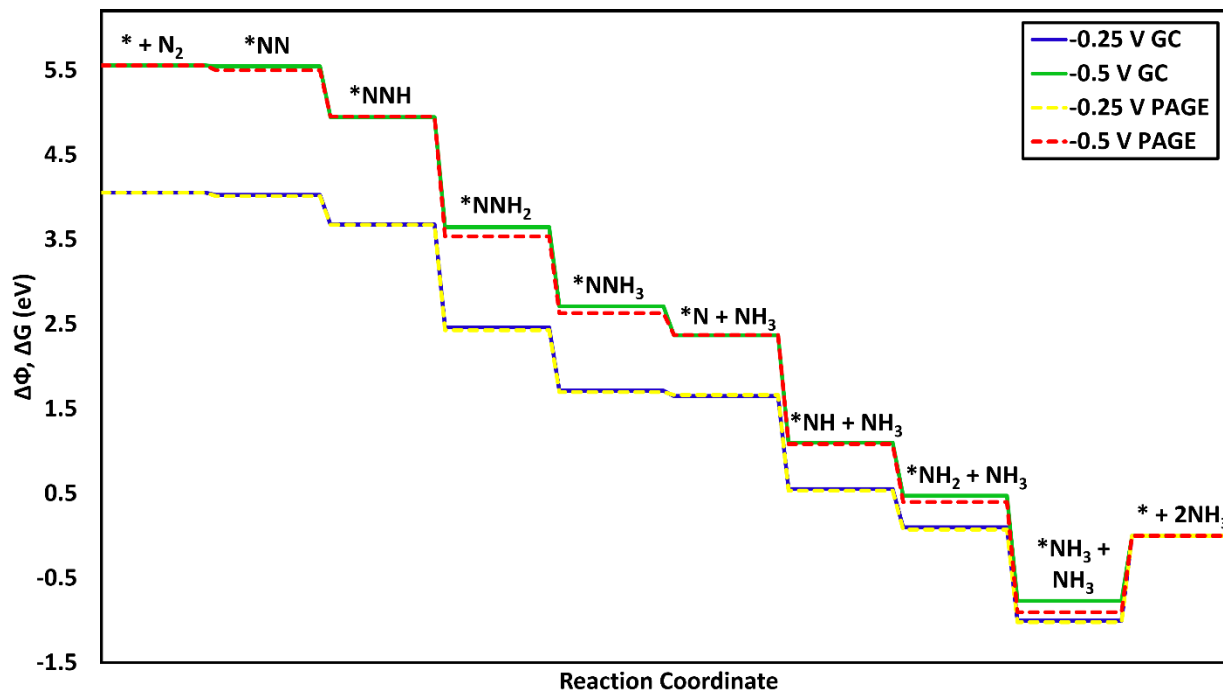


Figure A2: Reaction coordinate diagram of NRR for comparison of GC-DFT and the Potential-Adjusted Grand Free Energy (PAGE) method on Co(111) surface at different applied potentials. The PAGE approach approximates to the GC-DFT with sufficient accuracy at both -0.25 V and -0.5 V applied potentials.

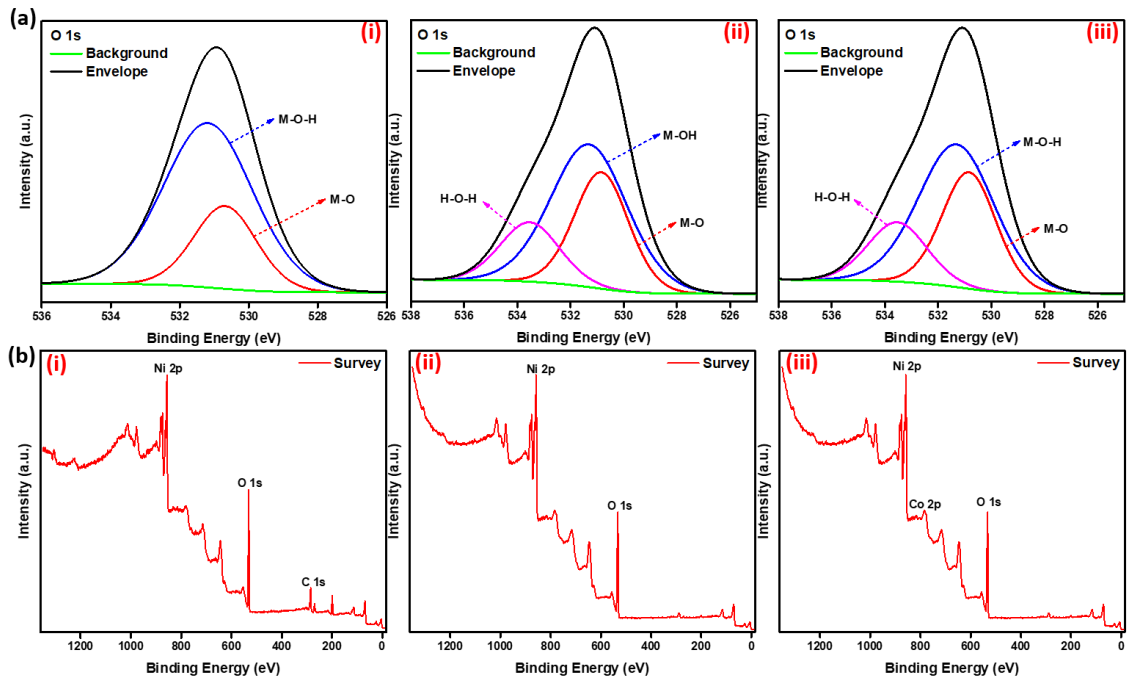


Figure A3: (a) XPS spectra of O 1s bare NF, Ni/NF, and Co/NF. The O 1s spectrum revealed a peak at 530.8 eV, corresponding to metal oxides, and a peak at 531.3 eV corresponding to metal hydroxides. On the modified electrodes, an additional peak at 533.5 eV was observed, corresponding to adsorbed water molecules; and (b) the survey of the XPS spectra in bare NF, Ni/NF, and Co/NF. The survey presents the entire sampling binding energy range scanned during the XPS procedure.

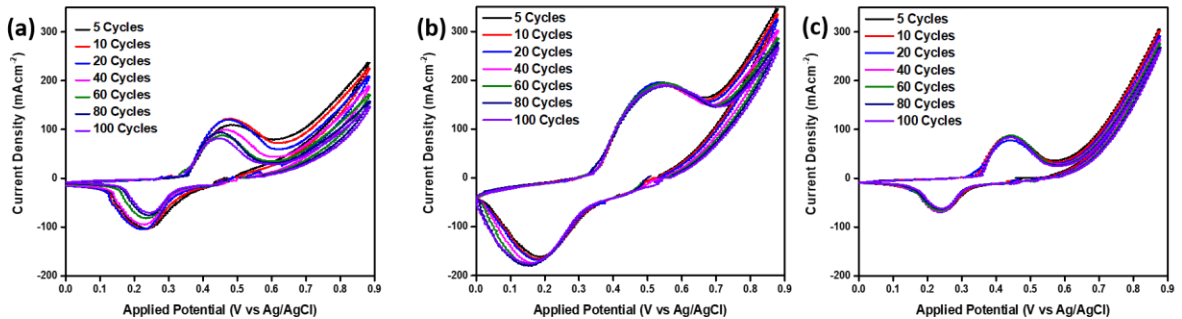


Figure A4: Effect of electrooxidation cycles on the AOR performance of NF, Ni/NF, and Co/NF electrodes. CV scans recorded over 5, 10, 20, 40, 60, 80, and 100 cycles for (a) bare NF, (b) Ni/NF, and (c) Co/NF. The bare NF electrode initially exhibited an increase in redox peak intensity, reaching a maximum at 10 followed by a decline, suggesting depletion of surface-active sites and reduced AOR performance. In contrast, Ni/NF and Co/NF electrodes demonstrated stable redox peaks throughout all cycles, indicating the presence of abundant and durable redox-active materials that sustain catalytic activity during prolonged cycling.

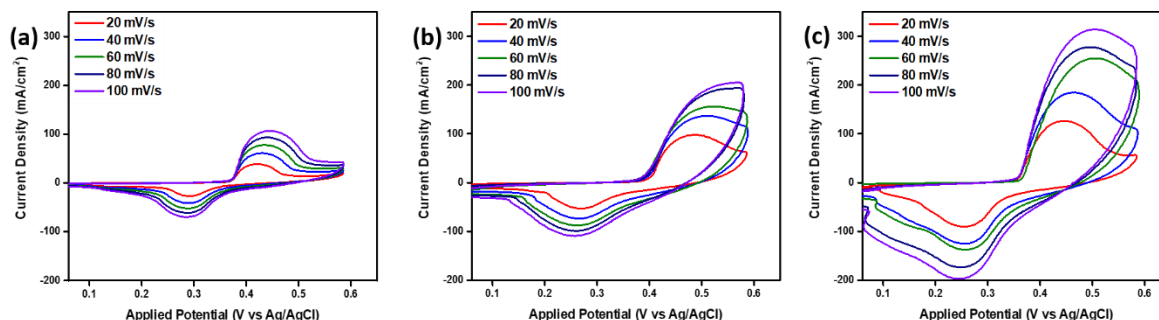


Figure A5: CV scans in the Faradaic region for NF, Ni/NF, and Co/NF electrodes at different scan rates. CV measurements for (a) bare NF, (b) Ni/NF, and (c) Co/NF were performed in 0.5 M NH_4OH and 1 M KOH at varying scanning rates (20 - 100 mV/s) to evaluate the effect of scan rate on redox kinetics and active site availability in the Faradaic region. The increase in redox peak intensity with increasing scan rate reflects an expansion in the active redox area, with the trend $\text{Co/NF} > \text{Ni/NF} > \text{bare NF}$. These results highlight the enhanced charge transfer capability and higher density of electroactive sites on the modified electrodes, particularly for Co/NF, which exhibits superior AOR activity.

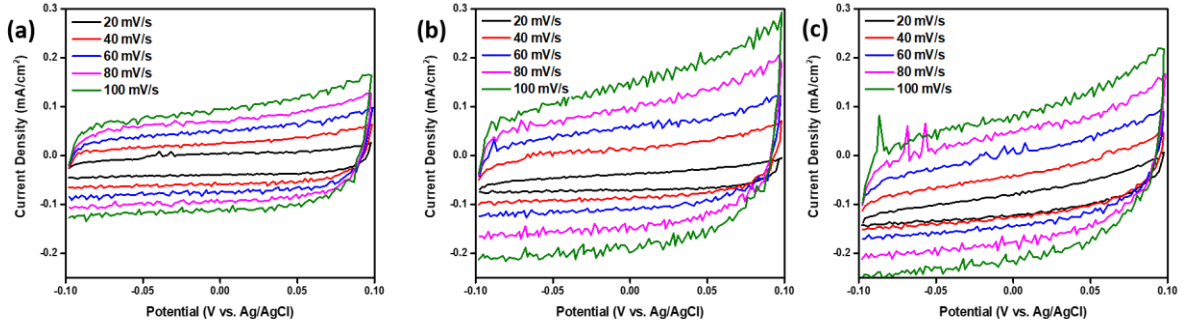


Figure A6: CV cycles in the non-Faradaic region for (a) NF, (b) Ni/NF, and (c) Co/NF in a solution of 0.5 M NH_4OH and 1 M KOH at different scanning rates. The data from these CV cycles, typically measured in a region where no redox reaction occurs, were used to calculate the electrochemical surface area of the electrodes. This allows for the full scan of all the available sites on the electrodes without interference from any reaction.

A.3 Calculations

Electrochemical Surface Area (ECSA):

The ECSA was determined using the double layer capacitance (C_{dl}) [122], calculated by measuring cyclic voltammetry across various scan rates (20-100 mVs^{-1}) within a non-Faradaic potential region (-0.1-0.1 V vs Ag/AgCl). To determine the C_{dl} , double-layer charging current density, $I_c = \frac{\Delta j}{2} = \frac{(I_{anodic} - I_{cathodic})}{2}$, was plotted against the scan rates.

The slope of the linear fitting line equals the C_{dl} , according to Equation A1. The ECSA is directly proportional to C_{dl} , calculated in Equation A2.

$$I_c = \Delta v C_{dl} \quad (\text{A1})$$

$$ECSA = \frac{C_{dl}}{C_s} \quad (A2)$$

Where Δj is the difference between the positive and negative current density (mA/cm^2), v is the scan rate, $ECSA$ (cm^2) and C_s is the specific capacitance, generally within the range of $0.022\sim 0.130$ (mF/cm^2) in alkaline solution, herein, 0.040 mF/cm^2 was used [123, 124].

Tafel Plot:

The Tafel slope is calculated using the Tafel equation:

$$V = a + b \log(j) \quad (A3)$$

where b is the Tafel slope relating to the electron transfer.

Ammonia Conversion:

$$\text{Ammonia Conversion (ppm)} = C_o - C_t \quad (A4)$$

Where C_o is the initial ammonia concentration (ppm), C_t is the ammonia concentration at a specified time (ppm).

Cell Efficiency:

The cell efficiency (ϵ , %) is calculated as:

$$\epsilon (\%) = \frac{3 \times \Delta H_{H_2}}{2 \times \Delta H_{NH_3} + 6 \times F \times E \times 10^{-3}} \quad (A5)$$

Where ΔH_{H_2} is the lower heating value of H_2 , ΔH_{NH_3} is the lower heating value of NH_3 , E is the applied potential (V), and F is the Faradaic constant (96480 C/mol) [21].

Energy Consumption:

The energy consumption of the process is calculated using Equation A6.

$$\text{Energy consumption (Whg}^{-1}\text{NH}_3) = \frac{I \times E \times t}{M_{\text{NH}_3}} \quad (\text{A6})$$

Where E is the applied potential (V), I is the corresponding current (A), t is time (h), and M_{NH_3} is the molar mass of ammonia (17.03 g/mol) [21].

Adsorption Isotherms:

From the cyclic voltammetry data in Figure 8(c) and 8(d), the Freundlich adsorption isotherm was fitted using the model represented by Equation A7 [125].

$$\theta = K_f C^{\frac{1}{n_f}} \quad (\text{A7})$$

The data is plotted in a linear form of the equation (Equation A8),

$$\ln \theta = \ln K_f + \frac{1}{n_f} \ln C \quad (\text{A8})$$

where θ is the surface coverage, given by $\frac{j_{\text{peak}}}{j_{\text{max}}}$, j_{peak} is the peak current at any given NH_3 concentration, j_{max} is the maximum peak current, K_f is the Freundlich constant, denoting the adsorption capacity, C is the NH_3 concentration, and n_f is an empirical constant related to the heterogeneity of the adsorbent surface. $0 < n < 1$ for a favorable adsorption, $n = 1$ for linear adsorption, $n > 1$ for unfavorable adsorption, and $n = 0$ for an irreversible adsorption process.

Table A1: Parameters of Freundlich model for NH_3 adsorption

S/N	Electrode	Freundlich Parameters		
		$1/n_f$	K_f	r^2
1	Ni/NF	1	1.32	1
2	Co/NF	1	1.09	1

Reaction Kinetics:

The reaction kinetics of Ni/NF and Co/NF were further investigated using the ammonia conversion data generated from the experiments (Figure 11(b)). By predicting the second-order reaction, the corresponding rate law was applied to calculate the reaction constants. The data were first converted from ppm to molarity using Equation A9, then fitted with the linear form of the second-order equation. The slope of the straight-line graph represents the reaction constant.

$$\text{Molarity (M)} = \frac{\text{ppm}}{M_{\text{NH}_3} \times 1000} \quad (\text{A9})$$

$$\frac{1}{C} = \frac{1}{C_0} + kt \quad (\text{A10})$$

Where C is the concentration in mol, M_{NH_3} is the molar mass of ammonia, k is the reaction constant, and t is time (min).

Table A2: Parameters of second-order kinetics for the NH_3 AOR

S/N	Electrode	Kinetic Parameters	
		K ($\text{mol}^{-1}\text{min}^{-1}$)	r^2
1	Ni/NF	0.005	0.9883
2	Co/NF	0.006	0.9888

Reaction Coordinate Diagrams Detailed Equations

Equations A11-A20 were used to calculate the free energies of each state in the reaction coordinate diagrams, which are plotted relative to the reactant states. The asterisk (*) denotes a solvated Ni or Co catalyst surface:

$$2G_{\text{NH}_3} + G_* + 6 G_{\text{OH}^-} = 0 \text{ (Reference)} \quad (\text{A11})$$

$$\Delta G_{*\text{NH}_3} = G_{\text{NH}_3} + G_{*\text{NH}_3} + 6 G_{\text{OH}^-} - \text{Reference} \quad (\text{A12})$$

$$\Delta G_{*\text{NH}_2} = G_{\text{NH}_3} + G_{*\text{NH}_2} + G_{\text{H}_2\text{O}} + 5 G_{\text{OH}^-} - \text{Reference} \quad (\text{A13})$$

$$\Delta G_{*\text{NH}} = G_{\text{NH}_3} + G_{*\text{NH}} + 2 G_{\text{H}_2\text{O}} + 4 G_{\text{OH}^-} - \text{Reference} \quad (\text{A14})$$

$$\Delta G_{*\text{N}} = G_{\text{NH}_3} + G_{*\text{N}} + 3 G_{\text{H}_2\text{O}} + 3 G_{\text{OH}^-} - \text{Reference} \quad (\text{A15})$$

$$\Delta G_{*\text{NNH}_3} = G_{*\text{NNH}_3} + 3 G_{\text{H}_2\text{O}} + 3 G_{\text{OH}^-} - \text{Reference} \quad (\text{A16})$$

$$\Delta G_{*\text{NNH}_2} = G_{*\text{NNH}_2} + 4 G_{\text{H}_2\text{O}} + 2 G_{\text{OH}^-} - \text{Reference} \quad (\text{A17})$$

$$\Delta G_{*\text{NNH}} = G_{*\text{NNH}} + 5 G_{\text{H}_2\text{O}} + G_{\text{OH}^-} - \text{Reference} \quad (\text{A18})$$

$$\Delta G_{*\text{NN}} = G_{*\text{NN}} + 6 G_{\text{H}_2\text{O}} - \text{Reference} \quad (\text{A19})$$

$$G_{*+\text{N}_2} = G_{\text{N}_2} + G_* + 6 G_{\text{H}_2\text{O}} - \text{Reference} \quad (\text{A20})$$

Table A3: Comparison of this work with other literature

Catalyst	Condition	Onset potential (V)	Current density (mA/cm ²)	EIS (R _{ct} , Ω)	Performance	Limiting step	Reference
NiCu/NF	0.3 M NH ₃ + 1 M KOH, 20°C	-	250	0.2	-	-	[126]
NiCu-NF	2 M NaOH + 0.4 M NH ₄ Cl, 25°C	0.36	~33	1.2	-	-	[86]
NiCu@NiCuOOH-NF	2 M NaOH + 0.4 M NH ₄ Cl, 25°C	0.36	90	0.5	-	-	[86]
Pt-Ru	5 M KOH + 1 M NH ₃ , 60°C	-	-	-	Cell Efficiency: ≈ 50% at 1.4 V	-	[127]
Pt-Ir	5 M KOH + 1 M NH ₃ , 60°C	-	-	-	Cell Efficiency: ≈ 68% at 0.8 V	-	[127]
Ni ₅₀ Cu ₅₀ /C	1 M KOH + 0.5 M NH ₃ , 25°C	-	110	-	Cell Efficiency: ≈ 50.2% at 1.4 V	-	[128]
Pt(100)	0.057 V vs. RHE	-	-	-	-	*NH – N (0.86 ev)	[38]
Pt(100)	0.62 V vs. RHE	-	-	-	-	*NH – N (0.29 ev)	[38]
Pt/NGA	0.1 M NH ₃ + 1 M KOH, 25°C	-	-	-	Cell Efficiency: ≈ 68.5% Vol. of H ₂ = 8.5 ml at 0.8 V in 180 minutes	-	[21]

NiCu/CP	55 mM NH ₃ + 0.5 M NaOH	0.47	52	3	-	-	[129]
Cu ₂ O/Ni	(i) O-S mechanism (ii) G-M mechanism	-	-	-	-	(i) *NH ₂ -*NH (1.41 eV) (ii) *NH ₃ - *NH ₂ (1.49 eV)	[130]
NiSe ₂ /Se-NiCuO _x /NF	O-S mechanism	-	-	~4	Vol. of H ₂ = 9 ml at 1.5 V in 25 minutes	*NH ₂ -*NH (0.87 eV)	[131]
Ni/NF	1 M KOH + 0.5 M NH ₄ OH, 25°C	0.31	522	2.50	Cell Efficiency: ≈ 62.9% Vol. of H ₂ = 9.51 ml at 0.8 V in 100 minutes	*NN - * + N ₂ (0.072 eV)	This work
Co/NF	1 M KOH + 0.5 M NH ₄ OH, 25°C	0.32	819	2.35	Cell Efficiency: ≈ 64.8% Vol. of H ₂ = 9.58 ml at 0.8 V in 100 minutes	-	This work

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VITAE

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EDUCATION

MSc Chemical Engineering

January 2023 – Present

King Fahd University of Petroleum and Minerals (KFUPM), Dhahran
Saudi Arabia

- **Thesis:** Electrochemical Ammonia decomposition to Hydrogen
- CGPA: 3.79/4.00

B.Eng Chemical Engineering (First Class Honors)

November 2021

Ahmadu Bello University (ABU), Zaria Nigeria

- CGPA: 4.63/5.00
- **Research Project:** Molecular Dynamics Study on the Miscibility of Polymer Blend of polylactic acid with polyethylene terephthalate, polystyrene, low-density polyethylene, high-density polyethylene, and natural rubber September 2021
- **Design Project:** Design of 18,000 tonnes per annum alkyd resin plant Aug. 2021
- **Industrial Project:** Investigating the effect of false air on the power consumption of Raw Mill at Ashaka Cement Plc. December 2019

WORK EXPERIENCE

Teaching Assistant (T.A)

January 2023 – Present

King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia

- CHE302: Heat Transfer (Term 241 & 242)
- CHE404: Hydrogen Production and Storage (Term 232)
- CHE204: Fluid Mechanics (Term 231)
- CHE303: Chemical Engineering Thermodynamics (Term 222)

National Youth Service Corp

March 2022 – February 2023

Defence Industries Corporation of Nigeria (DICON), Kaduna State, Nigeria

- Posted to Materials Testing Laboratory of the Research and Development Centre, DICON

Sales Manager

April 2020 – March 2022

Emjays Empire, Gombe State, Nigeria

- Wholesale and retail of soft and carbonated drinks

Intern

July 2019 – December 2019

Ashaka Cement Plc, Gombe State, Nigeria

- Students Industrial Working Experience Scheme (SIWES) at the process section

ACADEMIC PUBLICATIONS, PRESENTATIONS AND CONFERENCES

- Presented a poster titled “Electrochemical Ammonia Decomposition over Nickel and Cobalt Nanostructures on Nickel Foam for Sustainable Hydrogen Production: An Experimental and Computational Approach” at the 5th Student Research Contest (SRC) at KFUPM in April, 2025
- Presented a poster titled “Electrochemical Ammonia Decomposition over Nickel and Cobalt Nanostructures on Nickel Foam for Sustainable Hydrogen Production” at the 33rd Annual Saudi-Japan Symposium at KFUPM Dhahran Techno Valley in February, 2025
- **Jafar, U., Nuhu, U., Khan, W. U., & Hossain, M. M. (2024).** A review on green ammonia as a potential CO₂ free fuel. *International Journal of Hydrogen Energy*, 71, 857-876. <https://doi.org/10.1016/j.ijhydene.2024.05.128>
- Presented a poster titled “Velocity Distribution of Laminar Flow in a Circular Tube” for Mathematical Methods for Engineers course at Department of Mathematics, KFUPM in May, 2024
- Participated in 51st International Conference and Annual General Meeting of Nigerian Society of Chemical Engineers (NSChE) themed ‘Chemical Engineering and The Changing World’, held at Federal Palace Hotel, Victoria Island, Lagos, in November 2021
- Presented at a Virtual Conference of the Faculty of Science, Obafemi Awolowo University, Ile-Ife, Nigeria on ‘Computational Dynamics Study for the Blend of polystyrene, polypropylene and natural rubber’ in June, 2021

SKILLS

- Microsoft Office Packages
- Basic Proficiency in Density Functional Theory (DFT) calculations using Quantum Espresso
- Basic Proficiency in Materials Studio for Polymer Blend Study
- Basic proficiency in MatLab, Aspen Hysys and AutoCAD
- Excellent Research Skill
- Excellent Leadership and Critical Thinking Intelligence

HONORS AND AWARDS

- Al-Ansar Annual Graduate School Application Scholarships 2022: covers the costs associated with application fees for graduate schools and proficiency tests

- 2nd Position, Nigerian Society of Chemical Engineers (NSChE) final year students design project competition, November 2021
- Shell Nigeria Exploration and Production Company (SNEPCo) Merit Scholarship, 2018 – 2021
- Federal Government of Nigeria Scholarship, 2018 – 2021
- Total E&P National Merit Scholarship, 2015 – 2020
- Gold Medalist, National Mathematics Olympiad of National Mathematical Center (NMC), 2015

EXTRACURRICULAR ACTIVITIES

Covid 19 Vanguard Team

March 2022 - April 2022

National Youth Service Corps (NYSC) Orientation Training Camp, Katsina

- Coordinated the activities to ensure strict compliance to COVID 19 safety protocols

Faculty of Engineering Induction Ceremony Organizer

November 2021

Faculty of Engineering, Ahmadu Bello University, Zaria

- Served as the technical secretary of the organizing committee of the maiden Induction Ceremony of the Faculty of Engineering graduates into the Nigerian Society of Engineers

Departmental Career Session Organizer

November 2021

Department of Chemical Engineering, Ahmadu Bello University, Zaria

- Head the 3-member committee of the career session for the 2019/2020 graduating students

Tree Plantation

October, 2021

Ahmadu Bello University Directorate of University Advancement, Zaria

- Participated in 3000 Orange Trees Plantation for carbon offset from our environment
- Served as my signature on the COP21 Paris Climate Agreement to reduce carbon footprint

University Electoral Committee Member

January 2017

Gombe State Students Association (GOSSA) Electoral Commission, Zaria

- Conducted the Student Association Election and Swearing-in Ceremony of the newly elected executives for 2016/2017 academic session
- Alongside the other members, acted as the caretaker of the association for the period

TRAININGS AND WORKSHOPS

TechShift Hackathon

October 2024

First hackathon on hydrogen economy, organized by Aramco

Density Functional Theory Fundamentals

September 2023

King Fahd University of Petroleum and Minerals (KFUPM), Saudi Arabia

- 3-day workshop on using Quantum Espresso for Density Functional Theory calculations

Transforming Nigerian Youths Program

August 2022

Young Africa Works-Mastercard Found - Enterprise Dev. Centre, Pan-Atlantic University

- Aimed to create a network of entrepreneurial and managerial change makers in youth

Skills Acquisition and Entrepreneurship Development (SAED)

March 2022

*NYSC Orientation Camp, Katsina State***Annual Statistical Workshop**

September 2021

Association of Statistics Students of Nigeria (ASSAN), ABU Zaria

- Achieving an Excellent Research Using Statistical Packages (SPSS, Excel and Minitab)

ACADEMIC AND PROFESSIONAL MEMBERSHIPS

- Member - American Institute of Chemical Engineers (AIChE)
- Member - Nigerian Society of Engineers (NSE)
- Member - Lead Generation Initiative (LGI)
- Student Member – Nigerian Society of Chemical Engineers (NSChE)
- Student Member – Society of Petroleum Engineers (SPE)