PLA DE RECERCA / PLAN DE INVESTIGACIÓN
CURS / CURSO 2020-21

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Programa de doctorat / Programa de doctorado Electrochemistry. Science and Technology	
Línea de recerca / Línea de investigación Fundamental and applied electrocatalysis	
Títol de la tesi / Título de la tesis Development of novel electrocatalysts for the electroreduction of nitrogen to ammonia	

MEMÒRIA DEL PLA DE RECERCA
MEMORIA DEL PLAN DE INVESTIGACIÓN

1. Antecedents i estat actual del tema / Antecedentes y estado actual del tema

Ammonia (NH3) is one of the most widely used chemicals on the planet. As a main feedstock chemical, NH3 is not only indispensable in agriculture, fertilizer and pharmaceutical production, but it also provides a solution to the problems of carbon-free chemical energy for the transportation sector [1]. It is considered as an alternative carbon-free fuel source, which does not contribute any CO2 emissions [2]. Also considered to be a promising hydrogen energy carrier to alleviate the fossil fuel scarcity and global climate change, for its high energy density, high hydrogen content, no carbon footprint and being easy to liquefy [3–5].

It is well known that fossil fuels are an important source of energy used for transportation, electricity generation, and many other applications. Nevertheless, their use has caused severe damage to the environment. In the coming years, there is a strong need for clean fuel sources such as ammonia and hydrogen. The strong demand for the carbon-free fuel technologies to replace fossil fuels makes ammonia generators a potentially viable option in the commercial market in the future [6].

Until today, the dominant method for industrial scale NH3 synthesis still depends on the traditional Haber–Bosch process which involves the coactivation of hydrogen (H2) and nitrogen (N2) under extreme conditions (High temperature and pressure) accompanied by large amounts of CO2 emission [7–9], this energy-intensive and environmentally unsafe process consumes 2% of the global annual energy and leads to 1% of the world's CO2 emission [10]. Therefore, it is of paramount importance to explore environmentally friendly and sustainable NH3 synthesis methods at mild conditions [1].

In this sense, several works have already been published focused on providing the best conditions and catalysts for ammonia synthesis in recent decades [11]. There are many types of production methods to synthesize NH3. These can be classified according to the source of ammonia or the type of electrolyte used in the synthesis [12]. Where natural gas is clearly presented as the major source among all other sources [13]. In this context, the electrochemical Nitrogen Reduction Reaction (NRR) has emerged as a sustainable and eco-friendly pathway for the synthesis of NH3 using renewable electricity under ambient conditions, represents a very promising alternative to the Haber-Bosch process.

The NRR can hydrogenate nitrogen molecules with protons and electrons at ambient temperature and pressure using catalysts. However, catalysts that selectively and efficiently reduce nitrogen to ammonia remain elusive due to the strong competition of Hydrogen Evolution Reaction (HER) [14, 15];

adding to this, the inertia of N2 molecule because of its extremely strong triple bond in elemental nitrogen (N≡N), the second strongest bond in any diatomic molecule after carbon monoxide (CO) [16]. On the other hand, another obstacle can be caused by the relatively low solubility of N2 in water (0.66 mmole L-1 at standard conditions) [17]. This is why, efficient catalysts are urgently required to activate and reduce nitrogen into ammonia [11]. The electrochemical N2 reduction process is undoubtedly one of the great challenges that we must face in the coming years.

For this reason, in this Doctoral Thesis, it is proposed the synthesis, characterization and study of the electrocatalytic properties for NRR of different nanomaterials with a very low cost like bismuth (Bi), Tin (Sn), and Antimony (Sb) compared to precious metals, as well as the combination of these materials. In adittion, the efect of other experimental parameters such as nature of the solution, pH and temperature will be systematically evaluated.

Finaly, it is also important to notice the difficulty in quantifying the products NH3. As shown in previous contribution [18], the solutions as well as the different materials can be easily contaminated, which makes quite complicated to mesure the exact quantity of produced ammonia during NRR experiment. The other aspect that can lead to contamination is the fact that NH3 is present as a pollutant both in the environment and in the N2 gas used as a reagent, it is even present in human breath and laboratory equipment. For this reason, it is necessary to follow a strict protocol that includes reagent purification steps and different experiments that exclude or allow distinguishing what is contamination from what is truly electrochemical reduction of N2.

2. Bibliografia més rellevant / Bibliografía más relevante

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[11]. Zang W, Yang T, Zou H, et al. Copper Single Atoms Anchored in Porous Nitrogen-Doped Carbon as Efficient pH-Universal Catalysts for the Nitrogen Reduction Reaction. ACS Catalysis. 2019;9(11):10166-10173. doi:10.1021/acscatal.9b02944

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3. Objectius de la investigació / Objetivos de la investigación

The main objective of this Doctoral Thesis is the development of new nanomaterials and electrodes with good properties in terms of activity, selectivity and stability for the electrochemical reduction of nitrogen to ammonia.

The specific objectives that are proposed in this research are:

- Synthesis and characterization of Bi, Sn, Sb nanoparticles and combitations of them.
- Preparation of electrodes employing the previously synthetized nanomaterials.
- Electrochemical studies for the electroreduction of nitrogen to ammonia.
- Analytical studies for the correct quantification of the ammonia produced.
- Stability tests of the electrodes during the electrochemical reduction of nitrogen to ammonia.

4. Metodologia, hipòtesi i planificació temporal / Metodología, hipótesis y planificación temporal

The different nanomaterials that are proposed to be used in this Doctoral Thesis will be synthesized using well-established methodologies previously used in the research group. In particular, colloidal and solvothermal routes will be explored.
All nanomaterials will be characterized using many different experimental techniques which are availlable in the Research Support Services of the University of Alicante. Among others, it is proposed the use of the Transmission Electron Microscopy, Inductively coupled plasma optical emission spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy.

The nanoparticles will be subsequently used for the fabrication of electrodes. These will be made by air-brushing approaches and using carbon paper substrates. The electrodes will be characterized by Scanning Electron Microscopy analysis.

The electrochemical characterization of the nanoparticles and electrodes will be perfomed using

different electrochemical stations avalaible in our research group (VMP3 (BioLogic), PGSTAT302N AUTOLAB (Metrohm Autolab, B.V.), and Origaflex (Origalys)).

The ammonia quatification will be perfomed using the colorimetric method of indophenol blue with a HACH Lange DR-3800 system. Other liquid and gas products will be also analysed by using the analytical unit of the research group (GC, GC-MS, IC and HPLC analyses)

Temporary planning (organized in 12 quarters (36 months)):

Year 1

• Quarters 1-2: Synthesis of Bi, Sn and BiSn nanoparticles with different Bi/Sn ratio. Physical characterization of different nanomaterials. Preparation of Bi and Sn electrodes. Characterization of the electrodes.
• Quarters 3-4: Electrochemical characterization of the Bi and Sn nanoparticles and electrodes. Electrocatalytic experiments for NRR. Analytical quantification of ammonia. Stability measurements.

Year 2

• Quarters 5-6: Synthesis of Sb, BiSb and SnSb nanoparticles with different Bi/Sb and Sn/Sb ratio. Physical characterization of the different nanoparticles. Preparation of Sb, BiSb, and SnSb electrodes. Characterization of the different electrodes.
• Quarters 7-8: Electrochemical characterization of the Sb, BiSb, and SnSb nanoparticles and electrodes. Electrocatalytic experiments for NRR. Analytical quantification. Stability measurements.

Year 3

• Quarters 9: Synthesis of multimetallic BiSnSb nanoparticles with different Bi/Sn/Sb ratios. Physical characterization of the different nanoparticles. Preparation of the BiSnSb electrodes. Characterization of the electrodes.
• Quarters 10: Electrochemical characterization of the BiSnSb nanoparticles and electrodes. Electrocatalytic experiments for NRR. Analytical quantification of ammonia. Satability measurements.
• Quarters 11 and 12: Writing and presentation of Doctoral Thesis.

5. Impacte esperat/ Impacto esperado

The results obtained will be published in high-impact journals. It is expected that the results will allow the publication of about 5-6 articles.

Possible scientific journals for the publication of the results:
Electrochemistry Communications
Electrochimica Acta
Journal of American Chemical Society
ACS Catalysis
Green Chemistry, among many others.

The results will be also presented in oral and poster format at different scientific national and international meetings.

Specific Meetings:
- Meetings of the ISE (International Society of Electrochemistry)
- Meetings of the GE (Electrochemistry Group) of the RSEQ
- Meetings of the ECS (The Electrochemical Society)

The results obtained will allow to increase the know-how of the research group. Protection of some results through patents will be also considered.

In summary, this Doctoral Thesis will generate:
• 5-6 Articles

• 10-15 contributions to congresses
• 1-2 book chapters

6. Implicacions ètiques o de bioseguretat/ Implicaciones éticas o de bioseguridad.

Indique si la memòria contempla algun dels següents aspectes que puguen tenir implicacions ètiques o relatives a la bioseguretat:

Indique si la memoria contempla alguno de los siguientes aspectos que puedan tener implicaciones éticas o relativas a la bioseguridad:

A. Recerca en humans o utilització de mostres biològiques d'origen humà
Investigación en humanos o utilización de muestras biológicas de origen humano
Si ☐ No ☒

B. Utilització de cèl·lules troncals embrionàries humanes, o línies derivades d'elles
Utilización de células troncales embrionarias humanas, o líneas derivadas de ellas
Si ☐ No ☒

C. Assaigs clínics
Ensayos clínicos
Si ☐ No ☒

D. Ús de dades personals, informació genètica, uns altres
Uso de datos personales, información genética, otros
Si ☐ No ☒

E. Experimentació animal
Experimentación animal
Si ☐ No ☒

F. Utilització d'agents biològics de risc per a la salut humana, animal o per al medi ambient
Utilización de agentes biológicos de riesgo para la salud humana, animal o para el medioambiente
Si ☐ No ☒

G. Ús confinat d'organismes modificats genèticament (OMG)
Uso confinado de organismos modificados genéticamente (OMG)
Si ☐ No ☒

H. Alliberament d'OMG
Liberación de OMG
Si ☐ No ☒

Si ha contestat afirmativament en alguna de les qüestions anteriors, explique els aspectes ètics referits a la recerca que es proposa, les consideracions, procediments o protocols a aplicar en compliment de la normativa vigent. En tot cas, la recerca en aquestes àrees requerirà de l'autorització del comitè d'ètica de la UA i/o dels organismes preceptius (més informació). Aquesta autorització, que ha de ser prèvia a l'inici dels treballs experimentals, serà exigible per al dipòsit de la tesi.

Si ha contestado afirmativamente en alguna de las cuestiones anteriores, explique los aspectos éticos referidos a la investigación que se propone, las consideraciones, procedimientos o protocolos a aplicar en cumplimiento de la normativa vigente. En todo caso, la investigación en estas áreas requerirá de la autorización del comité de ética de la UA y/o de los organismos preceptivos (más información). Esta autorización, que tiene que ser previa al inicio de los trabajos experimentales, será exigible para el depósito de la tesis.

41st Meeting of the Electrochemistry Group of the Spanish Royal Society of Chemistry
1st French-Spanish Atelier/Workshop on Electrochemistry

Current Trends in Electrochemistry

" Development of novel Electrocatalysts for the Electroreduction of Nitrogen to Ammonia "

Roumayssa Amrine

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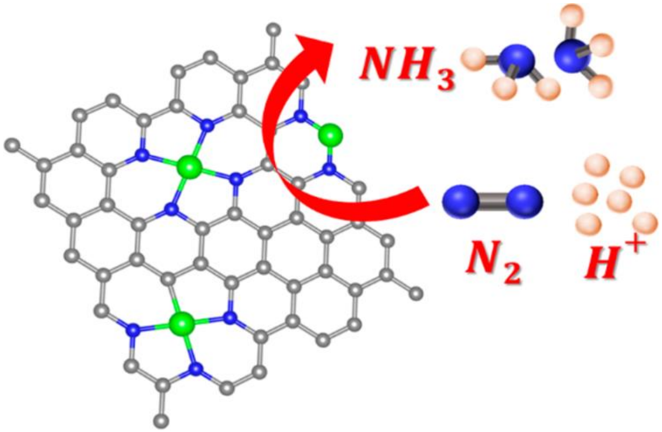

Directors:

José Solla Gullón
Vicente Montiel Leguey

July 2021, Paris

Universitat d'Alacant
Universidad de Alicante

INSTITUTO DE ELECTROQUÍMICA
UNIVERSIDAD DE ALICANTE

LEQA
GRUPO DE ELECTROQUIMICA APLICADA Y ELECTROCATALISIS

Outline

1. INTRODUCTION
2. OBJECTIVE
3. METHODOLOGY
4. PLAN
5. INITIAL RESULTS

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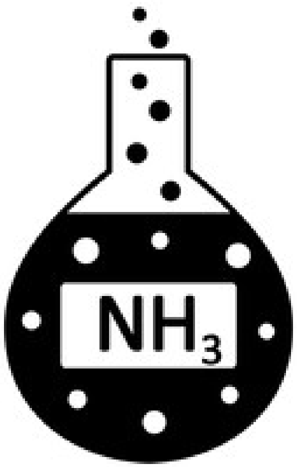
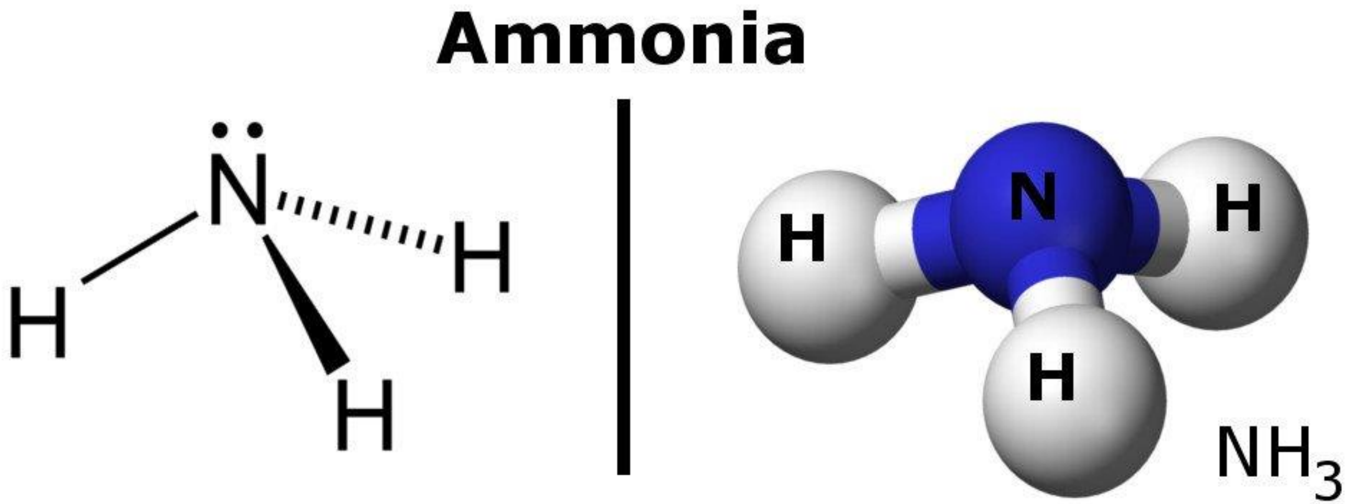
1. INTRODUCTION

- **What is ammonia (NH_3) ?**



Ammonia is an inorganic compound composed of a single nitrogen atom covalently bonded to three hydrogen atoms.



1. INTRODUCTION

- **Applications of ammonia**

Fertilizers
(85%)

-Chemicals
-Textiles
-Pesticides
-Dyes

Cleaning Ammonia solutions

Pharmaceuticals

Ammonia

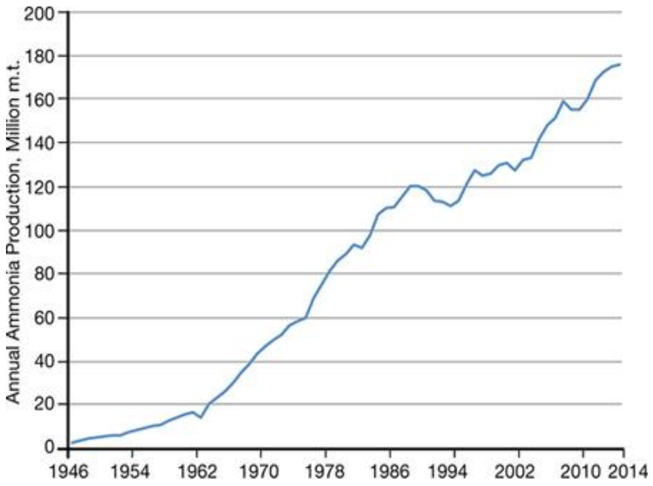
Transportation sector (carbon free fuel source)

-Refrigerant gas
-Purification of water

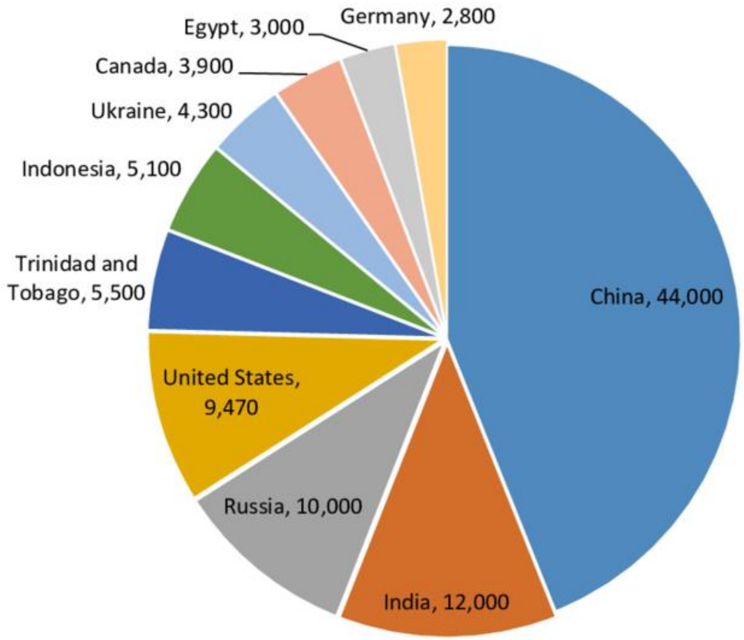
-Fibers, plastics
-Metallurgy
-Pulp and paper

1. INTRODUCTION

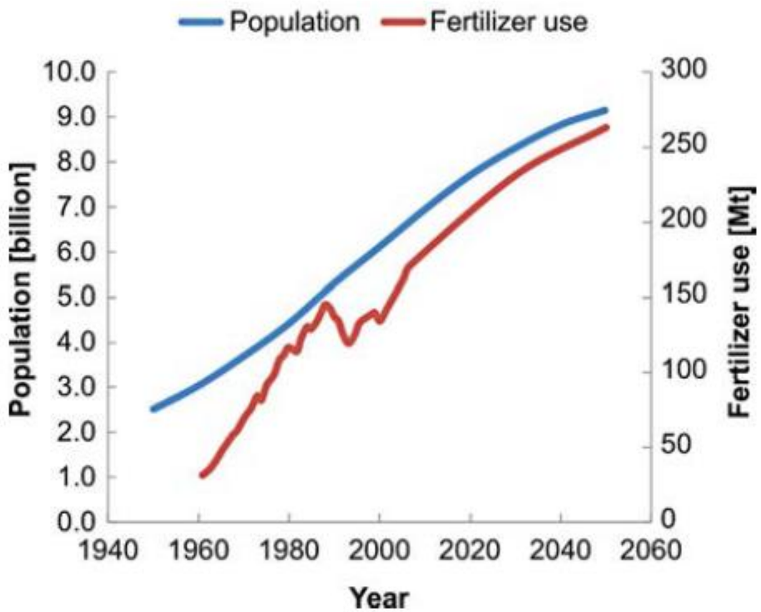
- **Ammonia production in the world**



V. Pattabathula et al., Chemical Engineering Progress. (2016), 9, 69-75



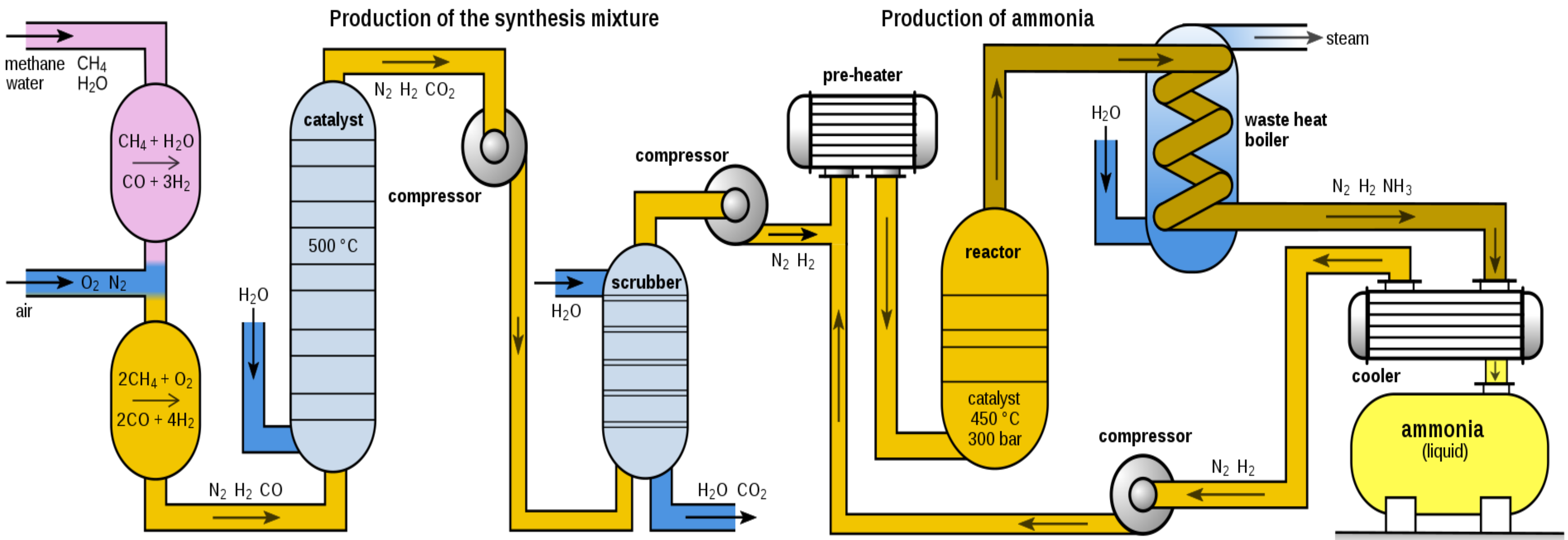
C. Egenhofer et al., CEPS Special Report, (2014), 85



S. Chen et al., Studies in Surface Science and Catalysis, (2019), 178, 31-46

- **The traditional Haber-Bosch process**

$$N_2 + 3H_2 \rightarrow 2NH_3$$

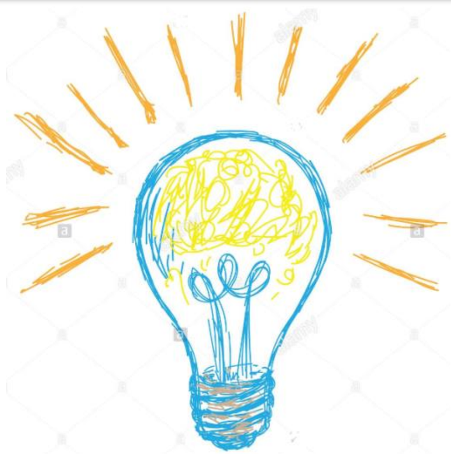


Extract of Wikimedia Commons.

300–500°C → 150–200 atm → CO_2 emission → Difficult and expensive to set up

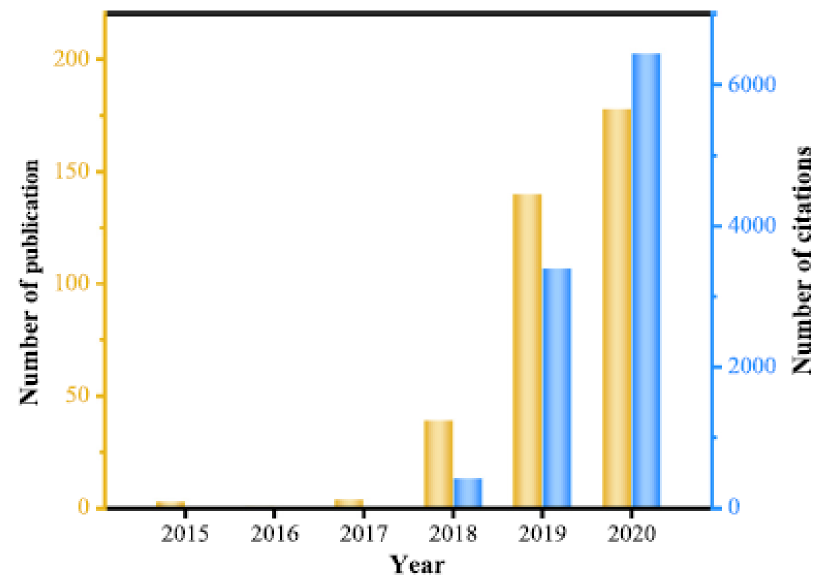
1. INTRODUCTION

It is of paramount importance to explore environmentally friendly and sustainable NH_3 synthesis methods at mild conditions!



- ✓ **Ambient conditions**
- ✓ **Green process**
- ✓ **Cost-effective and easy set up**

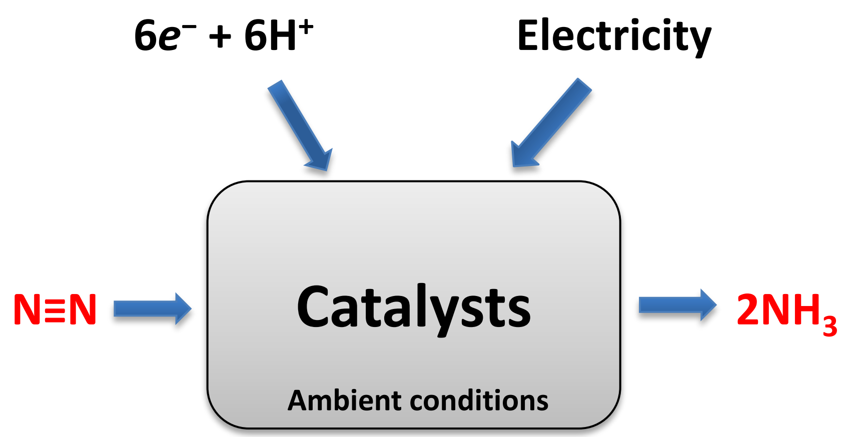
The Electrochemical Nitrogen Reduction Reaction (NRR).



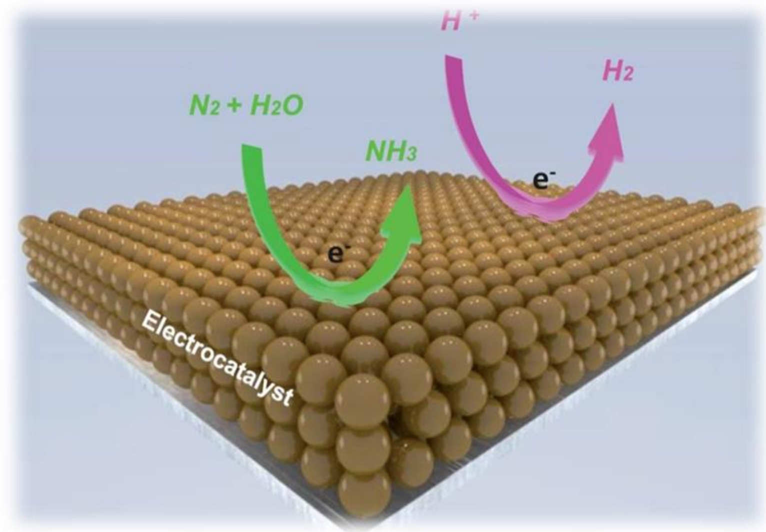
Number of publications (yellow bar) and citations (blue bar) related to the field of NRR from 2015 up to December 23, 2020, which were obtained by searching keywords electrochemical NRR, ammonia and nitrogen reduction in Web of Science.

H. Liu et al., Journal of Energy Chemistry. (2021), 61, 149-154

- **The Electrochemical Nitrogen Reduction Reaction (NRR)**



$$N_2\,(g) + 6H_2O\,(l) + 6e^- \rightarrow 2NH_3\,(aq) + 6OH^-\,(aq)$$



J. Mater. Chem. A, (2020), 8, 1545–1556

$$2H^+\,(aq) + 2e^- \rightarrow H_2\,(g)$$

Bond	*D* (kJ/mol)	r (pm)
N≡N	942	110

The electrochemical N_2 reduction process is undoubtedly one of the great challenges that we must face in the coming years!

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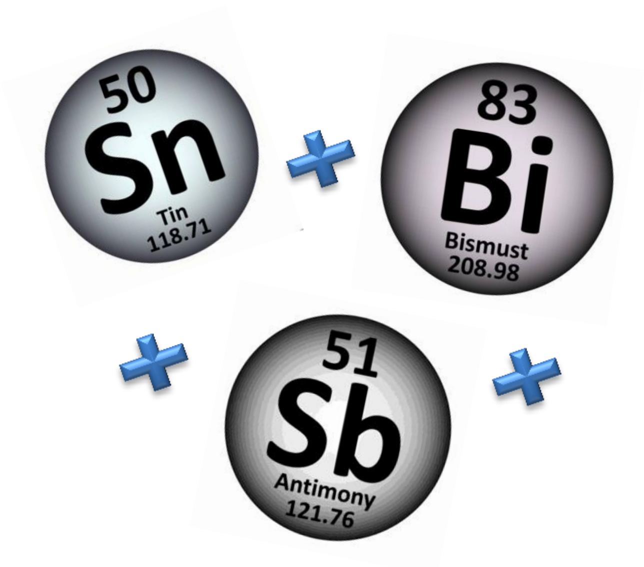
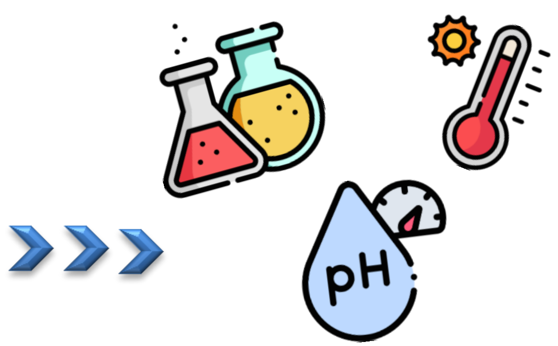
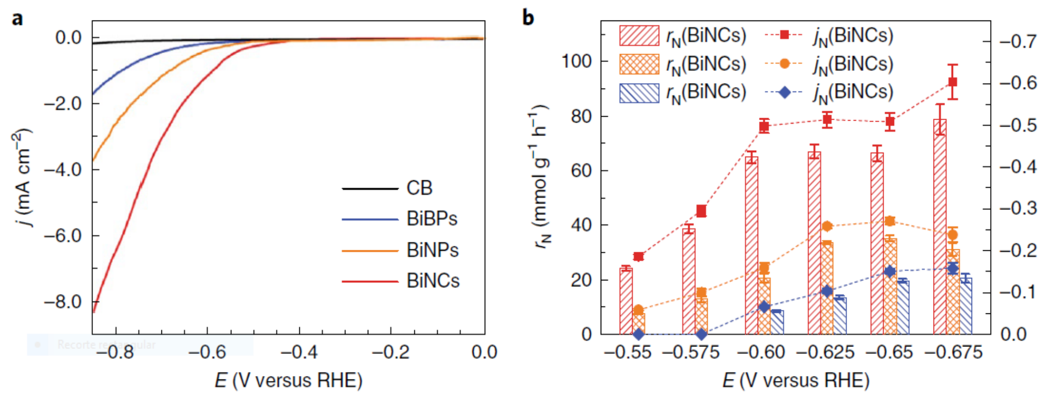
2. OBJECTIVE

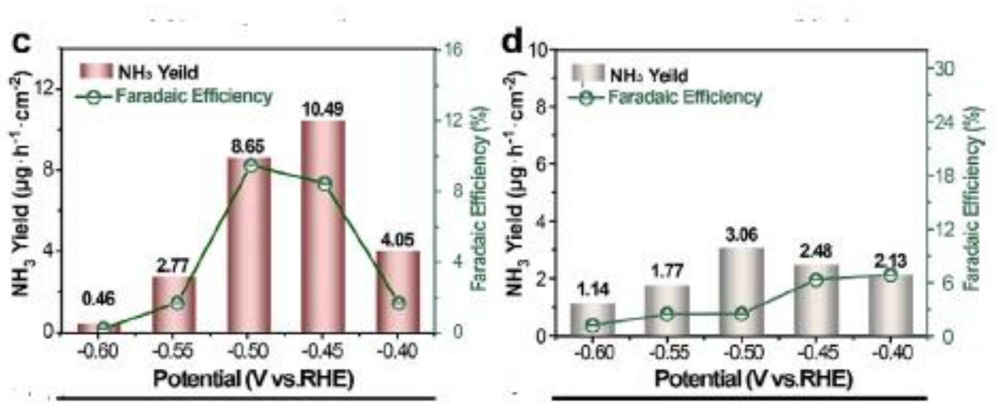
The main objective of this Doctoral Thesis is the development of new nanomaterials and electrodes with good properties in terms of activity, selectivity and stability for the electrochemical reduction of nitrogen to ammonia.







Y. Hao et al., Nature Catalysis. (2019), 5, 448-456



N. Cao et al., Journal of Colloid and Interface Science. (2011), 588, 242-247

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3. METHODOLOGY

- **Synthesis of nanomaterials**

1. NPs Synthesis → **2. Filtration** → **3. Drying**

$\underbrace{BiCl_3 / SnCl_2 \cdot 2H_2O + PVP}_{}$

DMF + NaBH$_4$ +

Carbon VULCAN XC-72R

Precipitation by using acetone

⇩

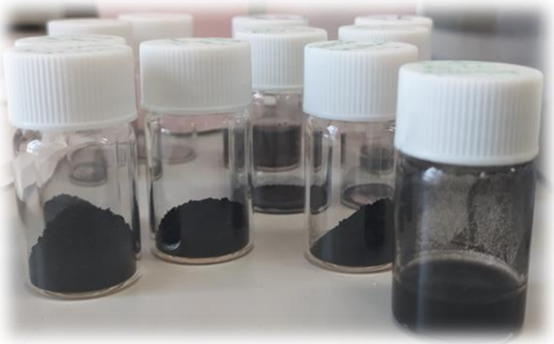
Filtration through a nylon membrane filter of 45 mm

t = overnight

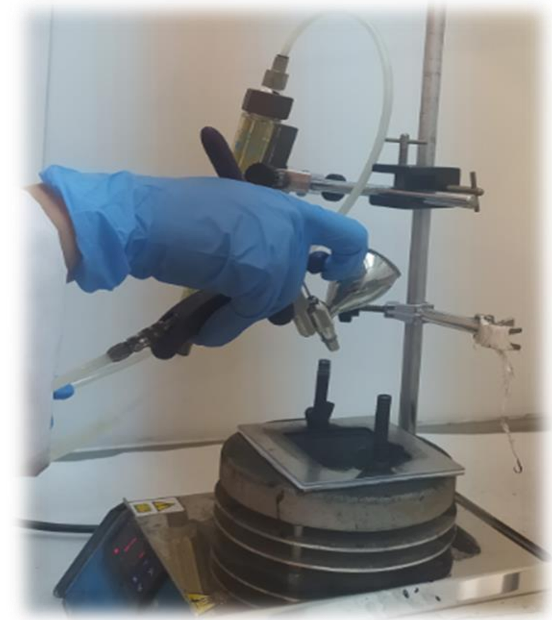
T = 60ºC

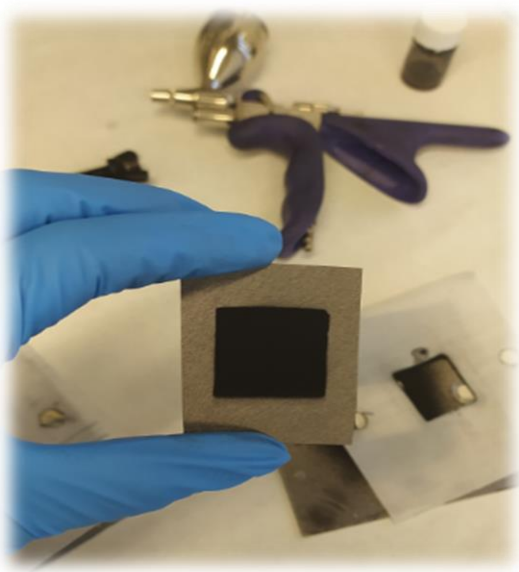
3. METHODOLOGY

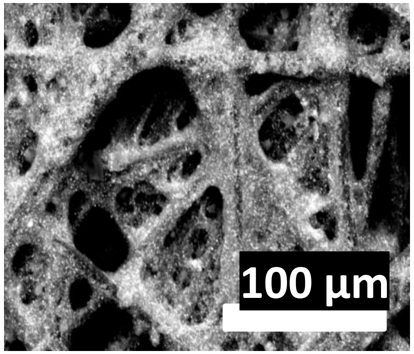
➢ **Preparation of catalytic ink and electrodes**



Ultrasonic agitation is used to homogenize the ink for at least 30 min.

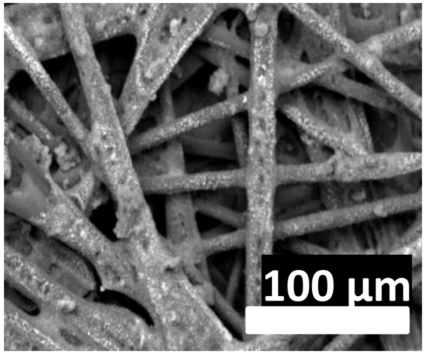






Bi/C

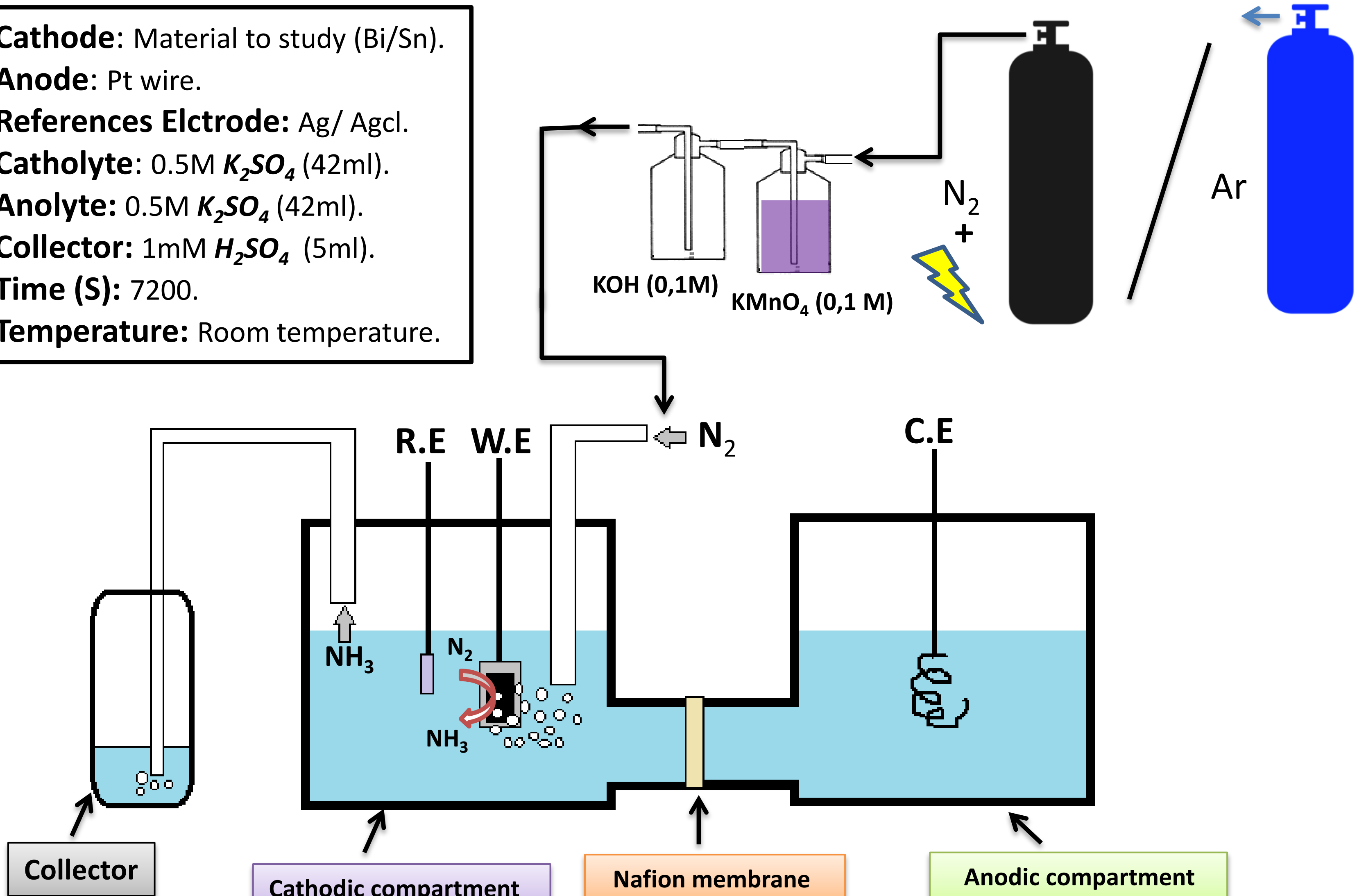
Sn/C



3. METHODOLOGY

- **Electrochemical synthesis**

- **Cathode**: Material to study (Bi/Sn).
- **Anode**: Pt wire.
- **References Elctrode:** Ag/ Agcl.
- **Catholyte**: 0.5M K_2SO_4 (42ml).
- **Anolyte:** 0.5M K_2SO_4 (42ml).
- **Collector:** 1mM H_2SO_4 (5ml).
- **Time (S):** 7200.
- **Temperature:** Room temperature.

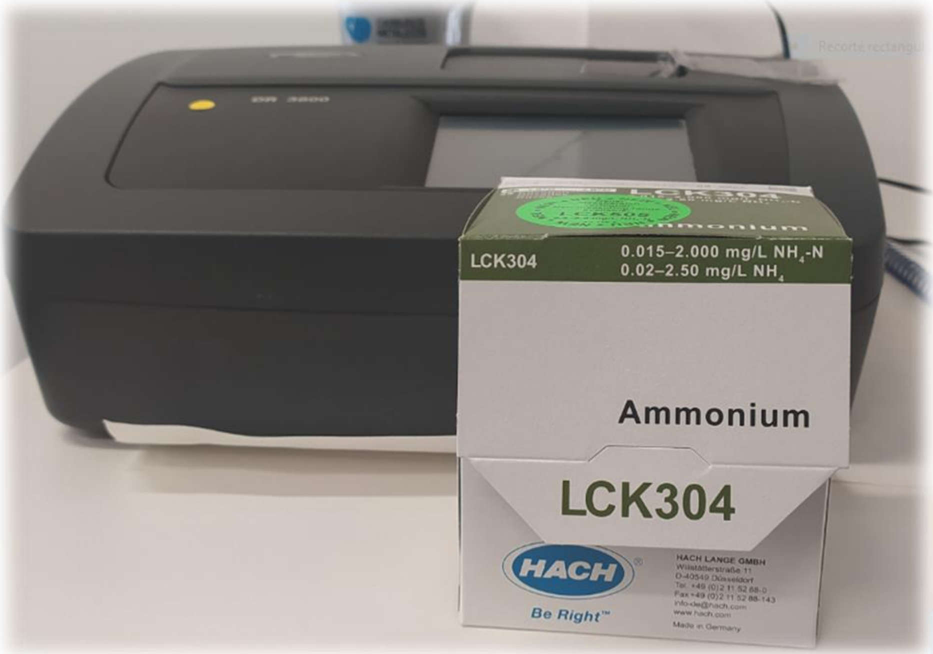


$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

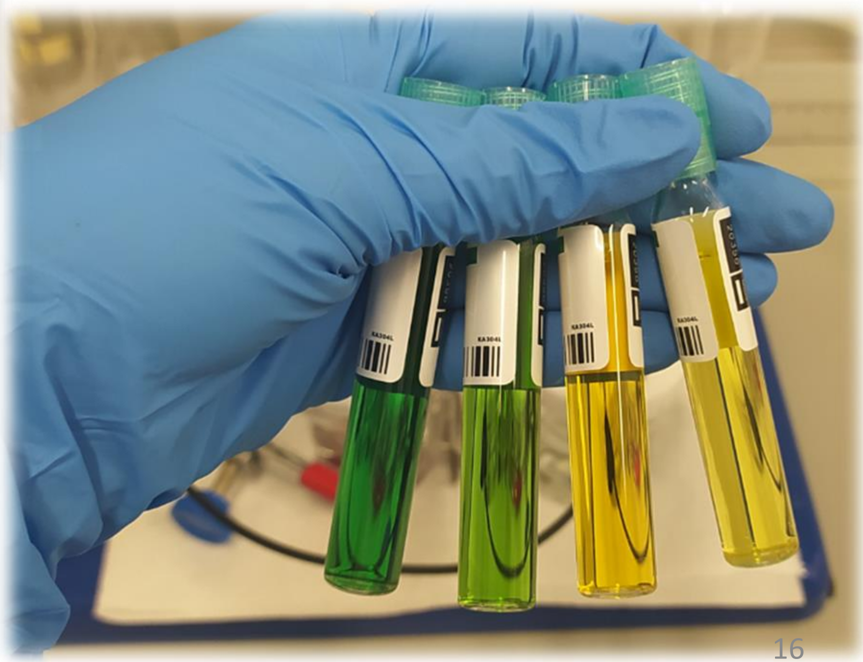
3. METHODOLOGY

➢ **Quantification of ammonia**



✓ The amounts of the produced ammonia in both alkaline and acidic electrolytes are measured by the indophenol blue method with a HACH Lange DR-3800 system.

✓ Ammonium ions react at pH 12.6 with hypochlorite ions and salicylate ions in the presence of sodium nitroprusside as a catalyst to form indophenol blue.



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4. PLAN

Quarters 1-2:
-Synthesis of Bi, Sn and BiSn nanoparticles.
-Physical characterization.
-Preparation of Bi and Sn electrodes.
-Characterization of the electrodes.

Quarters 3-4:
-Electrochemical characterization of the Bi and Sn nanoparticles and electrodes.
-Electrocatalytic experiments for NRR.
-Analytical quantification of ammonia.
-Stability measurements.

Year 1

Quarters 5-6:
-Synthesis of Sb, BiSb and SnSb nanoparticles.
-Physical characterization of the nanoparticles.
-Preparation of Sb, BiSb, and SnSb electrodes.
-Characterization of the electrodes.

Quarters 7-8:
-Electrochemical characterization of the nanoparticles and electrodes.
-Electrocatalytic experiments for NRR.
-Analytical quantification.
-Stability measurements.

Year 2

Quarters 9:
-Synthesis of multimetallic BiSnSb nanoparticles with.
-Physical characterization of the nanoparticles.
-Preparation of the BiSnSb electrodes.
-Characterization of the electrodes.

Quarters 10:
-Electrochemical characterization of the nanoparticles and electrodes.
-Electrocatalytic experiments for NRR.
-Analytical quantification of ammonia.
-Stability measurements.

Quarters 11 and 12:
Writing and presentation of Doctoral Thesis.

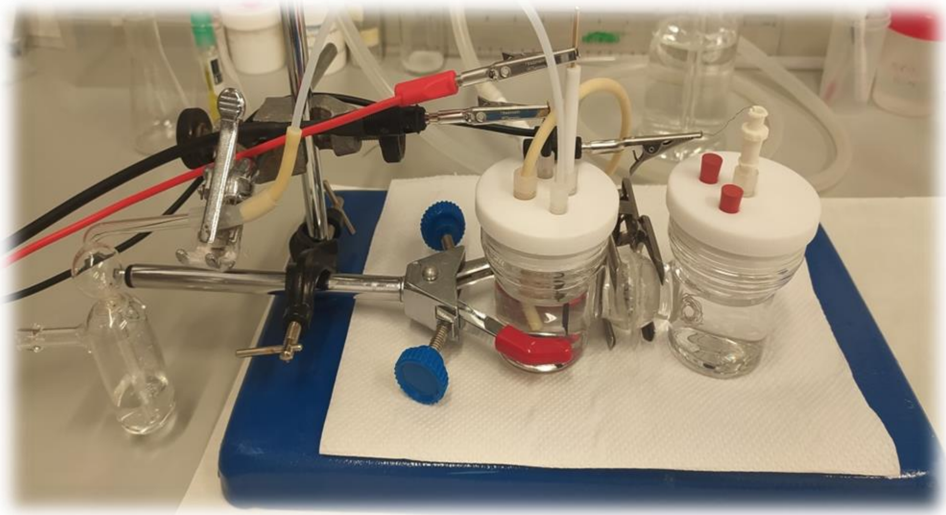
Year 3

Outline

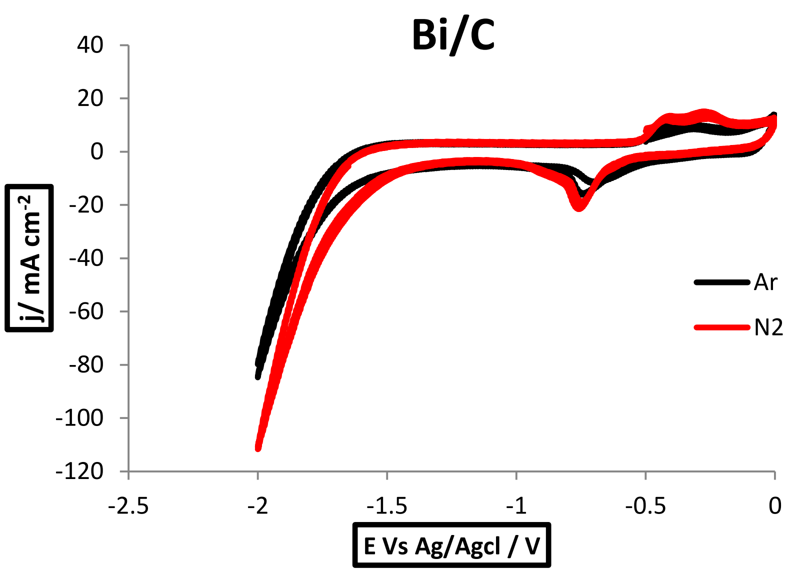
1. INTRODUCTION
2. OBJECTIVE
3. METHODOLOGY
4. PLAN
5. INITIAL RESULTS

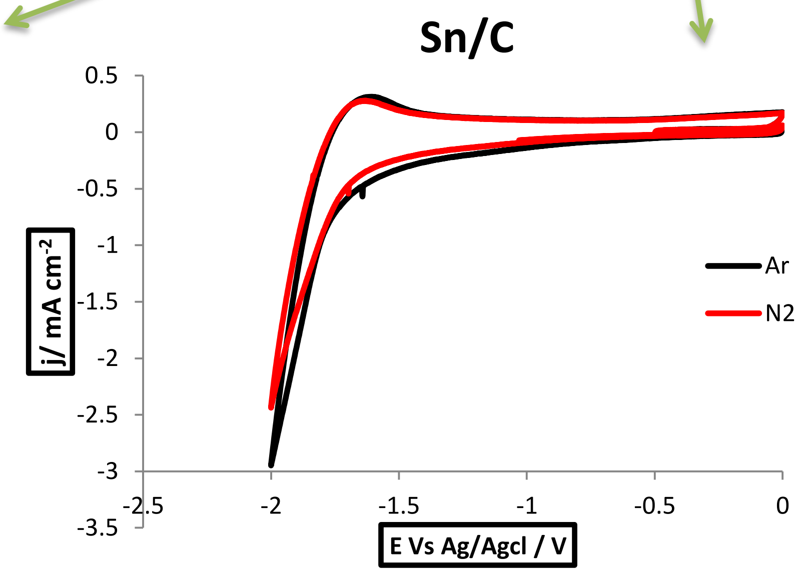
5. INITIAL RESULTS

H-cell electrochemical system

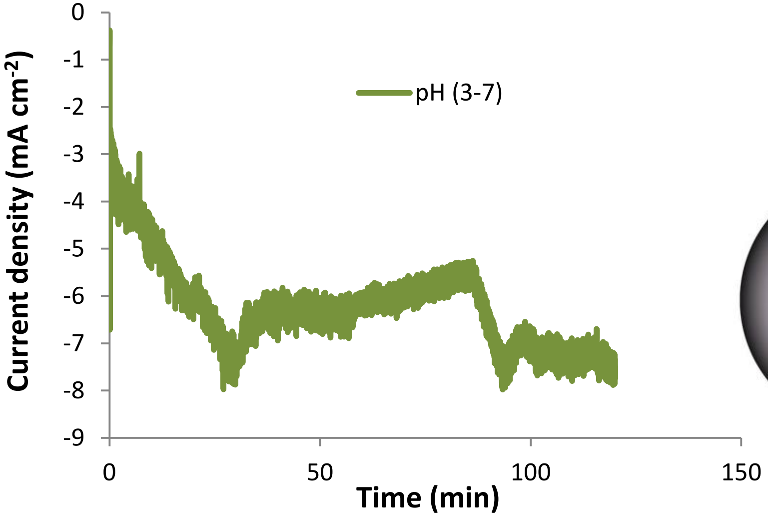


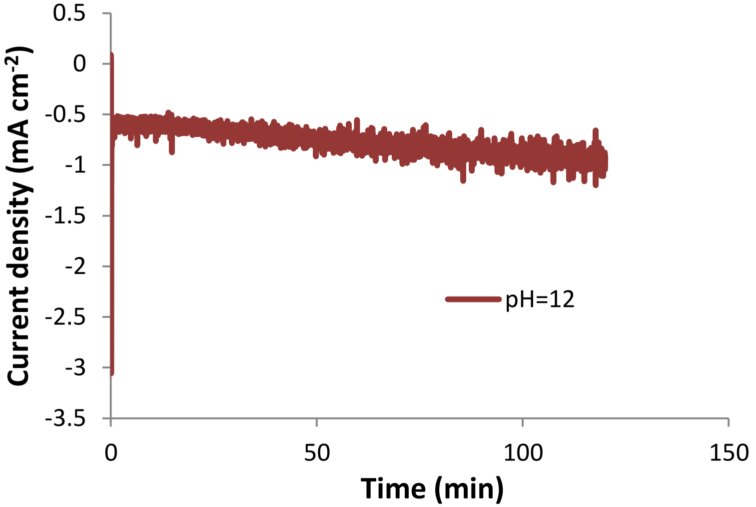
Potentiostat, Galvanostat "Origaflex"





5. INITIAL RESULTS





pH	Catalyst	Electrolyte	Potential (V vs Ag/Agcl)	Faradaic Efficiency (%)
Acidic media (3-7)	Bi/C electrode (1mg cm^{-2})	0.5M K_2SO_4	-1.7	0.25%
Alkaline media (12)	Bi/C electrode (1mg cm^{-2})	0.5M K_2SO_4	-1.7	1.75%

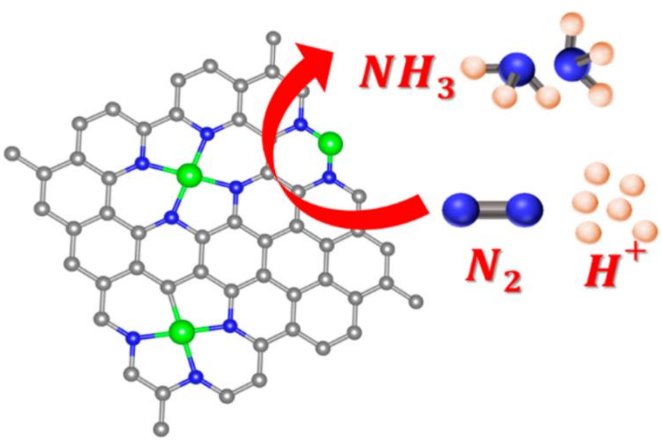
41st Meeting of the Electrochemistry Group of the Spanish Royal Society of Chemistry
1st French-Spanish Atelier/Workshop on Electrochemistry

Current Trends in Electrochemistry

“ Development of novel Electrocatalysts for the Electroreduction of Nitrogen to Ammonia ”

Roumayssa Amrine

e-mail: ra65@alu.ua.es



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July 2021, Paris

Universitat d'Alacant
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