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Master's Degree Thesis

Electrochemical Assessment of CuNi Catalysts Supported on Mesoporous Carbon Nitride for Nitrate Reduction to Ammonia

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Abstract

The electrochemical reduction of nitrate (NO_3RR) to ammonia has emerged as a promising strategy for the simultaneous removal of nitrate pollutants and the recovery of nitrogen in the form of ammonia. Unlike the centralized Haber-Bosch process, which requires high temperatures and pressures and is associated with high energy consumption and significant CO_2 emissions, NO_3RR could enable a more decentralized approach to nitrogen valorization, particularly when coupled with renewable electricity. In this context, NO_3RR is not intended to replace the Haber-Bosch process, but rather to offer a complementary route for nitrate remediation and ammonia recovery from nitrate-contaminated streams. However, nitrate reduction is a complex multielectron and multiproton reaction, involving several intermediates, multiple reaction pathways and the possible formation of different by-products. Moreover, the selectivity towards ammonia is governed by a delicate balance between nitrate adsorption, intermediate conversion, and competing side reaction, which are strongly affected by the applied potentials and the catalyst surface properties. In particular, at more cathodic potentials, the hydrogen evolution reaction can compete with nitrate reduction, limiting the Faradaic efficiency towards the desired product. Therefore, the development of low-cost, active, selective, and scalable electrocatalysts for nitrate reduction is critical to advancing this field. This work focuses on the study of four electrocatalysts based on copper-nickel (CuNi) alloys supported on mesoporous carbon nitride (MCN). The study systematically investigates the effect of different synthesis strategies on the physicochemical and electrocatalytic properties of the materials, with particular attention to the introduction of H_2SO_4 during the impregnation step and a subsequent post-synthesis acid treatment (AT). The prepared catalysts were characterized and evaluated in an H-type electrochemical cell, where they were immersed in an electrolyte solution to assess its catalytic activity at different applied potentials. Among the investigated materials, the catalyst synthesized in the presence of H_2SO_4 and without subsequent acid treatment showed the most promising performance under the tested conditions, although the improvement with respect to the analogous material prepared without H_2SO_4 was moderate. The results suggest that the synthesis environment can slightly influence the electrocatalytic response, while the post-synthesis acid treatment has a more pronounced effect, leading to changes in the metal loading and Cu/Ni ratio that may negatively affect nitrate reduction performance. Overall, these findings highlight the importance of controlling both the impregnation conditions and post-treatment steps to optimize CuNi/MCN-based catalysts for nitrate electroreduction.

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Chapter 1

Introduction

The nitrogen cycle is one of the primary and most important biogeochemical cycles on Earth, essential for interlinking humanity with the ecosphere and ensuring life on our planet. Throughout this cycle, nitrogen transitions through various oxidation states, ranging from +5 (NO_3^-) to -3 (NH_3). The cycle begins with a critical initial step known as nitrogen fixation, where inert atmospheric nitrogen gas (N_2) is converted into ammonia. This step is essential because it dictates the input of bioavailable nitrogen into our ecosystems. In natural systems, this fixation is primarily carried out by nitrogen-fixing organisms, such as rhizobia bacteria found in the root nodules of leguminous plants. Once nitrogen enters the soil, microorganisms transform it into organic nitrogen compounds that can be absorbed and utilized by plants and animals. However, this delicate natural balance has been severely disrupted by anthropogenic activities, which have unbalanced the nitrogen cycle. Driven by the rapid global population growth and consequent increase in food demand, the need for artificial nitrogen fixation has increased exponentially, with the production of ammonia via the Haber-Bosch process playing a central role in the synthesis of agricultural fertilizers. This massive overuse of chemical fertilizers, combined with the combustion of fossil fuels and the disposal of nitrogen-containing industrial waste, has altered the global nitrogen circulation, generating enormous quantities of nitrate-based pollutants (NO_3^-). Today, nitrates represent one of the main widespread contaminants in groundwater, rivers, and lakes. Due to their high chemical stability and extreme water solubility, nitrates are difficult to remove using traditional methodologies. The excess of nitrates that leaches and accumulates in surface waters is a primary cause of the phenomenon of eutrophication, a process that devastates aquatic ecosystems by reducing dissolved oxygen and destroying biodiversity. Moreover, nitrate pollution has a severe and direct effect on human health. The ingestion of water contaminated with high concentrations of nitrates, and particularly their much more toxic reduction products, such as nitrites, is strongly associated with severe pathologies, including

thyroid disease, birth defects, cancers, and methemoglobinemia (the so-called "blue baby syndrome") in infants. Faced with this emergency, scientific research is called upon to provide sustainable solutions. Moving beyond traditional biological and physicochemical methods, which are often slow and expensive, directs us today toward the electrochemical reduction of nitrates. This is an innovative technology capable not only of decontaminating wastewater under mild ambient conditions but also of converting pollutants directly into high-value-added ammonia, taking a fundamental step toward the restoration of a sustainable nitrogen cycle. [1-3]

1.1 Ammonia Production

Ammonia (NH_3) is a foundational chemical essential to multiple industries with fertilizer production accounting for the vast majority of its use (78%), alongside industrial chemicals, refrigeration, food and beverages, and pharmaceuticals, and it is increasingly recognized as a vital carbon-free energy carrier and storage medium. Driven by the needs of a growing global population, worldwide production currently stands at approximately 200 million tons per year, and this demand continues to rise. [1-3] The ammonia production still relies heavily on the traditional Haber-Bosch process, which was first industrialized in 1905. The German chemist Fritz Haber demonstrated ammonia could be successfully synthesize from nitrogen and hydrogen using a catalyst, but only under severe operational conditions i.e., high temperatures (350–600 °C) and extreme pressures (15–35 MPa). This fossil-fuel-dependent route is remarkably energy-intensive. According to the International Energy Agency (IEA), the production of conventional natural gas and coal-based ammonia represents 1 to 2% of the total global energy consumption. Furthermore, it releases around 450 million tons of CO_2 annually, representing approximately 1.5% of total global greenhouse gas emissions. Today, in the shadow of global decarbonization goals, ammonia is highly prized as a zero-carbon fuel for hard-to-abate sectors like marine shipping, heavy industry, and stationary power generation. Consequently, the severe environmental footprint of traditional manufacturing makes the development of sustainable, milder-condition synthesis routes an urgent global priority. [4]

1.2 Haber-Bosch Process

The Haber-Bosch process still represents the primary industrial method for large-scale ammonia production today. The innovation began in 1909 with the laboratory-scale demonstrations of chemist Fritz Haber and was later translated to an industrial scale by Carl Bosch, an achievement for which both received the Nobel Prize in subsequent years. The core of the process consists of the direct synthesis of

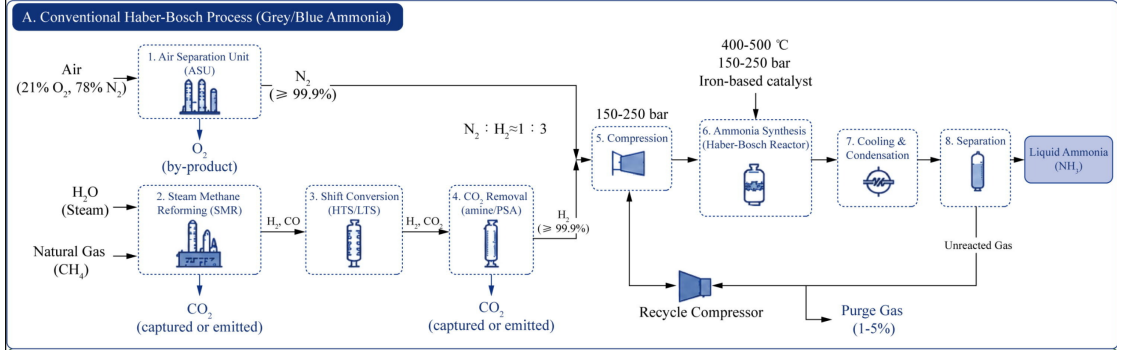
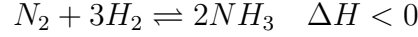


Figure 1.1: Conventional Ammonia production taken from [7]

ammonia from nitrogen gas (N_2) and hydrogen gas (H_2) according to the following exothermic and reversible reaction:



Nitrogen is obtained directly from atmospheric air (of which it constitutes roughly 78%), while hydrogen is currently generated primarily through upstream natural gas steam reforming processes.[5]. Ammonia synthesis poses a significant engineering challenge due to the balance between thermodynamics and kinetics. Since it is an exothermic reaction involving a reduction in the number of gaseous moles (from 4 moles of reactants to 2 moles of products), Le Châtelier’s Principle dictates that the equilibrium yield of ammonia is favored by high pressures and low temperatures. However, at low temperatures, the chemical inertness of nitrogen—due to the extremely strong covalent triple bond of the molecule ($N \equiv N$)—makes the activation energy prohibitive and the reaction rate practically zero. The actual process operate at temperatures between 400 and 600 °C and pressures ranging from 150 to 300 bar, feeding the reactants at an $H_2 : N_2$ molar ratio of 3:1. The commercial catalyst employed in the ammonia synthesis process is primarily based on metallic iron (Fe^0) as the active element. Specifically, the active phase consists of α -Fe, which is capable of easily decomposing nitrogen gas (N_2) at temperatures around 500 °C, leading to the formation of surface nitrides such as Fe_4N , Fe_3N and Fe_2N . The catalyst is manufactured starting from more or less stoichiometric magnetite (Fe_3O_4). This base material is mixed with specific promoters for example Al_2O_3 , K_2O , and CaO —and then fused in a furnace. After the melting process, the solid is cooled and crushed into suitably sized granules before undergoing reduction to obtain the active α -Fe phase. Due to the thermodynamic limits inevitably imposed by the high operating temperatures, the single-pass conversion of reactants into ammonia within the reactor is relatively low, typically settling between 20% and 35%. To make the process economically viable, the plant is

structured as a continuous loop system. The gases exiting the catalytic beds are rapidly cooled, utilizing highly integrated heat exchange networks to recover thermal energy. By cooling the mixture (in some separation sections even below $-20\text{ }^{\circ}\text{C}$), the ammonia condenses and is extracted from the system in liquid form. Conversely, the unreacted gases remain in the vapor phase, are recompressed, and pumped back into the reactor. Thanks to this separation and recycling operation, the overall conversion of the plant can exceed 98%.

1.3 Green Ammonia Production

To overcome the severe environmental and energy drawbacks associated with conventional ammonia synthesis, various sustainable strategies have been developed. This section outlines the primary alternative pathways for green ammonia production operating under mild conditions, specifically examining Biological Nitrogen Fixation, the Electrochemical Nitrogen Reduction Reaction (ENRR), and Nitrate Electroreduction (NO_3RR) and the Photocatalytic Conversion of Atmospheric Nitrogen (N_2) to Ammonia (NH_3).

1.3.1 Biological Nitrogen Fixation

Biological nitrogen fixation (BNF) is an essential reaction in the global nitrogen cycle. BNF accounts for roughly two-thirds of the fixed nitrogen produced on Earth and is catalyzed by the nitrogenase complex. The nitrogenase complex is a two-component metalloenzyme consisting of an electron-delivering iron (Fe) protein and a catalytic dinitrogenase protein (which can contain Mo, V, or Fe at its active site). Together, these two components catalyze the essential, ATP-dependent biological reduction of inert atmospheric dinitrogen (N_2) into bioavailable ammonia (NH_3). Three main variants of this enzyme exist in nature, they all share a basic architecture consisting of two separate, extremely oxygen-sensitive metalloproteins.[16] A unifying mechanistic principle among nitrogenases is that the activation of the nitrogen molecule is strictly coupled to a reductive elimination process: the enzyme must first accumulate protons and electrons (in the form of bridging hydrides) at the cofactor, which then combine to release hydrogen gas (H_2), thus making the site available for the binding and subsequent reduction of N_2 . The main differences among the various nitrogenase systems is the nature of the metal integrated into the active site cofactor, which classifies the enzymes into molybdenum (Mo), vanadium (V), and iron-only (Fe) nitrogenases.[14]

1. **Mo-nitrogenase:** This is the canonical system, the most widespread in nature, and by far the most efficient. Its catalytic protein (MoFe) hosts the FeMo-cofactor. Under optimal N_2 pressure conditions, the Mo-nitrogenase

limits waste production to a single H_2 molecule for each N_2 molecule reduced into two NH_3 molecules, maximizing energy efficiency. The other two systems are usually expressed by microorganisms under environmental molybdenum deficiency. Structurally, the catalytic protein of both alternative variants differs from the Mo-nitrogenase by the inclusion of an additional subunit, assembling into heterohexamers.

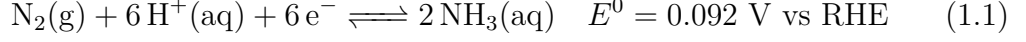
2. **V-nitrogenase:** It contains the FeV-cofactor, in which vanadium replaces molybdenum. It is less efficient than the Mo system in reducing nitrogen and "wastes" more electrons in the form of H_2 . But it is able to produce traces of ethane during acetylene reduction and, moreover, it can reduce carbon monoxide (CO) into complex hydrocarbons.
3. **Fe-nitrogenase:** Its active center, the FeFe-cofactor, contains exclusively iron atoms. Typically expressed when both Mo and V are lacking, it represents the nitrogenase with the lowest overall catalytic efficiency. For every N_2 molecule fixed, it produces 7 to 9 molecules of H_2 . That's because this enzyme has a much lower affinity (Michaelis constant, K_m) for atmospheric nitrogen compared to the Mo-nitrogenase. Consequently, at normal ambient partial pressures, N_2 struggles to compete with aqueous protons, leading to massive production of hydrogen gas instead of ammonia.

In summary, although all systems obey the same fundamental necessity to generate H_2 to activate nitrogen reduction, the substitution of the heterometal at the apex of the cofactor drastically alters the enzyme's substrate affinity and catalytic efficiency, demonstrating a fine adaptation of biochemical processes to fluctuations in trace metal availability across global ecosystems.[15][17]

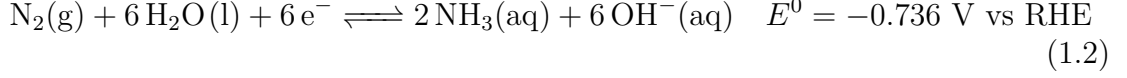
1.3.2 Electrochemical Nitrogen Reduction Reaction (NRR)

The direct electrochemical Nitrogen Reduction Reaction (NRR) is a highly promising technology for the sustainable production of green ammonia because it offers a carbon-free, decentralized alternative to the energy-intensive and fossil-fuel-dependent Haber-Bosch process by directly utilizing atmospheric nitrogen (N_2) and water under ambient conditions, powered entirely by renewable electricity. In an aqueous electrochemical cell, the NRR operates through a complex proton-coupled electron transfer (PCET) process, requiring the transfer of six electrons and six protons to convert one inert N_2 molecule into two NH_3 molecules. The reduction of nitrogen to ammonia is thermodynamically possible and ammonia exist in two different forms depending on the pH. At $pH < 9.25$, it exists in the ionic form and it is in neutral form at $pH > 9.25$. The reduction potential depends on the pH as

shown in the following equations: In acidic pH = 0:



In alkaline pH = 14:



The overall mechanism involves three fundamental steps: the adsorption of N_2 onto the electrocatalyst surface, the cleavage of the remarkably strong $\text{N}\equiv\text{N}$ triple bond (941–945 kJ/mol) accompanied by successive hydrogenation, and finally, the desorption of the synthesized ammonia.

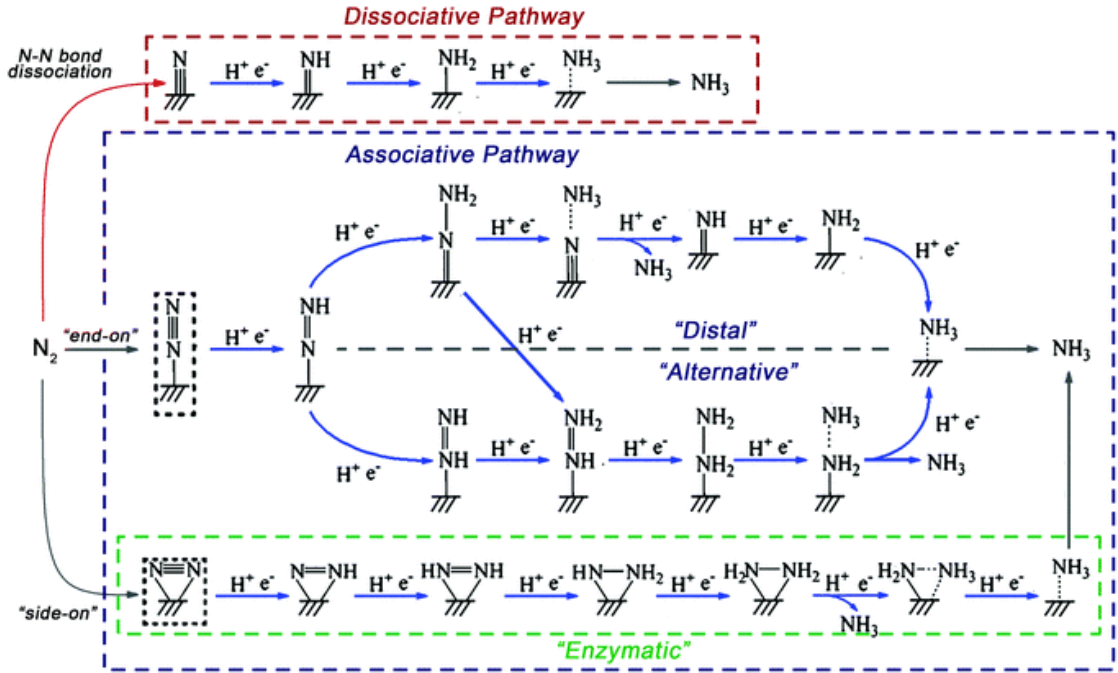


Figure 1.2: reaction pathways for the NRR by proton-coupled electron transfer taken from [12]

Mechanistically, the hydrogenation process is broadly classified into two main routes: the dissociative pathway, in which the $\text{N}\equiv\text{N}$ bond breaks immediately upon adsorption to form two isolated N -adatoms that are subsequently hydrogenated independently, and the associative pathway, where the $\text{N}\equiv\text{N}$ bond cleavage occurs simultaneously with progressive hydrogenation. The associative route is further subdivided into the distal pathway, where the remote, uncoordinated nitrogen atom is fully hydrogenated and released as the first NH_3 molecule before the remaining coordinated nitrogen atom is reduced, and the alternating pathway, where protons

and electrons are added alternately to both nitrogen atoms until the N-N bond breaks at the very end to release two NH_3 molecules. Additionally, for specific catalysts like transition metal nitrides, a Mars-van Krevelen (MvK) mechanism has been proposed, wherein a surface lattice nitrogen atom from the catalyst is directly protonated and released as ammonia, leaving behind a nitrogen vacancy that is subsequently replenished by dissolved N_2 gas from the electrolyte. Despite severe kinetic challenges such as the poor solubility of N_2 in water and fierce competition from the parasitic hydrogen evolution reaction (HER) that limits FE, NRR remains one of the most attractive solutions for green ammonia synthesis, as it completely eliminates direct CO_2 emissions and enables flexible, scalable, and on-site production of both fertilizers and clean energy carriers. [12-13]

1.3.3 Nitrate Electroreduction (NO_3RR)

The electroreduction of nitrates (NO_3^-) represents an emerging technological strategy with a dual environmental and energetic benefit. Unlike ammonia synthesis from molecular nitrogen (N_2), whose activation is thermodynamically hindered by the high dissociation energy of its triple bond, the Nitrate Reduction Reaction (NO_3RR) allows for the direct valorization of a widespread pollutant in water basins. By using electrical energy from renewable sources and operating under standard temperature and pressure conditions, this process enables the conversion of nitrate into ammonia (NH_3), transforming a waste product into a high-value-added resource.

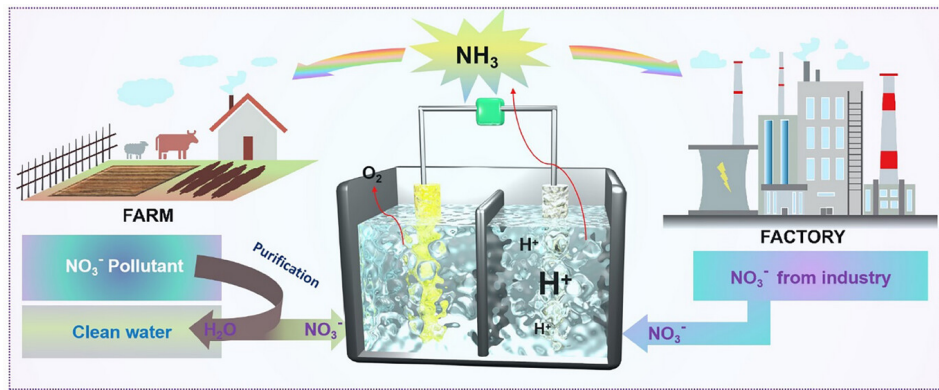


Figure 1.3: NO_3 reduction uses taken from [3]

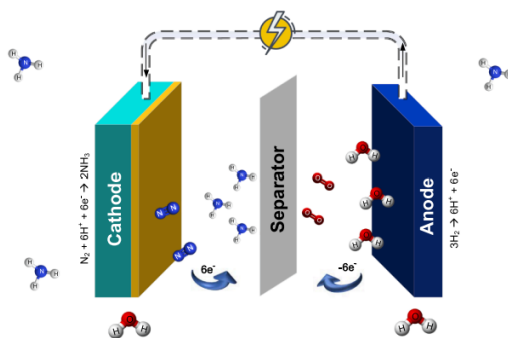
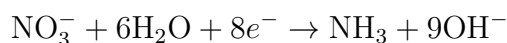


Figure 1.4: electrochemical ammonia synthesis process, taken from [24]

From a mechanistic perspective, the conversion of NO_3^- to NH_3 is an intricate reaction pathway governed by a Proton-Coupled Electron Transfer (PCET). The overall equation requires the transfer of a total of eight electrons, utilizing liquid water as the proton donor[3][2] [6].:



1.4 Ammonia as Energy Carrier

In the context of the energy transition and the global drive towards deep decarbonization, ammonia (NH_3) is emerging as one of the most promising zero-carbon energy carriers. Its role as a "hydrogen carrier" offers a technologically and economically viable solution to the stringent intrinsic limitations associated with the global storage and transportation of pure hydrogen. From a thermodynamic and physico-chemical perspective, ammonia has an exceptional gravimetric hydrogen content of approximately 17.6–17.8 wt% and a remarkable volumetric energy density, ranging between 11.6 and 15.6 MJ/L in its liquid form—significantly outperforming compressed or liquefied hydrogen. The primary engineering advantage lies in its mild liquefaction conditions: ammonia condenses at -33°C at atmospheric pressure, or at approximately 8.6–10 bar at room temperature. Conversely, hydrogen requires extreme cryogenic temperatures (-253°C) or exceptionally high compression (350–700 bar). The energy penalties and infrastructure costs for specialized containment vessels associated with these hydrogen storage processes are often prohibitive for large-scale applications[21].

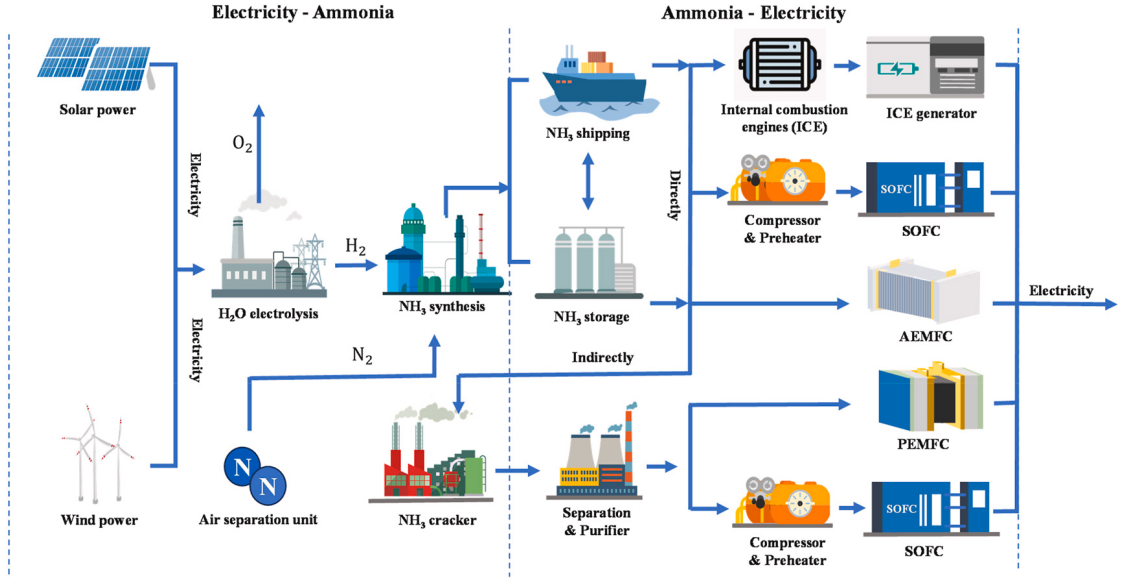


Figure 1.5: Renewable energy conversion and storage via electricity-ammonia-electricity routes. taken from [21]

This ease of storage consolidates ammonia as the medium of choice for the "power-to-ammonia-to-power" paradigm, which is designed for the long-term and long-distance storage of energy generated by intermittent renewable sources (e.g., solar and wind). To reconvert its chemical energy into electricity, ammonia can be utilized indirectly by undergoing an endothermic cracking process to release pure hydrogen, which is then fed into Proton Exchange Membrane Fuel Cells (PEMFCs). Alternatively, NH_3 can be fed directly into Solid Oxide Fuel Cells (SOFCs). Operating at elevated temperatures (600–1000 °C), SOFCs enable internal reforming and achieve very high overall system efficiencies, typically ranging from 45% to 65%. Ammonia is widely recognized as the ultimate destination fuel for the decarbonization of heavy-duty transport. It is particularly strategic in the maritime sector to meet the stringent emission reduction targets set by the International Maritime Organization (IMO). Its large-scale adoption is significantly facilitated by the existence of a mature global infrastructure network and supply chain: a pre-existing market valued at over 60 billion dollars that handles tens of millions of tons annually via dedicated vessels, pipelines, and port terminals. However, the implementation of ammonia as a direct fuel for thermal oxidation in Internal Combustion Engines (ICEs) or gas turbines presents formidable kinetic challenges[22]. Thermodynamically, its combustion is hindered by a very low laminar flame speed (approximately 6–7 cm/s), a high autoignition temperature (650 °C), and narrow flammability limits (15–28%). To stabilize combustion and mitigate the risk of misfires, ongoing research is focusing on strategies such as blending the ammonia

flow with hydrogen or other highly reactive fuels, alongside the optimization of the engine's compression ratio. Finally, the utilization of ammonia necessitates rigorous environmental and safety management. Its combustion inherently generates fuel-bound nitrogen oxides (NO_x), making it imperative to adopt efficient catalytic exhaust aftertreatment systems—such as Selective Catalytic Reduction (SCR)—to prevent severe ecological damage. Furthermore, its high toxicity dictates stringent handling procedures. Although its pungent odor is detectable at merely 5 ppm, inhalation becomes hazardous at concentrations above 25 ppm. This requires the mandatory adoption of anti-corrosive materials and the implementation of robust engineering safety protocols to prevent leakages and ensure the protection of human health across the entire value chain [23][24].

Chapter 2

NO₃RR State of Art and Theoretical Background

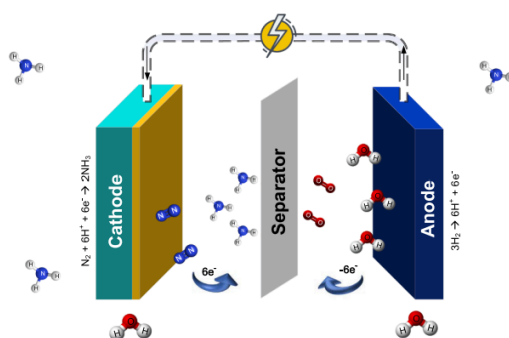


Figure 2.1: electrochemical ammonia synthesis process, taken from [24]

The selectivity of this reaction is highly dependent on parameters, such as overpotential and current density. The possible reactions routes are depicted in Figure 2.2.

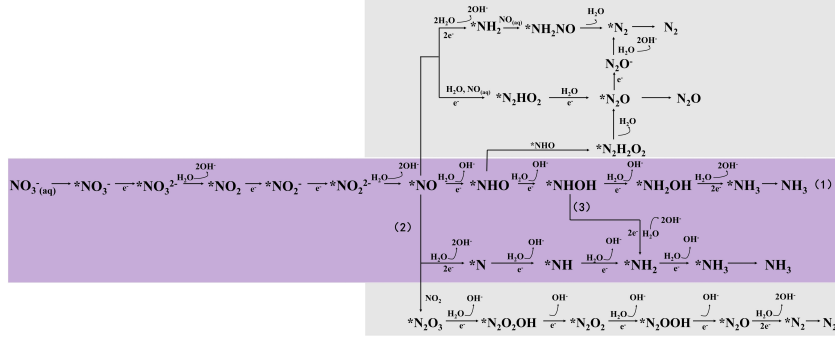
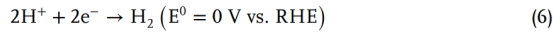
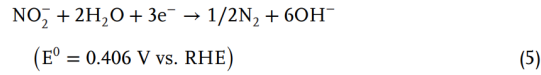
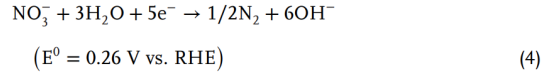
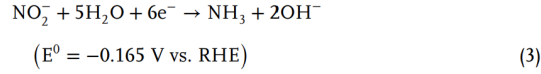
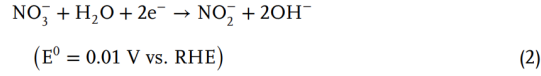
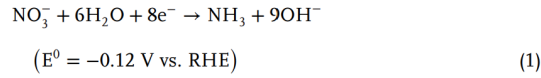


Figure 2.2: Possible reaction routes for electrochemical nitrate reduction. taken from [1]

The initial step of reducing NO_3^- to NO_2^- is considered the rate-determining step. Subsequently, NO_2^- is converted to adsorbed NO (NOads), which is then further reduced to either NH_3 or N_2 . The selectivity toward ammonia in this pathway remains a significant technical challenge



*NO is a key intermediate in steering the selectivity of nitrate reduction. If *NO is hydrogenated into *HNO, NH_3 will be the dominant product, while other reaction pathways will lead to the formation of N_2 (Equations 4 and 5). During NO₃RR, hydrogen evolution reaction (Equation 6) is an inevitable parasitic reaction due to the similar thermodynamic potentials between NO₃RR and HER, especially at high current densities[9]. To increase the FE of NO₃RR, HER was considered to be completely suppressed at the beginning of catalyst design. However, a fact is

that active hydrogen (*H) is indispensable in the successive hydrogenation steps to form NH_3 , and therefore a balance between *H supply and consumption should be carefully maintained. Deficient *H supply will slow down the production rate of ammonia, while excess *H supply will bring severe dimerization of hydrogen atoms to produce H_2 . Basically, the nitrate reduction includes three critical stages: (1) adsorption of nitrate ($NO_3^- \rightarrow *NO_3$); (2) reaction of intermediates on the surface of electrocatalysts (multi-steps of deoxygenation and hydrogenation); (3) desorption of ammonia ($*NH_3 \rightarrow NH_3$) [7][25]

2.1 Materials

Literature indicates that Rh, Fe, and Cu electrodes can be “selective” for ammonia production when selectivity is defined as conversion of only nitrogen species to ammonia, usually over a long period of hours. Despite the excellent selectivity and stability of noble metal catalysts, their high cost and limited availability present significant obstacles to widespread application. Consequently, increasing attention has been directed toward non-noble metal catalysts, which offer advantages, such as low cost, abundant availability, and potential for large-scale deployment. Among them, copper (Cu) stands out as a representative non-noble metal catalyst for nitrate reduction. The rationale behind copper’s exceptional catalytic performance lies in its unique electronic configuration. Specifically, the highest occupied d-orbital (HOMO) of copper aligns perfectly with the empty π -type lowest unoccupied molecular orbital (LUMO) of the nitrate ion[1]. This optimal orbital overlap enables Cu to inject electrons into the N–O bond with remarkable efficiency, thereby facilitating the initial deoxygenation of nitrate to nitrite ($NO_3^- \rightarrow NO_2^-$), which thermodynamically represents the most demanding kinetic bottleneck of the entire process. Furthermore, copper possesses a naturally high affinity for nitrogenous species relative to hydrogen. This intrinsic property ensures a low surface coverage of active adsorbed hydrogen (*H), effectively suppressing the parasitic Hydrogen Evolution Reaction (HER) and driving the faradaic selectivity toward ammonia synthesis. Despite these advantages, pure monometallic copper exhibits several critical vulnerabilities that hinder its direct industrial implementation. Specifically, it suffers from poor long-term chemical stability, tending to accumulate strongly bound reaction intermediates that lead to the progressive poisoning of the active sites. Moreover, under operational electrocatalytic conditions, the material is subject to profound and continuous morphological reconstruction. The active surface undergoes dynamic phase transitions, reducing from oxidized states—such as copper(II) oxide (CuO) and copper(I) oxide (Cu₂O)—to ultimately coalesce into aggregated metallic copper nanoparticles (Cu⁰). [3] To overcome the intrinsic limitations of pure copper and maximize both yield and selectivity, current research

is focusing on advanced nanometric architectures and targeted engineering strategies. Alloying copper with other transition metals allows for the modulation of its d-band center, thereby optimizing the binding energies of the reaction intermediates. In Cu – Ni alloys, for instance, Cu sites preferentially adsorb nitrate, while nickel captures the atomic hydrogen required for hydrogenation; this synergy rapidly converts the nitrite intermediate into ammonia, effectively suppressing hydrogen gas evolution. An even more compelling result is achieved with ordered CuPd intermetallic nanocubes: here, the Pauli repulsion generated by the d-orbitals of subsurface palladium destabilizes the nitrogen-containing intermediates, allowing the system to bypass classical thermodynamic limitations (i.e., scaling relations) and drastically lower the reaction barrier. Furthermore, Single-Atom Catalysts (SACs) represent the frontier of material efficiency by isolating individual metal atoms on conductive supports, thereby achieving 100% atomic utilization. By dispersing single copper atoms within a nitrogen-doped carbon matrix (Cu – N – C), a rigid coordination environment—often Cu – N₄—is established, which prevents the release of toxic intermediates like nitrites and directs the entire eight-electron cascade strictly toward ammonia. X-ray spectroscopy has revealed that these catalysts are structurally dynamic: under applied electrical potential, individual Cu atoms temporarily aggregate into active nanoparticles to drive the reaction, subsequently spontaneously redispersing into their single-atom configuration once the potential is removed. Given the multi-step nature of nitrate reduction, tandem catalysis and biomimetic design draw inspiration from natural enzymes, such as nitrate reductase, to compartmentalize the catalytic workload. Bimetallic tandem systems, such as Cu – Co core-shell structures, operate via spatially separated domains: copper sites perform the initial reduction of nitrate to nitrite, which then instantly migrates to the adjacent cobalt (or cobalt oxide) interface, where it acts as an ultra-fast hydrogenator to complete the conversion to ammonia. Concurrently, to directly mimic the enzymatic active site, biomimetic inorganic complexes based on sulfur-coordinated molybdenum (oxo – MoS_x) have been developed, ensuring exceptionally high selectivity under neutral pH conditions. Finally, defect and lattice strain engineering provide additional mechanisms to physically trap reactants and tune electronic structures. The deliberate introduction of oxygen vacancies in semiconductors like TiO_{2-x} or Co₃O₄ generates cavities where the oxygen atoms of nitrate are accommodated, forcibly weakening the N–O bond. Additionally, the application of mechanical deformations—such as compressive or tensile strain—to crystalline lattices offers profound electronic control. Inducing structural strain in materials like bismuth (Bi) or generating tensile strain in ruthenium nanoclusters via subsurface oxygen insertion leads to electron delocalization, which excellently inhibits the thermodynamic competition of the HER and drives the FE toward ammonia to a near-total extent[1][2][3][25]

Chapter 3

Materials And Methods

3.1 Synthesis of Ni–Cu@NMC

Ni–Cu@NMC was synthesized using SBA-15 as a hard template through a two-step impregnation process. D-glucosamine, urea, nickel nitrate hexahydrate, and copper nitrate hydrate were dissolved in acidified deionized water and added dropwise to SBA-15 under stirring, maintaining a Ni:Cu molar ratio of 1:1. After stirring for 1 h, the material was thermally treated by heating to 100 °C for 6 h, then to 140 °C for 2 h, and finally to 160 °C for 6 h. The resulting solid was ground and pyrolyzed under an inert atmosphere at 900 °C. Finally, the silica template was removed by treatment with 6 M NaOH, followed by washing with deionized water until neutral pH and drying overnight at 70–80 °C. Two samples were prepared following the same synthesis procedure. For the first sample (Ni–Cu@NMC, mb4 with H₂SO₄), D-glucosamine, urea, nickel nitrate hexahydrate, and copper nitrate hydrate were dissolved in deionized water containing H₂SO₄ and added dropwise to SBA-15 under stirring, maintaining a Ni:Cu molar ratio of 1:1. For the second sample (Ni–Cu@NMC, mb5 without H₂SO₄), the same procedure was followed, except that H₂SO₄ was omitted from both impregnation steps. In both cases, the Ni:Cu molar ratio was maintained at 1:1 and D-glucosamine: Urea at 1:10 throughout the synthesis. For comparison, pristine nitrogen-doped mesoporous carbon (NMC) was synthesized using the same hard-template procedure in the absence of metal precursors.

3.2 Working Electrode Preparation

The preparation of the working electrode is divided in three main phases: ink formulation, ultrasonic homogenization, and thermo-assisted deposition. The following material were used for the production of the working electrode:

- AV-Carb carbon paper
- nafion solution 5%wt
- ethanol
- Cu:Ni based powder

Catalytic Ink Formulation: The preparation began with the formulation of a homogeneous catalytic ink. Specifically, 13.3 mg of the solid catalyst powder (serving as the active phase) was carefully weighed and combined with 29.63 mg of Nafion solution. These quantities were precisely calculated to achieve a uniform catalyst loading of 4 mg/cm² on a carbon paper substrate (AvCarb) measuring 4 x 1 cm. Following the coating procedure, the coated AvCarb strip was cut into four identical 1 cm² sections. Each individual square was subsequently employed as the final working electrode for the electrochemical evaluations. In this system, Nafion plays a crucial dual role it acts as a polymeric binder to ensure the mechanical adhesion of the powder to the final substrate. This mixture was subsequently dispersed in 450.86 mg of ethanol, which was selected as the optimal dispersing solvent due to its volatility and compatibility with the components **Ultrasonic Homogenization:** To ensure the disaggregation of powder agglomerates to achieve a nanometric dispersion and maximize exposed catalytic sites the resulting suspension was subjected to an ultrasonic homogenization process. Specifically, the sonication was carried out using a tip sonicator at an amplitude intensity of 35% for a continuous duration of 15 minutes. **Thermo-Assisted Deposition (Spray-Coating):** The final stage involved the transfer of the homogenized ink onto the structural substrate via a thermo-assisted spray-coating technique. The prepared ink was nebulized using an airbrush and directed onto a piece of porous carbon paper (AV-CARB), which acted as the conductive backbone of the working electrode. During the deposition process, the carbon paper substrate was placed on a hot plate maintained at a strictly controlled, constant temperature of 80 °C. This thermal control is a critical engineering parameter: the elevated temperature forces the instantaneous evaporation of the ethanol droplets immediately upon contact with the heated substrate. Rapid solvent evaporation is vital to prevent the uneven segregation and peripheral accumulation of the solid particles, a macroscopic unevenness that typically occurs during slow drying phases when the solute migrates toward the edges of the droplet. As a result, this thermo-assisted approach successfully avoided any non-uniform deposition, ensuring the formation of a highly compact, structurally homogeneous, and strongly adhesive catalytic film across the entire surface of the electrode.

3.3 Cell Setup

A classical H-type cell was employed; this cell consists in an anodic and a cathodic chamber divided by a membrane. The anodic site contains:

- counter platinum electrode
- 380 rpm magnetic stirring

while the cathodic part contains:

- the working electrode, prepared as described above
- Ag/AgCl reference electrode
- Argon injection
- 190 rpm magnetic stirring

In both chambers 35 ml of an aqueous solution 0,2M of K_2SO_4 and 0,1M of KNO_3 is present as electrolyte.

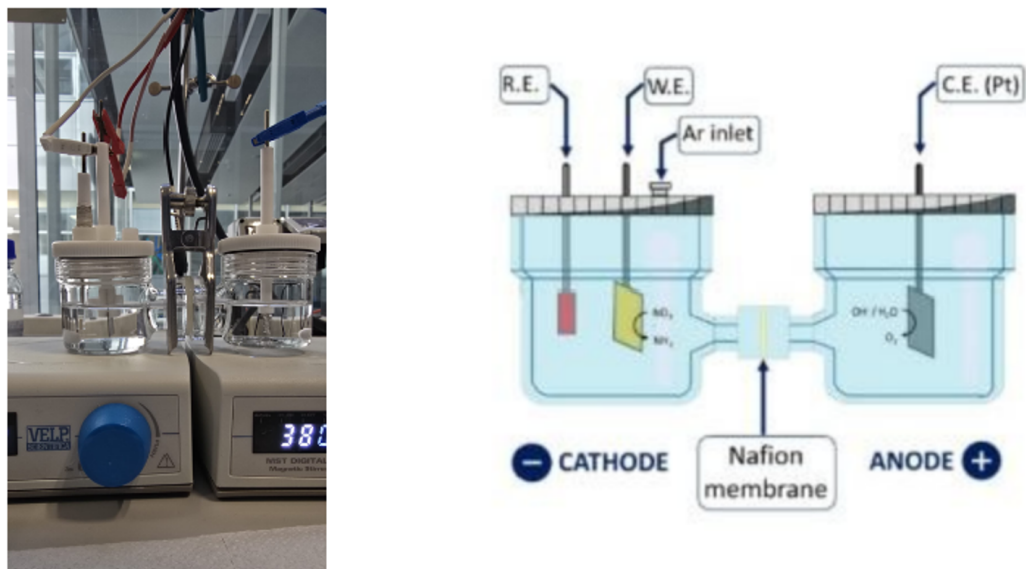


Figure 3.1: Experimental setup utilized for the electrochemical nitrate reduction tests. On the left, a photograph of the actual H-type glass cell placed on magnetic stirrers in the laboratory. On the right (taken from a Lorenzo Sibella work), a detailed schematic illustration of the two-compartment configuration, highlighting the three-electrode system (Working Electrode, W.E.; Reference Electrode, R.E.; and Platinum Counter Electrode, C.E.), the Ar-purged cathodic chamber, and the central Nafion proton-exchange membrane separating the two half-cells.

3.4 Electrochemical Characterization Protocol

To systematically evaluate the intrinsic redox behavior and the specific electrocatalytic activity of the material toward the nitrate reduction reaction, a dedicated electrochemical characterization protocol was executed. This procedure was explicitly designed to compare the catalyst's response in both the absence and presence of nitrate ions (NO_3^-). The initial characterization was performed in a nitrate-free electrolyte consisting of a 0.3 M K_2SO_4 solution to isolate the baseline response of the system. The following steps were executed:

3.4.1 OCV

The sequence began with an Open Circuit Voltage (OCV) measurement for 30 minutes. This technique monitors the resting potential of the cell without applying any external current, allowing the working electrode to thoroughly wet and reach a

stable thermodynamic equilibrium with the surrounding electrolyte.

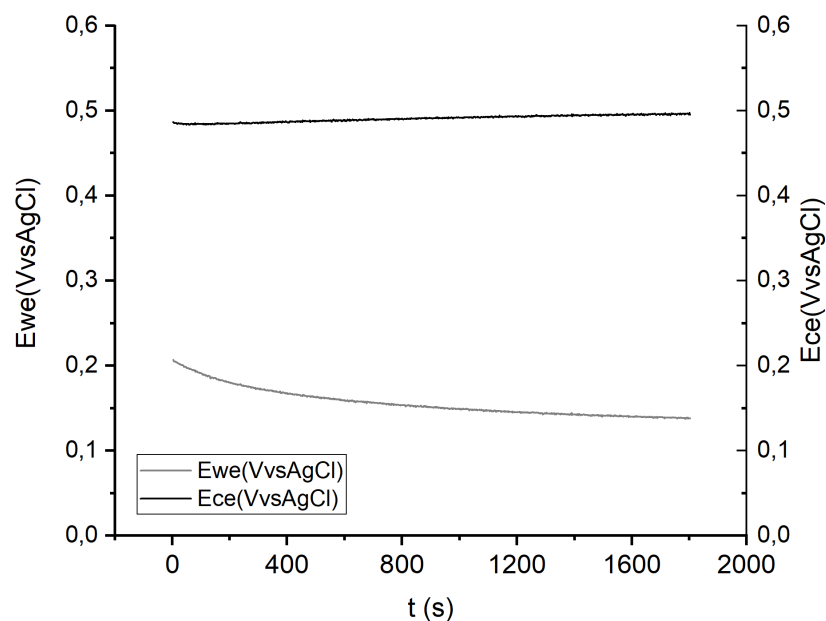


Figure 3.2: Example of an OCV curve

3.4.2 ECSA

Subsequently, the Electrochemically Active Surface Area (ECSA) was evaluated. The ECSA measurement is a fundamental diagnostic technique used to estimate the double-layer capacitance, allowing to quantify the actual physical area of the catalyst that is accessible to the electrolyte and capable of actively participating in the electron transfer. To accurately quantify the physical area of the catalyst that is accessible to the electrolyte, the ECSA was evaluated by measuring the electrochemical double-layer capacitance (C_{dl}). This assessment was conducted using Cyclic Voltammetry (CV) under strictly defined kinetic parameters to ensure the isolation of capacitive phenomena from faradaic processes. The CV sweeps were performed in a defined potential window, ranging from -0.05 V to +0.05 V vs AgCl. The selection of this restricted voltage range is because it corresponds to a strictly non-faradaic region for the bimetallic catalyst in the utilized electrolyte. Within this specific window, no electron transfer (neither oxidation nor reduction) occurs. Consequently, the recorded current response is purely capacitive, originating solely from the physical electrostatic charging and discharging of the electrical double layer at the solid-liquid interface, without the interference of any underlying chemical reactions. The CV cycles were executed at progressively increasing scan rates,

sweeping from 10 to 200 mV s^{-1} . Than in orther to evaluate the double layer capacitance (C_{dl}) value an intermediate value of potential is choosen and, for each scan rate value, the anodic and ctodic current is readed (respectivety the positive value and the negative value), it is possible to read it in the intersection between the CV curve and the line parallel to the y axis and perpendicular to the choosen potential.

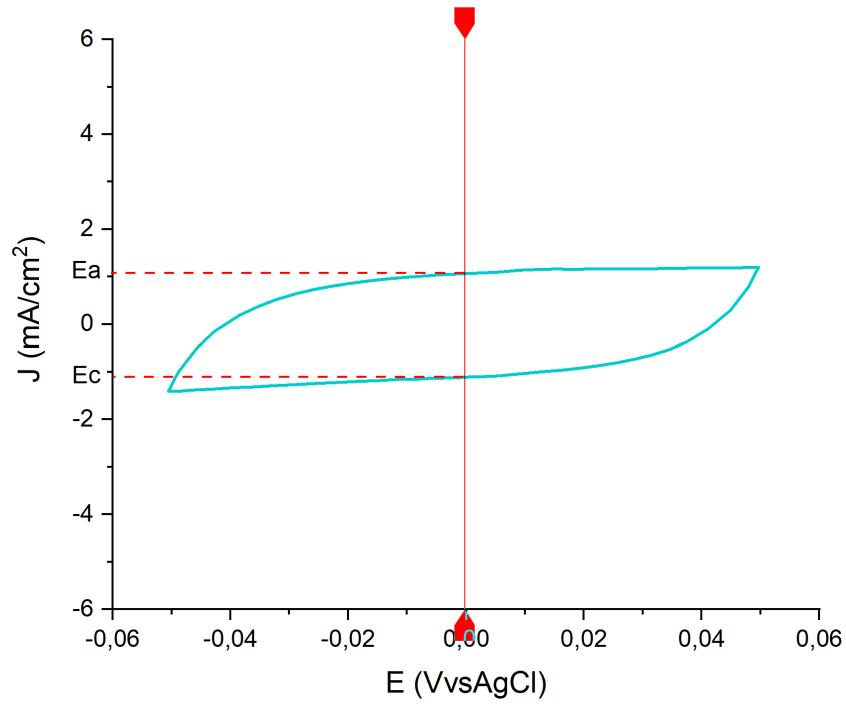


Figure 3.3: Ea and Ec value

The figure above describe how to take the correct value of Ea and Ec in orther to evaluate the C_{dl} value. Than the difference between these two values is calculated and divided by 2. This procedure is applied for each scan rate value, in this way by plotting the $(E_a - E_c)/2$ vs the scane rate curve it is possible to calculate the slope of this curve that is the actual value of the C_{dl} .

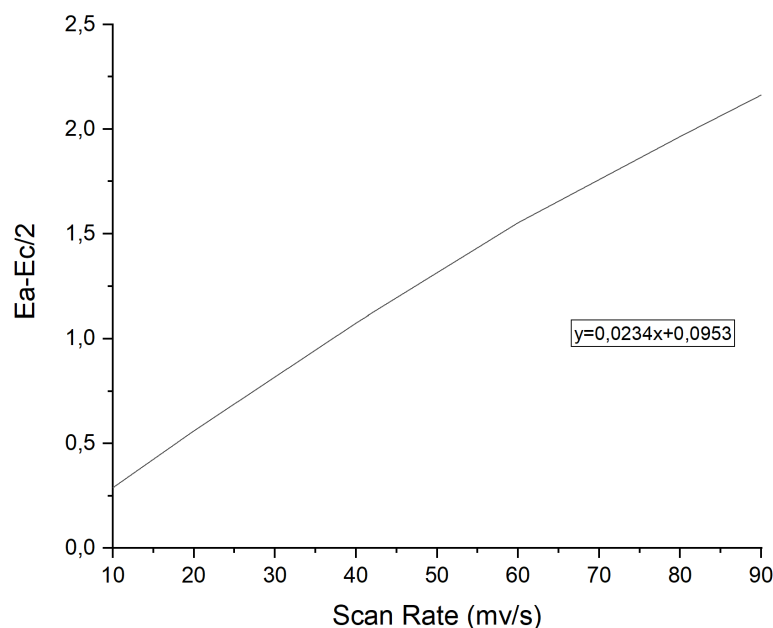


Figure 3.4: Example of a $E_a-E_c/2$ vs Scan rate curve

Finally in order to evaluate the Electrochemically Active Surface Area the C_{dl} must be divided by the specific capacitance of the ideal and perfectly smooth material (C_s , a standard value found in the literature). Then, a 5 mL baseline sample of electrolyte was extracted from the cell to serve as a blank reference ("point zero") for the subsequent spectrophotometric analyses.

3.4.3 Full Cyclic Voltammetry

A full Cyclic Voltammetry (CV) was then conducted, encompassing both the anodic (oxidation) and cathodic (reduction) regimes. Specifically, the CV was performed for 5 cycles over a potential window ranging from 0 to -2 V at a scan rate of 10 mV/s. This complete CV sweeping is essential to map the intrinsic surface redox transitions of the metallic species without the interference of the main faradaic reduction process.

3.4.4 LSV

To conclude this phase, a Linear Sweep Voltammetry (LSV) was recorded to establish the baseline current-potential profile of the blank system, applying a continuous potential ramp from 0 to -2 V at a slower scan rate of 5 mV/s.

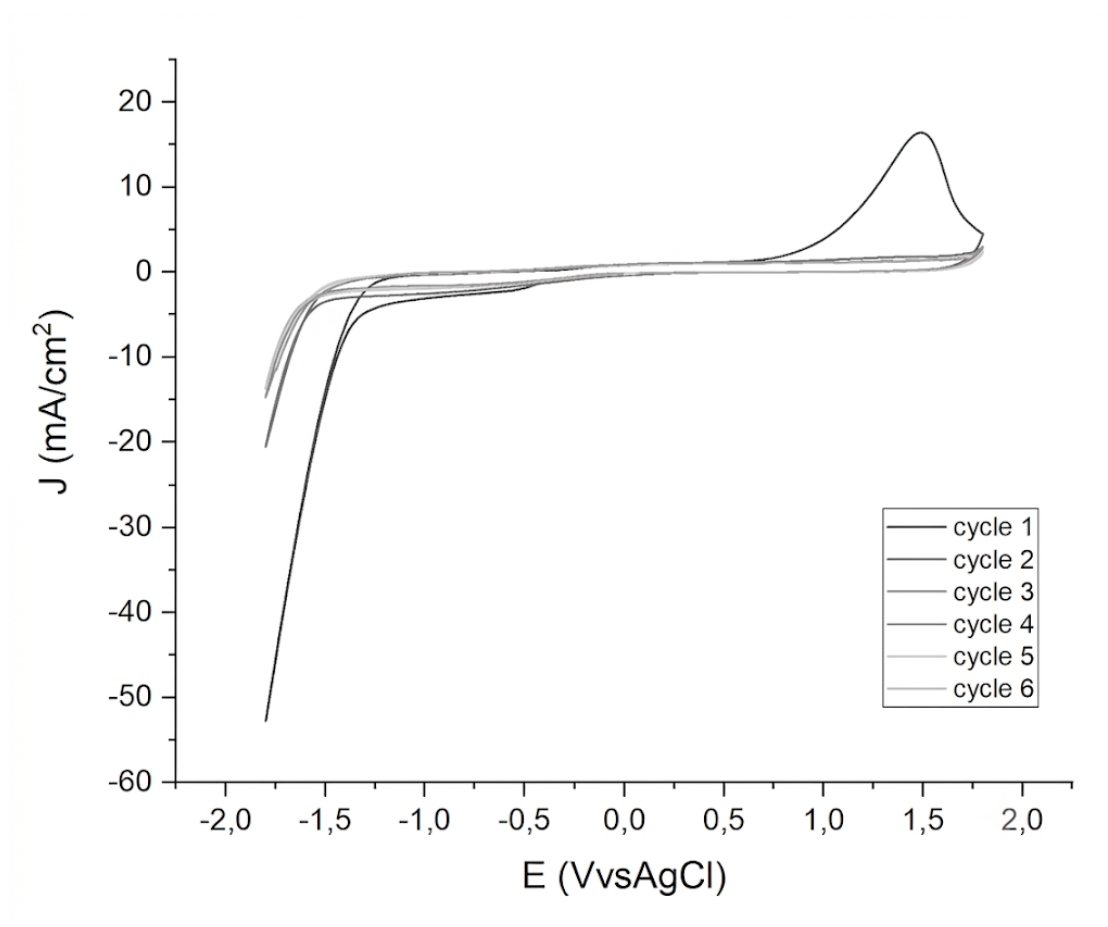


Figure 3.5: Example of a Complete CV curve

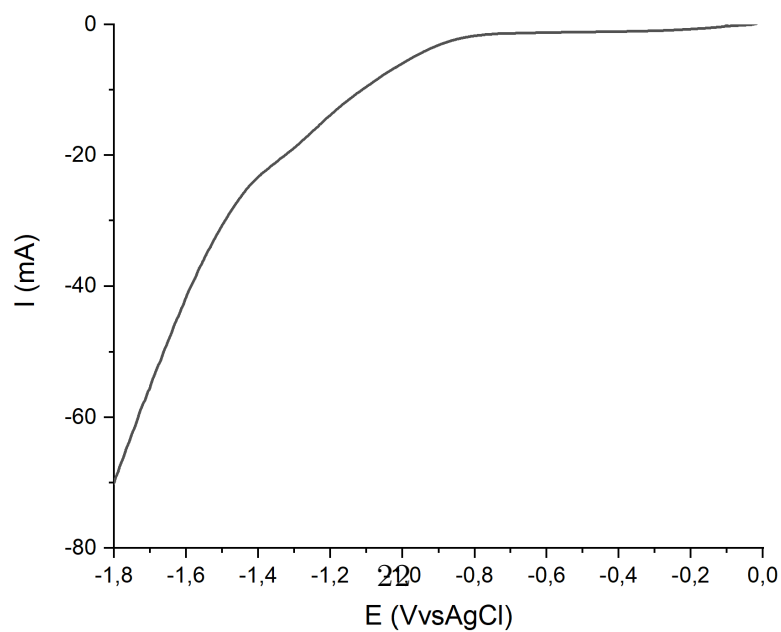


Figure 3.6: Example of an LSV curve

Subsequently, the catalytic activity was assessed by introducing the target reactant. The blank solution was replaced with a nitrate-rich electrolyte composed of 0.2 M K_2SO_4 and 0.1 M KNO_3 . The cell was allowed to restabilize under an OCV for 10 minutes, after which a new LSV was performed. This step allows for a direct comparison with the blank LSV, highlighting the onset potential shift and the preliminary catalytic response triggered by the presence of nitrates. To conduct the bulk electrolysis and evaluate the steady-state performance, the cell was drained and replenished with a fresh solution of the identical nitrate-containing electrolyte (0.2 M K_2SO_4 and 0.1 M KNO_3). The primary objective of the electrochemical characterization was to evaluate and compare the catalytic activity of the material both in the presence and absence of the target reactant (NO_3^-).

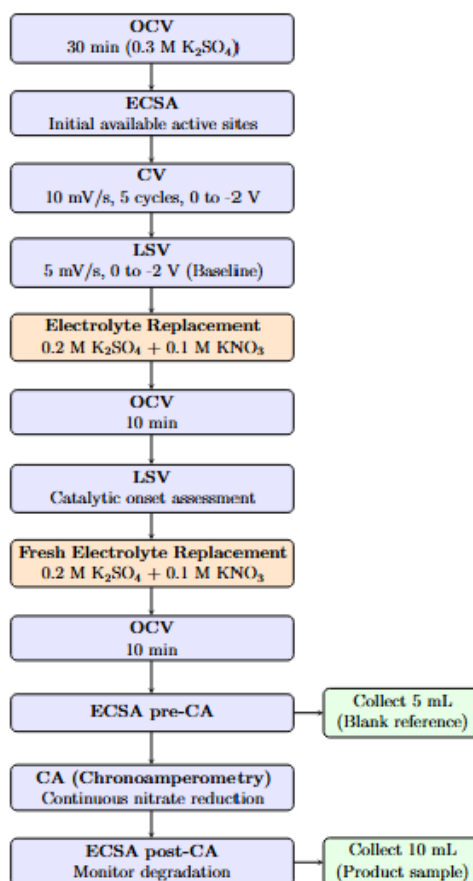


Figure 3.7: Comprehensive lowchart of the electrochemical characterization testing protocol

3.4.5 Evaluation of Electrocatalytic Activity

To evaluate the intrinsic electrocatalytic activity toward the nitrate reduction reaction, the linear sweep voltammetry (LSV) profile obtained in the blank electrolyte was directly compared with the LSV recorded in the nitrate-containing solution. Beyond the assessment of the onset potential and current density shifts, the reaction kinetics under both conditions were quantitatively analyzed by extracting and comparing their respective Tafel slopes. The Tafel plots were constructed by converting the LSV data, specifically by plotting the applied potential (E) on the x-axis against the base-10 logarithm of the absolute current density ($\log |j|$) on the y-axis. The Tafel slope for each system was then calculated by performing a linear regression fit strictly within the domain of the curve exhibiting the most pronounced linear behavior, which corresponds to the activation-controlled kinetic regime of the catalytic process. The initial low-current portion of the curve was deliberately excluded to avoid inaccuracies from capacitive contributions and signal instability, while the high-current region was omitted to prevent interference from mass transport limitations, ohmic drops, and gas bubble formation. While similar potential ranges were generally targeted for all samples, the exact fitting intervals were allowed to vary slightly between different materials to ensure the optimal linear segment was accurately captured for each specific catalyst. For clarity, the selected linear fit lines are explicitly shown on the plotted curves in the corresponding figures. Fundamentally, the Tafel slope indicates the additional potential required to increase the current by one order of magnitude; therefore, a lower slope signifies more favorable reaction kinetics. However, it is important to specify that the values reported in this study must be considered as apparent Tafel slopes, given that the formal overpotential was not explicitly calculated and no iR drop (the ohmic voltage drop caused by the electrical resistance of the electrolyte and the setup) correction was applied to the experimental data.

3.5 Electrochemical Evaluation Protocol

The electrochemical evaluation was conducted following a, multi-step protocol designed to activate the catalyst, establish baseline metrics, and quantify its performance during the target reduction reaction. The sequence of techniques is the following:

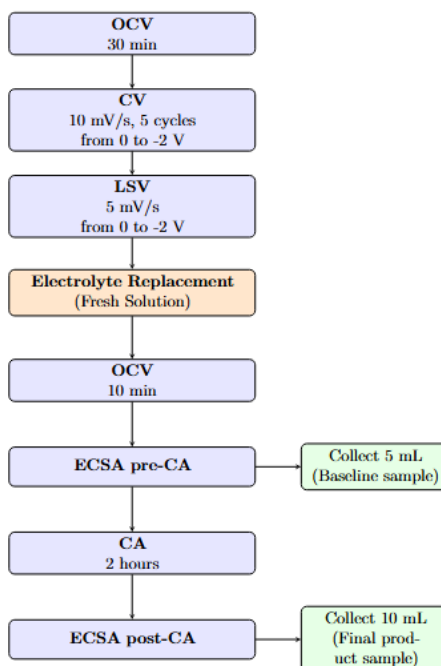


Figure 3.8: Detailed flowchart of the electrochemical evaluation protocol

The testing sequence commenced with an OCV measurement for 30 minutes.

3.5.1 Reduction CV

Once stabilized, the electrode was subjected to CV to perform an in-situ reduction. Specifically, the CV was conducted for 5 cycles over a potential window ranging from 0 to -2 V at a scan rate of 10 mV/s. This sweeping process is crucial to strip away native oxides from the Cu-Ni active sites, thereby fully activating the metallic catalyst surface.

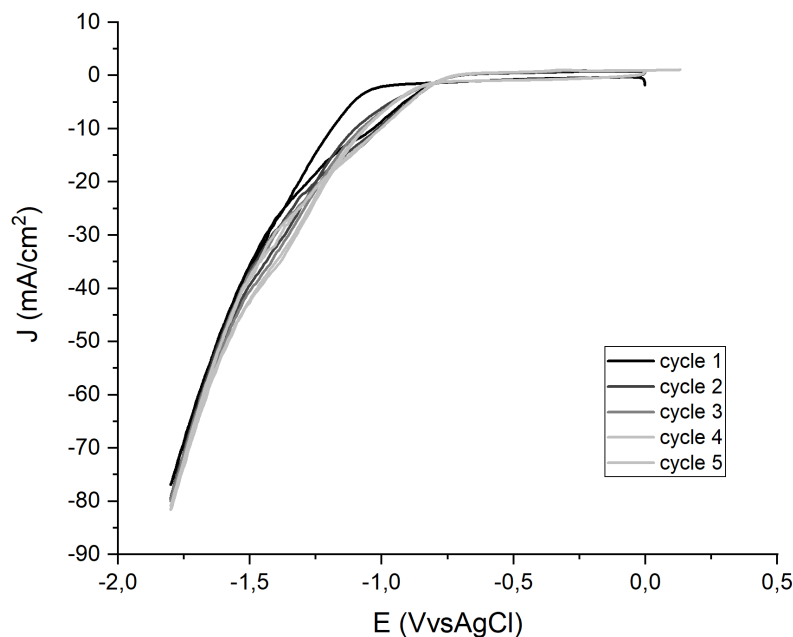


Figure 3.9: Example of a CV curve

Following this activation, a LSV was performed to map the baseline catalytic activity. To guarantee a pristine environment for the main performance evaluation, the exhausted electrolyte was completely drained from the cell and replaced with a fresh solution. A shorter OCV step of 10 minutes was then executed to re-establish thermodynamic equilibrium in the newly introduced environment. Subsequently, the ECSA was evaluated.

3.5.2 Chronoamperometry

The core of the electrochemical performance evaluation consisted of a Chronoamperometry (CA) test. During CA, a constant potential is applied to the working electrode over a prolonged period while the current is continuously monitored. This bulk technique drives the targeted reduction reaction under steady-state conditions for a continuous duration of 2 hours, facilitating the continuous accumulation of the desired products (such as ammonia).

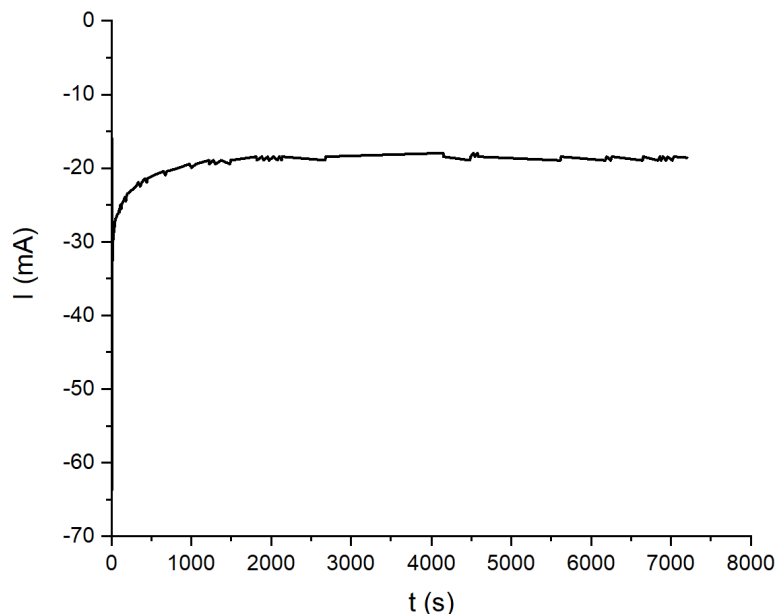


Figure 3.10: example of a CA curve

Upon completion of the CA test, a final ECSA measurement (denoted as post-CA) was conducted. Comparing the pre-CA and post-CA ECSA values provides critical insights into the structural integrity of the material, making it possible to assess any potential morphological degradation, catalyst poisoning, or loss of active sites that may have occurred during the harsh reaction conditions. Finally, a 10 mL sample of the final enriched electrolyte was collected from the cell. This sample contains the synthesized products and is strictly necessary for downstream chemical quantification and the calculation of the overall FE%.

3.6 Product Quantification Methods

Following the electrochemical evaluation, the precisely collected electrolyte samples were analyzed to quantify the synthesized products. Prior to any colorimetric analysis, a crucial sample preparation step was performed: the pH of all extracted aliquots was meticulously adjusted to a neutral window, strictly maintained between 5 and 8. This adjustment is essential to ensure the optimal chemical reactivity and stability of the colorimetric reagents used in the subsequent assays. The quantification of the target products was carried out using a UV-Vis spectrophotometer, relying on two distinct colorimetric protocols:

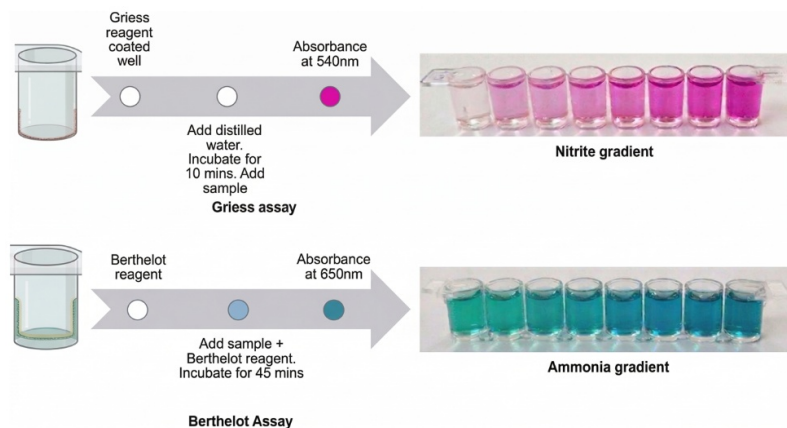


Figure 3.11: Greiss and Berthelot assay

The concentration of the synthesized ammonia was determined utilizing the Berthelot (indophenol blue) method. To accurately track the reaction progress and isolate the catalytically produced ammonia from any background noise, the analysis was systematically conducted on four specific cell aliquots: the anode and cathode electrolytes collected before the bulk electrolysis (pre-CA), and their respective solutions collected after the two-hour test (post-CA). For the analytical procedure, 2 mL of each pH-adjusted sample was mixed with the Berthelot reagents. The resulting solution was then incubated for 45 minutes to allow for the complete development of the characteristic blue-green indophenol complex. After the incubation period, the optical absorbance of the liquid was measured at a specific wavelength of 650 nm using the UV-Vis spectrophotometer. The exact ammonia concentration was subsequently calculated by interpolating the recorded absorbance values against a pre-established standard calibration curve. Alongside the main product, the concentration of nitrite species was evaluated using the standard Griess assay. For this colorimetric test, 1 mL of the targeted sample was diluted with 2 mL of distilled water and subsequently mixed with 1 mL of the Griess reagent. The mixture was allowed to incubate for a shorter duration of 10 minutes, leading to the formation of a distinct pink azo dye, whose color intensity is directly proportional to the nitrite concentration. The absorbance of the treated sample was then recorded at 540 nm via UV-Vis spectrophotometry, and the precise nitrite concentration was similarly derived using its corresponding specific calibration curve.

NH ₃	
ppm	abs
0	0,122
0,1	0,159
0,2	0,274
0,4	0,439
0,6	0,612
0,8	0,799
1	0,952
1,5	1,374
2	1,786

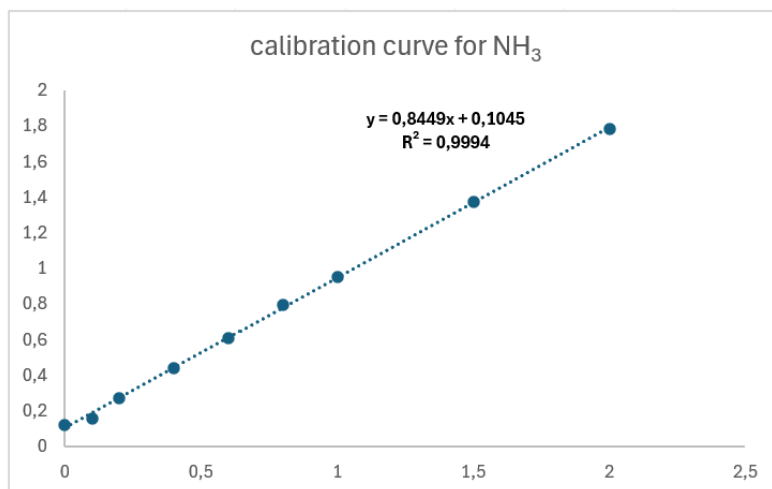


Figure 3.12: Calibration curve for ammonia (NH₃) quantification. The linear regression was established by measuring the UV-Vis absorbance of standard solutions with precisely known concentrations.

NO ₂ ⁻	
ppm	abs
0	0,04
0,1	0,061
0,25	0,093
0,5	0,149
1	0,255
2,5	0,571
5	1,084

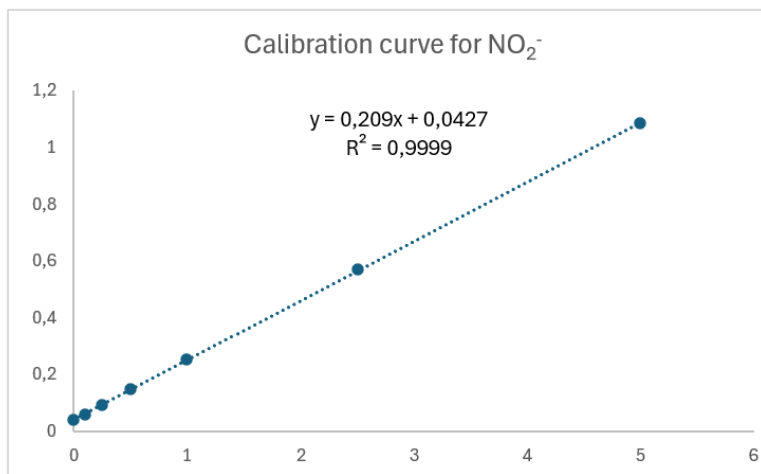


Figure 3.13: Calibration curve for nitrite (NO₂⁻) quantification. The linear regression was established by measuring the UV-Vis absorbance of standard solutions with precisely known concentrations.

3.6.1 Calculation Methodology for Faradaic Efficiency(FE%)

The absolute mass of the products was initially determined by multiplying the concentration obtained via UV-Vis spectrophotometry by the specific electrolyte volume present in the cell (e.g., 25 mL for the pre-CA baseline samples and 20

mL for the post-CA final samples). The resulting mass (in mg) was subsequently converted into moles. The FE%, which represents the selectivity of the catalyst in utilizing the transferred electrons for the desired reaction, was calculated using the following general equation:

$$FE(\%) = \frac{n \cdot F \cdot N_{product}}{Q} \times 100$$

Where:

- $N_{product}$ represents the quantified moles of the specific product. n is the number of transferred electrons required for the specific reduction pathway ($n = 8$ for the reduction of nitrate to NH_3 , and $n = 2$ for the reduction to NO_2^-).
- F is the Faraday constant (96485 C/mol).
- Q is the total accumulated charge (in Coulombs), calculated by mathematically integrating the corresponding CA current-time curve over the 2-hour operational period ($Q = \int I dt$).

3.7 Performance Parameters

To comprehensively evaluate the electrocatalytic performance of the synthesized materials towards the NO_3RR to ammonia, two primary figures of merit were investigated: FE% and Ammonia Yield Rate. These two metrics are the most commonly utilized parameters in current literature, as they provide a complete assessment of both the reaction selectivity and the absolute production capability of the catalyst under specific operational conditions.

3.7.1 Calculation Methodology for Yield Rate

Furthermore, the production Yield rate, normalized by the geometric area of the electrode and the total reaction time, was calculated according to the following equation:

$$Yield = \frac{m_{product}}{t \cdot A}$$

Where:

- $m_{product}$ is the total mass of the synthesized product (ammonia or nitrite) present in the electrolyte, expressed in milligrams (mg).
- t is the total duration of the steady-state bulk electrolysis (Chronoamperometry), expressed in hours (h).

- A is the geometric surface area of the working electrode immersed in the solution, expressed in square centimeters (cm^2).

Chapter 4

Results and discussion

4.1 Physicochemical Characterization of the Catalysts

The experimental work was conducted using a series of externally supplied (by Prof. Juqin and Phd student Mitra) bimetallic Copper-Nickel (Cu-Ni) catalysts supported on Mesoporous Carbon Nitride (MCN). The underlying carbon nitride support was synthesized using an SBA-15 silica template impregnated with D-glucosamine and urea. To evaluate the influence of different precursor environments on the final material properties, two distinct batches were provided and investigated:

- mb4 (prepared with the addition of sulfuric acid, H₂SO₄)
- mb5 (prepared without sulfuric acid).

Prior to the electrochemical evaluations, the supplied materials were analyzed at two different chemical functionalization stages: before acid treatment (denoted as -NaOH) and after an acid treatment (denoted as -AT).

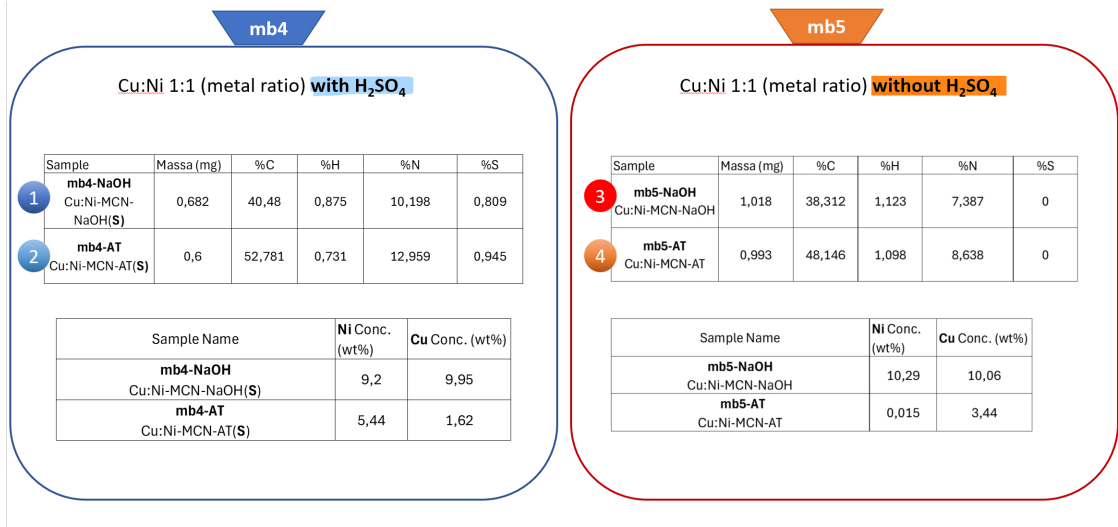


Figure 4.1: Enter Caption

A key distinguishing feature between the two batches is the sulfur content. The deliberate introduction of H_2SO_4 during the initial preparation of the mb4 batch resulted in a stable sulfur doping (ranging from 0.80 wt% to 0.95 wt%), which remained embedded in the support framework even after the severe final acid treatment. Conversely, as expected, the mb5 samples exhibited a complete absence of sulfur (0 wt%). The exact mass fractions of the active metals were quantified to evaluate the actual Cu and Ni loadings compared to the initial nominal 1:1 metallic ratio. While both catalyst batches exhibited a well-balanced bimetallic composition (around 9 to 10 wt% for both metals) before the final acid treatment, the elemental analysis revealed a critical structural difference after it:

- Impact on mb5 (Sulfur-free): The final acid treatment on this batch induced severe and detrimental metal leaching. The acidic environment nearly depleted the active sites, stripping away almost all the nickel (which plummeted to a negligible 0.015 wt%) and significantly reducing the copper content to 3.44 wt%.
- Impact on mb4 (Sulfur-doped): The sulfuric acid-treated batch demonstrated a noticeably higher resistance to acidic degradation. Despite the harsh final wash, the material retained a much more robust metal loading, successfully preserving 5.44 wt% of nickel and 1.62 wt% of copper.

These compositional profiles strongly suggest that the incorporation of sulfur species within the mb4 framework plays a vital role in modifying the chemical environment. Sulfur dopant facilitates water adsorption and dissociation and the heterogeneous interface is beneficial for hydrogen adsorption[26][27].

4.1.1 X-ray Diffraction (XRD)

The X-ray diffraction (XRD) analysis confirms that copper and nickel have successfully combined to form a single, uniform alloy. The bimetallic sample shows a series of peaks whose positions fall exactly between those of pure nickel and pure copper. This intermediate shift happens because adding larger copper atoms into the nickel framework causes a slight expansion of the overall crystal structure. Furthermore, the analysis shows no isolated peaks corresponding to separate, unmixed copper or nickel. This complete absence of individual metal phases is strong evidence that the two elements have perfectly and homogeneously merged within the carbon framework.

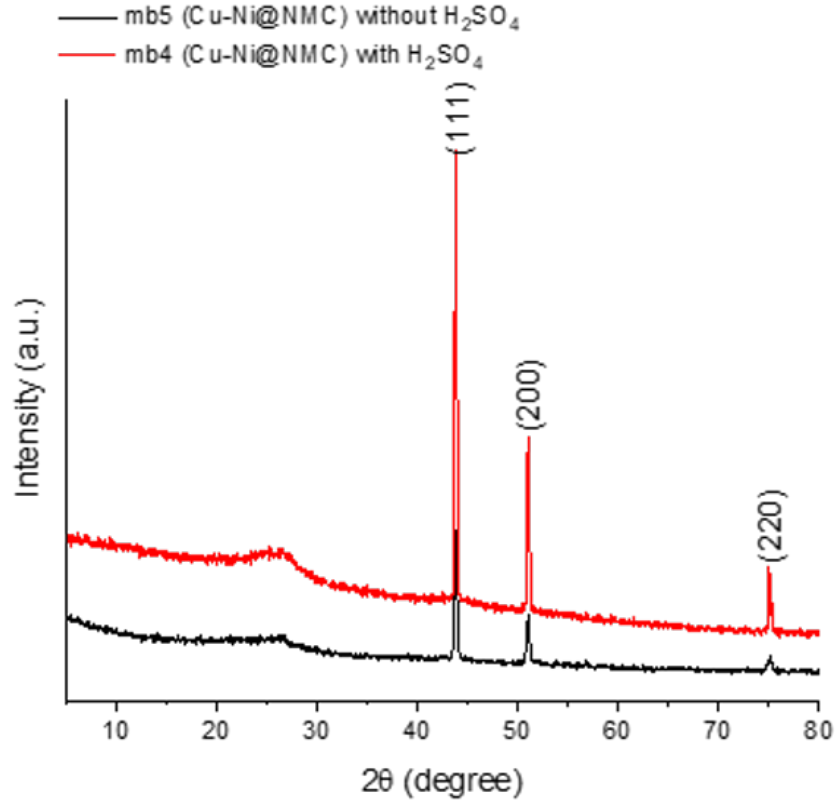


Figure 4.2: XRD analysis

4.1.2 Thermogravimetric Analysis (TGA)

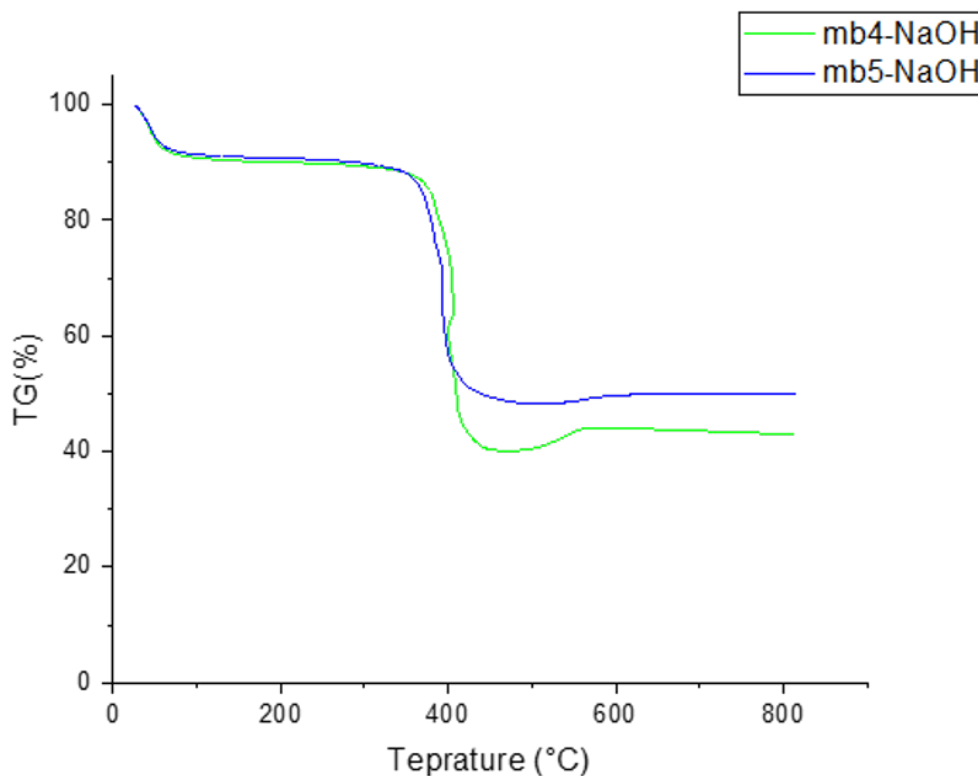


Figure 4.3: Thermogravimetric analysis (TGA) up to 800 °C under an air atmosphere

The TGA profiles of the samples exhibit an initial, minor weight loss below 150 °C, which can be entirely ascribed to the desorption of physically adsorbed water and residual surface moisture. Following this initial phase, the materials demonstrate remarkable thermal stability, maintaining a constant mass with no structural degradation observed up to approximately 400 °C.

4.2 Electrochemical Behavior and Nitrate Activity

Before evaluating the bulk ammonia production yields, it is fundamental to investigate the intrinsic electrochemical behavior of the prepared CuNi/MCN electrodes

and verify their specific activation toward the NO_3RR . This section details the preliminary electrochemical characterization conducted through CV and LSV. The analysis aims to identify the characteristic redox transitions of the bimetallic active sites in a pristine, reactant-free electrolyte, and subsequently demonstrate the catalytic onset shift upon the introduction of nitrate species into the system.

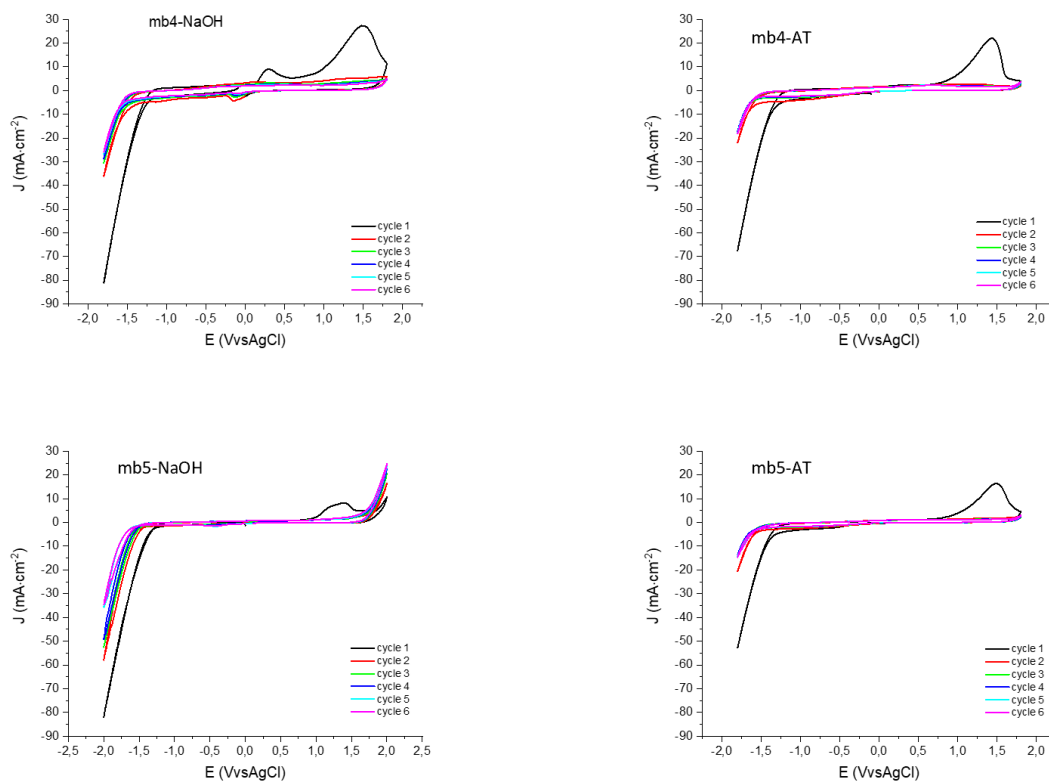


Figure 4.4: complete CV without NO_3^-

To evaluate the baseline electrochemical characteristics of the prepared Cu-Ni/MCN catalysts, full-range Cyclic Voltammetry (CV) was performed in a pristine 0.3 M K_2SO_4 aqueous solution. Figure 4.1 displays the resulting voltammograms for the four catalyst variants (mb4-NaOH, mb4-AT, mb5-NaOH, and mb5-AT) over six continuous cycles. The voltammograms reveal a strikingly distinct electrochemical behavior during the initial potential sweep (Cycle 1). Across all samples, the first cycle is characterized by a prominent and broad anodic peak in the highly positive potential region, approximately between +1.0 V and +1.5 V vs AgCl. Concurrently, a severe capacitive current is recorded in the cathodic sweep. This massive first-cycle response is highly irreversible. It can be attributed to the initial electro-oxidation and stripping of unstable native oxides formed on the bimetallic

surface during exposure to air, along with the irreversible oxidation of adventitious carbon or surface functional groups on the support matrix. Following this initial activation phase, a drastic stabilization occurs. From the second cycle onwards (Cycles 2 to 6), the large anodic feature completely vanishes. The voltammograms rapidly converge into a highly reproducible, narrow, and steady-state profile. This immediate stabilization confirms that the in-situ electrochemical cleaning was successful, leaving behind a structurally robust and electrochemically stable active surface for the subsequent reduction tests. Finally, in the highly negative potential regime (beyond -1.5 V vs AgCl), all samples exhibit a sharp, exponential increase in cathodic current density. Since this test is conducted in a nitrate-free environment, this faradaic current is most probably attributed to the onset of the HER.

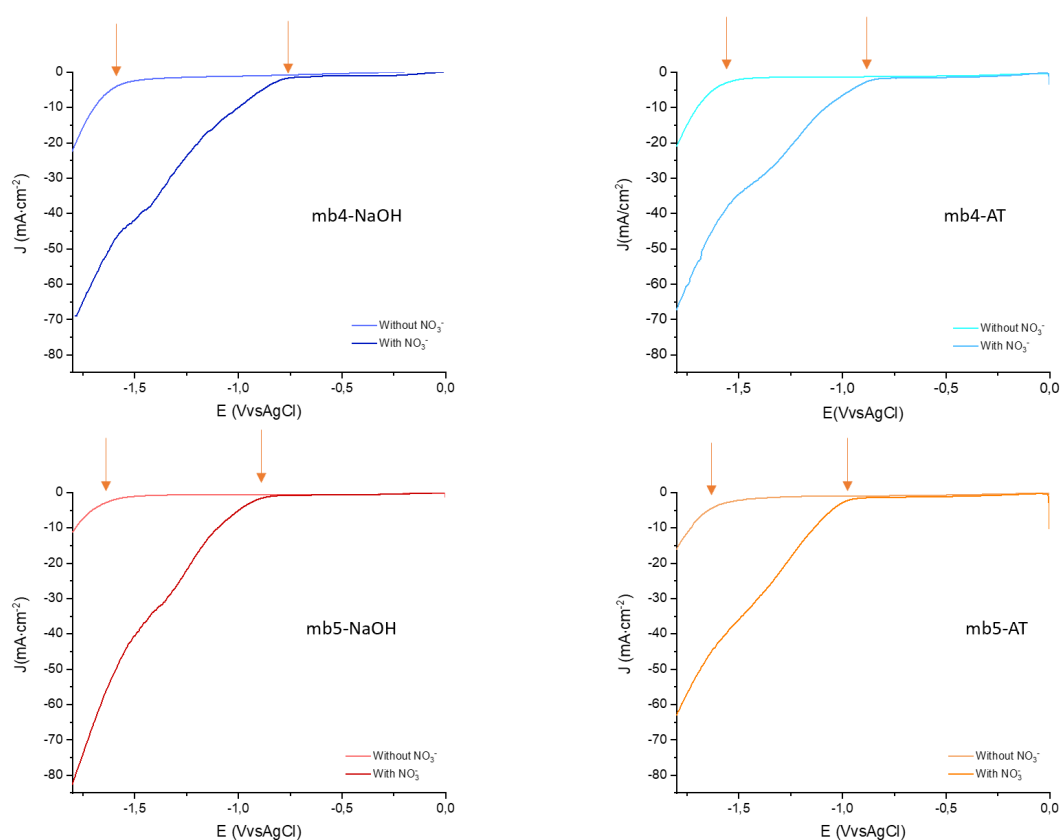


Figure 4.5: Comparison of the LSV profiles for the four synthesized catalysts recorded in the blank electrolyte versus the nitrate-containing solution. The orange arrows are used to highlight the onset potential for each specific catalytic system.

Building upon the baseline stability established through cyclic voltammetry, LSV was employed to definitively evaluate the catalytic activation toward the

Nitrate Reduction Reaction (NO₃-RR). Figure 4.2 illustrates the LSV polarization curves for the four catalyst variants. The primary focus of this analysis is the critical difference in the onset potential—defined as the exact point where the curve breaks away from the flat baseline and starts to sharply descend, indicating a surge in cathodic current—between the blank and the reactant-rich environments. As observed in the light-colored curves, when the test is conducted in the absence of nitrates, the current remains essentially zero across a wide voltage window. The curve only begins its steep downward descent at highly negative potentials (beyond -1.4 V vs AgCl). This late onset represents the thermodynamic activation of water splitting, where the Hydrogen Evolution Reaction (HER) becomes the dominant process. However, a dramatic shift in the electrocatalytic behavior is triggered upon the introduction of nitrates into the solution (dark lines). The defining feature of these graphs is the massive positive shift in the onset potential. In the presence of the reactant, the dark curve begins to drop and clearly separates from the flat baseline much earlier, typically around -0.7 V to -0.8 V vs AgCl. This pronounced difference between the two onset points is the fundamental proof of the material's specific catalytic activity. It visually and physically demonstrates that the Cu-Ni bimetallic active sites successfully trigger the electroreduction of nitrate species at significantly lower overpotentials, effectively initiating the NO₃-RR well before the competing hydrogen evolution can even begin. Following this early onset, the nitrate-rich curves exhibit a massive and continuous descent, reaching remarkable current densities (up to -60 to -80 mA/cm²) in the highly negative regime, thereby confirming the robust capability of the electrodes to sustain high reaction rates for bulk electrolysis.

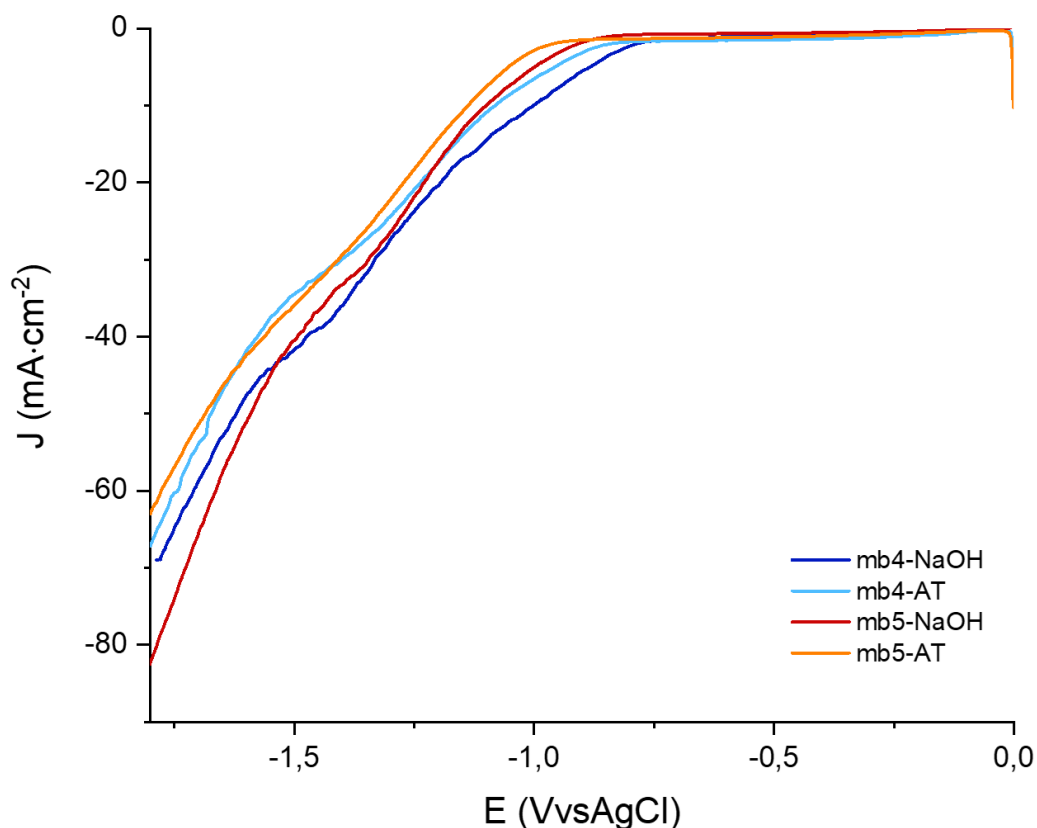


Figure 4.6: Direct comparison of the LSV profiles for the four synthesized materials. The curves were recorded in the presence of nitrates (NO_3^-) to evaluate and compare their relative electrocatalytic activity toward the nitrate reduction reaction.

Figure 4.6 shows a direct comparison of the LSV profiles and it's possible to observe that all four synthesized materials exhibit an overall comparable electrocatalytic behavior towards the nitrate reduction reaction. However the mb4-NaOH sample demonstrates a slightly superior performance. Its polarization curve exhibits a marginal shift towards less negative potentials, indicating a slightly earlier onset of the catalytic reduction and reaching higher cathodic current densities at lower overpotentials compared to the other tested catalysts. While all samples exhibit a consistent catalytic activation characterized by an early onset, the specific profile of the current density descent provides critical insights into the reaction dynamics. As the applied cathodic voltage increases, the reduction current steadily rises. To maximize the FE% and the ultimate ammonia yield, it is paramount to identify the exact potential where the target nitrate reduction rate is at its highest, just before the parasitic Hydrogen Evolution Reaction (HER) inevitably takes over the

system. Analyzing the slope of these polarization curves, a critical kinetic region is observed around -1.3 V vs AgCl. At this specific potential, the electrodes achieve a substantial and sustained cathodic current density (clustering between -25 and -35 mA/cm², with mb5-NaOH showing the most aggressive current response). This region represents a highly active kinetic regime for the target reaction. As the potential is pushed further into the negative direction (particularly beyond -1.4 V and approaching -1.8 V), the curves steepen dramatically. This late, massive surge in current is primarily attributed to the overwhelming thermodynamic onset of bulk water splitting, meaning the extra electrons would be wasted on generating hydrogen gas rather than converting nitrates to ammonia. Therefore, the region around -1.3 V vs AgCl emerges as the optimal electrochemical sweet spot. It provides the maximum specific activity for the NO₃RR while effectively mitigating the competitive and energy-wasting hydrogen evolution. Consequently, this exact voltage was specifically selected as the fixed operational parameter to drive the subsequent steady-state CA bulk electrolysis tests across all the characterized materials.

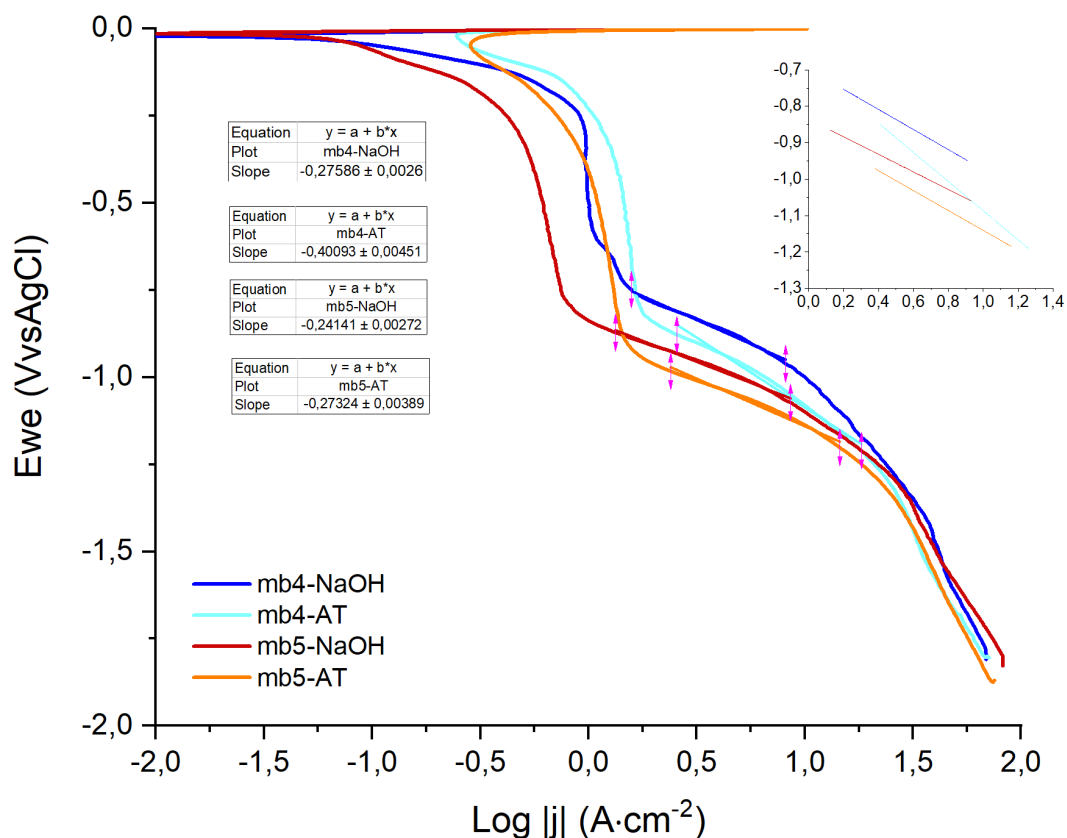


Figure 4.7: Tafel plots (potential versus the logarithm of current density) for the mb4-NaOH, mb4-AT, mb5-NaOH, and mb5-AT electrocatalysts evaluated in a nitrate-enriched electrolyte. The main graph shows the experimental polarization curves, where the vertical pink arrows denote the intermediate linear region selected for the data fitting. The inset in the upper right corner displays an enlarged view of the linear fitting lines. The embedded tables report the calculated Tafel slope value for each corresponding material

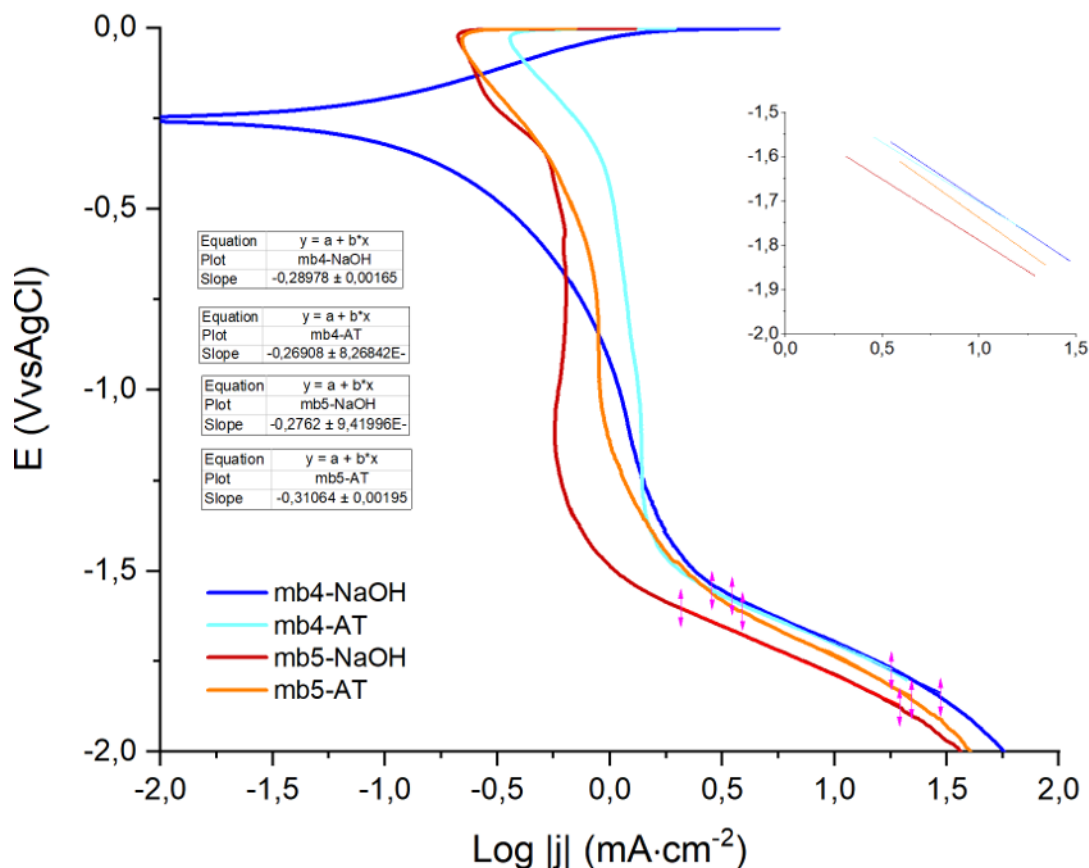


Figure 4.8: Tafel plots (potential versus the logarithm of current density) for the 4 electrocatalysts evaluated in a nitrate-free electrolyte. The main plot displays the experimental polarization curves, with vertical pink markers indicating the specific potential boundaries selected for the linear fitting. The top-right inset provides a magnified view of the resulting linear regression lines. The embedded tables report the calculated Tafel slope value for each corresponding material

Figure 4.7 presents apparent the Tafel plots (potential E vs. $\log |j|$) for four electrocatalysts evaluated in a nitrate-containing electrolyte. The polarization curves exhibit a pronounced reduction wave originating near 0.0 V, which is characteristic of the nitrate reduction reaction (NO_3RR). Tafel slopes, extracted from the intermediate linear regime (approximately -0.7 V to -1.2 V), are calculated as -0.276, -0.401, -0.241, and -0.273 V/dec for mb4-NaOH, mb4-AT, mb5-NaOH, and mb5-AT, respectively. The mb5-NaOH sample demonstrates the lowest Tafel slope, indicating the most favorable NO_3RR kinetics among the tested materials. A comparative analysis of the polarization curves demonstrates a distinct shift in both

the reaction onset and the underlying electrochemical mechanisms upon nitrate addition. In the nitrate-free electrolyte, the cathodic process is exclusively governed by the HER, characterized by a delayed onset potential (e.g., -0.75 V vs. Ag/AgCl for mb4-NaOH) and smooth, continuous current profiles. Consequently, the linear Tafel region is localized in the deep cathodic regime (-1.5 V to -1.9 V vs. Ag/AgCl) to evaluate background HER kinetics. On the other side, the nitrate-enriched system exhibits an immediate current response with an onset potential near 0.0 V vs. Ag/AgCl, followed by a prominent reduction wave between -0.5 V and -1.0 V vs. Ag/AgCl. This well-defined shoulder confirms that the electrocatalysts actively drive the nitrate reduction reaction (NO_3^- reduction) before the onset of massive hydrogen evolution. Accordingly, the kinetically controlled Tafel regime shifts to a significantly lower overpotential window (-0.7 V to -1.2 V vs. Ag/AgCl), directly capturing the specific kinetics of the NO_3RR process rather than the water-splitting background. The electrochemical evaluation reveals a nuanced catalytic behavior when comparing the intrinsic kinetics to the global performance. From a kinetic perspective, Tafel analysis demonstrates that the mb5-NaOH catalyst possesses the most favorable reaction kinetics for nitrate reduction, exhibiting the lowest Tafel slope (241 mV dec^{-1}). This indicates a highly efficient electron transfer process at low-to-intermediate overpotentials. However, the overall polarization (LSV) curves highlight the superior global activity of the mb4-NaOH material. Notably, at highly negative potentials, a distinct crossover (inversion) between the mb4-NaOH and mb5-NaOH curves occurs. Beyond this potential threshold, mb4-NaOH overtakes mb5-NaOH and is able to sustain significantly higher absolute current densities, demonstrating a greater overall catalytic capacity when operating under strong cathodic driving forces.

4.3 Active Surface Area Evolution Before Chronoamperometry

To thoroughly assess the morphological stability and the evolution of the catalyst-electrolyte interface during the bulk nitrate reduction, the ECSA was evaluated immediately before and after the 2-hour CA test. The ECSA is directly proportional to the electrochemical double-layer capacitance (C_{dl}), which was extracted by performing CV at varying scan rates (from 10 to 200 mV s^{-1}) in a strictly non-faradaic potential window (-0.05 to +0.05 V vs AgCl).

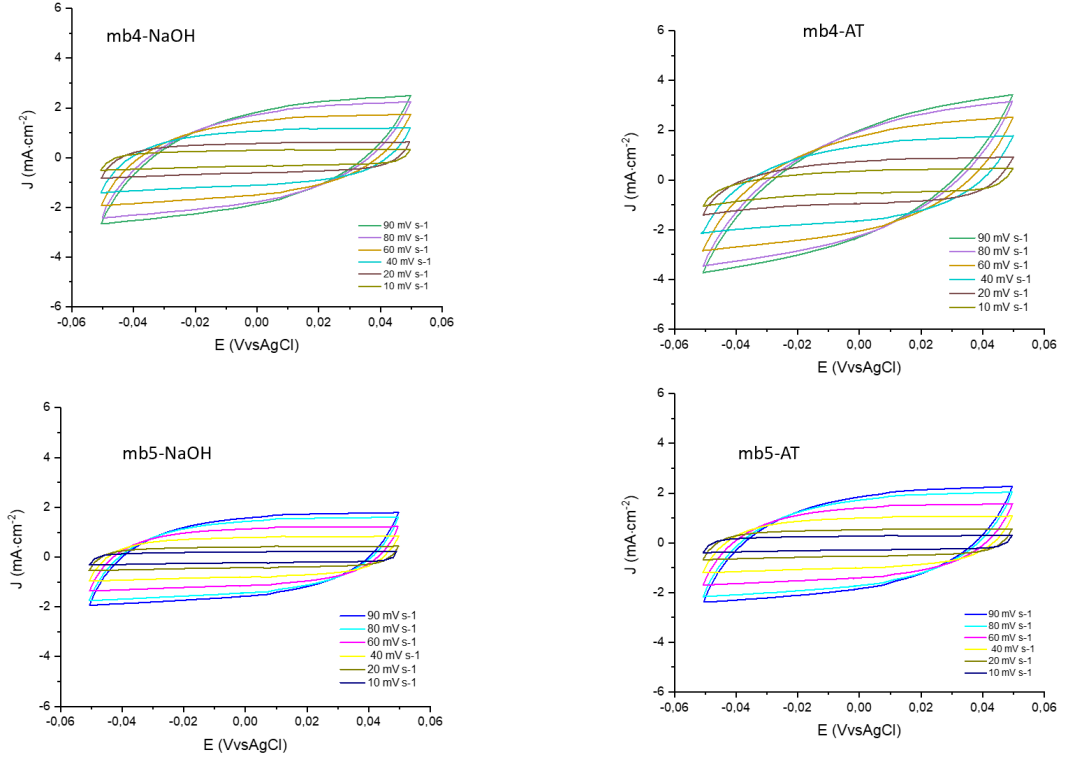


Figure 4.9: ECSA pre-CA

The C_{dl} value for the ecsa per are the following:

Material	C_{dl} pre-CA (-1.3 V)
mb4-NaOH	0.0182
mb4-AT	0.0252
mb5-NaOH	0.0166
mb5-AT	0.0190

Table 4.1: Double-layer capacitance (C_{dl}) values measured prior to bulk electrolysis at -1.3 V.

By looking at the C_{dl} values is possible to observe a consistent structure-activity trends across the tested materials. In the initial pre-CA state, mb4-AT material seems to have a higher electrochemically active surface area compared to the others. However, the overall variance across the four samples is negligible, suggesting essentially similar surface properties.

4.4 Electrocatalytic Performance (Ammonia Synthesis)

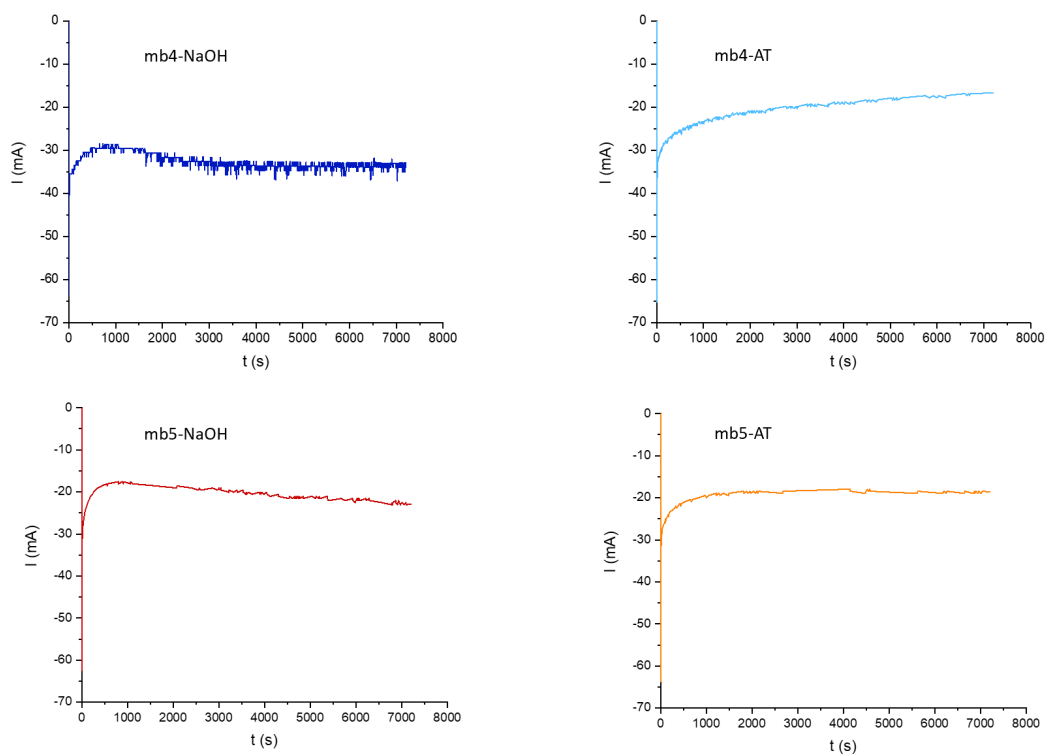


Figure 4.10: Time-dependent current profiles (chronoamperometry) of the four synthesized materials recorded during prolonged electrolysis (7200 s). These measurements illustrate the operational stability of the electrodes under the applied potential to drive the continuous nitrate reduction reaction.

Building upon the kinetic analysis derived from the LSV polarization curves, CA was employed to evaluate the steady-state catalytic performance of the materials. Based on the optimal onset-to-HER ratio identified previously, a fixed cathodic potential of -1.3 V vs AgCl was applied continuously for 2 hours (7200 seconds) in the nitrate-rich electrolyte. This bulk electrolysis step is fundamentally required to drive the reaction into a steady-state kinetic regime and ensure the continuous accumulation of the synthesized ammonia, achieving a sufficient concentration for downstream spectrophotometric quantification. Figure 4.11 illustrates the CA current-time profiles for the four tested catalysts. Across all samples, an initial sharp capacitive transient is observed in the first few seconds, corresponding to the electrical double-layer charging, followed by a rapid leveling of the faradaic

current. This behavior confirms that the catalysts quickly reach the desired steady-state kinetics for the nitrate reduction reaction. Despite the common operating potential, the samples exhibit distinct current behaviors, partially influenced by their specific mass loadings (ranging from 0.91 to 1.35 mg/cm²). The mb4-NaOH sample, possessing one of the highest loadings, achieves the highest absolute current, settling around -30 to -35 mA. However, its current profile displays noticeable and continuous fluctuations. In electrocatalysis, this noisy pattern is typically attributed to the vigorous formation, accumulation, and subsequent detachment of gas bubbles (predominantly hydrogen gas from the competing HER process) on the electrode surface, which temporarily block and release the active sites. Conversely, the mb5-NaOH sample maintains a relatively smooth current profile, leveling off in the range of -20 to -25 mA, indicating a more consistent electrocatalyst-electrolyte interface. Notably, both acid-treated catalysts (mb4-AT and mb5-AT) display exceptionally flat current responses throughout the entire 2-hour duration, settling at approximately -15 to -20 mA. The smoothness of these AT curves suggests a highly uniform reaction rate and a more controlled management of local gas evolution. Overall, the CA profiles demonstrate that all variants of the CuNi/MCN material can successfully sustain the required faradaic current over the 2-hour testing period without suffering from abrupt electrochemical deactivation, ensuring reliable and continuous product generation for the subsequent efficiency calculations.

4.4.1 Effect of Applied Potential on Current Density

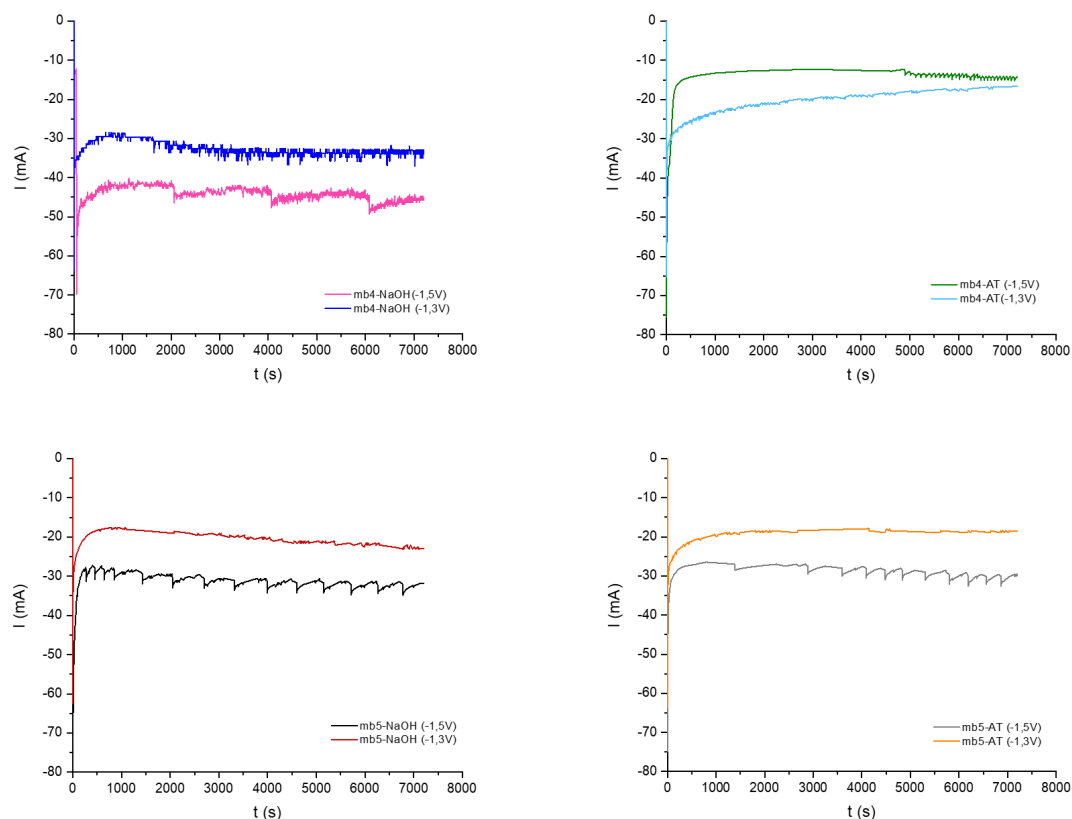


Figure 4.11: Chronoamperometric (CA) curves recorded during a 2-hour (7200 s) bulk electrolysis for the four synthesized electrocatalysts. Each panel compares the time-dependent current profiles obtained at two different applied potentials: -1.3 V and -1.5 V.

The CA curves recorded at -1.3 V and -1.5 V illustrate the distinct electrochemical stability of the prepared catalysts under varying applied potentials. At the optimal potential of -1.3 V, the current profiles for all tested materials rapidly reach a stable steady-state, characterized by smooth and constant traces over the entire test duration. This stable behavior indicates a well-controlled, continuous nitrate reduction process. Conversely, at the more negative potential of -1.5 V, while the absolute magnitude of the current generally increases, the signals become significantly noisier. The curves at -1.5 V exhibit a characteristic sawtooth pattern, which is particularly evident in the mb5-NaOH and mb5-AT samples. These continuous current fluctuations are typical of vigorous gas bubble formation and detachment on the electrode surface. This physical phenomenon confirms that at

more negative potentials, the competitive HER becomes highly active, mechanically disrupting the steady-state conditions on the active sites and competing with the targeted ammonia production.

4.5 Product Quantification, Faradaic Efficiency, and Products Yield

Following the 2-hour CA tests, the synthesized ammonia (NH_3) and the nitrite (NO_2^-) by-products were quantified to evaluate the absolute electrocatalytic performance of the materials. Two fundamental metrics were calculated: FE% and Yield rate.

4.5.1 Electrocatalytic Performance Analysis

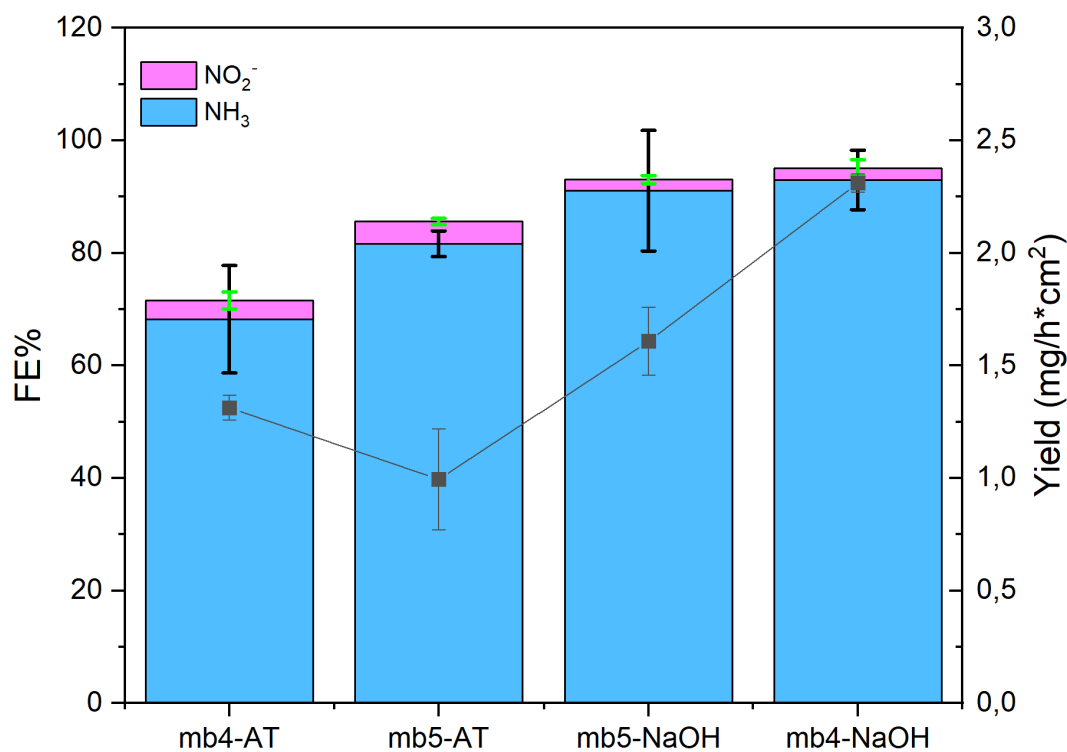


Figure 4.12: Comprehensive electrocatalytic performance of the four investigated materials. The stacked bar chart (left y-axis) illustrates the FE% partitioned into ammonia (NH_3 , blue) and nitrite (NO_2^- , pink) production. The overlaid line plot with square markers (right y-axis) represents the corresponding ammonia yield rate ($mg\ h^{-1}\ cm^{-2}$). Error bars indicate the standard deviation across multiple independent experimental runs.

Figure 4.12 summarizes the calculated FE% (left axis, stacked bars) and the normalized Yield rates (right axis, line plot) for the four investigated catalysts operating at -1.3 V vs AgCl. The data reveals a striking structure-performance relationship, heavily influenced by the pre-treatment of the MCN support. The sodium hydroxide-treated catalysts (mb5-NaOH and mb4-NaOH) overwhelmingly outperform their acid-treated counterparts (mb4-AT and mb5-AT) in both selectivity and total production capability. The mb4-NaOH sample exhibits the highest overall performance, achieving a remarkable FE% of approximately 95%. Crucially, the vast majority of this efficiency (around 93%) is selectively driven toward ammonia synthesis, with only a negligible fraction diverted to nitrite production. This outstanding

selectivity is coupled with the highest recorded Yield, peaking at approximately $2.3 \text{ mg/h} \cdot \text{cm}^2$, identifying mb4-NaOH as the optimal electrocatalyst among the tested batch. Similarly, the mb5-NaOH variant demonstrates excellent selectivity, reaching a total FE% of over 90% (with NH_3 FE% around 91%), although it registers a lower absolute Yield ($1.6 \text{ mg/h} \cdot \text{cm}^2$) compared to mb4-NaOH, likely due to variations in the specific mass loading and accessible surface area. Conversely, the acid-treated samples exhibit significantly restricted catalytic performances. While mb5-AT reaches a moderate NH_3 FE% of roughly 82%, its Yield drops significantly to roughly $1.0 \text{ mg/h} \cdot \text{cm}^2$. The mb4-AT sample displays the poorest metrics across the board, with the lowest ammonia selectivity (68%) and a restricted yield. This stark contrast suggests that the alkaline treatment (NaOH) plays a pivotal role in optimizing the surface chemistry, metal-support interactions, or the exposure of the Cu-Ni bimetallic active sites, thereby maximizing the kinetic conversion of nitrates directly into ammonia while severely suppressing side reactions.

4.5.2 Effect of Applied Potential on Faradaic Efficiency and Yield

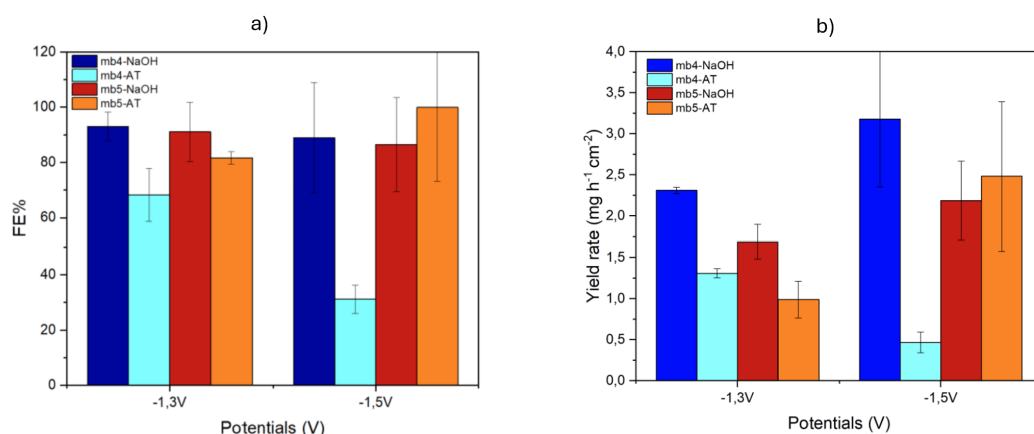


Figure 4.13: Figure a) Faradaic Efficiency (FE%) towards ammonia production for the four investigated electrocatalysts (mb4-NaOH, mb4-AT, mb5-NaOH, and mb5-AT) evaluated at two distinct applied potentials (-1.3 V and -1.5 V). The error bars represent the standard deviation across multiple independent measurements. Figure b) Ammonia yield rates for the four investigated electrocatalysts (mb4-NaOH, mb4-AT, mb5-NaOH, and mb5-AT) evaluated at two distinct applied potentials (-1.3 V and -1.5 V). The yield values are normalized by the geometric area of the electrode and time ($\text{mg h}^{-1} \text{cm}^{-2}$). The error bars represent the standard deviation across multiple independent measurements.

The analysis of the FE% reveals a clear trend of performance degradation for ammonia production when the applied potential is shifted from the optimal -1.3 V to a more negative -1.5 V. This decline in selectivity is primarily attributed to the intensified competition from the HER. As the potential becomes more cathodic, the thermodynamic and kinetic conditions increasingly favor water reduction. Consequently, a significant fraction of the supplied electrons is diverted away from the targeted nitrate-to-ammonia pathway and wasted on generating hydrogen gas. This performance drop is most dramatic in the mb4-AT sample, which suffers a drastic collapse in FE% from approximately 68% at -1.3 V to barely 31% at -1.5 V. While the alkaline-treated catalysts (mb4-NaOH and mb5-NaOH) maintain a higher overall efficiency, they also exhibit a slight reduction in their average FE% values at -1.5 V. Furthermore, the tests conducted at -1.5 V are characterized by noticeably larger error bars across almost all samples. This increased standard deviation highlights a severe loss of system stability and reproducibility at higher overpotentials. Although the mb5-AT sample displays a superficially higher average FE% at -1.5 V, its exceptionally large error bar confirms a highly erratic electrochemical behavior. Overall, these results corroborate that operating at -1.5 V triggers important hydrogen bubbling, which mechanically blocks active sites, disrupts local mass transport, and ultimately compromises the efficiency and stability of the ammonia synthesis process. From the graph is possible to notice that the pre acid treatment mb4-NaOH catalyst emerges as the best-performing material. At the optimal potential of -1.3 V, it achieves the highest ammonia yield rate (approximately $2.3 \text{ mg} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$) coupled with exceptionally low statistical variance. This confirms a highly stable, efficient, and reproducible catalytic process. On the other side, the mb4-AT sample represents a notable anomaly. Unlike the other materials, its yield rate collapses drastically at -1.5 V, dropping below $0.5 \text{ mg} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$. This severe failure, perfectly mirroring its collapse in FE%. In general The analysis of the ammonia yield rate, expressed in $\text{mg} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$, provides a crucial perspective that complements the FE% data and highlights a fundamental electrochemical trade-off. While the previous FE% analysis demonstrated a widespread decline in selectivity at -1.5 V, the yield rate data shows that for most catalysts (mb4-NaOH, mb5-NaOH, and mb5-AT), the absolute quantity of ammonia produced per unit area and time actually increases at this higher overpotential. The analysis of the ammonia yield rate, expressed in $\text{mg} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$, provides a crucial perspective that complements the FE% data and highlights a fundamental electrochemical trade-off. While the previous FE% analysis demonstrated a widespread decline in selectivity at -1.5 V, the yield rate data shows that for most catalysts (mb4-NaOH, mb5-NaOH, and mb5-AT), the absolute quantity of ammonia produced per unit area and time actually increases at this higher overpotential. This can be explained because at the more cathodic potential of -1.5 V, the total current passing through the electrochemical cell is significantly larger. Consequently, even though a smaller

percentage of these electrons is utilized for nitrate reduction (resulting in a lower FE%), the sheer volume of transferred charge still drives a higher absolute accumulation of ammonia. However, this enhanced production comes at the severe cost of system stability. The dramatically enlarged error bars observed at -1.5 V for these samples corroborate the physical instability induced by vigorous hydrogen evolution, which mechanically disrupts the reaction interface and leads to highly erratic production rates.

4.6 Active Surface Area Evolution

Based on the provided electrochemical data, a consistent increase in the double-layer capacitance (C_{dl}) is observed for all materials after bulk electrolysis at -1.3 V. This trend is visibly corroborated by the cyclic voltammograms, which display expanded capacitive loop areas and higher current densities in the post-CA measurements compared to their initial pre-CA states.

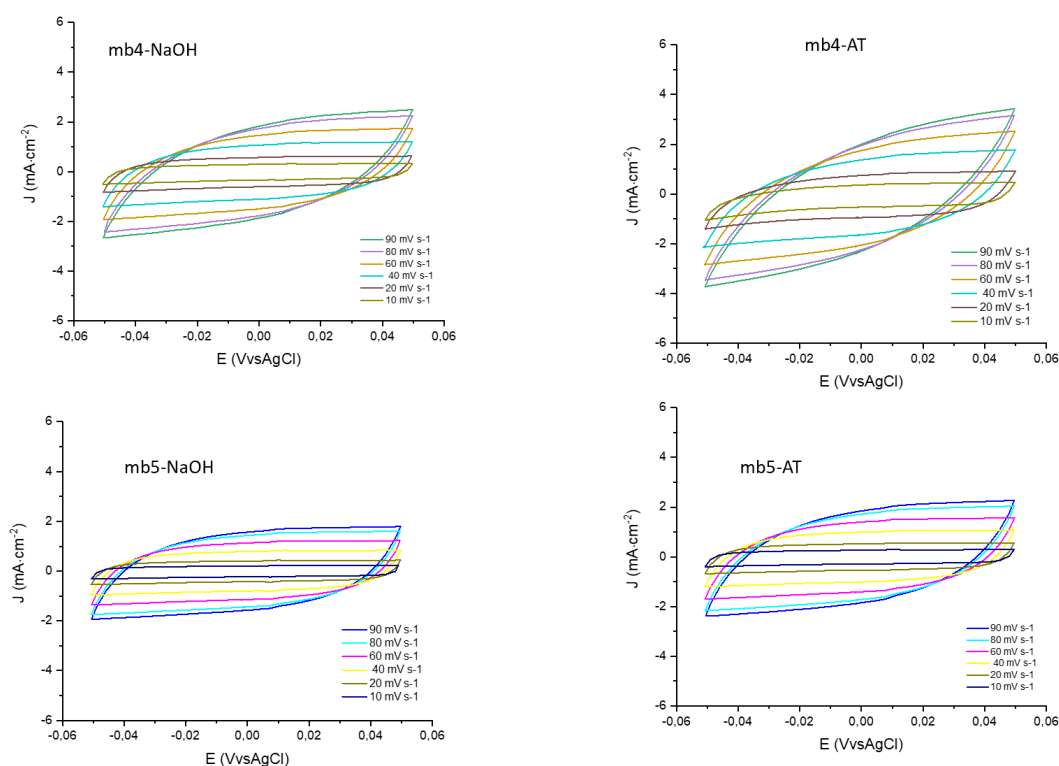


Figure 4.14: ECSA pre-CA

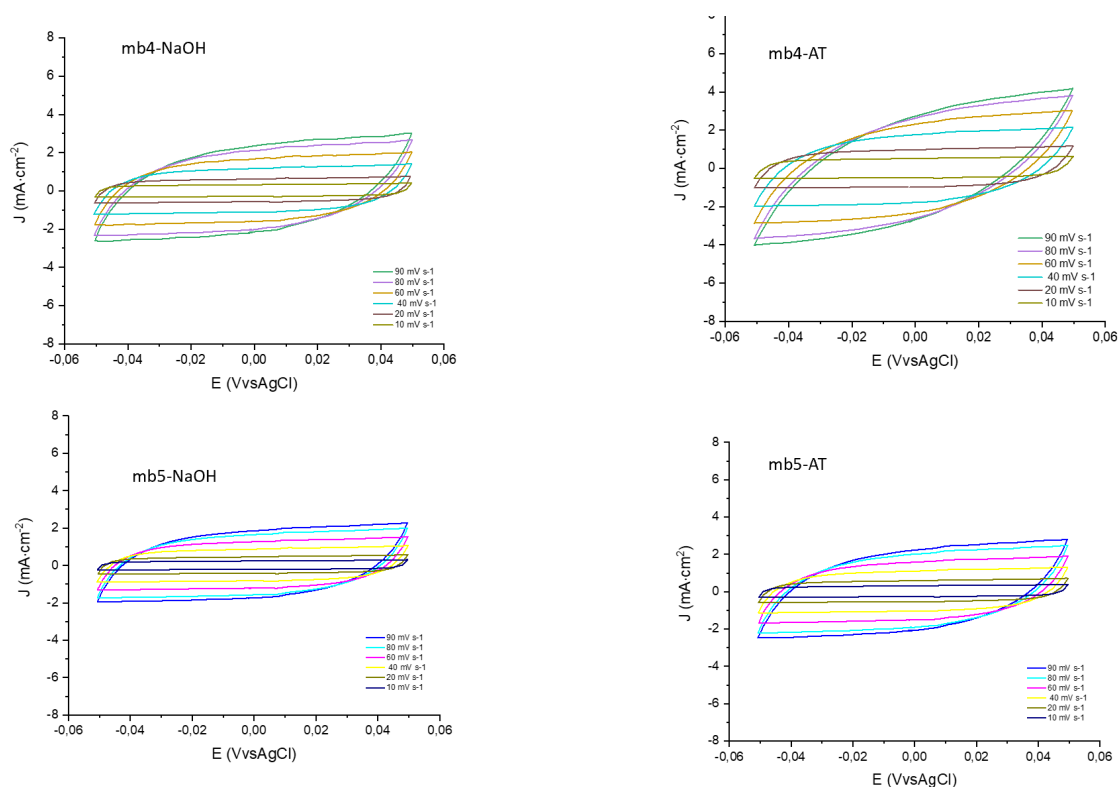


Figure 4.15: ECSA post-CA

After 2 hours of continuous electrolysis at -1.3 V vs AgCl, the CV loops for all samples, most notably mb4-NaOH and mb4-AT, display a significant vertical expansion, reaching higher absolute capacitive currents. This widening of the voltammograms provides direct physical evidence of an increase in the double-layer capacitance, indicating that the actual accessible surface area of the electrodes expanded during the operational period. This phenomenon is highly beneficial and is commonly attributed to in-situ surface roughening. The prolonged cathodic polarization, combined with the continuous, localized mechanical action of the hydrogen gas bubbles evolving and detaching from the surface, effectively modify the catalytic layer. This dynamic process likely opens up the internal porosity of the MCN matrix or exposes previously inaccessible Cu-Ni bimetallic active sites to the electrolyte. Consequently, these results confirm that the catalysts do not suffer from severe active site loss, structural collapse, or poisoning during the steady-state reaction; rather, they undergo a favorable electrochemical activation that further maximizes the exposed catalytic sites. By looking at the C_{dl} values is possible to observe that following bulk electrolysis at -1.3 V, all samples undergo a moderate C_{dl} increase, indicative of a controlled surface activation process rather than structural degradation. Notably, the mb4-NaOH sample exhibits the most pronounced relative

capacitance enhancement. That was aspected, as mb4-NaOH corresponds to the highest FE% within the study; such a correlation suggests a highly dynamic and reactive surface that readily undergoes morphological adaptation under the cathodic regime to maximize the exposure of active catalytic sites. Conversely, the mb4-AT sample, despite possessing the highest absolute initial ECSA, demonstrates the greatest morphological stability, undergoing the smallest relative structural change during the electrolytic process.

Material	C_{dl} pre-CA (-1.3 V)	C_{dl} post-CA (-1.3 V)
mb4-NaOH	0.0182	0.0245
mb4-AT	0.0252	0.0279
mb5-NaOH	0.0166	0.0197
mb5-AT	0.0190	0.0234

Table 4.2: Double-layer capacitance (C_{dl}) values before and after bulk electrolysis at -1.3 V.

Chapter 5

Conclusions and Future Perspectives

5.1 Conclusion

The main purpose of this study was to characterize, and systematically evaluate bimetallic CuNi/MCN electrocatalysts for the highly selective Nitrate Reduction Reaction ($\text{NO}_3^- \rightarrow \text{NH}_3$). Through a comprehensive electrochemical evaluation, the proposed materials demonstrated robust catalytic capabilities, with their macroscopic performance being heavily dictated by the specific chemical pre-treatment applied to the support matrix. Initial voltammetric characterizations successfully confirmed the in-situ activation of the bimetallic active sites. The introduction of nitrate species into the electrolyte triggered a massive positive shift in the onset potential, physically proving the specific catalytic activation of the electrodes well before the thermodynamic onset of the competing Hydrogen Evolution Reaction (HER). Subsequent kinetic analysis identified -1.3 V vs AgCl as the optimal operational sweet spot to maximize the target reaction rate while suppressing parasitic hydrogen generation. During steady-state bulk electrolysis, the mb4-NaOH sample emerged as the optimal electrocatalyst among the investigated batch. It achieved an outstanding overall FE% of approximately 95%, with 93% specifically directed toward ammonia synthesis, strictly minimizing nitrite by-product generation. This exceptional selectivity was coupled with a maximum production yield of $2.3 \text{ mg/h} \cdot \text{cm}^2$. Conversely, the acid-treated variants exhibited significantly diminished selectivity and restricted yields, underscoring the critical, beneficial role of alkaline surface modification in optimizing the catalyst-electrolyte interface. Furthermore, ECSA evaluations revealed a beneficial in-situ surface roughening phenomenon during operation, confirming that the bimetallic active sites do not suffer from rapid deactivation, but rather expand their accessible

surface area.

5.2 Future Prospective

While the evaluated CuNi/MCN electrocatalysts demonstrate remarkable intrinsic performance, it is essential to contextualize this technology within the broader industrial landscape. Electrochemical ammonia synthesis can't completely replace the established Haber-Bosch process, which remains unparalleled and highly optimized for massive, centralized global fertilizer production. Instead, the NO_3^- -to- NH_3 electroreduction can be a vital complementary technology. It offers a decentralized, small-to-medium-scale alternative that operates entirely under ambient conditions and can be driven directly by intermittent renewable energy sources. Most importantly, it provides a dual-purpose solution: simultaneously remediating nitrate-polluted agricultural and industrial wastewater while recovering ammonia as a value-added chemical carrier. To further bridge the gap between this fundamental proof-of-concept and practical implementation, several key areas of future research are proposed:

- **Long-Term Durability Testing:** While the 2-hour Chronoamperometry proved short-term stability, extended electrolysis tests (100+ hours) are required to evaluate the long-term resistance of the catalysts against degradation, structural collapse, or poisoning in industrial-grade electrolytes.
- **Flow Cell Integration:** Transitioning the testing setup from a standard H-cell to a continuous flow cell architecture to overcome mass transport limitations and scale up the overall production yield.