ELECTROLYSIS OF AMMONIA EFFLUENTS: A REMEDIATION PROCESS WITH CO-GENERATION OF HYDROGEN

A thesis presented to
the faculty of
the Fritz J. and Dolores H. Russ College of Engineering and Technology of Ohio University

In partial fulfillment
of the requirements for the degree
Master of Science

Egilda Purusha Bonnin
August 2006
This thesis entitled

ELECTROLYSIS OF AMMONIA EFFlUENTS: A REMEDIATION PROCESS WITH CO-GENERATION OF HYDROGEN. CATALYST DEVELOPMENT

by

EGILDA PURUSHA BONNIN

has been approved for

the Department of Chemical and Biomolecular Engineering

and the Russ College of Engineering and Technology by

Gerardine G. Botte
Associate Professor of Chemical and Biomolecular Engineering

Dennis Irwin
Dean, Russ College of Engineering and Technology
ELECTROLYSIS OF AMMONIA EFFLUENTS WITH CO-GENERATION OF HYDROGEN (54 pp.)
Director of Thesis: Gerardine G. Botte

The electrolysis of ammonia (NH₃) was studied to propose a remediation process for the removal of ammonia from waste water and produce hydrogen while returning clean water to the environment. An electrocatalyst able to support such reaction at low concentrations of ammonia was designed. Two substrates were tested, Raney nickel and carbon fiber. The performance of noble metals such as Rh, Pt and Ir, electroplated on the surface of the substrates was also evaluated. Electrodes made on the carbon fiber substrate presented more reactivity towards the electrolysis of ammonia than the Raney nickel substrate at the conditions tested. The best catalyst found was Rh-Pt-Ir with 5.1 mg cm⁻¹ of carbon fiber bundle, based on the highest current response of the system. Electrochemical techniques such as cyclic voltammetry and galvanostatic polarization were used to evaluate the electrocatalysts. An Ion Selective Electrode Meter was used to measure the ammonia concentrations. The minimum solution concentration was determined for ammonia (1.83 mM) and potassium hydroxide (0.2 M). The maximum conversion determined at the initial concentrations typically found in sewage water was 91.488 ± 0.003% and faradaic efficiency (η) of 91.81 ± 0.13%.

Approved:

Gerardine G. Botte
Associate Professor of Chemical and Biomolecular Engineering
Acknowledgments

I would first like to acknowledge the ideas, motivation, guidance and financial support of my advisor, Gerardine G. Botte. I appreciate her fervent belief in me and my work as well as giving me the space to use my creativity into the development of this project. I also would like to thank my coworkers at the Electrochemical Engineering Research Laboratory for supporting me throughout this process and maintaining a positive, and professional working environment. I would like to thank Juan Gonzalez for designing the carbon fiber electrodes as well as for answering all my technical questions. I would like to thank Yolanda De Abreu for being my mentor. Without Yolanda’s guidance I would not have pursued my dream of graduating from the Master’s program.

I would like to give a special recognition to Elizabeth Cellar and Zachary Bender for their help and support with the experiments in the lab. I would like to recognize Pamela Meggyesy, for her dedication in revising the documents submitted for publications. To the people, the university organizations, and the institutions that supported the publications, thank you. Thank you very much also to the members of my committee, Dr. Hla and Dr. Crist, for believing in me as a student and professional.

I would like to thank my caring friends for lending words of support every time I needed it. To Jeff Nartker, thank you for giving me the strength to persevere through this process and also for making me believed in myself by supporting me with your love. Finally, and most importantly, I would like to thank my wonderful family for giving me all the necessary tools to make me be the person I am today, for helping me overcome every difficult or challenging situation, and for always being by my side to provide me with the moral support that I needed.
Dedications

To My Mother, Father and Brother, for guiding me on the path of personal discovery, for inspiring me to follow my dreams, and for sharing in the understanding that distance is nothing when the family’s bond is strong.

To Jeff Narther, for showing me the meaning of Love
# Table of Contents

Abstract ............................................................................................................................... 3  
Acknowledgments ............................................................................................................... 4  
Dedications ......................................................................................................................... 5  
List of Tables ...................................................................................................................... 8  
List of Figures ..................................................................................................................... 9  

Chapter 1 – Introduction ................................................................................................... 12  
  1.1. Project Overview ................................................................................................... 12  
  1.2. Statement of Objectives ......................................................................................... 14  
  1.3. Significance of the Research ................................................................................. 15  

Chapter 2 – Literature Review .......................................................................................... 17  

Chapter 3 – Experimental Procedure ................................................................................ 21  
  3.1. Electro-catalyst Preparation and Composition....................................................... 21  
  3.2. Electrochemical Techniques ................................................................................. 22  
  3.2.1. Electroplating of Noble Metals on the Surface of Substrate.............................. 22  
  3.2.2. Electrochemical Techniques ........................................................................... 22  
  3.2.3. Characterization Techniques .......................................................................... 23  
  3.2.4. Equations for Calculations .............................................................................. 23  

Chapter 4- Electrolysis of Ammonia Effluents with Co-generation of Hydrogen. Catalyst Development ..................................................................................................................... 26  
  4.1. Introduction ............................................................................................................ 26  
  4.2. Experimental .......................................................................................................... 29  
  4.2.1. Electro-catalyst Preparation .............................................................................. 29  
  4.2.2. Polarization Techniques .................................................................................... 34  
  4.2.3. Catalyst Characterization ................................................................................ 35  
  4.2.4. Conversion and Faradaic Efficiency ................................................................ 36  
  4.3. Results and Discussion .......................................................................................... 37  
  4.3.1. Performance of Different Substrates ................................................................ 37  
  4.3.2. Performance of Carbon Fiber Substrate Electrodes at Low Concentrations of Ammonia ........................................................................................................... 40  
  4.3.3. Effect of Different Noble Metals on the Electro-oxidation of Ammonia at Low Concentrations ................................................................................................. 42  
  4.3.4. Galvanostatic Performance of the Electrodes .................................................... 44  
  4.3.5. Efficiency and Conversion .............................................................................. 46  
  4.4. Conclusions ............................................................................................................ 48
List of Tables

Table

2.1  H$_2$O and NH$_3$ Electrolysis. Using Solar Energy at $0.214$/KW-h$^1$ ......................18

4.1 Experimental Conditions Used for Electro-plating Pt-Ir on the Raney Nickel Substrates........................................................................................................................................32

4.2 Experimental Matrix Used for Testing the Carbon Fiber Electrocatalyst. The total loading of each electrode was fixed at 5 mg cm$^{-1}$ of carbon fiber bundle........................................................................................................................................33
List of Figures

Figure

2.1 Technological Analysis of the Proposed Technology. Using a clean energy supply and extracting the ammonia from a cheaper/no cost source, the ammonia electrolysis will give a byproduct of hydrogen and nitrogen. The hydrogen could be fed to a fuel cell in order to produce energy that is used to power the ammonia source (waste water) and/or it could be also sold into the market. The nitrogen is either released to the environment or sold for other purposes………………………………………….17

3.1 Experimental Procedure for the Construction of Carbon Fiber Electrodes2. Titanium gauze is connected to a titanium wire, cleaned with acetone and measured for weight. Poliacrylonitrile (PAN) (Celion G30-500), approximately 35 cm long, 7 μm diameter carbon fiber from BASF was wrapped and attached into the titanium gauze, cleaned and measured for weight. The electrode was cleaned with acetone, air dried and measured for total weight. Finally, the amount of noble metal deposited on the surface of the catalyst was measured……………………………………21

4.1 Typical Morphology for Carbon Fiber Catalyst of 20% Rh, 80% Pt-Ir. Magnification at X500. Pt-Ir-Rh-7.6 mg cm⁻¹ of fiber bundle. The morphology is characterized by a uniform coverage layer of Pt-Ir-Rh on the carbon fiber substrate………………………………………………………………………………………………36

4.2 Cyclic Voltammetry Curves for Pt-Ir on Raney Nickel and Carbon Fiber Substrates at 1 M NH₃, 1 M KOH, 25°C, and 10 mV s⁻¹. The carbon fiber electrode showed
better performance towards the electro-oxidation of ammonia, since surface blockage effect is not observed………………………………………………………………………………38

4.3 Cyclic Voltammetry performance of the Pt-Ir Raney Nickel Electrode with Time at 1 M NH₃, 1 M KOH, 25°C, and 10 mV s⁻¹. A decrease in reactivity over time was observed. From week 1 to week 4, the current decreased 200 mA………………..39

4.4 Comparison of the Electrochemical Performance of the Pt-Rh Carbon Fiber Electrode with Marincic and Leitz³ electrode (Platinized Pt on Pt foil) at 1.03 mM NH₃ and 0.1 M KOH. The currents were normalized by geometric area and noble metal loading to correct for the differences. The peak of current density is observed in the literature at 1.5 mA cm⁻² approximately, whereas with the carbon fiber substrate, the peak current density is observed at 15 mA cm⁻². Carbon fiber substrates showed 10 times higher currents than platinized Pt catalysts……………42

4.5 Cyclic Voltammetry Curves for Carbon Fiber Electrodes with Different Noble Metals Materials at 20 mM NH₃, 0.2 M KOH, and 25°C. The currents are normalized per noble metal loading to correct for any difference. Electrodes 3, and 4 (Table 4.2), seemed to have the same current response (2 mA mg⁻¹ of total loading). Electrodes 2 and 5 showed some reactivity by having a current peak response of 1 mA mg⁻¹ of total loading. The electro-oxidation of ammonia is not observed on Electrode 1 (only Rh)…………………………………………………………..44

4.6 Galvanostatic Performance of the Most Promising Electrodes (Electrode 3 to 5), based on the result of Figure 4.5. The experiments were performed at 20 mM NH₃, 0.2 M KOH, and 25°C. Pt-Ir-Rh was used as the cathode. Electrode 4 (Pt-Ir-Rh) showed the highest current and the lowest voltage for all the current tested. This
electrode was selected as the best at the conditions for low ammonia concentrations.

4.7 Galvanostatic Performance of Pt-Ir-Rh Electrode at 100 mA, Initial concentration of 20 ± 3 mM NH$_3$, 0.2 M KOH, and Room Temperature. The experimental elapsed time was the same as the theoretical time calculated by Faraday’s Law for a total of 13.78 h. The final NH$_3$ concentration was 1.83 ± 0.000006 mM, with a process conversion of 91.488 ± 0.003% and faradaic efficiency (η) of 91.81 ± 0.13%.
1.1. Project Overview

There are negative effects on the environment that are the result of poorly applied technological procedures such as waste water treatments that release toxic and dangerous chemicals. Chemical compounds used in the waste water treatment processes are detrimental to the normal environmental conditions. One of the common compounds present in waste water or sewage plants is ammonia (NH$_3$).

Ammonia can be used as a hydrogen carrier. Recently, Botte$^1$ has developed a new technology for the production of hydrogen on demand by the electrolysis of ammonia at the Electrochemical Engineering Research Laboratory (EERL)$^4$. The ultimate goal of the project is to use the ammonia that is already available in waste water, for instance, sewage plants, fertilizer pretreatment plants, and lagoons near farms with collection of animal manure, which deal with ammonia content from animal manure.

Within this context, the overall research objective of this project is to remove ammonia from effluents using waste water and return clean water and nitrogen to the environment with simultaneous production of hydrogen. The electrochemical destruction of the ammonia will produce hydrogen within environmental regulations. The environment will be protected at lower costs and the economics in the processes involved in the production of energy will be improved. Within this context, the specific objectives are: 1) to design an electrocatalyst able to electrolyze ammonia at the concentrations found in sewage and fertilizer plants; 2) to evaluate the performance of different noble metals electroplated on the surface of the selected substrates mentioned in the previous
objective(1); and 3) to determine the effect of variables on the ammonia electrolysis such as minimum initial ammonia and potassium hydroxide concentrations, minimum ammonia concentration removed with the process, ammonia conversion, and Faradaic efficiency.

Electrochemical techniques as well as materials characterization methods will be used to accomplish these objectives.

The economic foundations of this study are what make this project so relevant because financial feasibility must be considered when new technologies are proposed. If successful with the technology, clean water will be produced and nitrogen will be released without any environmental damage. Furthermore, the process will reduce energy costs as a result of the production of hydrogen from waste. For example, waste water plants could use the hydrogen to produce energy for their own purposes. The future projections guarantee that if every ammonia effluent reservoir in the United States applies the described technology, the savings for the country in terms of water purification and hydrogen production would be incalculable. Also, fertilizer plants could possibly produce energy from waste. Based on preliminary results, the electrolysis of ammonia can generate hydrogen at $0.89 per kg of hydrogen produced, when the ammonia average price is ($175/ton). If the electrolysis of ammonia is performed on waste waters, which contain the ammonia already, the cost of ammonia will be minimal. Therefore, hydrogen could be generated at $0.33 per kg of hydrogen produced. This will represent savings of 83.5% in the production of hydrogen.
1.2. Statement of Objectives

Fuel cells are one of the most clean and efficient devices that combine fuel (most commonly hydrogen) with oxygen to generate electricity with water as a by-product. However, there are some problems that limit the commercialization of fuel cells: the high hydrogen production costs for distributed power generation, hydrogen transport and storage. As a solution to these problems, a new technology has been developed to produce hydrogen by electrolyzing ammonia.\(^1\) This process has been developed at the EERL, under the direction of Dr. Gerardine G. Botte. The technology uses high concentrations of NH\(_3\) in an alkaline solution of potassium hydroxide (KOH) and low temperatures (25-50ºC). The electrolysis of ammonia is environmentally sound as it produces pure hydrogen which can be used in fuel cells, and releases nitrogen without any hazardous consequences. However, three problems were identified with developing the proposed process: 1) the concentrations of ammonia in these effluents are low, and it was unknown if the suggested technology was going to be successful at the typical concentrations of ammonia found at the effluents (0.5-2 mM/L),\(^3\),\(^6\) however, this was investigated in this present project; 2) the effluents in these plants also contain other species such as phosphorous, chlorines, and suspended solids, among others, and it is still unknown if the presence of these species in the effluents will affect the electrolysis of ammonia; and 3) even though hydrogen produced by the electrolysis of ammonia has significant low costs when compare to other technologies for distributed power generation (electrolysis of water and natural gas reforming), the process is sensitive to the prices of ammonia, that sometimes can be as high as $300/ton.\(^5\)
1.3. Significance of the Research

Having understood the economical and technological implications of this project, it is important to notice some of the most important aspects that are involved in this research. In relation to the economical point of view, the more impressive issue will be the saving projections. Based on the generation of hydrogen through the electrolysis of ammonia at $0.89 per kg of hydrogen produced, the highest price of ammonia is $300/ton. However, if the ammonia content is obtained from waste water as a common effluent and also from fertilizers plants, farms livestock, and animal manure, the price of this source will be significantly reduced. As a consequence, the hydrogen production could be reduced at $0.33 per kg, representing a saving of 83.5% in the production of H₂.

Even though the current stage of the research is actually based on a bench-scale, the expectations are higher every time. The goal will be the development of this current technology in order to make it as feasible as possible. Then, the dimensions will increase the actual design to small water facilities with the ammonia electrolysis application in order to make them as productive as possible. The last step will be increasing the amount of fertilizer, farms, and livestock’s sources with this technology with the objective to make the country more efficient and productive. The savings in terms of water purification and hydrogen production will be incalculable.

The idea is to contribute one more time to the development of the future, helping current knowledge to improve with time taking into account the environmental considerations that are now mandatory aspects for the survival of the race.

In order to be able to produce the electrochemical reaction that is occurring, the electrode material has to be ideal. Economical considerations are important at this point,
because the used material should be accessible and easy to work with. Also, the reactivity of the material must last for a considerable period of time. For these reasons, it is important to develop an efficient electrode composition.
Chapter 2 – Literature Review

The technological analysis of this study can be summed up with Figure 2.1.

Figure 2.1: Technological Analysis of the Proposed Technology. Using a clean energy supply and extracting the ammonia from a cheaper/no cost source, the ammonia electrolysis will give a by-product of hydrogen and nitrogen. The hydrogen could be fed to a fuel cell in order to produce energy that is used to power the ammonia source (waste water) and/or it could be also sold into the market. The nitrogen is either released to the environment or sold for other purposes.

The equations that are involved in the overall reaction are.

Anode: Ammonia Oxidation

\[ 2NH_3(g) + 6OH^{-}(aq) \rightarrow N_2(g) + 6H_2O(l) + 6e^- \quad E^0 = -0.77 \text{ V/SHE} \quad (2.1) \]
Cathode: Water Reduction

\[ 6H_2O_{(l)} + 6e^- \rightarrow 3H_2(g) + 6OH^-_{(aq)} \quad E^0 = -0.82 \text{ V/SHE} \quad (2.2) \]

Overall Reaction:

\[ 2NH_3(l) \rightarrow N_2(g) + 3H_2(g) \quad E^0 = 0.059 \text{ V} \quad (2.3) \]

The economical analysis of this project is based on the comparison of two technologies, water and ammonia electrolysis. Table 2.1 shows the most important prices that operate under actual costs. These costs represent savings in 95.3% lower energy and 87.3% cheaper hydrogen\(^1\).

<table>
<thead>
<tr>
<th></th>
<th>Water Electrolysis</th>
<th>Ammonia Electrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Energy</strong></td>
<td>33.0</td>
<td>1.55</td>
</tr>
<tr>
<td>(W-h/g H(_2))</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>H(_2) Cost</strong></td>
<td>7.10</td>
<td>0.90</td>
</tr>
<tr>
<td>($/Kg H(_2))</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is also important to mention where the ammonia sources are available. The technology proposed is looking to obtain the ammonia from highly toxic pollutants found in industrial waste water in gaseous and aqueous forms. Also, from agricultural runoff from fertilizers (NH\(_4^+\)), from municipal wastewater effluents that have ammonia
concentrations in the ranges of (0.5-2 mM/L), pH between 5-10^7, chicken farms, pig farms, and chemical plants. If the ammonia is extracted from all these type of sources, the cost of the technology will be reduced to the minimum or it will not have any cost involved.

However, hydrogen fuel cells have encountered several limitations that have to do with the high hydrogen production costs, hydrogen transportation, storage and availability of sources. The ammonia electrolysis will overcome these challenges. The costs as it was described above will be reduced to a minimum by using cheaper or free ammonia sources. Also, the transportation of the hydrogen will not be needed from the fact that the production of the hydrogen will be done in situ, where the technology is applied. For that reason, the hydrogen will be produced and consumed immediately by feeding it into the fuel cell that will generate the necessary energy to operate into the system for what it was designed. The hydrogen storage will not longer be a limitation, due to the fact that it is produced and consumed at the same time. Finally, the sources of ammonia are available as it was mentioned before, and there are several ones available in the environment.

Previous studies revealed that the ammonia electrolysis from effluents was a method used to convert ammonia into no environmentally hazard products. The current technology proposed at the EERL have overcome these previous results by using better catalyst that support the reaction much more, specially under the particular case of low concentrations in which the difficulty for the reaction to take place is higher. Marincic and Leitz studied the electro-oxidation of ammonia at low concentrations to evaluate the possibility of ammonia removal from waste-water. Catalysts of different
compositions such as platinized platinum were tested for reactivity and economic feasibility of the electro-oxidation at room temperature. The authors tested the effect of: different catalyst loadings (in the range of 0.5-20 mg cm\textsuperscript{-2}), pH (between 5.55 and 12.8), concentrations of ammonia (between 0.12-10mM or 2-170 ppm), electrolytes such as NaCl, K\textsubscript{2}SO\textsubscript{4}, phosphate buffer and K\textsubscript{2}HPO\textsubscript{4}, and current density on the electro-oxidation of ammonia. It was found that only platinum electrodes were able to support the electro-oxidation of ammonia at a reasonable rate. However, the cost of the materials was very high due to the electrode area required for the reaction. The maximum current density obtained was 11.2 mA cm\textsuperscript{-2} in dynamic conditions, and 2.20 mA cm\textsuperscript{-2} in static conditions. On the contrary, this present study proves the efficiency of the process to be 91.5% by using carbon fiber electrodes with noble metals plated on the surface of the substrate, such as Rh, Pt and Ir, to be a feasible technology on the ammonia electro-oxidation at low concentrations. That is why one of the most important parts of this research is based on the selection of the material, to increase the active surface area and make it reactive enough for the reaction to take place with time.\textsuperscript{1, 8}
Chapter 3 – Experimental Procedure

3.1. Electro-catalyst Preparation and Composition

One of the electrodes examined in this work was based on Raney nickel substrate plated with noble metal materials. The idea was to determine the optimum composition of material deposited on the surface of the electrode that will increase the performance of the electrode. In order to understand the methodology of designing Raney nickel electrodes, it is recommended to see reference.\(^8\)

The other electro-catalysts evaluated in this project were made on a carbon fiber substrate. Figure 3.1 shows the experimental procedure followed for the designing.\(^2\)

![Figure 3.1: Experimental Procedure for the Construction of Carbon Fiber Electrodes.](image)

Titanium gauze is connected to a titanium wire, cleaned with acetone and measured for weight. Polyacrylonitrile (PAN) (Celion G30-500), approximately 35 cm
long, 7 μm diameter carbon fiber from BASF was wrapped and attached into the titanium gauze, cleaned and measured for weight. The electrode was cleaned with acetone, air dried and measured for total weight. Finally, the amount of noble metal deposited on the surface of the catalyst was measured.

3.2. Electrochemical Techniques

3.2.1. Electroplating of Noble Metals on the Surface of Substrate

The next step is the electroplating technique which is developed in several steps, depending on the desired loading (mg cm\(^{-1}\) of carbon fiber bundle or mg cm\(^{-2}\) of Raney nickel) deposited on the surface. The technique was performed through several layers. Each layer corresponded to a particular noble metal. The first layer was made of rhodium, and the second layer was made of a co-deposition of platinum and iridium.

The electrode prepared previously was subjected to an electroplating process as described below to form first a rhodium (Rh) layer and then a platinum-iridium (Pt-Ir) layer by an electrolytic procedure. Figure 4.2 shows the experimental set up for the electro-deposition technique. Also, Table 4.2 gives information about the catalyst used.

3.2.2. Electrochemical Techniques

Electrodes must be tested in an electrolytic cell to analyze their performance. For that purpose, electrochemical techniques known as cyclic voltammograms (potentiostatic) will be performed. Figure 4.3 shows the experimental procedure to test the catalysts. Cyclic Voltammetry tests will set a potential range and it will get a current response. This test is a qualitative test more than a quantitative one\(^9\).
The conditions for the potentiostatic technique were: potential fixed (between -0.8 V to 0.1 V), sweep rate of 10 mV/s, Hg/HgO reference electrode, and a Luggin-Haber capillary located at a distance of 3 mm to the working carbon fiber electrode to allow a selective transport of species between the electrodes since the hydrogen ion selective transport is a phenomenon that needed to be enhanced. The measurement equipment used was a state-of-the-art ARBIN Cycler BT2000 (Potentiostat). The number of cycles performed was 20, to observe the stability of each cycle and the overall tendencies.

On the contrary, galvanostatic test presented a constant current and the potential response of the system was tested.

An all glass, closed electrochemical cell of conventional design was used in which the working electrode (anode) was tested versus the counter electrode (cathode).

3.2.3. Characterization Techniques

Furthermore, Electrode characterization was performed using techniques such as Scanning Electron Microscopy (SEM). This characterization technique was performed before and after the treatment. After treatment characterization was made in order to analyze the noble metal deposition coverage.

3.2.4. Equations for Calculations

The equation that explains the electrical efficiency of the electrolysis of ammonia reaction is Faraday’s law, which is described as it follows:
\[ t = \frac{m \times n \times F}{s \times M \times I} \]  \hspace{1cm} \text{(Equation 3.1)}

Where:

\( m \) = mass needed (gr) \( \rightarrow \) depending on the concentration fixed

\( n \) = equivalent mol \( \rightarrow \) 3 eq

\( F \) = Faraday’s constant \( \rightarrow \) 26.8 A-h/eq

\( s \) = stoichiometric factor \( \rightarrow \) 1 mol

\( M \) = molecular weight \( \rightarrow \) 17.03 gr/mol

\( I \) = current applied (A)

To calculate the ammonia conversion of the process, the following equation was applied:

\[ Conversion_{NH_3} = \frac{C_o - C_f}{C_o} \times 100 \]  \hspace{1cm} \text{(Equation 3.2)}

Where:

\( C_o \) = Initial Concentration of NH\(_3\)

\( C_f \) = Final Concentration of NH\(_3\)

\textit{Faradaic Efficiency of the Process}- The efficiency of the process was calculated using Eqn. 3.3 through Eqn. 3.7. The theoretical amount of ammonia (mmoles) was found with Faraday’s Law.

\[ m_{\text{theoretical}} = \frac{s \times I \times t}{n \times F} \times 1000 = [mmM] \]  \hspace{1cm} \text{(Equation 3.3)}
The real amount of ammonia (mmoles) was calculated with the initial and final concentration.

\[ \text{Conc}_{\text{NH}_3(\text{initial})} \rightarrow \left( \frac{\text{mmoles}}{L} \right) \times (\text{Volume}_{\text{solution}}) = [\text{mM}]_{\text{initial(\text{real})}} \quad \text{(Equation 3.4)} \]

\[ \text{Conc}_{\text{NH}_3(\text{final})} \rightarrow \left( \frac{\text{mmoles}}{L} \right) \times (\text{Volume}_{\text{solution}}) = [\text{mM}]_{\text{final(\text{real})}} \quad \text{(Equation 3.5)} \]

\[ [\text{mM}]_{\text{initial(\text{real})}} - [\text{mM}]_{\text{final(\text{real})}} = [\text{mM}]_{\text{real}} \quad \text{(Equation 3.6)} \]

Finally the faradaic efficiency is calculated as it follows:

\[ \eta = \frac{\text{real}\_{\text{mole\text{OS}NH}_3}}{\text{theoretical}\_{\text{mole\text{OS}NH}_3}} \times 100 \quad \text{(Equation 3.7)} \]

Also, the power consumption of the systems evaluated was calculated, the Eqn. states the following.

\[ P = V \cdot I \quad \text{(Equation 3.8)} \]

Where: P: power (W), V: potential (V), and I: current (A).
Chapter 4- Electrolysis of Ammonia Effluents with Co-generation of Hydrogen.

Catalyst Development

This chapter contains a manuscript that intends to be submitted for publication to the Journal of Electrochemical Society (or another similar peer review journal) by Egilda P. Bonnin, Elizabeth Cellar, and Dr. Gerardine G. Botte.¹⁰

4.1. Introduction

There are negative effects on the environment that are the result of poorly applied technological procedures. Ammonia emissions are an example of these inadequate processes. Ammonia is related to eutrophication and particulate matter, therefore the removal of ammonia from wastes is imperative.¹¹, ¹² It is widely known the presence of ammonia in sources such as industrial waste water in both gaseous and aqueous forms. This contaminant could also be found in agricultural runoff from fertilizers in the form of NH₄⁺. Typical ammonia concentrations in municipal waste water effluents are in the range of 0.5-2 mM (8.5-34 ppm) with pH values between 5 and 8,³, ⁶ and 0.6-6 mM (10-102 ppm) with pH values of 10.8-11.5.¹³

Marincic and Leitz,³ studied the electro-oxidation of ammonia at low concentrations to evaluate the possibility of ammonia removal from waste-water. Catalysts of different compositions such as platinized platinum, graphite, titanium, and tantalum, as well as, titanium coated with platinum black were tested for reactivity and economic feasibility of the electro-oxidation at room temperature. The authors tested the effect of: different catalyst loadings (in the range of 0.5-20 mg cm⁻²), pH (between 5.55
and 12.8), concentrations of ammonia (between 0.12-10mM or 2-170 ppm), electrolytes such as NaCl, K\textsubscript{2}SO\textsubscript{4}, phosphate buffer and K\textsubscript{2}HPO\textsubscript{4}, and current density on the electro-oxidation of ammonia. It was found that only platinum electrodes were able to support the electro-oxidation of ammonia at a reasonable rate. However, the cost of the materials was very high due to the electrode area required for the reaction. The maximum current density obtained was 11.2 mA cm\textsuperscript{-2} in dynamic conditions, and 2.20 mA cm\textsuperscript{-2} in static conditions.

In order to improve the process, an electrode-catalyst which provides higher current densities needs to be developed.

Recently, Botte\textsuperscript{1} and Vitse et al.\textsuperscript{14} have proposed a new technology for the production of hydrogen on demand based on the electrolysis of ammonia, since ammonia can be used as a hydrogen carrier. According to the authors the reactions involved are:

\[
2NH_3(g) + 6OH^-(aq) \rightarrow N_2(g) + 6H_2O(l) + 6e^- \quad E^0 = -0.77 \text{ V/SHE} \quad (4.1)
\]

\[
6H_2O(l) + 6e^- \rightarrow 3H_2(g) + 6OH^-(aq) \quad E^0 = -0.82 \text{ V/SHE} \quad (4.2)
\]

where reactions (1) (ammonia oxidation), and (2) (water reduction), take place at the anode and cathode of the ammonia electrolytic cell, respectively; yielding the following overall reaction:

\[
2NH_3(g) \rightarrow N_2(g) + 3H_2(g) \quad E^0 = 0.059 \text{ V} \quad (4.3)
\]

The electrolysis of ammonia has several advantages:\textsuperscript{14} low operating temperature, hydrogen is produced on demand without the need of storage, the technology can use sustainable renewable energy sources, and the process can be extended as a waste water treatment process.
Botte have suggested that the technology can be used as a remediation process with hydrogen co-generation. However, the authors worked at high concentrations of ammonia, for the technology to be extended as a water remediation process, an electrocatalyst able to oxidize ammonia at the concentrations found in the effluents with significantly high current densities when compared to Marincic and Leitz needs to be developed. The proposed technology can be used as an application for purification of ammonia effluents with hydrogen cogeneration. This paper presents results based on the catalyst testing in the presence of low concentrations of ammonia, at the characteristic effluent concentrations.

Within this context, the objectives of this paper are:

1. Design an electrocatalyst able to electrolyze ammonia at low concentrations. The new catalyst should have a high surface area with low loading of noble metals. In this sense, two different substrates were tested, Raney nickel, as suggested by Cooper and Botte, as well as carbon fibers. Therefore, the first part of this paper deals with the identification of the best substrate between this selection.

2. Evaluate the performance of different noble metals electroplated on the surface of the selected substrates mentioned in objective 1. Previous studies have suggested that the presence of noble metals enhance the electrolysis of ammonia. According to Copper and Botte, Rh enhances the activity towards the OH adsorption, which seems to be a limitation for the reaction due to the competition between the adsorption of ammonia and OH on platinum electrodes, causing a blocking effect on its active zones. The authors also found that Rh fills effectively the empty active sites on the Pt surface for the ammonia oxidation reaction. Sathe and Botte mentioned that Rh is characteristic for its
electronic conductivity on carbon fibers, improving the adherence and deposition. Giner et al.\textsuperscript{17} reported that catalyst materials from the platinum group such as Pt and Ir, enhanced the kinetics of the electro-oxidation of ammonia. McKee et al.\textsuperscript{18} also proposed the usage of Pt-Ir as a catalyst material for the dissociation of ammonia for ammonia fuel cells. Based on this background information, different metals such as Rh, Pt, and Ir at different loadings and combinations were tested to determine their effect on the electrolysis of ammonia at low concentrations.

3. Determine the conversion and Faradaic efficiency of the reaction as well as the effect of ammonia and hydroxyl radical concentrations on the ammonia electrolysis using the best catalyst found in objective 2.

A second publication\textsuperscript{19} reports a cascade-continuous process for the development of the electro-oxidation of ammonia at two scales of different dimensions and currents applied at galvanostatic conditions. The conversion of ammonia and electric efficiency is also presented, as well as the ammonia and potassium hydroxide concentration minimization, based on the findings of this current paper.

4.2. Experimental

4.2.1. Electro-catalyst Preparation

Two catalyst materials were used, Raney nickel and carbon fiber substrates plated with noble metals. The substrates presented a geometric area of 6 cm\textsuperscript{2} for Raney nickel, and 4 cm\textsuperscript{2} for carbon fiber formed by wrapping the fibers on a titanium gauze as described by Sathe and Botte\textsuperscript{2} (titanium gauze 18 mesh woven, 0.28 mm diameter, wire open area of 64.3\%, and 100\% purity). The titanium gauze was attached to an annealed,
99.7% pure titanium wire, 0.81 mm diameter, and 20 cm long; both titanium gauze and wire were purchased from Alfa Aesar. Raney nickel substrate was deposited on titanium gauze using the procedure described by Cooper and Botte.8

The carbon fiber substrates were prepared by wrapping poliacrylonitrile (PAN) (Celion G30-500), 7 μm diameter carbon fibers from BASF on the titanium gauze as described in the literature.1,2,15 Each bundle of fiber consisted of 6000 filaments with an average length of 35 cm. Titanium gauze was chosen as the support of the carbon fibers to increase the electronic conductivity of the substrate. Furthermore, electrodeposition of noble metals on titanium does not take place unless the surface is properly treated (chemically or mechanically),20,21 which guaranteed that the noble metals would deposit only on the fibers preferentially. The carbon fiber substrates were cleaned with acetone, and air dried before the electrodeposition. The weight of each of the electrodes was recorded before and after the deposition with noble metals.

All the plating salts for the electrodeposition were 99.9% pure, obtained from Alfa Aesar. Dihydrogen hexachloroplatinate (IV) acid hydrate (H₂PtCl₆·6H₂O), with 38% Pt content, rhodium (III) chloride trihydrate (RhCl₃·3H₂O) with 38.5% of Rh content, and iridium (III) chloride trihydrate (IrCl₃·3H₂O) with 55% of Ir content were used to performed the electrodeposition of Pt, Rh, and Ir; respectively.

One of the objectives of the paper was to select the best substrate for the process of ammonia electrolysis. In order to do this, the two substrates chosen were both electroplated with Pt-Ir based on the findings of Vitse et al.14 The authors observed that this combination of noble metals provided the lowest voltage for the ammonia electrolysis and the highest efficiency from the materials tested when Pt foil was used as
substrate. Both substrates, Raney nickel and carbon fiber, were electrodeposited
galvanostatically with the combination of noble metals in a glass cell using platinum foil
as the counter electrode. The counter platinum electrode had 20 cm$^2$ of geometric area,
0.1 mm of thickness, 99.95% of purity, and it was purchased from ESPI Metals. In this
sense, the counter electrode was 3 times larger than the geometric area of the Raney
nickel working electrode, and 5 times larger than the geometric area of the carbon fiber
working electrode.

The electrodeposition of Pt-Ir on the Raney nickel substrate was performed with a
simultaneously deposition of Pt-Ir. The plating conditions are summarized in Table 4.1.
The plating bath for Pt-Ir was prepared by dissolving the corresponding quantities of
H$_2$PtCl$_6$·6H$_2$O and IrCl$_3$·3H$_2$O salts (keeping a weight ratio of 1:5 Pt to Ir), in order to
achieve a concentration of 0.1 mg ml$^{-1}$ (Table 4.1) in a total volume of 250 ml of solution
containing 95 ml of 32% w/v NaOH/L and 155 ml of high performance liquid
chromatography (HPLC) water/L. The solution was stirred with a stirring bar and kept at
room temperature. The electroplating process was done by fixing the current
systematically in increasing steps. The current was changed from 1.5 to 30 mA with
increments of 6 mA every 10 min (see Table 4.1). The apparatus used to control the
current was an ARBIN cycler BT2000, in which the voltage range was kept between -
0.015 and -1.2, avoiding the hydrogen evolution region that tends to form Pt black. The
total experimental time depended on the desired amount of noble metals to be deposited
on the substrate. After every step of current applied, the weight of the Raney nickel
electrode was measured to assure the desired loading of 8 mg cm$^{-2}$. 
### Table 4.1: Experimental Conditions Used for Electroplating Pt-Ir on the Raney Nickel Substrates

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pt-Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salts</td>
<td>$\text{H}_2\text{PtCl}_6\cdot6\text{H}_2\text{O}$ (38% Pt) + $\text{IrCl}_3\cdot3\text{H}_2\text{O}$ (55% Ir)</td>
</tr>
<tr>
<td>Chemicals</td>
<td>NaOH/L 32% w/v and High performance liquid chromatography (HPLC) water</td>
</tr>
<tr>
<td>Concentration of Salt (mg ml$^{-1}$)</td>
<td>0.1</td>
</tr>
<tr>
<td>Temperature of plating bath ($^\circ$C)</td>
<td>25</td>
</tr>
<tr>
<td>Loading [mg/cm$^2$ of Substrate]</td>
<td>4</td>
</tr>
<tr>
<td>Steps of current (mA)</td>
<td>1.5-30</td>
</tr>
<tr>
<td>Increment of current (mA)</td>
<td>6</td>
</tr>
<tr>
<td>Steps time (min)</td>
<td>10</td>
</tr>
<tr>
<td>Voltage range (V)</td>
<td>-0.015 to -1.2</td>
</tr>
</tbody>
</table>

Carbon fiber electrodes were electroplated with different noble metals (Rh, Pt, Pt-Rh, Pt-Ir, and Rh-Pt-Ir), the experimental matrix used is given in Table 4.2. The total loading of noble metals was kept at about 5 mg cm$^{-1}$ of carbon fiber bundle, such that, the effect of the different materials tested could be determined. Rhodium was deposited as a first layer in all the electrodes that contains this metal (in order to increase the electronic conductivity of the fibers,$^2$ increase the adherence of the other noble metals, minimize OH$^-$ surface blocking effect,$^{16}$ and provide complete coverage of the fibers), while the second layer was formed by either Pt or Pt-Ir (simultaneously co-deposited). The procedure described by Sathe and Botte$^2$ was used for the electrodeposition of the different metals on the carbon fibers (see Table 4 of the reference for a summary of the plating conditions). The plating procedure for Pt-Ir on carbon fiber substrates is
described as an example. The plating bath was prepared by dissolving the required quantities of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ salts (in order to achieve a concentration of 0.4 and 1.04 mg ml$^{-1}$ of Pt and Ir, respectively) in 250 ml of 1 M HCL solution (prepared with HPLC grade water). The solution was heated at 80°C and mixed with a stirring bar. The plating was done galvanostatically at a current of 250 mA in intervals of 20-30 min, the current was controlled using an ARBIN cycler BT2000. The voltage was kept below -1.3, avoiding the formation of Pt black. After every time interval the weight of the electrode was measured to assure the loading initially fixed of 5 mg cm$^{-2}$ of carbon fiber bundle.

Table 4.2: Experimental Matrix Used for Testing the Carbon Fiber Electrocatalysts. The total loading of each electrode was fixed at 5 mg cm$^{-1}$ of carbon fiber bundle.

<table>
<thead>
<tr>
<th>Number</th>
<th>Electrode</th>
<th>Loading (mg cm$^{-1}$ of carbon fiber bundle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh</td>
<td>5.0</td>
</tr>
<tr>
<td>2</td>
<td>Pt</td>
<td>5.3</td>
</tr>
<tr>
<td>3</td>
<td>Pt-Rh</td>
<td>5.2</td>
</tr>
<tr>
<td>4</td>
<td>Pt-Ir-Rh</td>
<td>5.1</td>
</tr>
<tr>
<td>5</td>
<td>Pt-Ir</td>
<td>4.6</td>
</tr>
</tbody>
</table>
4.2.2. Polarization Techniques

The electrochemical performance of the electrodes was determined by using cyclic voltammetry and galvanostatic polarization techniques. An ARBIN cycler BT2000 was used to perform the experiments. An all glass three electrode closed cell 1-L was used. The polarization potentials in the cyclic voltammetry experiments were measured vs. an Hg/HgO reference electrode. A Luggin-Haber capillary was located at 3 mm of the working electrode (anode) filled with a solution of 20% vol. KOH was used. A sweep rate of 10 mV s\(^{-1}\) was used during the experiments, the potential scan rate varied from -0.8 V to 0.1 V for a total of 20 cycles (to guarantee the sustainable periodic response. A 20% Rh, 80% Pt-Ir on carbon fiber counter electrode was used for the cyclic voltammetry experiments. At the same time, the galvanostatic experiments used the same Pt-Ir-Rh carbon fiber as cathode (to decrease the over-potential of the cathodic reaction; see Eq. 4.2. The electrode had a loading of 7.6 mg cm\(^{-1}\) of carbon fiber bundle, a geometric area of 4 cm\(^2\), and it was prepared following the procedures described before. Different constant currents were set, and the stable potential response of the system was observed. Also, current changes were fixed with increments of 10 mA each between 10-150 mA, each current was set for 30 min; with a resting time of 1 min. A 1 V limit was set for the experiments to finish in order to protect the catalyst materials, as well as to guarantee that the potential response was under the water electrolysis standard potential of 1.23 V.\(^{22}\) The solution was mixed with a stir bar during the galvanostatic experiments.

The electrochemical measurements were done at different concentrations of ammonia (between 0.001 and 1 M) and potassium hydroxide (between 0.2 and 1 M). The
chemicals used were 99.9% purity provided by Fischer Scientific. The volume of the solution used in the electrochemical cell was 800 ml and all the experiments were performed at room temperature. The conductivity and the pH of the solution were measured with the usage of a Multi-sense Conductivity/pH Cell, Mettler Toledo, MC 226.

4.2.3. Catalyst Characterization

The morphology of the electrodes was determined using a Scanning Electron Microscope (JEOL JSM-5300), operating at 30kV and 80 mA. The electrodes were observed after the electrodeposition with noble metals in order to analyze deposition coverage, and the uniformity and adherence of the deposited layers. Typical morphologies of the electrodes tested in this publication are similar to the ones shown and described by Sathe and Botte.\(^2\) As an example, a typical morphology for the 20% Rh-80% Pt-Ir counter carbon fiber electrode with 7.6 mg cm\(^{-1}\) of carbon fiber bundle used in the polarization techniques is shown in Figure 4.1. The photo-micrography at 10 \(\mu m\) of scale and magnification of 500X shows a typical morphology for a Pt-Ir-Rh carbon fiber electrode, in which it is noticed a uniform coverage layer of noble metals on the carbon fiber substrate. The deposition of the noble metals (Pt-Ir) on the Raney nickel electrode showed pre-selected areas in which the deposition was performed, showing a not uniform coverage. This is in agreement with the results reported by Cooper and Botte,\(^{16}\) even though the authors reported Pt-Rh.
Figure 4.1: Typical Morphology for Carbon Fiber Catalyst of 20% Rh, 80% Pt-Ir. Magnification at X500. Pt-Ir-Rh-7.6 mg cm$^{-1}$ of fiber bundle. The morphology is characterized by a uniform coverage layer of Pt-Ir-Rh on the carbon fiber substrate.

4.2.4. Conversion and Faradaic Efficiency

The ammonia concentration was measured with an Ion Selective Electrode Apparatus$^{23}$ from Thermo Electron Corporation, Model Orion 710A+. The concentrations were tested before and after the experiments in order to calculate the ammonia conversion, and the Faradaic efficiency of the process. The experimental time tested was compared to the theoretical time calculated based on Faraday’s Law. The values reported were measured following the error propagation and the appreciation of the instruments.
4.3. Results and Discussion

4.3.1. Performance of Different Substrates

Figure 4.2 presents the sustained periodic response of Pt-Ir Raney nickel and carbon fiber electrodes during cyclic voltammetry at a scan rate of 10 mV s$^{-1}$. The reported current was normalized by geometric area and total loading of noble metals in order to correct for the differences between the two substrates evaluated. The experiments were performed at 25$^\circ$C using a solution of 1 M ammonia and 1 M KOH. A high concentration of ammonia was chosen to evaluate the substrates avoiding diffusion limitations that may be present at low concentrations of ammonia. The oxidation currents reported above -0.5 V vs. Hg/HgO reference electrode are due to the electro-oxidation of ammonia as described by others.$^{14, 16}$ The slopes of the curves for both electrodes seem to be similar, which indicates that the ammonia electro-oxidation rate is about the same (per geometric area and total noble metal loading); however, the reaction on the Raney nickel electrode is not continuous (observed peak at -0.2 V vs. Hg/HgO reference electrode). The decrease on the current on the Raney nickel electrode with the polarization potential may be caused by the blockage of the catalyst active sites by absorbed OH$^-$ radicals as explained by Botte (diffusion limitations should not be the reason because of the high concentrations of ammonia used).$^1$ The surface blockage in the Raney nickel may be due to a non-uniform coverage of the substrate, which also causes a lower active (noble metal area) surface area for the reaction when compared to carbon fiber electrode. Carbon fiber electrodes may present a higher surface area than Raney nickel electrodes that possibly is contributing with the reactive capacity. Cooper and Botte reported exposed Raney nickel
zones after the electroplating of noble metals, which indicated a non adherent deposition of the catalysts.\textsuperscript{16}

Figure 4.2: Cyclic Voltammetry Curves for Pt-Ir on Raney Nickel and Carbon Fiber Substrates at 1 M NH\textsubscript{3}, 1 M KOH, 25\textdegree C, and 10 mV s\textsuperscript{-1}. The carbon fiber electrode showed better performance towards the electro-oxidation of ammonia, since surface blockage effect is not observed.

Based on the discussion supported by Cooper and Botte\textsuperscript{16} related to the non-uniform coverage of noble metals on the Raney nickel substrate, one of the consequences may be the degradation of the material with time. To evaluate the stability of the Raney nickel electrode with time (the electrode was exposed to air during the operating time), the same electrode was tested weekly for a moth at the same conditions set in Figure 4.2. The results are shown in Figure 4.3, in which the uniform and sustained periodic state of
the Pt-Ir Raney nickel electrode reported a significant decrease in the current with time. A decrease in approximately 200 mA of current is an indication of reactivity lost of the catalyst. A reactive catalyst able to perform at similar current conditions for a specific voltage range (-0.8 V → +0.1 V → -0.8 V) with time is needed. Raney nickel catalyst did not show the desired behavior towards the ammonia electro-oxidation reaction.

![Cyclic Voltammetry performance of the Pt-Ir Raney Nickel Electrode with Time at 1 M NH₃, 1 M KOH, 25°C, and 10 mV s⁻¹.](image)

**Figure 4.3:** Cyclic Voltammetry performance of the Pt-Ir Raney Nickel Electrode with Time at 1 M NH₃, 1 M KOH, 25°C, and 10 mV s⁻¹. A decrease in reactivity over time was observed. From week 1 to week 4, the current decreased 200 mA.

Another important comparison between the substrates is the weight of the electrodes. The total weight of the Raney nickel substrate (excluding the loading of noble metal) was 1170 mg, which is considerably heavier than the weight of the carbon
fiber electrode (886.2 mg). Based on the results shown in Figures 4.2 and 4.3, and the weight of the electrodes, carbon fiber was selected as the best substrate for the electro-oxidation of ammonia. The advantages over Raney nickel include: (1) uniform coverage by noble metals, (2) no surface blockage effect, (3) large surface area, and (4) light weight.

4.3.2. Performance of Carbon Fiber Substrate Electrodes at Low Concentrations of Ammonia

The results from the previous section were performed at high concentrations of ammonia; however, the electrochemical performance of the electrodes needs to be tested at the concentrations of ammonia found in waste water. Figure 4.4 presents a comparison of a Pt-Rh carbon fiber electrode (electrode # 3 of Table 4.2) with a 0.13 cm$^2$ platinized Pt foil electrode developed by Marincic and Leitz.$^3$ The reason why a Pt-Rh carbon fiber was selected for comparison purposes, instead of a Platinized Pt electrode was based on the electronic conductivity and adherence properties that Rh had shown in previous applications.$^2$ It was also a purpose of the investigation to determine the improvement on Rh over Pt, as well as the different substrates. The experiment was performed at the conditions described by the authors:$^3$ 1.03 mM NH$_3$ and 0.1 M KOH (equivalent to 12.8 pH), at 25$^\circ$C. The apparatus used to test the Pt-Ir carbon fiber electrode was a Solartron 1287 Electrochemical Interface. The data from Marincic and Leitz was digitalized using the software Get Data Version 2.17,$^{24}$ their potential was measured vs. a SHE and it was corrected to a Hg/HgO reference electrode by adding - 0.092 V. The sweep rate used was 3.33 mV s$^{-1}$, at static conditions. In the first cycle represented by the carbon fiber
substrate, two peaks can be observed; the first peak occurs at a potential of \(-0.65 \text{ V vs. Hg/HgO electrode}\) and it is associated with the electro-adsorption of OH\(^{-}\) as described elsewhere.\(^{16, 25}\) The second peak occurs at a potential of \(-0.4 \text{ V vs. Hg/HgO electrode}\) and it is related with the electro-oxidation of ammonia. The decrease in the current density as the potential increases is associated with diffusion limitations as the concentration of ammonia in solution is low. The electro-oxidation of ammonia in the Pt-Rh electrode took place at a lower potential than Marincic and Leitz,\(^3\) which could have been caused by the difference in the electrode compositions. This fact represents an improvement for the electrolysis of ammonia at low concentration as the energy consumed by the process will be reduced. Furthermore, the peak of current density observed in the carbon fiber electrode is 10 times higher than the one reported by the authors,\(^3\) which could be caused by an increased in the surface area. After 10 cycles the ammonia in solution was depleted, as no ammonia peak was observed in the last cycle.
Figure 4.4: Comparison of the Electrochemical Performance of the Pt-Rh Carbon Fiber Electrode with Marincic and Leitz$^3$ electrode (Platinized Pt on Pt foil) at 1.03 mM NH$_3$ and 0.1 M KOH. The currents were normalized by geometric area and noble metal loading to correct for the differences. The peak of current density is observed in the literature at 1.5 mA cm$^{-2}$ approximately, whereas with the carbon fiber substrate, the peak current density is observed at 15 mA cm$^{-2}$. Carbon fiber substrates showed 10 times higher currents than platinized Pt catalysts.

4.3.3. Effect of Different Noble Metals on the Electro-oxidation of Ammonia at Low Concentrations

The different electrode materials shown in Table 4.2 were tested for the electro-oxidation of ammonia at low concentrations. The experiments were performed at 20 mM NH$_3$ and 0.2 M KOH. Figure 4.5 shows the cyclic voltammetry of the different electrodes at a scan rate of 10 mV s$^{-1}$ and 25°C. The current reported were normalized
with respect to electrode loading to account for any differences. Electrodes 3 and 4 showed the same current peak value of approximately 2 mA mg⁻¹ of total loading. The kinetic behavior of the electrodes tested was slightly different, which indicates an effect associated with the noble metal material used. It can be noticed that for the Rh Electrode 1, the electro-oxidation of ammonia is not observed, which indicates the capacity of the Rh to improve the OH⁻ adsorption, but the inefficiency to enhance the ammonia electro-oxidation (probably due to a weak ammonia adsorption when compared to OH⁻ adsorption). Electrode 2 and 5 showed a current peak, but not as high as electrode 3 and 4. In order to determine which electrodes present the best performance further analysis should be performed to compare the capacity of developing higher currents at lower potentials. Electrodes 2-5 exhibited a good performance in cyclic voltammetry conditions. Pt-Rh Electrode has a significant kinetic improvement over Rh or Pt electrodes (1 and 2), probably due to the synergistic effect of the Rh (adherence, electrical conductivity),² and Pt (activity towards ammonia electro-oxidation).¹⁷,¹⁸ The presence of Pt-Ir also enhances the oxidation of ammonia at low concentrations. Also, the presence of Rh-Pt-Ir may be the perfect combination for the best catalyst at the conditions tested, by combining all the characteristics provided by each one of the catalyst materials used.
4.3.4. Galvanostatic Performance of the Electrodes

The most promising electrodes selected based on the results shown in Figure 4.5 (electrodes 3 to 5) were tested galvanostatically. As mentioned in the experimental description a Pt-Ir-Rh electrode was used as counter electrode to minimize the voltage of the cell (decrease cathodic over-potentials). The intention of this test is to determine the
electrode that achieves the highest current at the lowest cell voltage. Figure 4.6 shows
the comparison of the performance of different electrodes at 20 mM NH₃, 0.2 M KOH,
and 25°C. In all the cases the solution was mixed using a stir bar. The current was
increased from 10 mA to the maximum achieve by each electrode in increments of 10
mA each. Each current was sustained for 30 minutes. Electrode 4 (Pt-Ir-Rh electrode)
showed the best behavior by giving the highest current response of the system (150 mA),
and the lowest potential in each of the steps of currents tested. Electrode 4 reported a
difference in potential of 100 mV approximately respect to electrode 2, and same
potential respect to electrode 5, both reaching 100 mA as the highest current. This
indicates a best catalyst for the ammonia electro-oxidation reaction, due to lower energy
consumption and the high current. In that sense, it seems like at low concentrations of
ammonia, the synergistic effect of Rh-Pt-Ir are a perfect complement to enhance the
ammonia electrolysis.
Figure 4.6: Galvanostatic Performance of the Most Promising Electrodes (Electrode 3 to 5), based on the result of Figure 4.5. The experiments were performed at 20 mM NH$_3$, 0.2 M KOH, and 25°C. Pt-Ir-Rh was used as the cathode. Electrode 4 (Pt-Ir-Rh) showed the highest current and the lowest voltage for all the current tested. This electrode was selected as the best at the conditions for low ammonia concentrations.

4.3.5. Efficiency and Conversion

The Faradaic efficiency and the conversion for the electro-oxidation of ammonia were determined on the best electrode chosen from Figure 6 (Rh-Pt-Ir-Electrode 4). The current was set constant at 100 mA, and the experiment was performed until the system reached 1 V, as the maximum voltage permitted. Higher voltages were not attempted to avoid the electrolysis of water. The experiment was performed in five (5) steps. Figure 4.7 shows the results of the electrochemical test. During the first trial the elapsing time
before reaching 1 V was 10.8 h. The reasons for the increase in the voltage could be that the ammonia was completely depleted from the bulk or concentration overpotential (depletion of ammonia concentration at the surface of the electrode). To determine the cause, the system was allowed to rest for 15 minutes and then it was polarized again at the same current (trial 2). The fact that the system was stable for a long period of time indicated the effect of concentration overpotential on the electrolysis. Same procedure was applied until the voltage rise immediately (at short elapsing time) to 1 V (trial 5). After trial 5, the concentration of ammonia in the solution was too low for the cell to operate at 100 mA. Finally, the time was accounted for a total of 5 trials and the total time was compared with the theoretical time calculated following Faraday’s law. The ammonia concentration was measured at the beginning and end of the test in order to determine the percentage of ammonia conversion, as well as the Faradaic efficiency of the process. The initial concentration was 21.5 ± 0.000006 mM ammonia, and the final concentration was 1.83 ± 0.000006 mM ammonia, yielding into a percentage of ammonia conversion of 91.488 ± 0.003%. The Faradaic efficiency was 91.81 ± 0.13%. This percentage based values are consider high but still they could be improved by cells operating at different currents and considering the power consumption as well as the conversion and efficiency of the process. This is the topic for a second publication. 19 The final ammonia concentration obtained was still a considerable high concentration to be released into the environment without any pollution consequences, which value should be in the order of 0.08 mM according to EPA. 26
Figure 4.7: Galvanostatic Performance of Pt-Ir-Rh Electrode at 100 mA, Initial concentration of 20 ± 3 mM NH₃, 0.2 M KOH, and Room Temperature. The experimental elapsed time was the same as the theoretical time calculated by Faraday’s Law for a total of 13.78 h. The final NH₃ concentration was 1.83 ± 0.000006 mM, with a process conversion of 91.488 ± 0.003% and faradaic efficiency (η) of 91.81 ± 0.13%.

4.4. Conclusions

Two different substrates were evaluated for the electro-oxidation of ammonia at low concentrations. Electrodes prepared on a Raney Nickel substrate presented lower reactivity for the electro-oxidation of ammonia at low concentrations when compared to the carbon fiber substrate. In summary, carbon fiber is a better substrate than Raney nickel for the electro-oxidation of ammonia at low concentration conditions based on: 1) uniform coverage by noble metals; 2) no surface blockage effect; 3) large surface area, and 4) light weight (886.2 mg vs. 1170 mg of Raney nickel weight)
The carbon fiber electrodes developed performed ten (10) times better than the electrodes reported in the literature\(^3\). The electrochemical performance of different noble metals deposited on carbon fibers was evaluated. Electrodes containing Pt-Ir-Rh seemed to be the most promising for the electrolysis of ammonia at low concentrations based on the cyclic voltammetry and galvanostatic results. The process presented a 91.488 ± 0.003% conversion of ammonia and Faradaic efficiency (\(\eta\)) of 91.81 ± 0.13% on the Pt-Ir-Rh electrode on carbon fiber substrate with a loading of 5 mg cm\(^{-1}\) of carbon fiber bundle. This implies that the electro-oxidation of ammonia at low concentrations and at a current density of 25 mA cm\(^{-2}\) follows Faraday’s law closely, which indicates conversion to nitrogen.

Further considerations will be taken based on these results to improve the efficiency and the conversion of the electrolysis. The future scope intends to find a strategy to decrease even more the concentrations of NH\(_3\) and KOH. EPA standard regulations for ammonia emissions in water sources should be accomplished\(^{10,13}\). In a second publication, adjustments to the current density are performed to decrease the concentration of ammonia in the solution and improve the efficiency and the conversion of the reaction\(^{10}\).
Chapter 5 – Conclusions and Recommendations

5.1. Catalysts

Electrodes prepared on a Raney nickel substrate presented lower reactivity for the electrolysis of ammonia reaction at low concentrations than electrodes made on carbon fiber substrates. Higher currents and lower potentials were reached with the carbon fiber substrate. In addition, SEM characterization technique supported the understanding of the catalysts morphology, as well as the determination of how the electro-deposition technique was performed for the materials under study. SEM showed that carbon fiber catalyst presented a more uniform coverage of noble metal materials than Raney nickel electrodes. Potentiostatic technique also supported the selection of carbon fibers over Raney nickel catalysts, by representing a similar trajectory in the oxidation-reduction curve than the trajectory presented for Raney nickel electrodes. In summary, carbon fiber is a better substrate than Raney nickel for the ammonia electrolysis at low concentration conditions.

In comparison with previous studies, the EERL carbon fiber catalysts selected performed ten (10) times better than the referenced literature\(^3\). The optimum catalyst evaluated in galvanostatic conditions of 100 mA and solution concentration of 20 ± 3mM NH\(_3\) and 0.2M KOH, presented an optimum composition of 23% Rh-77% Pt-Ir.

5.2. Minimization of NH\(_3\) and KOH Concentrations

The optimum minimum concentrations reached in galvanostatic conditions were 1.83 mM NH\(_3\) and 0.2M KOH.
5.3. Conversion and Electrical Efficiency of the Electrolysis of Ammonia

The process presented a 91.488 ± 0.003% conversion of ammonia and Faradaic efficiency ($\eta$) of 91.81 ± 0.13% on the Pt-Ir-Rh electrode on carbon fiber substrate with a loading of 5 mg cm$^{-1}$ of carbon fiber bundle. This implies that the electro-oxidation of ammonia at low concentrations and at a current density of 25 mA cm$^{-2}$ follows Faraday’s law closely, which indicates conversion to nitrogen.

5.4. Recommendations

Recommendations for this particular project will be based on the future understanding of the overall process from the natural source into the electrolytic cell where the electrolysis is occurring. By understanding the chemistry of the natural source, and assuring that the composition of that source is compatible with the catalyst-electro-oxidation of ammonia the whole integral problem will be solved. The future scope includes the development of a systematic testing for contaminants also present in the natural sources of ammonia. For instance, it is important to test the compatibility of these contaminants when they are involved in the same environment. The production of hydrogen could be affected or not by the presence of phosphates, suspended solids, chlorines, sodium, metallic traces, among others. In addition, if these contaminants are mixed in the same place, the objective will be to understand if that is detrimental or beneficial for the normal operation condition of the NH$_3$ electrolysis reaction.
References


