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Iron Nitrate Hexahydrate Nanoparticles Embedded in Porous Carbon Nanofibers as Catalyst for Efficient Reduction of Nitrate to Ammonia

Pedro Aparicio
Master’s Thesis for the Master of Science in Sustainable Energy Engineering
Division of Heat Transfer
Department of Energy Sciences
Faculty of Engineering | Lund University

ISRN LUTMDN/TMHP-24/5592-SE
ISSN 0282-1990

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June 2024, Lund

This degree project for the master's in sustainable energy engineering was done in Chengdu, China at the University of Electronic, Science and Technology of China in association with Lund University. It was supervised by Dr. Martin Andersson and Dr. Thing Shuai Li, with the examiner being Dr. Marcus Thern.

Abstract

As global energy demands rise and the need for sustainable solutions becomes more urgent, so efficient ammonia production is fundamental. Traditional methods, such as the Haber-Bosch process, are both energy-intensive and environmentally harmful. This research investigates an alternative by developing a catalyst for the electrochemical reduction of nitrate to ammonia, using Iron Nitrate Hexahydrate Nanoparticles embedded in Porous Carbon Nanofibers (CNFs). This synthesized catalyst showed high ammonia yield (18.5 mg h^{-1} mg^{-1} cat) and faradaic efficiency (70.9%), with its structural and morphological integrity verified through XRD and SEM analyses. This catalyst can be a good choice for more environmentally friendly ammonia production, potentially providing ecological advantages over other conventional methods. Future research focus will be on optimizing synthesis parameters and scaling up the production process under real-world conditions to fully harness its potential.

Keywords: nitrate reduction to ammonia, electrochemical ammonia synthesis, catalyst, iron nitrate hexahydrate, porous carbon nanofibers

Preface

The master's thesis research project was a 14-week experience that evolved through extensive research, lab experimentation, fantastic cultural activities, and new friendships in China. The University Of Electronic Science and Technology of China (UESTC) located in Chengdu, Sichuan, provided all the conditions needed for a successful project. The project is associated with the Department Of Energy Sciences at Lund University, which has a partnership with the previous University mentioned. The main goal of this research was to create an efficient method for ammonia synthesis, using advanced nanostructured catalysts. I am very grateful to Martin Andersson who served as my supervisor in Sweden and Lund University for providing me with this opportunity and guidance, as well as to Dr. Ting Shuai Li, for his support during my stay in China. Also, mention a deep thank you note to my lab partners Zhi Ruo, Hai Tao, and Niu who put some time aside from their duties as students and researchers to help me and answer some of my questions during the process.

Chengdu, June 2024

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List of Abbreviations and Symbols

@: Embbeded in X
CNF : Carbon nanofiber
Iron (II) Nitrate: Fe(NO3)2·6H2O
NO_3 RR: Nitrate Reduction Reaction
SEM: Scanning electron microscopy
NRR: Nitrogen reduction reaction
XRD: X-ray diffraction
PVA: Polyvinyl alcohol
PTFE: Polytetrafluoroethylene
CV: Cyclic Voltammetry
LSV: Linear sweep voltammetry

Introduction

Background and Context

Ammonia is usually manufactured through techniques that rely mostly on fossil fuels and generate high CO2 emissions. These are becoming less prominent since it is critical to identify more environmentally friendly options. To achieve the net-zero goal of emissions by 2050, researchers are investigating green technologies for ammonia production. These show initiatives toward dedication to sustainability and environmental preservation, opening ways for a shift in the way ammonia is produced. Ammonia's influence is felt in many industries, its adaptability and continuous development of technology and industrial techniques place it as one of the highest priorities to create a more prosperous and sustainable future. Ammonia, or NH_3, is also very adaptable which makes it an essential component of many different industries, including energy, agriculture, and chemistry (IEA, 2021).

Chemicals, Fertilizers, Pharmaceuticals, and Plastics

Around 70% of ammonia is used in the fertilizer business to enhance crop growth. It links the nutrients that plants need from the soil and nitrogen in the atmosphere. The fertilizers that contain ammonia are fundamental for keeping healthy soil and raising crop yields, these are both necessary for the prosperity of agriculture. Ammonia ensures the nitrogen needs of plants are met, and consequently the availability of food for humans. Ammonia is a critical component in the chemical and plastics industries as well, where it is used to produce synthetic fibers, explosives, and plastics. Due to its adaptability and use, it is a necessary component of many manufacturing processes, making sure the production of crucial materials is successful. Ammonia is also essential in the production of pharmaceuticals, which include medications, essential for the development of healthcare and medicine. With all this, it plays a wide and crucial function in all sectors of the economy, including agriculture, manufacturing, and healthcare. Adding up, ammonia is also a very good option for carrying energy (IEA, 2021).

Carbon-Neutral Energy Carrier

With the current search for renewable sources and fossil-free options, ammonia has an advantage which is that it can solely burn nitrogen and water when used as a fuel, meaning it emits no carbon dioxide into the atmosphere. It can also efficiently store and transfer hydrogen, helping to overcome some of the drawbacks of hydrogen as a renewable energy source. This means ammonia has a great potential to participate heavily in the transition to renewable energy sources. With all this, ammonia still can be produced in a green manner, further explored in this paper, also participating in combating issues with wastewater pollution (Spatolisano et al., 2023; Zhai et al., 2023).

Electrochemical Nitrate Reduction Reaction (NO_3 RR) and Wastewater treatment

Domestic water when left untreated usually has ammonia in its composition. The process of nitrification, driven by microbial activity, converts it into nitrite and then nitrate. The compliance standards for this treatment, demand the removal of the resultant nitrate from this water, so denitrification methods are necessary as well. This process evolves reducing the nitrate to non-dangerous nitrogen gas, which can safely go into the atmosphere. Denitrification techniques include the denitrifying of filters, which not only eliminate nitrate but also filter out solids that were suspended from the liquid waste.

Nitrification is related to the metabolic activity of nitrifying bacteria. These special microbes gather energy from nonorganic sources like ammonia or nitrite to generate organic molecules. Initially, ammonia-oxidizing bacteria catalyze the conversion of ammonia to nitrite, as expressed in equation (1):

$$NH_3 + O_2 \rightarrow NO_2^- + 3H + 2e^- \qquad (1)$$

Subsequently, nitrite-oxidizing bacteria will oxidize nitrite into nitrate, as shown in equation (2):

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H + 2e^- \qquad (2)$$

In another process, denitrification promotes the reduction of nitrates to gaseous nitrogen by helpful anaerobes. These versatile species, which include some fungi, survive and develop in environments with low levels of oxygen, using oxygen-containing compounds like nitrate to help them survive. Once nitrogen enters the water, it exists in different forms such as dissolved nitrogen gas, ammonia, nitrate, and nitrite, as well as organic nitrogen, often as proteinaceous matter or dissolved in particulate phases (U.S. EPA, 2019).

Nitrogen gas (N_2) is often used for ammonia generation but with it a great challenge arises due to its strong N–N triple bond, meaning its activation energy for product formation is very high. The Haber–Bosch process has been used for a long time, where nitrogen from the air and hydrogen in gaseous form from natural gas or other sources react at high pressure and high temperature. This process is very demanding due to its energy consumption. In addition, a catalyst, usually based on iron, is used to speed up the reaction. Under these conditions and with the catalyst helping the reaction, nitrogen and hydrogen overcome their tendency to remain inert, and react, forming ammonia (Jeon et al., 2024).

With the emergence of the technique for the Nitrate Reduction Reaction (NO_3 RR) a promising and environmentally friendly way to fight nitrate (NO_3^-) contamination in wastewater reservoirs, by using electrochemical methods to convert nitrate into ammonia, it is possible to sidestep the negative aspects associated with the Haber–Bosch process and have another route for the nitrate from wastewater. This reduction reaction is shown below in equation (3) in a simplified manner:

$$NO_3^- + 6H^+ + 6e^- \rightarrow NH_3 + 3H_2O \qquad (3)$$

Nitrate ions (NO_3^-) undergo reduction by acquiring electrons (e^-) and protons (H^+), resulting in the formation of ammonia (NH_3) and water (H_2O) (Jeon et al., 2024).

Researchers have been on the search for different catalysts to enhance the efficiency of the nitrate reduction reaction. These have been made through:

1. Transition Metals: Taking advantage of the d-orbital energy levels, facilitating electron transfer during the reaction, enhancing its efficiency.

2. Alloys and Single Atomic Catalysts: Combining transition metals into alloys or harnessing them in single atomic configurations optimizes NO_3 RR performance by making small changes on crystal planes or inducing oxygen vacancies.

3. Metal-Free Catalysts: By manipulating electronic properties in metal-free catalysts it can help to reduce side reactions, resulting in increasing ammonia yield and Faradaic efficiency (Jeon et al., 2024).

It is complicated to address environmental issues caused by livestock manure wastewater causes. Recovering ammonia from this is an important step. New electrochemical techniques offer efficient ways to achieve this. This not only helps to reduce pollution levels but also frees up important resources for further use. It encourages a comprehensive way to manage wastewater and its nutrients, and the co-production of compounds (R. Wang et al., 2023).

Aim of the Degree Project

The main goal of this degree project is to develop a catalyst that enhances the electrocatalytic reduction of nitrate to ammonia. This aim is connected to general goals focused on improving wastewater treatment and the promotion of green ammonia production.

By improving the efficiency of the electrocatalytic reduction process, the catalyst aims to facilitate the conversion of harmful nitrate (NO_3^-) into ammonia (NH_3).

This problem evolves a design of a catalyst that could greatly enhance the activity of the electrocatalytic reduction reaction.

To make sure this challenge was successfully overcome, some specific goals were identified:

1. **To fabricate an effective catalyst**: One goal was to develop an adequate catalyst with desired properties that could significantly optimize the conversion rate of nitrate to ammonia. This would involve synthesizing materials with appropriate structures and compositions to optimize catalytic activity.

2. **Understand underlying mechanisms:** It was important to comprehend the fundamental mechanisms that the electrocatalytic process is based on. This would include the reaction kinetics, surface interactions, and intermediate species involved in the conversion of nitrate to ammonia on the catalyst surface.

3. **Evaluate catalyst stability and efficiency:** It is fundamental to evaluate the stability and efficiency of the developed catalyst, this includes conducting electrochemical testing to analyze the catalyst's performance over time and the concentration of reactants.

Limitations

A great part of the work for the master's thesis research project was performed at the University of Electronic, Science and Technology of China (UESTC). Due to time restraints, the porous carbon fiber couldn't be refined for optimal hydrothermal growth of what was the initial catalyst of copper oxide. The first 4 times that the electrospinning was attempted, the carbon fibers were not uniform and with the same diameter, which made the growth of CuO impossible to achieve in the desired timeframe. The possible cause could be the parameters of the viscosity of the polymer, the needle being too narrow, or errors in humidity in the display of the electrospinning machine. Optimizing these could have given better results. So the catalyst was decided to be used as Iron Nitrate Hexahydrate and pre-mixed with the CNF for the electrospinning. The lab instruments were also shared with other students which caused the limited use at certain times. The SEM images were retrieved from another university, due to a lack of equipment at UESTC. Other factors such as lack of experience in lab procedures, language barriers, and lack of time for students to supervise some parts of the experience limited partly the outcomes of the final result. Even tho, results attained were successful and very positive.

Outline of the Report

The outline of the report is as follows:

1. Theoretical Framework
2. Methodology
3. Results
4. Discussion
5. Conclusion and Future Directions
6. References
7. Appendix A
8. Appendix B

Theoretical Framework

Disciplinary Foundation

The project acknowledges its disciplinary foundation, which draws from these key areas:

1. **Semiconductor physics.**
2. **Solid physics.**
3. **Electrochemistry**

Semiconductor physics

When applying semiconductor physics to catalyst design for electrocatalysis, there are several concepts evolved, which are explored below.

Electronic Band Structure:

The property that distinguishes semiconductors from other materials is related to the behavior of their electrons, particularly the existence of gaps in their electronic excitation spectra. The microscopic behavior of electrons in a solid is most easily specified in terms of the electronic band structure (Yu & Cardona, 1996).

The semiconductor band structures influence catalytic activity, and to get the maximum efficiency possible bandgap engineering is evolved, allowing to tailor the energy levels of catalyst materials to match specific redox reactions (Ye et al., 2023).

Doping strategies

Another aspect is the doping of semiconductors, this can be helpful by carefully and specifically changing and optimizing the charge carrier type and concentration in a specific and controlled methodology, it is a key technology foundation for modern electronics and optoelectronics (Y. Wang et al., 2021)

It introduces impurities into a semiconductor lattice, changing its electronic properties. In catalysts, doping can enhance charge carrier concentration, modify band structures, and improve catalytic activity (Ye et al., 2023).

Charge transfer dynamics

When electrons or holes move from one material to another, the process is called charge transfer. This movement is important for many scientific and technical applications.

A good example of when the potential of charge transfer dynamics is used is Mixed-Dimensional Heterojunctions (MDHJs). These are when different types of materials are combined, such as mixing different shapes of materials and sizes. These combinations have special properties at their meeting points that the individual materials don't have. One example is when a mix of MoS_2 (metal) and VOPc (an organic semiconductor) is shining light on the MoS_2, it takes about 710 trillionths of a second for the holes to jump to the VOPc. But when shining light on the VOPc, the electrons move to the MoS_2 almost instantly, in less than 100 trillionths of a second. This super-fast separation of charges creates an interlayer exciton (Schwinn et al., 2022).

General charge transfer dynamics can occur in various contexts, such as vibrational energy flow in large polyatomic molecules and the motion of protons in solution (May & Kühn, 2023).

Another process is called charge-transfer excitons, when these form when photoexcited electrons and holes undergo charge transfer when two materials meet (Bian et al., 2020).

Semiconductor physics provides insights into the behavior of charge carriers (electrons and holes) within materials, and by understanding charge transfer dynamics, it is possible to design catalysts that facilitate efficient charge transport during electrochemical reactions, such as the one performed in this research. Optimizing the band structure of a semiconductor catalyst can improve its ability to transfer charges in reactions like hydrogen evolution or oxygen reduction (Boudjemaa, 2020). Understanding charge transfer dynamics is very important for designing efficient devices and getting the best result possible from the unique properties of mixed-dimensional heterojunctions.

Surface States and Defects

Sometimes semiconductors have surfaced in different states. These impact catalytic performance, and when understanding how to manage these, can help design catalysts with optimal surface properties. For example, controlling surface defects in metal oxides can increasingly enhance their electrocatalytic activity (Ye et al., 2023).

Nanostructuring and Interfaces

Here, semiconductor nanoparticles or nanosheets can provide high surface area due to their area-to-volume ratio and unique electronic properties. When designing catalysts with well-defined interfaces enhances charge transfer and catalytic efficiency, also due to quantum effects (Boudjemaa, 2020).

Materials Selection

Many semiconductor materials (e.g., metal oxides, carbon-based materials, layered structures) can serve as catalysts. The electronic properties that they carry, as well as stability, and reactivity are important considerations when designing a catalyst (Boudjemaa, 2020).

Photocatalysis and Solar Energy Conversion

One known example is how semiconductor catalysts can harness solar energy for electrochemical reactions. When investigating these light-matter interactions and excitation of photons, can help guide the design of photocatalysts (Ye et al., 2023).

In sum, semiconductor physics principles help us with the design of catalyst materials, how to get an increase of charge transfer, work on the surface engineering for proper surface band structure interactions, and very refined band structures for efficient electrocatalysis. But to harness the full potential of the reaction, the physical properties of each material are fundamental, so a good understanding of solid physics is important.

Solid Physics

Solid physics focuses on the arrangements and physical properties of materials in the solid state, involving how the atoms in these materials are positioned and how they interact with one another. This field encompasses many subparts that are fundamental to understanding the behavior of solid materials at a microscopic level, which include electrical, magnetic, and thermal properties. To develop new materials and technologies, such as semiconductors, this field gives us fundamental insights and teachings (Harrison, 2008).

It also has a prominent role in catalyst fabrication and characterization. For example, a catalyst's porous structure has a large specific surface area. Solid physics can help in understanding these properties. Techniques such as BET analysis to determine surface area and pore size distribution investigations are important to show how molecular transport and reaction pathways are affected by changes in the pore structure. For this paper, analysis of the porous structure of the carbon nanofiber was previously examined. Another aspect to examine is pore geometry, which considers the pore width and shape. Terms such as nanopores include micropores and mesopores which can have an interval for width length, which allows to focus research on the overall behavior of these in general, instead of fixed pore size scales (Neimark et al., 2008).

Regarding catalyst characterization, solid physics presents techniques such as solid-state NMR spectroscopy, investigating atoms, surface sites, reactants, adsorbate complexes, and reaction intermediates on solid catalysts (F. Chen, 2014). To further understand catalyst characterization, one has to have a good understanding of electrochemistry.

Electrochemistry

Electrochemistry focuses on the study of electron movement during oxidation-reduction reactions, at anode-cathode electrochemical cells. Measurements of potential, current, or charge are used to determine concentrations of species or characterize chemical reactivity (Electrochemical Methods, 2021).

It is traditionally seen as a branch of physical chemistry that deals with how different materials conduct electricity and convert between chemical and electrical energy. It also is related to biology and chemical physics, especially in bio-electrochemical systems and electrocatalysis. In electrochemistry reactions happen at interfaces between phases with different conductivity. Oxidation and reduction reactions involve the transfer of electrons between electrodes in an electrochemical cell, with this, electrical and chemical energy are converted back and forth. In electrochemical cells, there are electrodes in contact with an electrolyte, here they conduct electricity and interface with ionic conductors. A great way to speed up reactions in the electrochemical cell is to use a catalyst without getting used up, and the type of electrode material affects reaction efficiency. The higher the catalytic activity the faster reactions happen, which in turn improves the process's overall efficiency. Electrocatalysis has applications in developing new power sources like fuel cells, as well as environmental protection, such as water purification (Gamburg, 2023).

Fuel Cells

Fuel cells serve are an excellent example of electrocatalytic reactions in action. Fuel cells convert the chemical energy of a fuel directly into electricity through electrochemical reactions, Figure 1 exemplifies the technology of a fuel cell. These differ from batteries since they don’t store energy, but they operate continuously while they are supplied with hydrogen and oxygen. In this cell, there is also an anode and a cathode, at the anode, hydrogen fuel undergoes oxidation, releasing electrons, these electrons then travel through an external circuit to the cathode, where oxygen is reduced. The reduction of oxygen at the cathode combines with hydrogen ions (protons) to form water, which completes the reaction. The electrolyte in a fuel cell allows ions to move between the anode and cathode while disallowing the mixing of hydrogen and oxygen gases. This is connected to electrocatalysis since they rely on catalysts to enhance the rate of the electrochemical reactions at the electrodes, where they play an important role in helping the oxidation of hydrogen and the reduction of oxygen with the choice of electrode material significantly impacting the efficiency of these reactions (Donev et al., 2024).

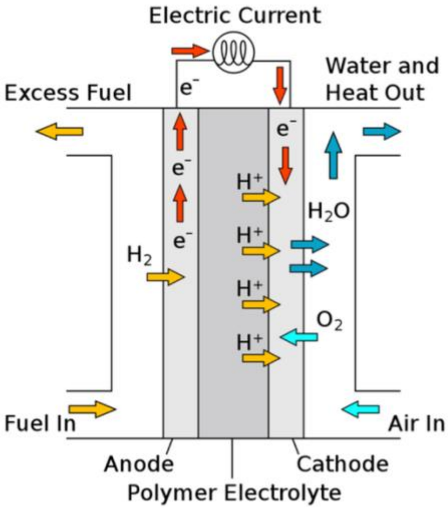


Figure 1- Functioning principle of a fuel cell (Donev et al., 2024)

Fuel cells have a wide range of applications for power generation from chemical energy to electrical energy, from portable devices to large-scale power plants, they offer a cleaner alternative to fossil fuels, with only water as the byproduct, with the use of green hydrogen (Leccese, 2013).

They are a great example of the advantages of electrocatalysis by offering a cleaner and more efficient alternative to traditional combustion engines. The high efficiency and low-temperature operation of electrocatalytic reactions contribute to the superior performance of fuel cells (Adzic & Marinkovic, 2020).

Hydrogen as an alternative fuel

Hydrogen boasts a high combustion velocity, around six times higher than that of petrol, which in turn contributes to higher engine efficiency. It allows for very lean mixtures, with over 5% higher efficiency compared to diesel-fueled engines. Hydrogen combustion is potentially free of hydrocarbons, CO, and CO2 emissions, making it a great alternative fuel for meeting specific emissions standards in spark-ignition engines. It can be produced with several different methods, like steam methane reforming coal gasification, and electrolysis, each with different efficiencies and related CO2 emissions. Still, even tho having many benefits, hydrogen faces challenges like high NOx emissions, lower power output, and issues with the durability and reliability of hydrogen-fueled engines (Stępień, 2021).

Catalyst Development

Catalysts are very important for industry, the environment, and all living things. They speed up reactions without being used up and don't change the final balance of the reaction. This means they help reactions happen faster without changing the amount of products and reactants at the end. Catalysts work by giving a different way for the reaction to occur that needs less energy. They increase the speed of both the forward and backward reactions in the same way, keeping the final balance unchanged. The way they do this is through a special interaction with the reacting substances (Lower, 2022).

Catalyst materials and performance in catalyzing nitrate reduction to ammonia.

In the context of the nitrate reduction to ammonia, Fe single-atom catalysts effectively prevent N-N coupling (required for N_2) due to their lack of neighboring metal sites. These catalysts can enhance NH3 selectivity due to the advantage of atomically dispersed Fe sites (Z.-Y. Wu et al., 2021).When comparing catalytic nitrate reduction to nitrogen gas reduction, the first offers higher conversion rates and energy efficiency, this is due to the solubility of nitrate and the conversion pathway playing crucial roles (Hao et al., 2021).

Regarding structural engineering catalysts, usually synthetic methods are used such as doping, alloying, single-atom engineering, nanoconfinement, and size-regulation. These methods enhance catalyst activity and selectivity for nitrate reduction, these continued advancements in catalyst design will contribute to efficient ammonia production (Qiu et al., 2024).

Other advancements are non-noble metal electrocatalysts, these materials aim to improve efficiency and reduce environmental impact (Cao et al., 2024).

Inside these, single-atomic metal catalysts are a good possibility in nitrate reduction as well as metal-free catalysts**,** which are being investigated for efficient ammonia production (Jeon et al., 2024).

Nitrogen Reduction Electrocatalyst

The development of efficient electrocatalysts for the nitrogen reduction reaction (NRR) has great importance in both industrial fuel production and value-added chemical synthesis. The NRR is crucial in ammonia synthesis. Usually, ammonia is produced through the energy-intensive Haber–Bosch process. However, electrocatalytic NRR is an alternative route that operates at ambient temperature and pressure. Efficient NRR electrocatalysts can significantly reduce energy consumption during ammonia production, making it more sustainable and economically viable. The NRR involves breaking the triple bond between nitrogen atoms (N≡N) and forming the N–H bond (ammonia). A well thought design and optimization of NRR electrocatalysts are very important for achieving this transformation efficiently. Despite recent progress, there are still challenges to solve, and new possibilities for improving NRR efficiency are still being explored. Future perspectives involve advancing our understanding of NRR mechanisms, exploring new catalyst materials, and optimizing their performance (Zhou et al., 2020).

Nitrate, ammonia, and efficient catalysis

Nitrate is a pollutant usually found in industrial, domestic, and agricultural wastewater. Its high solubility and stability are some factors that make the extraction of this substance complicated. The electrocatalytic reduction can be used as an efficient and environmentally friendly method to convert nitrate into ammonia, removing the limitations of traditional methods. By electrochemically reducing nitrate, it is possible to simultaneously remove nitrate contaminants and generate ammonia.

The ability to produce ammonia directly from nitrate using renewable electricity has significant implications for agricultural nutrition supply. Besides agriculture ammonia is also used in pharmaceuticals as a reagent, in metallurgy where it is essential in various metallurgical processes, in explosives as an important component, and textile industry, used in dyeing and finishing. Besides that ammonia is being considered as a next-generation carbon-free energy carrier since it has a large energy density and a simple production and transportation.

Regarding efficient electrocatalysts for nitrate reduction, transition metals with occupied d-orbitals (similar energy levels to nitrate's lowest unoccupied molecular orbital) help electron transfer during the reduction process. Some strategies such as pore structure regulation, alloying, heterostructure construction, and single-atom catalysts have been used to design efficient electrocatalysts. Critical factors affecting performance include nitrate adsorption, exposed active sites, mass transfer rate, and stability of electrocatalysts.

Efficient electrocatalysts for nitrate reduction are extremely important in sustainable ammonia production, environmental protection, and energy savings. It also contributes to cleaner water and greener industrial practices. So to refine an efficient catalyst for this, material design has to be considered (Theerthagiri et al., 2022).

Material design considerations

The surface properties of materials play a crucial role in their effectiveness. Making sure that a high number of exposed sites is active is essential for efficiently adsorbing and reducing nitrates. Also, efficient electron transfer is achieved when the electrocatalyst contains transition metals with d-orbitals that match the energy of nitrate's lowest unoccupied molecular orbital (Heerthagiri et al., 2022).

Another factor is a higher surface area which allows more active sites for nitrate adsorption and electrical conductivity to facilitate charge transfer during the reduction process. Conductive materials, such as carbon-based materials, are often used to support the active metal sites, which were used in this research experiment (CNF) (Niu et al., 2023).

Finally stability and recovery, stability is crucial for long-term performance, ensuring that the catalyst remains active during continuous operation. Recovery of ammonia from the electrocatalyst is essential for practical applications. An efficient electrocatalyst for nitrate reduction should have accessible active sites, good electrical conductivity, and stability. A well-defined composition and suitable crystal structure are also important, which are mentioned later in the report (Zhou et al., 2020).

Selectivity strategies

The design of electrocatalysts with many exposed active sites is very important for nitrate adsorption and reduction. Surface modification and the creation of heterostructures are also strategies used to improve selectivity toward ammonia formation (Qin et al., 2022).

Electrolyte optimization is very important when adjusting the electrolyte pH and optimizing ionic strength these enhance nitrate adsorption and selectivity for ammonia production (Jung & Hwang, 2021).

Operating at ambient temperature and pressure to minimize side reactions and controlling electrode potential are also practiced to enhance ammonia formation, to suppress the hydrogen evolution reaction, where a side reaction of a hydrogen proton is reduced to form hydrogen gas, co-catalysts, and electrolyte additives are added to improve the selectivity of the reaction (Ren et al., 2021).

Recent research on this topic evolves interface engineering, where the interface between different materials can enhance selectivity (Xiao et al., 2024) , as well as amorphous catalysts, such as cobalt-based catalysts, which have shown very good results (X. Li et al., 2022). A combination of catalyst design, electrolyte optimization, and reaction conditions can enhance selectivity for NRA, and with new insights into nanoscale design and nanomaterials, the efficiency of electrocatalysts can be further explored, which is discussed next.

Nanoscale Design

Regarding nanoscale design, there have been developments that allow an increasing efficiency in electrocatalysts, cu-based materials show promise due to their electrocatalytic activity and cost-effectiveness, these were the first plan for the catalyst of this report (CuO@CNF) (Xu et al., 2022), as well as R alloy nanosheets and tandem catalysts (You et al., 2024). Nanocatalysts can effectively remove nitrate contaminants from water systems, but the challenges are in the gap between lab-scale and real-world applications.

Types of Electrocatalysts

The main categories of electrocatalysts include transition and noble metals, metal-free electrocatalysts, and perovskite-type catalysts.

1. Transition Metals and Noble Metals

Transition Metals and Noble Metals are both crucial in the field of catalysis, specifically for nitrate reduction. Transition metals like Fe (Iron), Co (Cobalt), and Ni(Nickel), and noble metals such as Pt (Platinum), Pd (Palladium), and Au (Gold) are usually used for their ability to reduce nitrates. These metals are preferred for their ability to speed up the reduction process, making it more efficient. Another aspect is that the surface properties of these metals can be adjusted to optimize their interaction with nitrate molecules. They can also be engineered to selectively target nitrates, which is very important for reducing by-products and improving efficiency. The arrangement of atoms around the metal center affects its reactivity and is a key area of study recently, research in the field shows that these metals are important in catalysis due to their unique electronic configurations and their ability to form various oxidation states, essential for the redox reactions involved in nitrate reduction (Q. Wu et al., 2024).

2. Metal-free electrocatalysts

Metal-free electrocatalysts research is a recent topic of interest in the field of catalysis, because of its applications such as nitrate reduction. They are cost-effective, and generally less expensive than noble and transition metals, which means they are economically more vib=able. They also have a lower environmental impact during production and use and have distinctive properties for catalyst processes (W. Guo et al., 2023). Recent research focuses on Sulfides, Oxysulfides, Oxides, Phosphides, and N-doped Materials (Y. Wu et al., 2023), and is directed towards understanding how these materials interact with different reactants and how they can be optimized for higher activity and selectivity (Liu et al., 2019; Y. Wu et al., 2023).

One of the main applications of metal-free electrocatalysts is in the reduction of nitrates to nitrogen or ammonia, it is possible to do this here without the use of chemical reductants or hydrogen gas, usually necessary in traditional processes (W. Guo et al., 2023).

3. Perovskite Type Catalysts

High-entropy perovskite oxides, a specific type of material known by a mixture of several metal elements, could be a good option in improving the performance of electrocatalytic nitrogen reduction reactions (eNRR), in this case talking about nitrogen reduction reaction, and not the subject of focus on nitrate reduction reaction. By changing the ratios of nonstoichiometric metal elements in these perovskite materials, it is possible to generate additional oxygen vacancies. These vacancies are important as they make both the production of ammonia (NH3) and the Faraday efficiency of the reaction improve. Within the perovskite structure, nickel has been chosen as a key catalytic site. The creation of more oxygen vacancies facilitates the adsorption and reduction of nitrogen, which are essential steps in the eNRR process. This connection between nickel sites and oxygen vacancies plays a critical role in boosting the overall efficiency and effectiveness of nitrogen reduction to ammonia (Chu et al., 2022; Q. Wu et al., 2024).

Electrocatalytic Mechanisms

The basic principles and mechanisms related to electrocatalytic reactions, including nitrate reduction to ammonia, are based on several key factors that lead to the reaction pathways and efficiencies.

Electron Transfer Process

Electrocatalytic reactions are heterogeneous chemical reactions where electrons are transferred between the electrode and reactants in the electrolyte. The electrode, usually a metal or another conductive material, interacts with reactants, intermediates, and products, facilitating the reaction without being consumed (Strbac & Adzic, 2014).

Adsorption/Desorption

The initial step of the reaction involves the adsorption of reactants onto the surface of the catalyst, which is the most important step and leads the way for the next reaction steps. After the reaction, desorption occurs, releasing the product from the catalyst surface and allowing new reactant molecules to adsorb and react. The electrocatalysis involves the breaking of bonds in the reactants and the formation of new bonds to create the products (Strbac & Adzic, 2014).

pH-Dependent Mechanisms

The performance of electrocatalysts, especially for nitrate reduction to ammonia, can be significantly influenced by the pH of the environment. Different pH conditions can make the reaction pathways, potential determining steps, and limiting potentials inferior affecting the activity and selectivity of the catalysts (Strbac & Adzic, 2014).

Nitrate Reduction and Ammonia Synthesis

Traditional ammonia conversion

The Haber-Bosch Process

The haber-bosch process revolutionized the production of ammonia and was essential for population growth. Over the past century, this process has become much more efficient, with energy consumption dropping from 100 GJ per ton of ammonia in the 1930s to about 26 GJ per ton today. However, there's a shift towards green ammonia production, which uses renewable energy sources. This transition is guided by the need for low-cost electricity from renewables and advancements in electrolyzer technology. Various technologies are being explored to improve ammonia synthesis, including electrochemical routes such as the one in this paper. These methods hold potential for decentralized fertilizer production, but there are still challenges to overcome, particularly in optimizing catalysts and reducing energy costs. Also, advancements in electrolysis are making green ammonia more competitive with traditional methods. In the near term, developments include transitioning to blue ammonia using less carbon-intensive hydrogen sources and adjusting existing plants for hybrid production methods. By 2025-2030, fully electrolysis-based technologies are expected to be commercially viable on an industrial scale. Research is also focusing on efficient and low-temperature ammonia decomposition to make hydrogen production more cost-effective and sustainable (Rouwenhorst et al., 2021).

In the Haber-Bosch process, nitrogen from the air combines with hydrogen under extremely high pressures and moderately high temperatures. A catalyst mostly made from iron allows the reaction to occur at a lower temperature. Ammonia is removed from the reaction as soon as it forms, keeping an equilibrium that shifts towards product formation. Commercial production occurs at pressures ranging from 200 to 400 atmospheres and temperatures ranging from 400°C to 650°C (750°F to 1200°F) (Briney, 2021). The overall reaction is shown in Equation 4, and the overall process in Figure 2.

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{4}$$

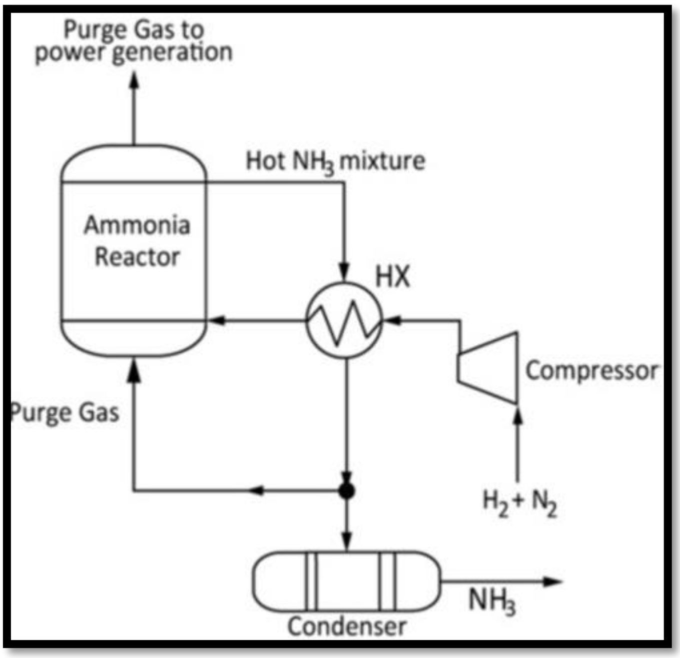


Figure 2- The functioning process of the Haber-Bosch method (Darmawan et al., 2022, p. 5)

Amomnia-based fertilizers play a fundamental role, contributing to over 40% of food production, this work was so important that they were awarded the Nobel Prize in Chemistry. Despite the food production impact, ammonia production still consumes a significant amount of energy and is a major source of CO2 emissions, accounting for 2% of global energy use and 1.6% of CO2 emissions. To tackle these environmental challenges, there is a pressing need to develop more sustainable methods that utilize renewable energy sources and reduce CO2 emissions (S. Chen et al., 2019, p. 2).

Recent advances in Ammonia Synthesis

New methods to enhance ammonia synthesis under milder conditions are continuously investigated especially at lower temperatures and pressures. The previously explored method typically requires high temperatures and pressures, resulting in significant energy consumption and carbon emissions. If ammonia can be produced under less energy-consuming conditions, it opens up exciting possibilities such as smaller-scale devices that could be used for ammonia generation. Renewable energy sources (such as atmospheric pressure electrolyzers) combined with low-pressure NH3 synthesis could lead the way to more sustainable practices. Exploring alternative pathways (photocatalysis, electrocatalysis, chemical simulation, and biological NRR) contributes to the journey for energy-efficient ammonia production (Movick et al., 2023).

Biological Nitrogen Reduction

To simulate nitrogen reduction, the process of this biological process is advantageous and necessary since it is a green and natural process. Atmospheric nitrogen gas (N_2) is converted into ammonia (NH_3), a form of nitrogen that living organisms can use. A marine alga hosts a cyanobacterium called UCYN-A inside its cells, the specialized bacteria capture nitrogen gas (N_2) from the air. Nitrogen gas is made up of two nitrogen atoms held together by a very strong bond. The bacteria can now use a special enzyme called nitrogenase to break these bonds, once the bond is broken, each nitrogen atom combines with hydrogen atoms to form ammonia

(NH_3). The ammonia formed can be absorbed by plants where it's used to make vital compounds like amino acids, which are the building blocks of proteins (Coale et al., 2024).

Nitrogen to ammonia synthesis in the laboratory

Electrochemical ammonia synthesis is an area of research that focuses on developing alternative methods to the traditional Haber-Bosch process. Some recent advancements include two electrochemical methods such as N2 electrolysis and the electrochemical reduction of atmospheric nitrogen, which can be conducted at a lower temperature (Jiao & Xu, 2018; Pavel, 2023).

The reaction mechanisms for the nitrogen-to-ammonia synthesis

The electrochemical ammonia synthesis is complex and evolves several pathways, but the main reaction mechanisms are the dissociative mechanism associative pathway, and the enzymatic pathway. On the dissociative mechanism, the N-N bond is broken before the nitrogen atoms are adsorbed onto the catalyst surface (Biswas et al., 2022).

For the associative pathway, there are two different sub-pathways. Firstly on the alternating pathway, nitrogen binds to the catalyst, and hydrogen atoms are added on at the same time. For the distal pathway, The nitrogen molecule binds to the catalyst with one nitrogen atom (end-on). Hydrogen atoms are added to the nitrogen atom that is not bonded to the catalyst (the distal nitrogen). After the distal nitrogen has been hydrogenated, the hydrogenation continues on the proximal nitrogen until ammonia is formed (Biswas et al., 2022).

Finally, the enzymatic pathway mimics the biological nitrogen reduction previously mentioned. These processes are usually enhanced by catalysts, and recent advancements in transition metal borides, carbides, and nitrides have demonstrated advantages in selectively adsorbing nitrogen and also reducing it. Both theoretical and experimental research, including density functional theory (DFT) analyses, are being developed to enhance the efficiency and selectivity of these mechanisms.

Advantages and disadvantages of nitrogen to ammonia synthesis

Even though the process is less energy-consuming the electrochemical nitrogen reduction reaction (NRR) requires a more energy-efficient approach due to its slow reaction rates. Getting a high selectivity is complicated since catalysts usually favor producing hydrogen over ammonia, which leads to energy waste. Also, the inherent stability of nitrogen molecules and competition from hydrogen evolution reactions (mentioned previously in this report) in aqueous solutions present big obstacles. Other issues arise with low partial current density for ammonia, low Faradaic efficiency, and difficulties in accurately measuring ammonia due to contamination. Developing catalysts that enhance activity, selectivity, and durability is crucial for advancing electrochemical ammonia synthesis. Strategies are needed to improve process activity and durability, with a focus on potential future industrial applications (Biswas et al., 2022; Fu et al., 2022).

Of course, despite these challenges, the advantages are significant and promising, it can potentially operate under milder conditions, reducing the energy required to break the strong nitrogen bonds. With this, it reduces carbon emissions associated with non-renewable power sources. Unlike the centralized production in the Haber-Bosch process, electrochemical synthesis can be done on-site, lowering transportation costs and making fertilizer more affordable. It allows for small-scale production, which can be scaled according to demand, providing flexibility and reducing waste. The process can produce high-purity ammonia, which can be an advantage in various applications, such as as a potential carbon-free fuel. Solid-state electrochemical synthesis has the potential to overcome the problems of conventional methods, such as limited conversion and severe environmental pollution. These advantages show a big potential for electrochemical ammonia synthesis to become a greener and more efficient alternative for ammonia production (Fu et al., 2022; Biswas et al., 2022; Amar et al., 2011).

Nitrogen Analysis

Dinitrogen, also known as molecular nitrogen (N_2), is interesting due to its specific properties and its important role in various chemical processes. It contains a strong triple bond ($N \equiv N$) with a high bond enthalpy. It is also the most abundant element in the Earth's atmosphere, and its composition is about 78.1% of the air by volume. It is one of the most produced industrial gases, used in different applications such as food preservation, fertilizers, and the production of steel and pharmaceuticals. Other than that Nitrogen is fundamental in almost all proteins, it is found in DNA as nitrogenous bases and in neurotransmitters (Chemistry of Nitrogen, 2023).

Nitrate Analysis

Nitrate is a compound that is present in several environmental systems, usually the result of natural activities and pollution. It is found in water bodies and can accumulate through the food chain. It is found here due to activities like the use of nitrogenous fertilizers, fossil fuel combustion, and nitrogen-fixing crops. Since the haber bosch process has been used, its presence has been increasing (Singh et al., 2022).

It is one of the essential macronutrients for plants. It is absorbed through the roots and serves as a primary source of nitrogen. Plants use nitrate to create amino acids, which are the foundation blocks for proteins. Proteins are essential for various cellular processes and overall plant health. Proper photosynthesis also relies on nitrate availability. During photosynthesis, plants absorb sunlight and convert it into energy, which is used for growth and development. Without nitrates, this process is not possible. Nitrate signaling also regulates the plants' response to abiotic stressors like nutrient deficiencies, unfavorable pH, ions, and drought (Ye et al., 2022).

Nitrates can also be of benefit to us, they occur naturally in our bodies and are found in both healthy and unhealthy foods. Medications containing nitrates widen blood vessels and help treat angina. Synthetic nitrates are added to processed meats (like bacon, sausage, and deli meats) to prevent bacterial growth and enhance flavor. Natural nitrates from vegetables (e.g., celery) are also used, but they convert to nitrites in the stomach, but potentially forming carcinogens. Leafy greens rich in nitrates could be also of benefit to heart health (Corliss, 2022).

There are some dangers associated with nitrates too, excessive nitrates or nitrites can convert the iron in hemoglobin to its ferric ($Fe3+$) state, resulting in methemoglobin, an abnormal form of hemoglobin that cannot bind oxygen. This condition, known as methemoglobinemia, leads to poor tissue oxygenation and anoxia (University of Washington, Department of Environmental & Occupational Health Sciences, 2014).

Electrocatalytic reduction of nitrate to ammonia.

The electrocatalytic reduction of nitrate to ammonia is an important area of research due to its potential for a sustainable method of ammonia production and nitrate waste management. It has been focusing on developing efficient electrocatalysts, the goal of this research experiment. Transition metals with occupied d-orbitals that match the energy levels of nitrate's lowest unoccupied molecular orbital have been found effective (Theerthagiri et al., 2022).

Understanding the intermediates and side reactions is crucial. Some researchers have achieved nitrate conversion rates from 53% to 99.8% and ammonia selectivity from 70% to 97.4% (Theerthagiri et al., 2022).

Both computational and experimental methods have been used extensively to understand the reaction mechanism and evaluate the properties of catalysts (K. Zhang et al., 2024).

The use of carbon-based materials for green electro-conversion has been a recent advance, with some environmental benefits in its use. In this report, carbon nanofiber were used as the support for the catalyst (Theerthagiri et al., 2022).

The reduction of nitrate to ammonia reaction mechanisms

The nitrate reduction to ammonia involves several steps and side reactions, Figure 3 gives a simple idea of the process in the electrocatalyst surface.

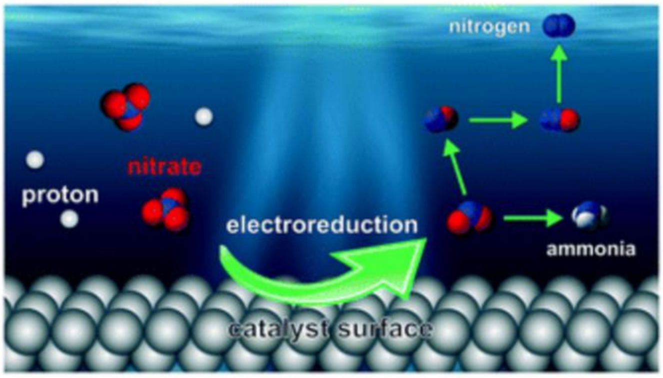


Figure 3- Simple visualization of nitrate reduction to ammonia at the catalyst surface (Z. Wang et al., 2021)

Initially Nitrate ions (NO_3^-) from the solution diffuse to the electrode surface. This stage is influenced by the medium (acidic or alkaline) and the concentration of nitrate ions. Then nitrate ions adsorb onto the cathodic electrode. This adsorption can be limited by the presence of other ions in the solution, here electrocatalysts with a high surface area and selective adsorption properties are crucial for efficient reduction. For the charge transfer, the electroreduction involves multiple stable nitrogen intermediates and products, like nitrite (NO_2^-), nitric oxide (NO), and ammonia (NH_3). The two mechanisms are as follows:

1. Indirect Autocatalytic Mechanism: Usually in acidic mediums, where NO_2^- and NO^+ serve as electroactive species, which lead to the formation of nitrous acid (HNO_2) by an autocatalytic process.

2. Direct Electrocatalytic Mechanism: In alkaline mediums with lower nitrate concentrations, it involves direct electron transfer to nitrate, which leads to its reduction by several intermediate steps.

Ammonia (NH_3) and dinitrogen (N_2) are the most thermodynamically stable products. Ammonia formation is favored under conditions that promote hydrogen adsorption, while nitrogen formation requires higher activation energy.

Regarding the pathways, the hydrogen-adsorbed pathway is where reduction of water to adsorbed hydrogen happens, which then reduces various nitrogen intermediates to ammonia. While for electrocatalytic pathway transition metal catalysts make the conversion of nitrate to nitrite, nitric oxide, and eventually to ammonia or nitrogen easier through electron transfer reactions (Theerthagiri et al., 2022).

The most favorable pathway involves several steps: $NO_3 \rightarrow NO_2 \rightarrow NO \rightarrow ONH \rightarrow ONH_2/HNOH \rightarrow NH_2/NH \rightarrow NH_2 \rightarrow NH_3$, ultimately producing valuable ammonia (Mahmood et al., 2023).

Some of the pathways are well identified in Figure 4.

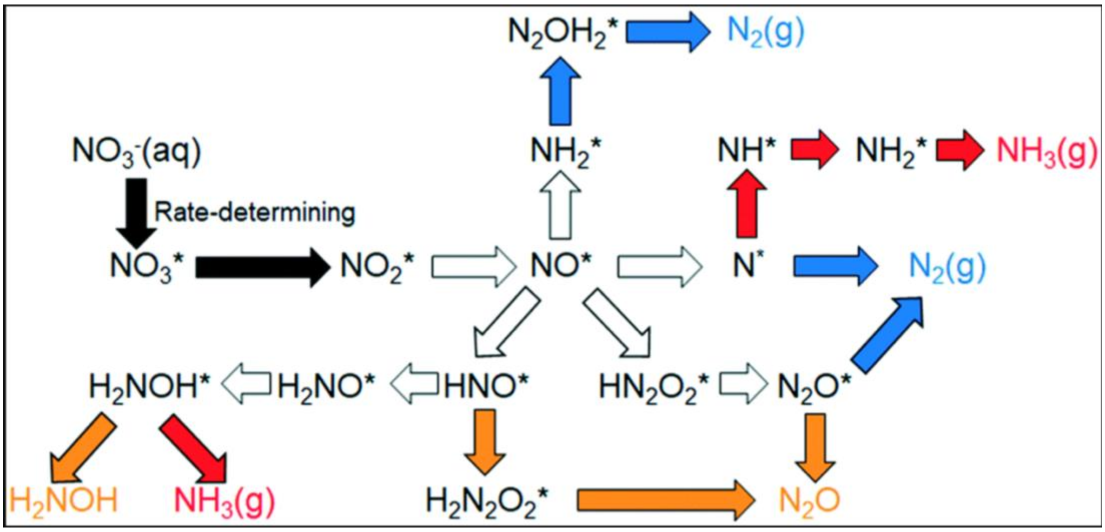


Figure 4- Pathways for nitrate to ammonia reduction reaction (Z. Wang et al., 2021)

The electrocatalytic reduction of nitrate to ammonia is promising but still shows some gaps and opportunities, as discussed ahead.

Gaps and Opportunities

The current research on the electrocatalytic reduction of nitrate to ammonia has made significant progress, but there are still limitations that present opportunities for further exploration. Current catalysts are not very good for its selectivity and stability. They may generate ammonia but also participate in other side reactions, which lower the efficiency, such as nitrite and hydrogen evolution. Also, it is needed for the catalyst to work for a long time, which is very important if it is meant to be used daily and at a large scale, and not only for one experiment. There are several reaction mechanisms, that are still not fully understood, the electrocatalytic reduction of nitrate to ammonia involves complex multi-electron and proton processes, and its pathways and intermediates are not always clear, which prevents the full efficiency of catalysts. There is a lot of room for innovation in catalyst design and synthesis, such as pore structure regulation, alloying, heterostructure construction, defect and interface engineering, crystal structure regulation, microenvironment modulation, and single-atom catalysts have been studied. These can enhance nitrate adsorption, increase the number of exposed active sites, improve mass transfer rates, lower intermediates barrier, and reduce side reactions. (Niu et al., 2023).

Iron-based catalysts

Fe-based catalysts are considered effective for nitrate reduction to ammonia due to several reasons. Fe/Cu diatomic catalysts have shown a maximum ammonia Faradaic efficiency of 92.51% at certain voltages, indicating most of the electrical charge contributes to the desired reaction (S. Zhang et al., 2023).

Computational and theoretical analyses suggest that the interaction between nitrate ions and Fe/Cu enhances the adsorption and discharge of nitrate anions, facilitating the reduction process. Fe-based materials, especially Fe2O3 nanoparticles supported on atomically dispersed Fe-N-C, demonstrate high NO3RR (nitrate reduction reaction) activity. The combination of these nanoparticles and single-atom Fe-N-C sites leads to a synergistic effect that enhances NO3RR performance. Studies have shown that the optimized 3xFe2O3/Fe-N-C catalyst achieves a maximum ammonia partial current density (jNH3) of 1.95 A cm-2, which is industrially relevant. The catalyst maintains a near unity Faradaic efficiency (FE) for NH3, indicating a high selectivity for ammonia production over other possible products (Murphy et al., 2023).

The process using Fe-based catalysts evolves reactants being adsorbed onto the surface of the at specific active sites. An interaction occurs between the catalyst's surface and the reactant molecules, which enhances their reactivity. The chemical reaction then takes place. The product molecules are desorbed from the catalyst surface. A good catalyst must adsorb reactant molecules strongly enough for them to react but not so strongly that product molecules remain permanently attached to the surface, and iron's ability to match this balance is confirmed (Clark, 2023).

Iron is a transition metal, which means it can exist in different oxidation states. For example, iron can form compounds like (FeO), iron(III) oxide (Fe_2O_3), and iron (II) the last being used in this research. These different oxidation states allow iron to participate in redox reactions, making it a versatile catalyst (Ashworth, 2014).

An interesting example involving iron as a catalyst is autocatalysis. In autocatalysis, a reaction is catalyzed by one of its own products. Iron ions (either iron(II) or iron(III)) can serve as the catalyst in such reactions (Clark, 2023).

Other than that iron is cheap and abundant which makes it a good pick for a catalyst (E. B. Bauer, 2015).

Carbon fibers as a support for catalysts

Carbon nanofibers (CNFs) can serve as excellent catalyst supports for various chemical reactions due to their unique properties. CNFs possess a high surface area due to their nanoscale dimensions and porous structure. This large surface area provides ample sites for catalysts to get attached, making the overall catalytic activity better, as well as their fibrous morphology which allows for efficient mass transport of reactants and products, reducing mass-transfer limitations.

CNFs also exhibit excellent electron conductivity due to their graphitic nature, enabling rapid redox processes at the catalyst sites. This property facilitates efficient charge transfer during catalytic reactions.

Another aspect is its stability under harsh reaction conditions. Their robust structure can withstand elevated temperatures, corrosive environments, and mechanical stress (Kim et al., 1994).

The surface chemistry of CNFs also allows for selective adsorption of specific reactants. CNFs can be paired with different groups (e.g., nitrogen, oxygen) to modulate their catalytic behavior, making them versatile for various reactions (Xia et al., 2022).

The compound $Fe(NO_3)_2{\cdot}6H_2O$@CNF consists of iron nitrate hexahydrate ($Fe(NO_3)_2{\cdot}6H_2O$) immobilized on carbon nanofibers (CNF). This composite material has great potential for electrocatalytic reduction of nitrate (NO_3^-) to ammonia (NH_3), and to achieve efficient results a strict methodology had to be followed.

Methodology

Before reaching the end goal of getting the ammonia yield and the faradaic efficiency, the experiment had several steps. These were divided by:

1. CNF and Iron(II) nitrate @CNF preparation.
2. XRD and SEM imaging
3. Working electrode preparation.
4. Electrocatalytic cell preparation.
5. Electrochemical testing.
6. Determination of ammonia yield and faradaic efficiency.

CNF and Iron (II) Nitrate@CNF preparation

The process for preparing Iron (II) nitrate@carbon nanofibers (CNFs) is described in detail. This method involves multiple steps to achieve the successful synthesis of the target material. The materials used include Iron (II) nitrate hexahydrate (Fe(NO3)2·6H2O), 1.5 grams of Polyvinyl alcohol (PVA) 67000, 10 milliliters of deionized water, and 5 grams of polytetrafluoroethylene (PTFE).

Overview of the compounds

PVA serves as a crucial component in the preparation process. It is highly water-soluble, making it an excellent choice for creating stable solutions or suspensions. It is cost-effective, which is advantageous for large-scale production. It can also be spun into fibers easily, making it suitable for creating nanofibers, and it can withstand moderate temperatures during processing. The role of PVA in the CNF is that it acts as a stabilizer, binder, and carrier for other components during the synthesis process. Deionized water plays a critical role in various stages of material synthesis. It is purified to remove ions, minerals, and impurities, resulting in ultra-pure water, the absence of these ensures that it won't interfere with chemical reactions. Deionized water serves as a solvent for dissolving and dispersing other materials. Deionized water could be also used in the electrolysis process to produce hydrogen (e.g., via High-Pressure Electrolysis). It provides a clean environment for splitting water molecules into hydrogen and oxygen. Sometimes deionized water may be involved in forming complexes (e.g., PVA–iodine complexes) that enhance material properties (Xu et al., 2019).

PTFE is known to be non-stick, resistant to adhesion by other materials, it also is highly unreactive, even at elevated temperatures. PTFE has low friction, making it suitable for applications where reduced wear and smooth surfaces are essential (C. Li et al., 2019).

Polymer preparation

First, 1.5 grams of Polyvinyl alcohol (PVA) 67000 was dissolved in 10 milliliters of deionized water. This solution was heated to 90°C using a water bath stirring machine, ensuring that the temperature of the water bath was higher than that of the solution in the beaker. Next, during the homogenization step, 10 grams of PTFE and 0.2 grams of Iron (II) nitrate hexahydrate were added to the PVA solution. The mixture was stirred at room temperature until it became homogeneous. Finally, the polymer was electrospun.

Electrospinning

Electrospinning was performed by using the polymer described previously to create very thin fibers by applying an electric field into a rotating cylinder. The process results in nanofibers with diameters ranging from nanometers to micrometers. Advantages of electrospinning include a wide range of available raw materials, a simple process, small fiber diameters, and high porosity. Researchers have extensively studied electrospinning, focusing on its influencing parameters, physical models, and computer simulations. These parameters include factors like solution viscosity, applied voltage, flow rate, and collector distance. To make the process more efficient, and the fibers to be homogenous and uniform these parameters have to be on the right value, as well as temperature and humidity inside of the electrospinning machine. Too much water vapor can cause the fibers to absorb water, which is not desired. Electrospinning is applied in various fields such as biomedicine where electrospun polymers play a vital role in biomedical engineering. They are used for tissue engineering, wound dressings, drug delivery systems, and others. Nanofibers can also enhance energy storage and conversion devices, such as supercapacitors and batteries. Electrospun nanofibers also serve as catalyst supports due to their high surface area and porosity, as in the case of this research. Electrospinning technology goes back to 1897 when Rayleigh et al. studied the phenomenon of charged liquid transforming from a cylinder to a bead. Even tho electrospinning started in the early twentieth century, it began real use around 2000 (Y. Guo et al., 2022). Figure 5 shows a simple schematic of the process.

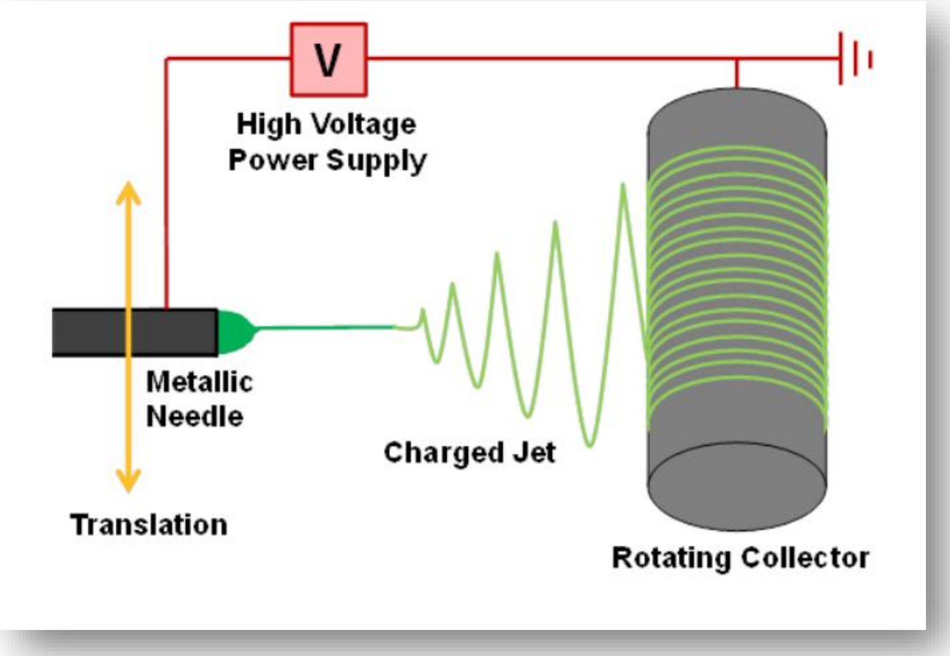


Figure 5- Exemplification of the electrospinning method (Electrospinning Services | NEI Corporation, n.d.)

The spinning voltage was set between 20 and 23 volts, and the push speed was adjusted to 0.05. The homogenized solution was then spun into the desired forms using appropriate spinning equipment. Both the voltage and push speed were continuously adjusted during the electrospinning process to ensure a uniform conic fiber release. As shown in Figure 6, the fibers would clog and needed to be cleaned every 20 minutes, making the entire process take nearly 8 hours. owing this, the fibers underwent a two-step heating process.

Figure 6- Prepared polymer inside of sirynge ready for electrospinning

Thermal Treatment

Thermal treatment is essential for developing carbon fibers with high mechanical strength. It finalizes the formation of carbon nanofibers (CNFs) and enhances the molecular orientation and ordering of graphitic domains, resulting in additional strengthening of the fibers. It is important to precisely control reaction parameters such as temperature, gas environment, time, choice of substrate, and tension applied during stabilization to optimize thermal treatments. It is also known that applying tension force during the carbonization process can improve the orientation of graphitic microstructures, thereby enhancing the mechanical properties of CNFs (Hu et al., 2020).

The fibers were then heated. The spun samples were placed in a muffle furnace preheated to 280°C and maintained at this temperature for two hours, with a ramp-up rate of 2°C per minute. After that, the samples were transferred to a tube furnace under an inert argon atmosphere, and preheated to 800°C. This temperature was also maintained for two hours, with the same ramp-up rate of 2°C per minute. After the thermal treatment, the samples were gradually cooled to room temperature under the inert gas atmosphere. The Iron (II) nitrate functionalized carbon nanofibers (CNFs) were then collected. For comparison, CNFs without Iron (II) nitrate were prepared using the same process but without the catalyst, to evaluate the differences in ammonia yield and faradaic efficiency. After being collected they were sent for imaging analysis.

XRD and SEM imaging

Imaging methods such as X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) are essential for characterizing materials and having a concrete visualization of the specific structure and composition of these.

X-ray diffraction (XRD)

X-ray diffraction is used to understand the crystal structure of materials. It helps identify the elements and structure of samples like the carbon nanofibers (CNF) and Fe(II) nitrate used in this experience. In XRD the sample is hit with X-rays. The X-rays then interact with the atoms in the sample, causing the X-rays to scatter and create a diffraction pattern. When the scattered X-rays have the same wavelength, they reinforce each other, creating stronger signals at specific angles. This is due to a key concept called Bragg's Law, in this law the diffraction angle is related to the wavelength of incident X-rays and the interplanar distance shown in equation (4).

$$\mathrm{n}\lambda = 2\mathrm{d} * \sin(\theta) \tag{4}$$

With:

Diffraction Angle (θ): The angle at which X-rays are diffracted.
n: An integer representing the order of the diffraction.
λ: The wavelength of the incident X-rays.
d: The distance between atomic planes in the crystal.

XRD measures the intensity of the diffracted X-rays at various angles, these measurements are plotted as intensity peaks against the angle (usually shown as 2θ). When seeing the results, it can provide information about the sample's composition, crystal structure, and phase purity. By analyzing these patterns, it is possible to confirm the presence of specific elements and assess the structural details of the material. This technique is used in various fields such as polymer science, metallurgy, structural biology, pharmaceutical science, catalysis, and many others (Dutrow & Clark, 2007; Kiani, 2023).

Scanning Electron Microscope (SEM)

In SEM An electron gun creates a beam of electrons, which is then focused to a very small diameter (0.4-5 nm) using condenser lenses, the focused beam is then directed in a rectangular scan over the sample by deflection coils that move the beam in the x and y axes. When the electron beam hits the sample, it loses energy through scattering and absorption. This interaction generates different signals, including secondary electrons, back-scattered electrons, and characteristic X-rays, which are detected by the SEM.

Secondary electrons are low-energy electrons coming out of the sample's surface because of inelastic scattering, they help create images showing the sample's surface topography. Another type of electron is back-scattered electrons these are electrons that bounce back from the sample. The intensity of this signal depends on the atomic number, giving information about the sample's elemental composition. Characteristic X-rays are emitted when the electron beam knocks out inner shell electrons, and higher-energy electrons fill the gaps.

The signals detected are then combined with the beam's position to produce detailed images. Secondary electron detectors are usually used to create gray-scale images that show surface details. Back-scattered electron detectors highlight differences in composition, with heavier elements appearing brighter (Nagle, 2022).

SEM instruments usually operate at accelerating voltages of 0.3–30 kV. SEM generates a variety of signals on the surface of solid specimens using a directed beam of high-energy electrons. These signals provide information about the sample's exterior morphology (texture), chemical composition, crystalline structure, and material orientation (Datye & DeLaRiva, 2023).

SEM is commonly used in physical, materials, and chemical sciences. It has found wide acceptance in medical studies, biological science, and pharmaceutical sciences. Advances in SEM have improved the imaging and study of various biological specimens. SEM also plays a role in nanotechnology, microchip production, and digital artwork (Kathirvel et al., 2022).

Working electrode preparation

First, 5 mg of catalyst was ground into a fine powder as shown in Figure 7, this increased its surface area, enhancing reactivity and making sure of an even dispersion in the solution. The ground catalyst was then added to a mixture of 655 µL ethanol, 325 µL deionized water, and 20 µL of a 5 wt% Nafion solution.

Figure 7- Grinded powder of the Fe (II) Nitrate@CNF

Next, the catalyst mixture was put through ultrasonic dispersion, where ultrasonic energy was used to break up any large aggregates, ensuring a uniform sample. This process was carried out for 60 minutes to ensure good mixing.

Once the sample was homogeneous, 20 µL of it was dropped onto a carbon paper substrate. Carbon paper is chosen for its high conductivity and stability as mentioned previously, making it ideal for electrochemical applications. This step anchors the catalyst particles onto the carbon paper surface.

Finally, the deposited suspension on the carbon paper was left to dry at room temperature on a lamp as shown in Figure 8. This allows the solvents (ethanol and water) to evaporate, leaving a thin, evenly distributed film of the catalyst on the carbon paper substrate.

Figure 8- Drying of carbon paper with the catalys

Electrocatalytic cell preparation

Electrocatalytic cell

Electrochemical cells generate electricity from spontaneous redox reactions or consume electricity to drive nonspontaneous redox reactions. These reactions involve the transfer of electrons from one chemical substance to another, driven by oxidation-reduction (redox) reactions. They consist of two electrodes (anode and cathode) connected by an external circuit and an electrolyte, which allows ions to transfer between electrode compartments, maintaining electrical neutrality.

There are two types of Electrochemical Cells:

1. Galvanic Cells (Voltaic Cells): They use the energy from spontaneous reactions to generate electricity.

In galvanic cells, oxidation happens in the anode, where there is a releasing of electrons, while at the cathode reduction happens, attracting electrons. The electrons flow from the anode to the cathode through the external circuit, producing an electric current.

2. Electrolytic Cells: Consume electrical energy to drive nonspontaneous reactions.

Electrolytic cells operate in the other way around, where an external voltage is applied to drive nonspontaneous reactions.

A salt bridge completes the circuit and maintains electrical neutrality by allowing ions to go between electrode compartments. A voltmeter is used to measure the potential difference between the two compartments of the cell and gives an indication of the cell potential (Ecell) in volts (Qayyum Kashif, 2018).

For the nitrate reduction of ammonia, all electrochemical tests were conducted in an H cell, divided by a Nafion membrane. The experimental setup used a three-electrode system: a carbon sheet coated with Fe (II) Nitrate@CNF as the working electrode, a platinum tablet as the counter electrode, and a saturated Ag/AgCl/KCl reference electrode for neutral electrolytes. The electrolyte for both the anode and the cathode was the same, Figure 9 shows this setup. For neutral conditions, the electrolyte was a 0.1 M PBS solution (prepared from Na2HPO4 and NaH2PO4) with a pH of 7, NaNO3 is added to the electrolyte as a nitrogen source after high-temperature impurity removal. The potential of the reference electrode relative to the reversible hydrogen electrode (RHE) is calculated using equation (5).

In 0.1 M PBS with 0.1 M NaNO3:

$$E(RHE) = 0.0591 \times pH + E\left(\frac{Ag}{AgCl}\right) + 0.197\,V \tag{5}$$

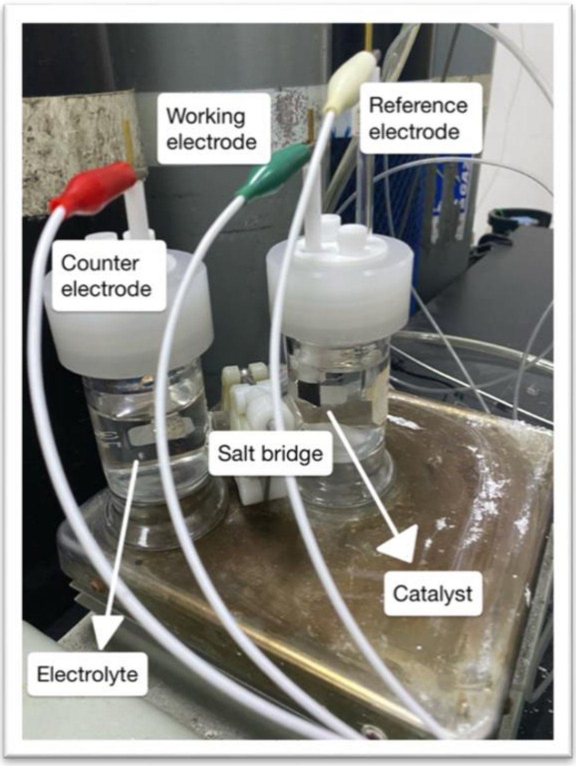


Figure 9- Electrochemical cell set-up

Electrochemical testing

Electrochemical methods

Some key techniques include potentiometric methods where the potential is measured under static conditions. In this case, no substantial current is flowing through the cell, and its composition remains unchanged. It is usually valuable for quantitative analysis of the system, through its electrical properties, Also, the coulometric method (Coulometry) converts the species that are being analyzed completely on another substance whether by oxidation or reduction with the goal of precise analysis of the analyte quantities and properties. Finally, voltammetric and amperometric methods. In voltammetry, a time-dependent potential is applied to an electrochemical cell measuring the resulting current as a function of that potential. This one also gives quantitive and qualitative information about the species involved, used repeatedly in the experiment performed for the nitrate reduction reaction (DePauw University, 2021).

Voltammetric and amperometric methods

Cyclic voltammetry (CV)

Cyclic voltammetry (CV) is a widely used and reliable technique for assessing the initial performance of electrochemical capacitors and gaining insights into complex electrode reactions. CV is an electrochemical method that measures current and voltage during reduction and oxidation reactions, it gives qualitative information about electrode processes. CV is also very effective in assessing electron transfer that is started by chemical reactions, including catalysis.

CV can measure the current as a function of the applied potential, with this it captures both reduction and oxidation reactions. It makes it important in analysing electron transfer in catalytic reactions, making it a crucial tool for studying electrocatalytic materials. In this test the x-axis represents the applied potential (V) and the y-axis represents the resulting current (i).

When performing CV testing, the the potential of the working electrode is cycled while measuring the current. In a two-electrode setup, the potential difference between the positive and negative electrodes is measured, while in a three-electrode configuration, the potential is measured between the reference and working electrodes. When this happens the measured currents during the anodic (oxidation) and cathodic (reduction) sweeps are recorded to characterize the electrochemical reactions. Data is then plotted as current (A) versus potential (V) to illustrate the electrochemical processes involved. These tests were performed and analyzed later in this report (Azam & Mupit, 2022).

This technique can be used to study the presence of intermediates in oxidation-reduction reactions and the reversibility of a reaction. It can also be used to determine the electron stoichiometry of a system, the diffusion coefficient of an analyte, and the formal reduction potential, which can be used as an identification tool (Quiroga, 2023).

Linear sweep voltammetry (LSV)

In Linear sweep voltammetry (LSV) a working electrode is used, also an unstirred solution containing an excess of supporting electrolyte helps to suppress the migration of charged species, making sure that the movement of electroactive species is mainly due to diffusion. The potential of the working electrode then changes linearly with time, the current is recorded throughout the experiment, resulting in a voltammogram (a plot of current vs. potential). There is a peak in this plot that can give us some insight into what is happening. The maximum current observed during the experiment and consequently the potential at which the peak current occurs. In the beginning, when the potential is in a range where no electrochemical reaction occurs, a small capacitive current is seen. This is due to the rearrangement of ions and molecules near the electrode surface. When the potential reaches the region where the electrochemical reaction occurs, the current starts to increase rapidly due to the electron transfer process. There is then the peak as the potential becomes more suitable for the redox reaction, and the rate of electron transfer increases. Then the peak starts going down, from the depletion of the analyte, which leads to a decrease in current. LSV is a powerful method for characterizing electrochemical reactions, especially when analyzing freely diffusing species in solution without significant interactions with the electrode surface or additional chemical reactions (Bontempelli et al., 2019).

This technique is used to analyze the kinetics of electron transfer, including catalysis, it can also be used for organic and inorganic synthesis, sensor, and biological system evaluation (Peroff, 2023).

Chronoamperometry (i-t test)

In an electrochemical cell that has a working electrode, a counter electrode, and a solution containing only the oxidized form of the analyte (O) a potential is applied between the working and counter electrodes so that no electrochemical reactions occur, this results in no net current flow. The potential is stepped 177 mV more negative, causing immediate reduction of “O” to “R” at the electrode surface, making “O” concentration nearly zero at the electrode surface. In the case of the experiment done, an electrochemical cell with a working electrode coated with Fe(II) nitrate on carbon nanofibers (CNF), a counter electrode and an electrolyte solution containing nitrate ions (NO_3^-) are initially at a potential where no significant reactions occurring, so there's no net current. The potential at the working electrode is then stepped to a more negative value. This negative potential will make the reduction reaction start to happen. At this new potential, nitrate ions (NO_3^-) at the electrode surface are reduced to ammonia (NH_3). The Fe(II) nitrate@CNF catalyst is helping this reaction by lowering the energy required and providing active sites for the reaction to occur efficiently. The Fe(IIII) nitrate is acting as a catalyst, which means it helps speed up the reduction of nitrate to ammonia without being consumed in the process. The carbon nanofibers (CNF) provide a large surface area and good electrical conductivity, which helps the process and the efficiency of the reaction. As the nitrate ions near the electrode surface are reduced to ammonia, more nitrate ions from the bulk solution diffuse to the electrode surface. This diffusion is driven by the concentration gradient created as nitrate is reduced at the surface. The current flowing in the circuit is related to the rate of the nitrate reduction reaction. When measuring the current, it is possible to determine how efficiently the catalyst is converting nitrate to ammonia (Franklin et al., 2016; Leslie & Mauzeroll, 2024).

Determination of ammonia yield and faradaic efficiency

Ammonia yield

The Indophenol Blue Method is a widely used colorimetric technique for measuring ammonia concentrations. This method is based on a chemical reaction where ammonia interacts with indophenol blue, resulting in the formation of a blue/green-colored complex . The depth of the blue color produced in this reaction is directly proportional to the amount of ammonia present in the sample. The Indophenol Blue Method is particularly valuable in various applications, including water quality monitoring and studies involving the Nitrogen Reduction Reaction (NRR). Its reliability and simplicity make it a preferred choice for researchers and professionals working in environmental science and analytical chemistry, ensuring precise ammonia quantification in diverse contexts. To quantify the ammonia concentration, the absorbance of the blue/green complex is measured using UV-visible spectroscopy. The principle of UV-visible spectroscopy involves measuring the absorbance of light by a compound. In the context of ammonia detection, this technique is used to measure the absorbance of the indophenol blue-ammonia complex. The resulting UV-visible spectra offer valuable information regarding the concentration of ammonia. By utilizing a calibration curve, which correlates absorbance to ammonia concentration, accurate quantification can be achieved. This method is essential for precise and reliable determination of ammonia levels in various analytical applications. This measurement allows for accurate determination of ammonia levels because the absorbance is directly correlated with the concentration of ammonia in the sample (Utomo et al., 2023).

UV-vis spectrophotometry for ammonia detection

The post-electrolyte from the experiment using Fe(II) Nitrate@CNF as the working electrode is diluted 40 times before testing. In contrast, the post-electrolyte using CNF as the working electrode is only diluted once before testing. Specifically, 2 mL of the solution after the reaction is mixed with 2 mL of a 1 M NaOH coloring solution containing 5% salicylic acid and 5% sodium citrate. Then, 1 mL of an oxidizing solution (0.05 M NaClO) and 0.2 mL of a catalyst solution ($C5FeN6Na2O$ at 1 wt%) are added to the mixture. After standing in the dark for 2 hours, the UV-Vis absorption spectra are measured, this is shown in Figure 10, going from right to left (-0.8 V to -1.2 V) it is possible to see a darker green. The concentration of NH3 is determined by measuring the absorbance at a wavelength of 655 nm. The concentration-absorbance relationship is calibrated using a standard NH4Cl solution in a 0.1 M NaOH solution.

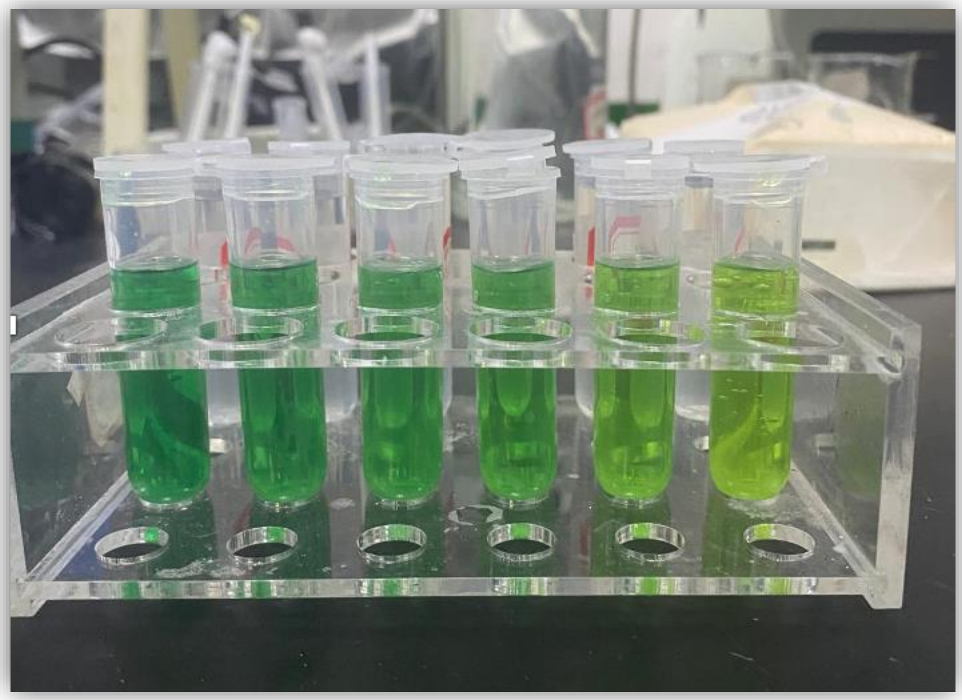


Figure 10- Indophenol blue method (one set of results)

Nitrite yield

The Griess Method is a widely used technique for detecting nitrite. The principle of this method involves a reaction between nitrite and the Griess reagent, which comprises an aniline derivative and a coupling agent in an acidic solution. This reaction produces a red-pink-colored compound that can be measured spectrophotometrically. The absorbance of this colored product is typically measured at a wavelength of 540 nm, providing a quantitative indication of nitrite concentration. The Griess Method is known for its simplicity and speed. It is highly sensitive and capable of detecting nitrite levels as low as 1 nmol per well. This makes it an excellent choice for applications requiring precise nitrite quantification (Ab234044 Griess Reagent, 2018).

Griess method for determination of nitrite (NO_2^-)

The concentration of nitrite is measured using the Griess reagent. To prepare the reagent, 0.2 g of N-(1-naphthyl)ethyl-diamine dihydrochloride, 2.0 g of sulfanilamide, and 5.88 mL of phosphoric acid are dissolved in 100 mL of deionized water and stirred until thoroughly mixed. The reacted electrolyte is then diluted 10 to 20 times. From this diluted solution, 1 mL is mixed with 1 mL of the Griess reagent and 2 mL of deionized water. The mixture is allowed to develop color in the dark at room temperature for 10 minutes. The resulting magenta solution is analyzed using UV-vis absorption spectroscopy over the range of 400 to 650 nm. The absorbance at 540 nm is then used to determine the nitrite concentration by comparing it to a standard curves.

In situ and operando techniques

The introduction of in situ and operando techniques has marked a significant advancement in catalysis research, propelling the field forward with unprecedented insights into catalyst behaviour. These innovative methods offer researchers the unique opportunity to study catalysts under authentic operating conditions, providing invaluable insights into catalytic mechanisms and dynamic behaviours that were previously inaccessible.

In situ techniques observe catalysts under conditions that closely mimic real-world environments, including factors like pressure and temperature, which were not used in this experiment. On the other hand, operando techniques involve simultaneous measurements of catalytic activity and selectivity during reactions, enabling real-time monitoring and analysis.

By enabling researchers to study catalysts in action, these techniques offer an immediate understanding of structural changes, bonding dynamics, and reactivity during reactions. The integration of in situ and operando techniques with machine learning tools accelerates catalyst optimization and enhances data interpretation, streamlining the research process.

Overcoming challenges such as radiation damage, instrumentation limitations, and complex data interpretation is essential for the continued advancement of these techniques. These techniques play a pivotal role in observing dynamic changes in catalysts during reactions, providing critical insights for the design and development of efficient catalytic systems. Their ability to capture real-time data is instrumental in fine-tuning and improving catalytic processes, making them indispensable tools in modern catalysis research (L. Chen et al., 2024; Mu et al., 2023).

Calculations of the FE and NH_3 yield rate

The yield of NH_3 is calculated using the equation (6):

$$Yield\ (NH_3)\ = C(NH_3) \times V \div (t \times m_{cat}) \tag{6}$$

The faradaic efficiency of NH_3 is calculated using equation (7):

$$FE_{NH_3} = 8 \times F \times C(NH_3) \times V \div (17 \times Q) \tag{7}$$

The faradaic efficiency of NO^{2-} is calculated using equation (8):

$$FE_{NO^{2-}} = 2 \times F \times C(NO^{2-}) \times V \div (46 \times Q) \tag{8}$$

Where:

$C(NH_3)$: Measured concentration of NH_3
$C(NO^{2-})$: Measured concentration of NO^{2-}
V: Volume of electrolyte in the cathode chamber
t: Time for which the potential is applied
m_{cat}: Mass of catalyst loaded on the working electrode.
F: Faraday constant (F = 96485 C mol^{-1})
Q: Total charge applied during the reaction

After following this detailed methodology, several results were obtained, which are shown in the next section.

Results

The results section follows the methodology with the presentation of experimental data and findings. Firstly, there is an analysis of electrochemical testing results, and then the characterization of catalyst composition and structure.

Electrochemical testing

Fe (II) Nitrate@CNF initial testing

This section shows the results of the relevant electrochemical tests for the analysis of this catalyst. In Figure 11 the LSV curve for the catalyst with and without nitrate electrolyte, it is possible to see a difference in the curves. In the curve without nitrate, no reactions are happening close to the optimal voltage of -1.1 V and even in the tested voltage ranges, while in the curve of the electrolyte with nitrate, the current is higher and there is a big peak until the reaction starts to slow down again. For the curve without nitrate, the current keeps steady close to zero while on the curve with nitrate, there is a noticeable increase.

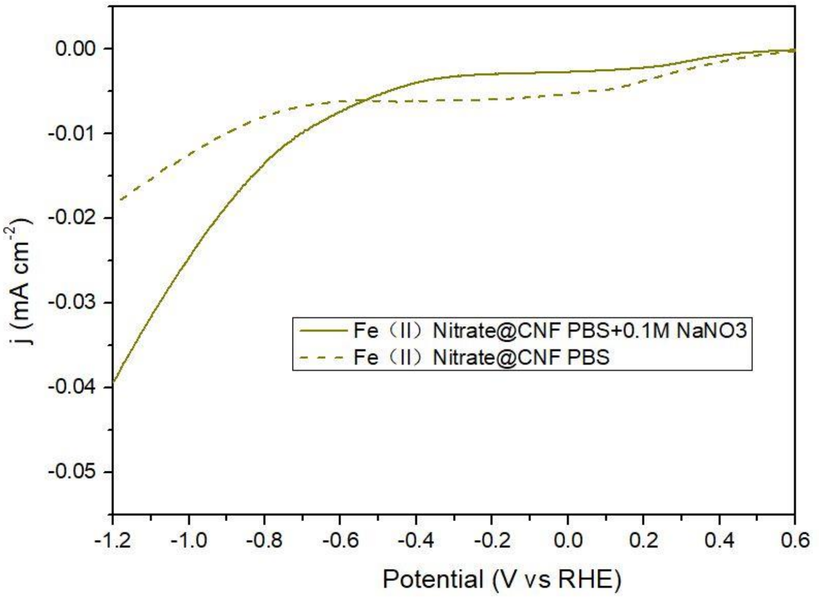


Figure 11- LSV curve of Fe (II) Nitrate@CNF with and without 0.1M $NaNO_3$

The noticeable range of highest reaction activity through this test was defined to be between -0.8V and -1.2V, so this range was further analyzed.

To further analyze this range the i-t tests shown in Figure 12 over the course of one hour for each of the voltage show an increasing current value for each increased voltage. In an electrolytic cell, applying a higher voltage increases the rate of redox reactions at the electrodes, thus increasing the current. Once the reactions stabilize, assuming no significant changes in concentration or temperature, the current remains steady.

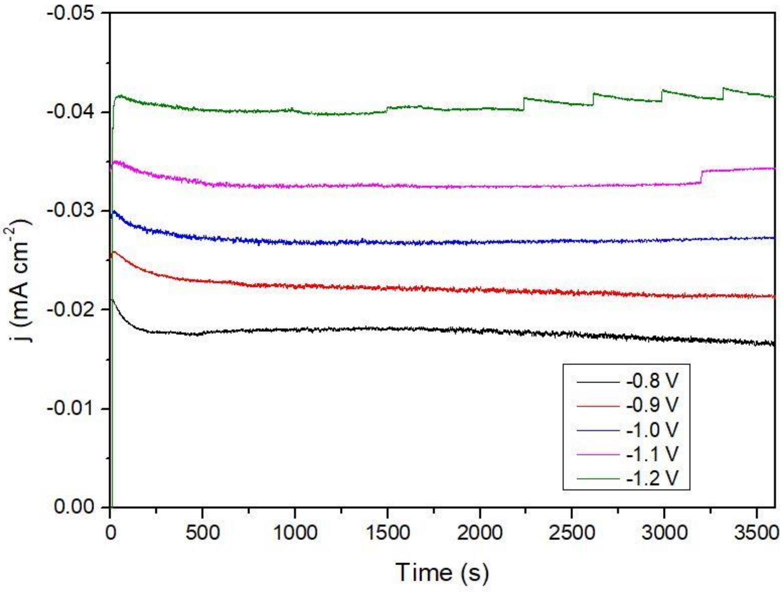


Figure 12- Chronoamperometric tests for each voltage

A U-vis spectrometry was also performed for each of the samples, resulting in higher absorbance for the highest voltages, Figure 13 shows these results.

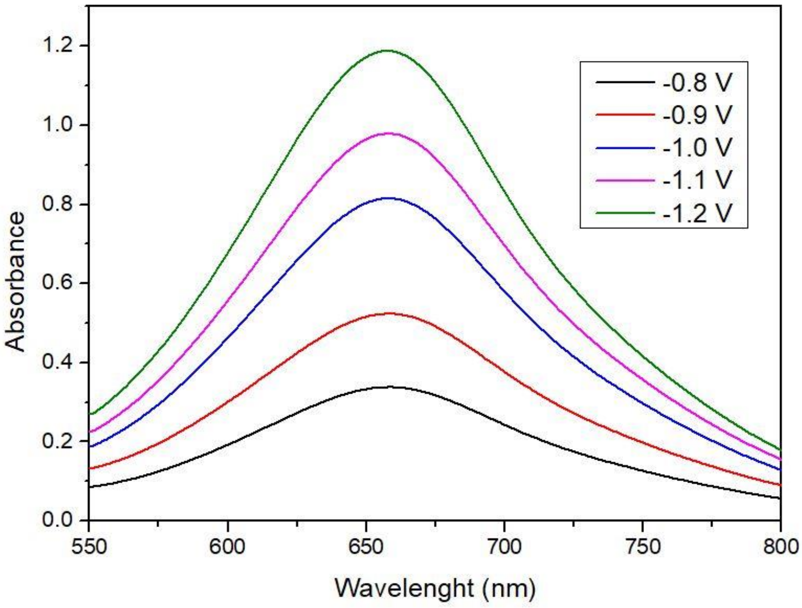


Figure 13- U-vis absorbance spectra curves for each of the 5 potentials

To get a sense of how these curves translated to actual results, the absorbance at 655 nanometers wavelength was retrieved, with these values and using the formulas mentioned in the methodology section, it was possible to reach the first results for faradaic efficiency and NH_3 yield shown in Table 1.

Table 1- Results for the first test of final solution at 5 different potentials

Test voltage (V)	Absorbance	Q (Coulombs)	FE (%)	NH3 yield (mg h^-1 mg^-1 cat)
-0.8	0.339	63.8	37.4	5.2
-0.9	0.524	80.8	48.7	8.7
-1.0	0.816	97.8	65.4	14.1
-1.1	0.979	118.6	65.5	17.1
-1.2	1.189	146.4	65.1	21.0

Table 2 shows the first testing results for each voltage potential, giving insights on absorbance, the Q in coulombs, the faradaic efficiency, and the NH_3 yield.

As seen in this table, the highest faradaic efficiency was -1.1 volts, and even though the highest yield was at -1.2 volts, the lower potential resulted in less energy-consuming results.

Not only the results of the ammonia yield and faradaic efficiency are of interest, but as mentioned before, side reactions may also produce nitrite. In this experiment, the nitrite efficiencies were also obtained, to get a sense of how well and selective the conversion was being made. This theory was previously analysed in the catalyst development section and translated into results here. Using the Griess method and formulas previously mentioned the results achieved are shown in Table 2.

Table 2- Analysis of the solution for nitrite, including absorbance, charge, voltage, and FE.

Test Voltage (Volts)	Q (Coulombs)	Absorbance	FE(%)
-0.8	63.7	3.5	45.3
-0.9	80.8	3.2	32.6
-1	97.8	3.0	25.6
-1.1	118.6	2.9	20.5
-1.2	146.4	2.9	16.6

To have a better idea of how these results compare to the NH_3 analysis Figure 14 shows a clear picture of the performance of each voltage.

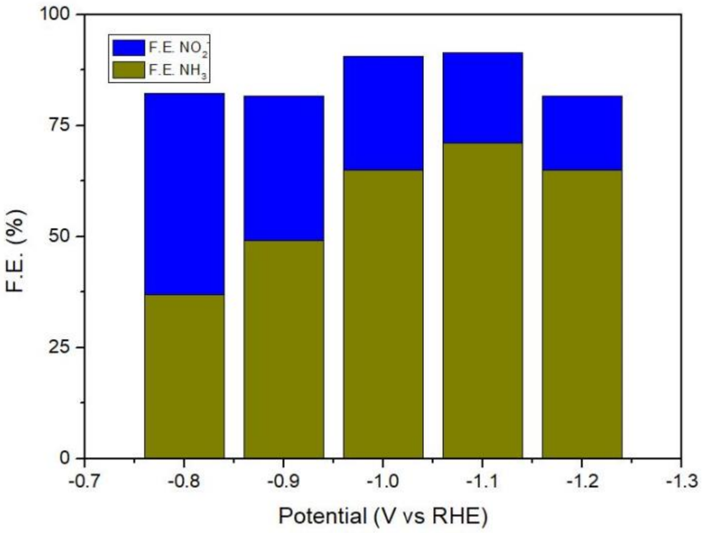


Figure 14- Faradaic efficiency of ammonia and nitrate conversion for each voltage.

In blue it is possible to see the nitrite conversion efficiency and in green the ammonia conversion efficiency. There is a clear difference, ammonia conversion is very selective, especially at the optimal voltage of -1.1 volts, which shows a good performance of the process and the catalyst. Now that the desired voltage was defined, several testing was performed to study the catalyst further and eventually achieve higher efficiency, even though a value of 65.5% was already promising.

Fe (II) Nitrate@CNF optimal voltage testing

As previously mentioned now that an optimal voltage was defined, further testing proceeded. The previous absorbance test with and without 0.1M $NaNO_3$ was repeated, but solely for a voltage of -1.1V, the U-vis absorbance spectra are shown in Figure 15.

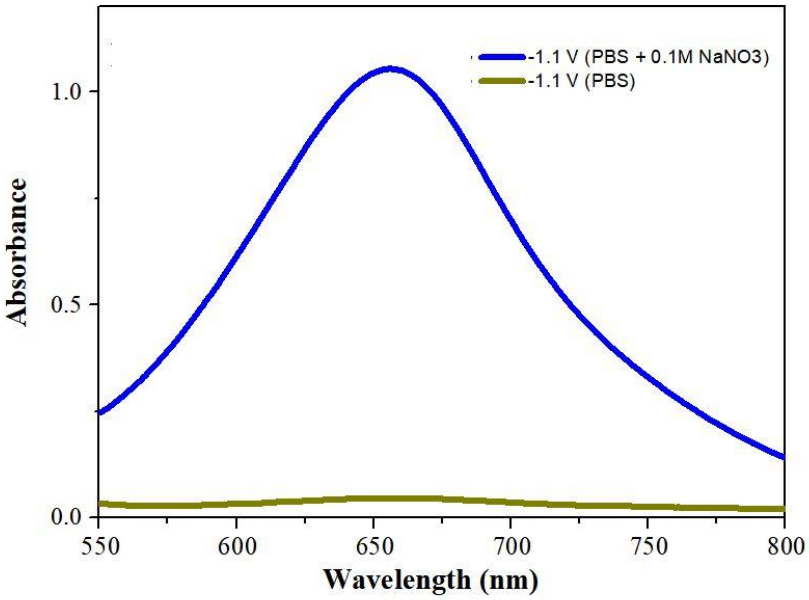


Figure 15- U-vis absorbance spectra for optimal voltage with and without 0.1M $NaNO_3$

These curves show a clear difference in absorbance, the electrolyte with PBS only serves as a reference, since no ammonia was formed, comparing it with the nitrate-containing electrolyte, confirms the reducing capacity of the catalyst.

To further analyze the yield and efficiency of the catalyst at the optimal voltage of -1.1 V and minimize error the experience was performed 5 more times, called recycling tests. Table 3 shows the experimental data of these tests and Figure 16 gives a graphic representation for better interpretation.

Table 3- Experimental data for recycling tests

Cycle number	Test voltage(Volts)	Absorbance	Q(Coulombs)	FE(Faradaic efficiency)	NH3 yield rate(mg h^-1 mg^-1 cat)
1	-1.1	0.979	118.6	65.5	17.1
2	-1.1	1.055	118.6	70.9	18.5
3	-1.1	0.953	118.2	63.8	16.6
4	-1.1	0.836	92.5	70.9	14.5
5	-1.1	0.742	90.9	63.5	12.7

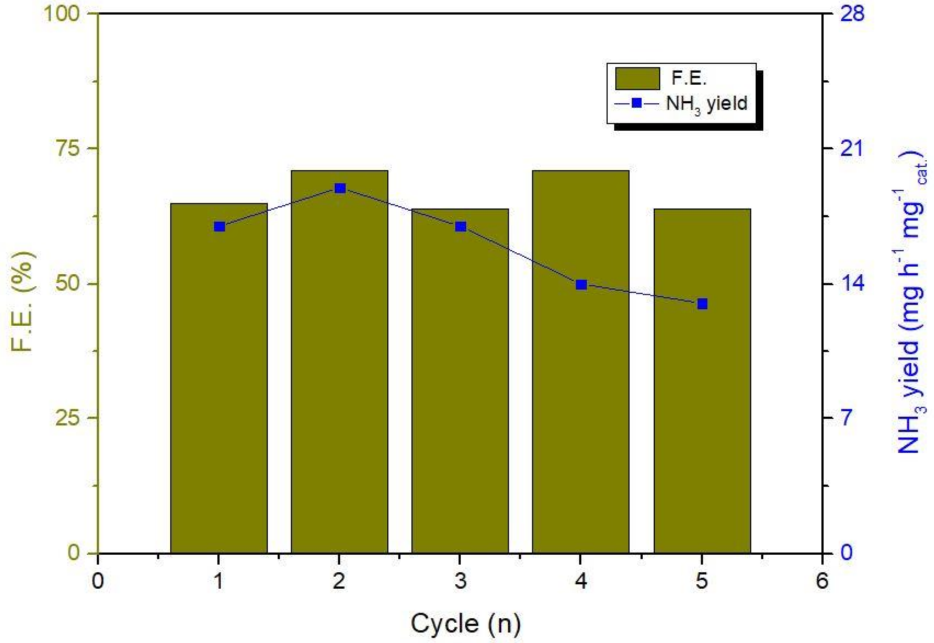


Figure 16- Recycling tests for Fe (II) Nitrate@CNF showing NH_3 yield and FE

The faradaic efficiency of the tests showed a further increase in the performance of the catalyst, the highest achieved efficiency was 70.9%, and a maximum NH_3 yield rate of 18.5 mg h^{-1} mg^{-1}_{cat} in cycle number 2.

Finally, the stability of the catalyst was another important aspect to access and mention, this was measured over 24 hours at optimal voltage and measured the current in terms of the time. Figure 17 shows that the performance of the catalyst was stable.

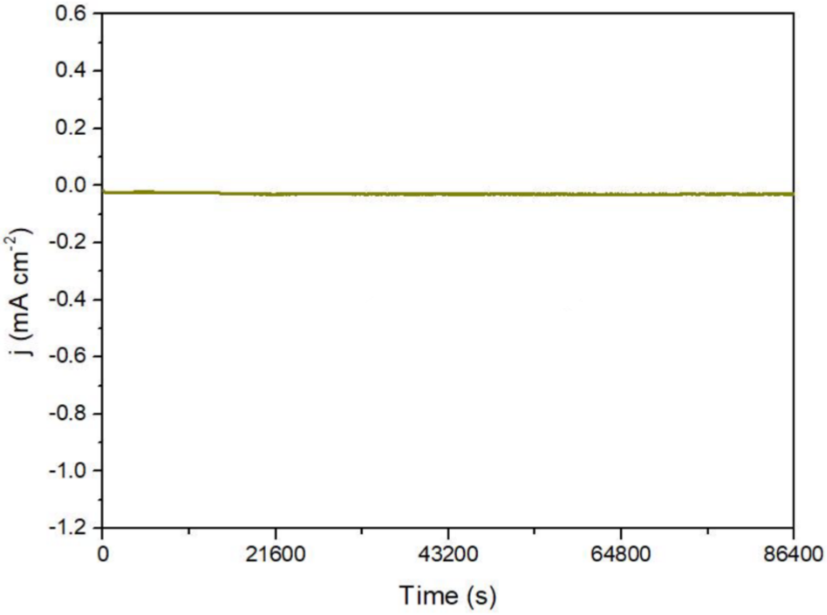


Figure 17- Chronoamperometry for 24 hours at optimal potential.

Carbon nanofiber testing and comparison to Fe (II) nitrate@CNF as a catalyst

Carbon nanofiber electrochemical testing involved similar practices as the Fe (II) nitrate@CNF catalyst as explained in the methodology section and served as a comparison. Table 4 shows the experimental data of the results attained for the CNF.

Table 4- Experimental results for carbon nanofiber at different voltages

Test voltage (V)	Absorbance	Q (Coulombs)	FE (%)	NH3 yield (mg h^-1 mg^-1 cat)
-0.8	0.198	54.2	22.1	2.6
-0.9	0.273	60.6	30.2	4.0
-1	0.475	85.6	41.2	7.8
-1.1	0.529	110.1	36.2	8.8
-1.2	0.806	160.0	39.4	13.9

The results show that the carbon nanofiber alone without the catalyst, achieves some efficiency, and NH_3 yield, but very far from the performance achieved by the previous material. Figure 18 shows an illustrative comparison between both.

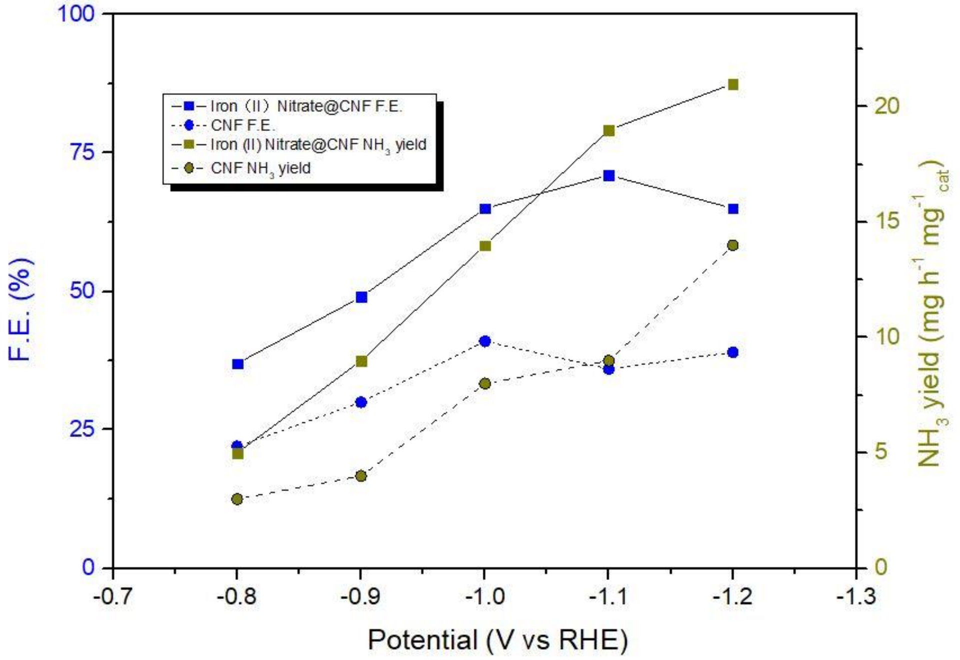


Figure 18- Comparison of FE and NH$_3$ yield between CNF and Fe (II) Nitrate@CNF

The circles here represent the CNF while the squares are the Iron (II) Nitrate@CNF, as it can be seen, both the FE (in blue) and NH$_3$ yield (in green) are higher with the squares, which shows that the catalyst in the carbon nanofiber performs better than the carbon nanofibers by themselves.

Material caracterization

XRD

As explored before, material characterization can help to make sure the materials are successfully synthesized. For this analysis, XRD and SEM were performed. Figure 19 shows the XRD pattern for the Fe (II) Nitrate@CNF, and solely the carbon nanofiber.

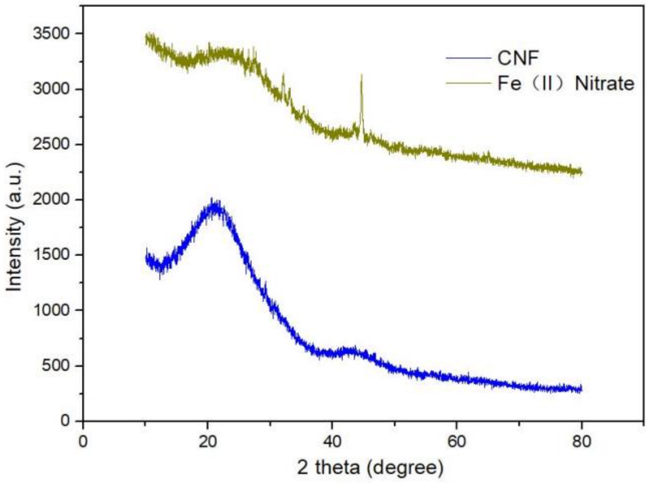


Figure 19- The XRD pattern for both synthesized materials

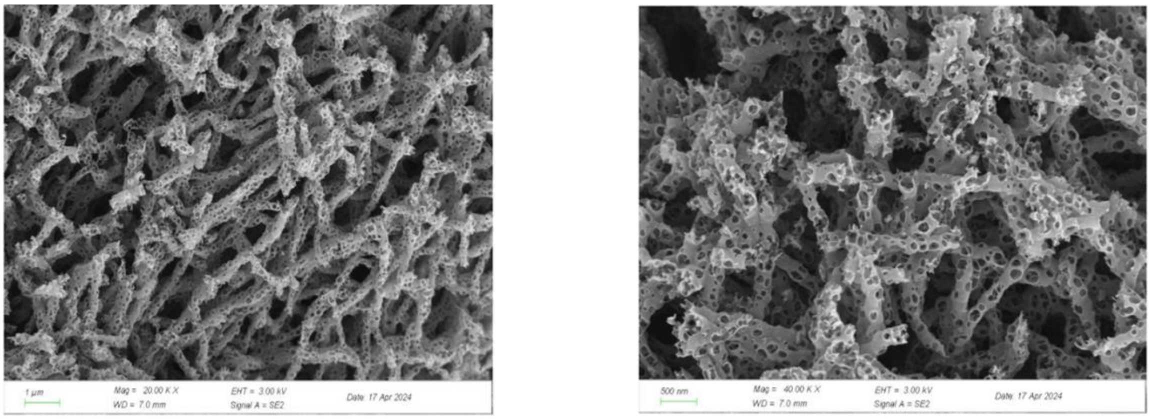
In blue, it is possible to see a clear peak at around 26° (JCPDS No. 75-1621) which indicates the presence of the graphitic carbon of CNFs also 42.44° (graphitic 101), these are the most prominent ones, and they provide valuable information about the crystalline structure of carbon nanofibers, and show a successful synthesis.

Regarding the Fe (II) Nitrate in the CNF, the previous peaks carry on and can be seen. Specifically for the iron, there is a prominent peak at around 44.673 from the Fe PDF card (JCPDS No. 06-0696), which shows the presence of iron in this compound and its successful synthesis.

The Powder Diffraction File (PDF), from the JCPDS-International Centre for Diffraction Data, is a widely used scientific database containing about 40,000 x-ray diffraction patterns, including metals and alloys, minerals, and forensic patterns. Each year, several new patterns are added from literature, private contributions, grants, and the JCPDS Associateship at the National Bureau of Standards (NBS) (Wong-Ng et al., 1982).

SEM

The morphology of the final synthesized material was analyzed, Figure 20 shows the SEM imaging of the Fe (II) Nitrate@CNF with different magnitudes.



a) 20.000x

c) 40.000

b) 100.000x

Figure 20- SEM imaging for Fe (II) Nitrate@CNF

These show that the fibers are uniform and have a consistent diameter of around 200nm with the porous varying between around 50 nm and 150 nm. However, the fibers are broken or interrupted in some areas.

Discussion

The primary goal of this project was to develop and evaluate the effectiveness of Fe(II) Nitrate@CNF as a catalyst for the electrochemical reduction of nitrate to ammonia. The results obtained during this research indicate that the synthesized catalyst significantly improves the Faradaic efficiency (FE) and ammonia (NH3) yield compared to carbon nanofibers (CNF) alone.

The initial tests conducted at various potentials (-0.8V to -1.2V) revealed that the highest Faradaic efficiency was achieved at -1.1V, despite the highest yield of NH3 being at -1.2V. At -1.1V, the FE was 65.5%, with an NH3 yield of 17.1 mg h^-1 mg^-1 cat. , at -1.2V, the FE dropped to 65.1%, with an NH3 yield of 21.0 mg h^-1 mg^-1 cat. The optimal performance at -1.1V suggests that this voltage strikes a balance between efficient energy use and high NH3 yield, highlighting the catalyst's potential for practical applications. The decrease in FE at -1.2V, despite the higher NH3 yield, can be attributed to increased side reactions that consume more electrons, thus lowering the efficiency. This insight emphasizes the importance of optimizing operational parameters to achieve the best balance between yield and efficiency.

The CNF alone, without the Fe(II) nitrate catalyst, showed significantly lower performance. At -1.1V, the FE was 36.2%, with an NH3 yield of 8.8 mg h^-1 mg^-1 cat. This big difference underscores the crucial role of the Fe(II) nitrate catalyst in enhancing the electrochemical reduction process. The introduction of Fe(II) nitrate likely provides additional active sites and facilitates electron transfer, leading to improved catalytic activity. This result validates the hypothesis that integrating Fe(II) nitrate into CNF significantly boosts the overall catalytic performance.

The UV-Vis absorbance spectra for the optimal voltage (-1.1V) with and without 0.1M NaNO3 were compared. The nitrate-containing electrolyte showed a clear absorbance peak, confirming the catalyst's effective reduction capability. This was not observed in the PBS-only reference, reinforcing the specificity and efficiency of the catalyst under the optimal conditions. The UV-Vis spectra thus provide a direct indication of the catalyst's activity in the presence of nitrate, affirming its targeted functionality.

To ensure the reliability of the results, recycling tests were performed at -1.1V. The FE and NH3 yield across five cycles were consistent, with a slight improvement observed in the second cycle. The highest FE recorded was 70.9% in cycle 2, with an NH3 yield of 18.5 mg h^-1 mg^-1 cat. The results demonstrated good reproducibility and stability of the catalyst, with minor variations attributed to operational conditions. The improvement in the second cycle might indicate na initial activation phase where the catalyst reaches its optimal state. This suggests that Fe(II) Nitrate@CNF can maintain high performance over multiple uses, which is critical for practical applications.

The chronoamperometry test over 24 hours at the optimal potential (-1.1V) indicated stable performance, with no significant degradation in current. This stability is crucial for long-term applications and further validates the practical utility of the Fe(II) Nitrate@CNF catalyst. The ability to maintain consistent current over extended periods highlights the robustness of the catalyst and its potential for industrial scale-up.

The chronoamperometric tests conducted at different voltages (-0.8V, -0.9V, -1.0V, -1.1V, and -1.2V) showed distinct patterns of current stability. At -1.1V, the current remained stable over the 24-hour period, indicating that this voltage is optimal not only for FE and NH3 yield but also for maintaining consistent catalytic activity. At -1.2V, although the NH3 yield was slightly higher, the current exhibited more fluctuations, suggesting increased side reactions and reduced stability. These observations underscore the need to balance voltage settings to achieve both high efficiency and stability.

The Linear Sweep Voltammetry (LSV) curves demonstrated a significant difference in catalytic activity with and without 0.1M NaNO3. The presence of NaNO3 resulted in a distinct peak, indicating active nitrate reduction. In contrast, the absence of NaNO3 showed a much lower current response, highlighting the specificity of the Fe(II) Nitrate@CNF catalyst for nitrate reduction. This result reinforces the effectiveness of the catalyst in targeting nitrate and converting it to ammonia efficiently.

The XRD analysis confirmed the successful synthesis of the catalyst, showing characteristic peaks for both CNF and Fe. SEM imaging illustrated the uniformity and consistent diameter of the fibers, although some areas exhibited breaks or interruptions. These structural features are important for understanding the catalyst's behavior and optimizing its performance. The uniform distribution of Fe within the CNF matrix, as indicated by XRD and SEM, is likely responsible for the enhanced catalytic properties observed.

In Figure 21 a comparison with similar catalysts is shown. Here we can see that this catalyst had one of the highest NH_3 yields, and a not-so-low FE, further showing its potential. A table with more details including references is shown in the APPENDIX A section.

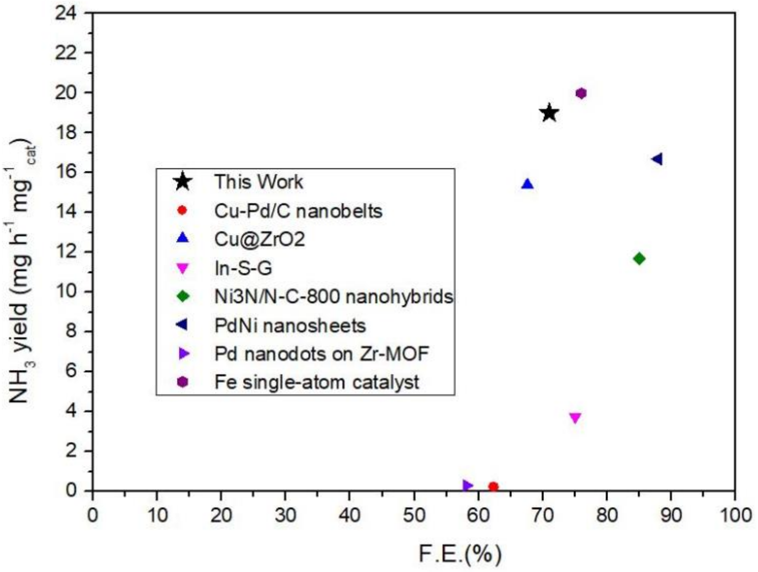


Figure 21- Comparison of Fe (II) Nitrate@CNF to other tested catalysts

Despite the promising results, several challenges were encountered. The presence of side reactions producing nitrite affected the overall efficiency. This was particularly noticeable at higher potentials, where the energy cost outweighed the benefits. These side reactions consume electrons that would otherwise contribute to nitrate reduction, thereby lowering the FE. Future work should focus on mitigating these side reactions through catalyst modifications or optimizing the reaction environment. Although the catalyst demonstrated good stability over 24 hours, longer-term stability tests are necessary to fully establish its durability. The initial stability tests are promising, but extended testing is required to ensure that the catalyst can withstand the demands of continuous operation in industrial settings.

While the recycling tests showed consistent results, minor variations indicate potential areas for improving operational consistency. Factors such as precise control of environmental conditions and uniform catalyst preparation methods need to be addressed to ensure reproducibility across different batches and experimental setups. Achieving uniform carbon fibers initially proved challenging due to variations in polymer viscosity, needle diameter, and humidity levels. These inconsistencies could have impacted the overall catalytic performance by creating areas with less optimal catalyst distribution. Addressing these issues through improved electrospinning protocols will be essential for future improvements. Shared use of laboratory instruments and facilities limited the time available for experimental work, impacting the overall project timeline. Easier access to dedicated equipment and resources would greatly benefit future research efforts.

Potential sources of error include, variations in absorbance measurements could lead to discrepancies in calculated yields and efficiencies. Ensuring accurate and consistent calibration of analytical instruments is crucial for reliable data. Impurities in the electrolyte solution might have influenced the reaction dynamics, affecting the observed results. Using high-purity reagents and maintaining a controlled experimental environment can help mitigate these issues. Errors in sample preparation, handling, and measurement can introduce variability in the results. Adhering to strict protocols and implementing quality control measures will minimize these sources of error.

The successful development and testing of Fe(II) Nitrate@CNF catalysts have broader implications for the field of sustainable ammonia synthesis. Traditional methods of ammonia production, such as the Haber-Bosch process, are energy-intensive and contribute significantly to greenhouse gas emissions. The electrochemical synthesis of ammonia using renewable energy sources presents a greener alternative. The high efficiency and stability of Fe(II) Nitrate@CNF catalysts make them promising candidates for scaling up this technology for industrial applications. Furthermore, this study provides insights into the importance of optimizing catalyst materials at the nanoscale to enhance their performance. The integration of metal nitrates with carbon nanofibers could be explored further with other metal ions to develop a range of high-performance catalysts for various electrochemical applications.

In conclusion, the study successfully demonstrated the potential of Fe(II) Nitrate@CNF as a catalyst for electrochemical ammonia synthesis. Despite encountering several challenges and limitations, the results obtained were highly encouraging, with the catalyst showing high Faradaic efficiency and stability. Future research should focus on further optimizing the electrospinning process and exploring the use of other metal nitrates to enhance catalyst performance. This work lays the foundation for developing more sustainable and efficient methods for ammonia production, contributing to the broader goal of reducing the environmental impact of industrial processes.

Conclusion and Future Directions

The primary aim of this research was to develop and evaluate the effectiveness of Fe(II) Nitrate@CNF as a catalyst for the electrochemical reduction of nitrate to ammonia. The experimental results indicated that the synthesized catalyst significantly enhanced both Faradaic efficiency (FE) and ammonia (NH_3) yield compared to carbon nanofibers (CNF) alone. Specifically, the highest FE recorded was 70.9%, with an NH_3 yield of 18.5 mg h^{-1} mg^{-1} cat, highlighting its potential for practical applications.

Additionally, the comparison with pure CNF revealed that Fe(II) Nitrate@CNF considerably outperformed CNF, emphasizing the crucial role of the Fe(II) nitrate component in enhancing the catalytic process. The UV-Vis absorbance spectra confirmed the catalyst's effective reduction capability and the recycling tests demonstrated its stability and reproducibility. The stability analysis showed consistent performance over 24 hours at optimal voltage, which is vital for long-term industrial applications. Material characterization via XRD and SEM validated the successful synthesis and uniformity of the catalyst.

The implications of these findings are significant. The high efficiency and stability of Fe(II) Nitrate@CNF suggest it could be a viable alternative to traditional ammonia synthesis methods, potentially reducing the environmental impact associated with the Haber-Bosch process. This study contributes to the growing body of research aimed at developing sustainable and efficient methods for ammonia production, with broader applications in agriculture and industry.

Reflection on the Project's Outcomes and Contributions to the Field

The outcomes of this project have made several valuable contributions to the field of electrochemical ammonia synthesis. Firstly, the successful development of Fe(II) Nitrate@CNF as a high-performance catalyst offers a promising alternative to more energy-intensive processes. The demonstration of its high Faradaic efficiency and stable performance provides a strong foundation for further research and potential commercialization.

Secondly, this research highlights the importance of integrating metal nitrates into carbon-based supports to enhance catalytic activity. The approach taken in this study can be extended to other metal ions and support materials, paving the way for the development of a range of high-performance catalysts for various electrochemical applications.

Moreover, the project has advanced the understanding of the structural and functional properties of nanofiber-based catalysts. The insights gained from material characterization and performance evaluation can inform future efforts to optimize catalyst design and synthesis processes.

Suggestions for Future Research and Potential Advancements in the Area

Building on the findings of this study, several areas of future research could further advance the field of electrochemical ammonia synthesis. Future studies should conduct extended-duration tests to ensure the consistent performance of Fe(II) Nitrate@CNF over longer periods. This will help establish the catalyst's durability and suitability for industrial applications. Fine-tuning the voltage and electrolyte concentrations could further enhance the efficiency and yield of ammonia synthesis. Investigating different electrochemical environments and optimizing operational parameters could be also important. Investigating other metal nitrates, concentrations and support materials could lead to the development of even more effective catalysts. Exploring the use of bimetallic catalysts or doping with additional elements may provide new pathways for improving catalytic activity and stability.

Conducting in-depth studies to understand the mechanistic pathways of nitrate reduction on Fe(II) Nitrate@CNF will provide valuable insights into the reaction kinetics and dynamics. Advanced characterization techniques, such as in situ spectroscopy, could be employed to monitor real-time changes in the catalyst during the reaction. Pilot-scale studies to evaluate the performance of Fe(II) Nitrate@CNF in larger systems will be essential for transitioning from laboratory research to practical applications. Assessing the economic feasibility and environmental impact at scale will be critical for commercialization.

Learning Outcomes

The project provided hands-on experience with advanced synthesis techniques, including electrospinning and material characterization methods such as XRD and SEM. These skills are essential for conducting high-quality research in materials science and nanotechnology. Overcoming challenges related to the electrospinning process and experimental setup required innovative problem-solving and adaptability. The ability to troubleshoot and refine experimental protocols is a crucial competency for researchers. Analyzing complex data sets and interpreting the results in the context of electrochemical catalysis deepened the understanding of the relationships between material properties and catalytic performance. This analytical capability is vital for driving scientific discovery. Writing this detailed report and presenting findings helped me develop effective communication skills while keeping it short and concise. Clearly articulating research outcomes and their implications is fundamental for explaining the gained knowledge and advancing the field. The project involved collaboration with other lab partners, and with some large language barriers, which contributed to skills of adaptability and the will to ask questions putting aside feelings of rejection and fear. Being a topic of little expertise, learning on the go and investigating while having to proceed with a very long process in a short period of time, made working under pressure and shooting for quality results a hard task which made the experience and great preparation for a future real life work scenario.

In conclusion, this project has successfully demonstrated the potential of Fe(II) Nitrate@CNF as an efficient and stable catalyst for electrochemical ammonia synthesis. The findings contribute to the development of sustainable ammonia production methods and offer valuable insights for future research. By addressing the challenges encountered and building on the project's successes, continued advancements in this field could lead to important and breakthroguh discoveries.

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APPENDIX A

Further electrochemical testing and catalyst performance comparison table

Further cyclic voltammetry tests are shown in figure Figure A.1 (CNF) and A.2 (Iron Nitrate Hexahydrate Nanoparticles). The comparison table to other catalysts is shown in Table A.1.

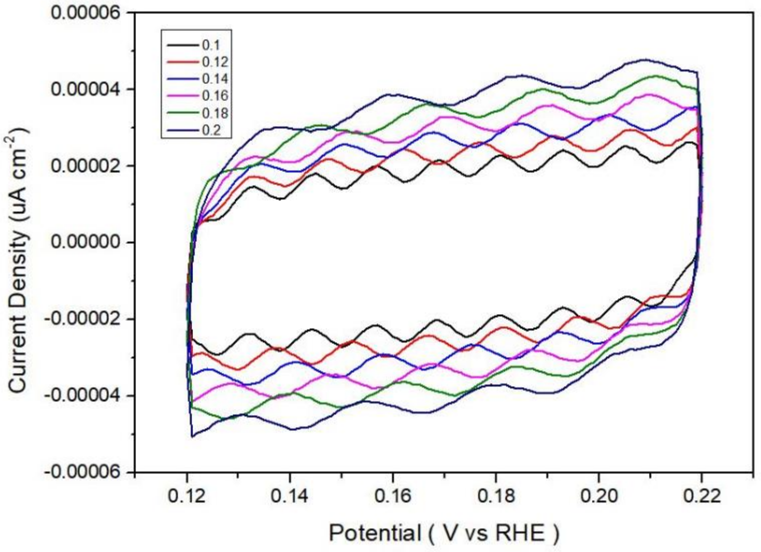

Figure A. 1- Cyclic voltammetry at different scan rates for CNF

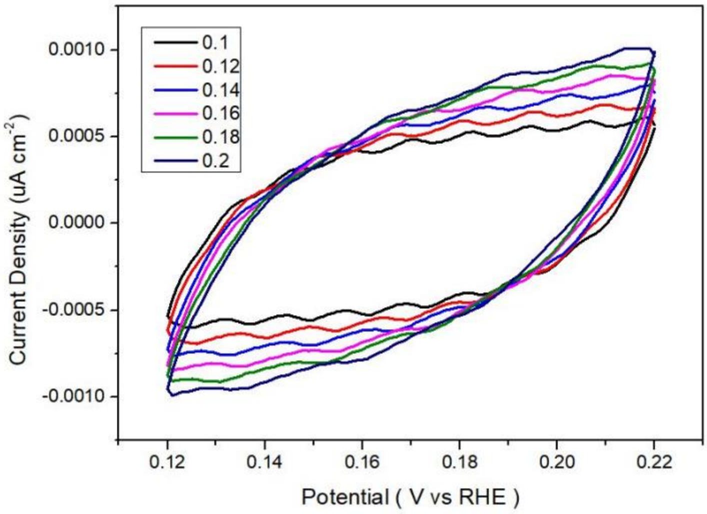

Figure A. 2- Cyclic voltammetry at different scan rates for Fe (II) Nitrate

Table A. 1- Comparison of different catalyst's performance of nitrate reduction to ammonia

Catalyst	**NH_3 yield (mg h^{-1} mg^{-1} cat)**	**FE (%)**	**Ref.**
Fe (II) Nitrate@CNF	18.5	70.9	This work
Cu-Pd/C nanobelts	0.221	62.3	(Wang et al., 2022)
Cu@ZrO_2	15.4	67.6	(Xia et al., 2022)
In-S-G	3.74	75	(Lei et al., 2021)
Ni_3N/N-C-800 nanohybrids	11.71	85	(Zhang et al., 2022)
PdNi nanosheets	16.7	87.9	(Zhang et al., 2022)
Pd nanodots on Zr-MOF	0.287	58.1	(Jiang et al., 2022)
Fe single-atom catalyst	20	76	(Wu et al., 2021)

APPENDIX B

Further SEM imaging

Further SEM imaging for Fe (II) Nitrate is shown in Figures B.1 and B.2.

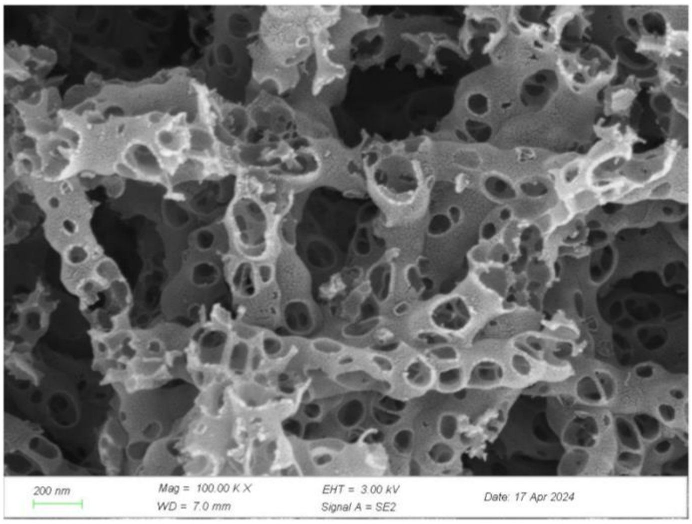

Figure B. 1- SEM imaging of Fe(II) Nitrate@CNF (100.000x)

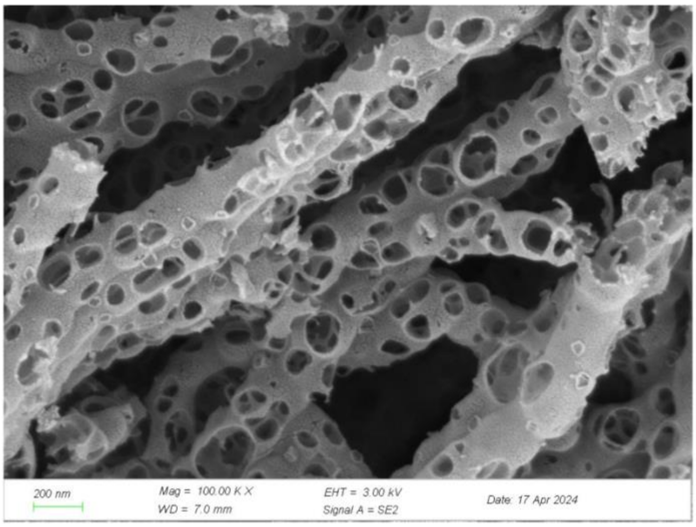

Figure B. 2- Another perspective of SEM imaging of Fe(II) Nitrate@CNF (100.000x)