



Small-scale electrochemical ammonia production: a quantitative literature review of promising catalysts for future development

Violet Perkins Phillippo

BSc (Hons) Chemistry, Year 3

University of Southampton

Department of Chemistry

Supervisor: Professor Phil Bartlett

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Abstract

This literature review identifies promising catalysts, for the sustainable and cost effective *in-situ*, small-scale electrochemical ammonia production, for agricultural applications. The research is motivated by the drive to improve the food and financial securities of African farmers, whose crop yields are limited by a lack of access to affordable fertiliser. In the last several years, this area of catalysis research has received an increasing amount of attention, however, viable alternatives to the metal nitride catalysts, used by Atmonia, remain elusive. The overarching barrier, to efficient ammonia production, is finding catalytic materials that sufficiently activate the N₂ bond for reduction or that can sufficiently suppress the hydrogen evolution reaction (HER), a significant competing reaction. Herein, I evaluate the performance of catalysts reported in both theoretical and experimental studies, in the areas of nitrogen doped carbon catalysts, nanomaterial catalysts and plasma based catalysts. The criteria discussed in this review are the overpotential required for N₂ reduction, the Faradaic efficiency (FE) achieved and the rate of ammonia production, reported in the literature. I identify the refinement of the use of defect engineering in nitrogen doped carbon catalysts and nanomaterial catalysts and activation of the N₂ bond with plasma, as future research aims.

1. Introduction

This literature review evaluates the progress that has been made, in catalytic development, for cost effective and sustainable electrochemical ammonia production. My interest lies in recognising the potential for the manufacture of cost effective and sustainable units, for Kenyan farmers to produce ammonia *in-situ*. I shall be discussing the nature of the catalysts used in an electrochemical cell for ammonia production, limited to the promise that materials show, in terms of cost effectiveness and sustainability.

Each section will focus on an area of catalyst development: nitrogen doped carbon catalysts, nanomaterial catalysts and plasma based catalysts. For each catalyst discussed, I will compare the overpotentials required to produce ammonia, the Faradaic efficiencies (FEs) and the rates of ammonia production that have been measured experimentally or predicted using density functional theory (DFT) calculations. Where the information is available, I will also comment on the stability and durability of the catalysts discussed. This is because these are key considerations in catalytic design for electrochemical ammonia production, in terms of evaluating the cost effectiveness and sustainability of a material. In addition to this, these are also the key issues that must be addressed, in order to find a catalyst that is commercially viable.

I will use these criteria to assess the viability of the proposed catalysts, in line with existing working examples of small-scale ammonia production, such as the renewable small scale Haber-Bosch units¹ and Atmonia's electrochemical ammonia production unit, which uses a metal nitride catalyst.² Consequently, electrochemical scientists and engineers can identify the most promising areas for future catalysis development (Figure 1 below).

One of the scientific partnerships to report the electrochemical fixation of nitrogen was Van Tamelen and Seeley, in 1969. The primary focus of this research was to investigate the catalytic role of tetraisopropoxide and naphthalene, present in the electrolyte. The solution was stirred under a pure nitrogen source, at 40 V and 10.2 mmol of ammonia was collected after 11 days, when the conductance of the cell had

diminished.³ In the 1980s, Masashi *et al.*⁴ and Becker and Poisin⁵ amongst others, demonstrated the electrochemical synthesis of ammonia at ambient conditions, using solid heterogeneous catalysts. Although the Faradaic efficiencies of below 1%, reported by Masashi *et al.*,⁴ have long since been superseded, the ability to produce ammonia at ambient conditions, was a remarkable development in sustainable technology. Over the last 10 years, the use of scientific innovation, such as nanomaterials and plasma technology have become more established, and this has led to significant progress in catalyst development, therefore, in this review, I will cover the literature published within the last 10 years. This research is more relevant to the context of this review, due to the particular focus on sustainable catalysts, which has become an increasingly prevalent issue. Crucially, 67% of the papers mentioned in the review and discussion section were published in the last 2 years, therefore, in the review it was important to highlight the merits and limitations of cutting-edge research.

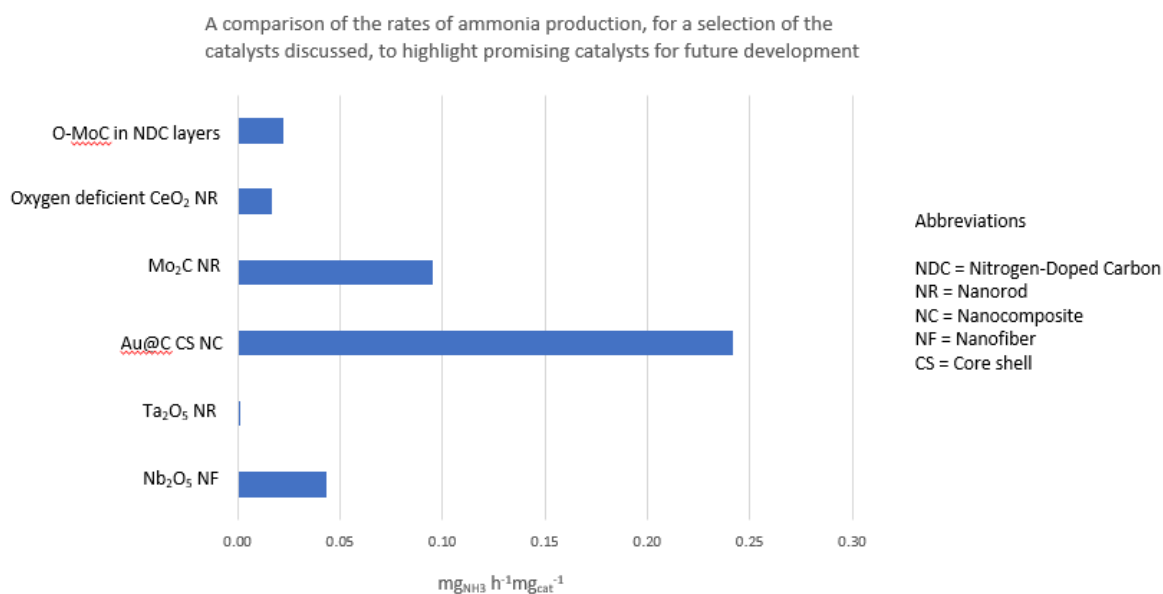


Figure 1 A comparison of the rates of ammonia production, for selected promising NRR catalysts, for future development. Compiled using experimental data from selected sources.^{25,28,38-40,42}

Kenyan agriculture is predominantly carried out on a small-scale, in areas of the highest agricultural potential. The average farm size is 0.2-0.3 ha and these small-scale farms, make a significant contribution to the agricultural sector by producing 70% of Kenya's marketed agricultural produce.⁶ Therefore, cost effective and sustainable *in-situ* ammonia production has the potential to significantly increase both the financial

and food securities of Kenyans. The context of this report has a specific focus on Kenya, due to its established solar technology industry,⁷ which means that the country already has the infrastructure and technology in place, to provide renewable energy, to operate an *in-situ* ammonia production unit. The information available, regarding farm sizes in Kenya, is also more precise than reported for other African countries. Therefore, a more accurate assessment can be made regarding the current viability of *in-situ* ammonia production, to produce ammonia cost effectively and sustainably.

However, overall, there are 41 million farms in Africa that are smaller than 2 ha in size,⁸ which shows that the impact of the research would be felt across the whole continent. In rural locations, where the typical population density is very low, many farmers are currently unable to benefit from fertiliser distribution networks and electricity distributed by the national grid.⁹ M-KOPA is a solar company established in 2013 that, to date, has connected 750,000 homes and businesses to solar power, with 46% of the customers using the installed system to generate income. The company provides affordable solar energy, by operating a daily payment system, which would allow farmers to spread the cost of the solar technology over the period of a year. M-KOPA currently operates in Kenya but also in Nigeria, Uganda and Tanzania,¹⁰ which implies that it would be equally possible to set up solar powered, *in-situ* ammonia production in these countries.

It seems that micro-dosing, the targeted application of small, affordable quantities of fertiliser to a crop,⁹ would be an ideal solution to increasing the economic potential of Kenyan farmland. A project in Southern Zimbabwe demonstrated the application of 10 kg of ammonium nitrate fertiliser to a 0.1 ha plot, using a micro-dosing method. This is approximately the equivalent of 17 kg N ha⁻¹, which is 25% of the recommended dose. Another plot, of equal size, was left untreated. The project revealed that, despite large variations in crop management, for example, the timing of fertiliser application, 92% of the sample of 89 farmers achieved an increased yield, compared to the untreated plot.¹¹ A later project, also in Zimbabwe, illustrated that applying 8-10 kg N ha⁻¹ increased the farmers' yields of maize and small grains by 50%,⁹ which shows that the cost effectiveness of fertiliser application can be increased, whilst still sufficiently increasing the output of the farm.

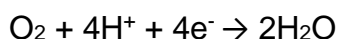
However, Kenyans depend on the international markets for their fertilisers, as local production is non-existent or limited.¹² This means that for many rural farmers, access to fertiliser remains a difficult issue. A project in Nigeria, funded by the UK's Department for International Development (DFID), led the distribution of over 2,000 metric tonnes of fertiliser, in small packs, to 570,000 farmers.¹³ This was beneficial to the farmers, as it allowed them to access small quantities of fertiliser, however, the costs, organisation and environmental impact associated with fertiliser distribution, remained. The project highlights that there is a need for *in-situ* electrochemical ammonia production, to allow farmers to be more self-sufficient, through reducing their reliance on the international supply chain of fertiliser and Government led projects. To be commercially viable to Non-Governmental Organisations (NGOs) and farmers alike, an electrochemical ammonia production unit would need to be cost effective, sustainable and provide sufficient yields of ammonia for micro-dosing applications.

At the working electrode, the significant reaction that competes with the reduction of N₂ gas to ammonia is the HER, which is the reduction of the proton source in the cell to H₂ gas.¹⁴⁻¹⁷ Skulason *et al.*¹⁵ acknowledge that the HER will always be a competing reaction, even in nitrogen fixation in biological systems, so the current research effort is focused on catalysts that can suppress, rather than eliminate the HER. Even in a basic solvent, there are a significant number of protons present, which are available to participate in HER,¹⁸ as well as the low solubility of N₂ in most electrolytes. Therefore, discovering ways to suppress HER, through catalytic design, is currently a major hindrance to achieving highly efficient electrochemical ammonia production.^{19,20} The selectivity of the catalyst for the desired reaction is measured quantitatively, in terms of the Faradaic efficiency that it demonstrates, over the time period in which the catalyst is tested. The Faradaic efficiency represents the proportion of electrons supplied to the catalyst, which participate in the desired nitrogen reduction reaction (NRR), compared to other, competing reactions. Therefore, developing a catalyst that could suppress the HER, would increase the rate of ammonia production, without the need to increase the overpotential or to use harsher reaction conditions.

The most prominent issue for economic and sustainability considerations is the activation of the N₂ triple bond for reduction. It would be preferable to carry out the reaction at ambient conditions, to minimise the energy demand and maximise the safety of the process but this is difficult to achieve at low overpotentials without

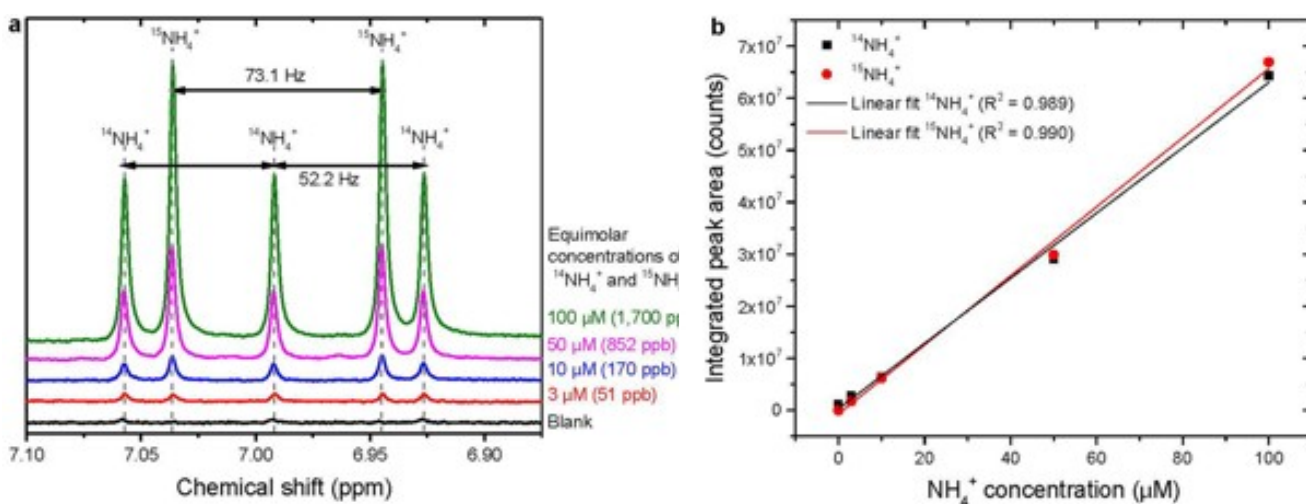
compromising the rate of ammonia production. At low overpotentials, the chemisorption of protons onto the surface of the catalyst, is more thermodynamically favourable than the protonation of N₂ present on the catalyst.¹⁹ This reduces the Faradaic efficiency of the catalyst and thus the rate of ammonia production, by reducing the number of active sites available for N₂ activation. It is clear, from the papers analysed, that scientists are motivated to design catalysts that are either able to activate the N₂ bond or to suppress the HER reaction.

A review article²¹ focused on the studies that have explored the electrochemical oxygen reduction reaction (ORR), in which molecular oxygen is reduced to water. There are two ways in which this reaction is different from the NRR. However, the knowledge gained from research into catalysts for ORR is still of value to scientists, as a benchmark for research on the NRR. The bond enthalpy of O=O is 498 kJ mol⁻¹ which is significantly less than the 941 kJ mol⁻¹ required to dissociate the N₂ triple bond.²² This implies that the catalyst for NRR will need to be more active, a higher overpotential will need to be applied or the reaction conditions will need to be harsher. In addition to this, the ORR is a 4 electron process, whereas the mechanism for NRR involves 6 electrons and, from the literature, it is clear that there are several possible mechanistic pathways for nitrogen reduction,²⁰ which appear to vary depending on the catalytic surface used.



The quantities of ammonia produced in laboratory tests, are currently very small. This means that there is significant uncertainty associated with the detection and determination of the rate of ammonia production. Liu *et al.*²³ emphasise that scientists need to develop more selective and accurate methods for ammonia detection. This is so that they can determine whether the ammonia detected has been produced *in-situ* or whether the system has been contaminated by small quantities of ammonia or nitrogen containing compounds. These impurities could come from sources such as the N₂ gas stream input, the catalyst or the surrounding air, which would lead to a false

positive result, for ammonia production. It is therefore the studies that attempt to address this issue, by undertaking appropriate tests, that have additional validity compared to those that do not. By replacing the N₂ gas stream with an Argon gas stream, studies have demonstrated that it is possible to show whether there is any ammonia present in the system as, in the presence of the Argon gas stream, *in-situ* ammonia production should be zero.²⁴⁻²⁷ In addition to this, isotopic labelling of nitrogen can be used to more definitively differentiate between ammonia produced *in-situ* and ammonia from other sources. In their experiments, scientists have used N₂ sources, which contain only the ¹⁵N isotope. They have used sensitive methods such as ¹H NMR, to qualitatively confirm that ¹⁵NH₃ has been produced *in-situ* by the electrochemical system and to quantitatively determine the mass of ammonia produced.²⁶⁻²⁸ Anderson *et al.*²⁹ show that the coupling between ¹H and ¹⁵N (*I* = ½) nuclei, in ¹⁵NH₄⁺ results in a doublet with a coupling constant of 73 Hz, whereas the interaction between the ¹H nuclei and the quadrupolar ¹⁴N nuclei, in ¹⁴NH₄⁺, results in a triplet with a coupling constant of 52 Hz. As ¹⁴N is by far the most abundant nitrogen isotope in the atmosphere, any contamination is identified by the detection of ¹⁴NH₄⁺, even when the experiment does not result in the production of ¹⁵NH₃. The ¹H measurements in this study were carried out using a Bruker AVANCE III HD 800 MHz spectrometer, equipped with a 5 mm TCI Cryoprobe, with solutions containing equal concentrations of ¹⁴NH₄⁺ and ¹⁵NH₄⁺, from NH₄Cl. Figure 2(a) shows that the peaks for ¹⁵NH₄⁺ can be detected at concentrations as low as 51 ppb, demonstrating the high sensitivity of the technique for the detection of ammonia. Figure 2(c) below, shows that the desired peaks are still very much identifiable on a more common, lower resolution 400 MHz spectrometer.



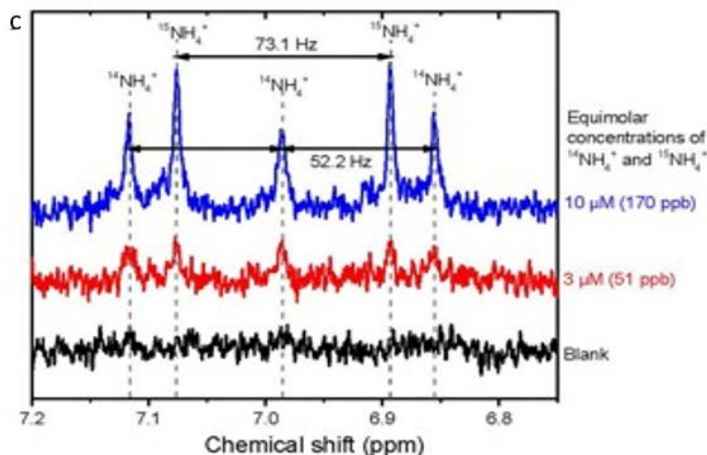


Figure 2 (a) ^1H NMR Spectrum of a solution of 600 μl 0.1 M KOH, acidified with 0.5 M H_2SO_4 to a pH of 1. CH_3OH (200 μM) was added as an internal reference. (b) The integrated peak areas from (a) for both $^{14}\text{NH}_4$ and $^{15}\text{NH}_4$, can be used to determine the quantity of $^{15}\text{NH}_3$ produced, by using the calibration curve shown. (f) The experiment was repeated using the solution outlined in (a), but the spectrum was collected using a Bruker AVANCE III HD 400 MHz spectrometer equipped with a 5 mm Prodigy probe. Adapted from S. Z. Anderson, V. Čolić, S. Yang, J. A. Schwalbe, A. C. Nielander, J. M. McEnaney, K. Enemark-Rasmussen, J. G. Baker, A. R. Singh, B. A. Rohr, M. J. Statt, S. J. Blair, S. Mezzavilla, J. Kibsgaard, P. C. K. Vesborg, M. Cargnello, S. F. Bent, T. F. Jaramillo, I. F. L. Stevens, J. K. Nørskov and I. Chorkendorff, *Nature*, 2019, **570**, 504-508.

None of the proposed catalysts discussed, have enabled the production of ammonia at a rate that is sufficient to supply a Kenyan farmer, in a reasonable production time. The lower bounds of the reported ranges have been used to estimate the minimum mass of ammonia required to supply a Kenyan farmer with sufficient ammonium nitrate fertiliser, for one season. Taking the lowest figure of a 0.2 Ha farm,¹² and an application of 10 kg Ha^{-1} of ammonium nitrate fertiliser,¹¹ the mass of ammonia required to fertilise the farm would be approximately 1.2 kg. The modal order of magnitude, for the rate of ammonia production, for the catalysts discussed in this review, is $10^{-5} \text{ g h}^{-1} \text{ mg}_{\text{cat}}^{-1}$. It would take 14,000 (to 2 sf) years to produce the 1.2 kg of ammonia needed, however, this is based on the use of only 1 mg of catalyst. The nitrogen doped carbon catalysts reported by Qu *et al.*²⁸ and Zhao *et al.*²⁷ demonstrate rates of ammonia production of 23.8 and 22.3 $\text{mg h}^{-1} \text{ g}_{\text{cat}}^{-1}$ respectively. At a rate of ammonia production of 20 $\text{mg h}^{-1} \text{ g}_{\text{cat}}^{-1}$, it would take 7 years, to the nearest year, to produce 1.2 kg of ammonia. This shows that by increasing the mass of the catalyst by a factor of a thousand, and thereby increasing the surface area on which the NRR can take place, the rate of ammonia production remains unviable for commercial application but does increase

considerably. However, the figures calculated, are gross underestimates, as the calculation assumes that the catalyst sustains a FE of 100%, a stable current density and has sufficient durability, for this length of production. Therefore, there is currently a gap in the research between established technology and catalysts that currently show insufficient rates of ammonia production, in a laboratory environment. This review indicates the catalysts, that demonstrate a promising performance in the electrochemical production of ammonia and thus where future research should be focused.

2. Literature review and discussion

2.1 A review of the small-scale Haber-Bosch process

The Haber-Bosch process is currently the most efficient process, for the large-scale production of ammonia. The energy intensive process involves passing gaseous N_2 and H_2 over a Ru or Fe based catalyst, at high pressures (150-350 atm) and high temperatures (350-550 °C), to form ammonia.¹⁶

There are currently several operational pilot plants around the world that produce ammonia on a small scale, using the Haber-Bosch process. This is advantageous because the efficiency of the process is well known and the energy consumption on a small-scale is much less, which makes it possible to make the process more sustainable, by providing the energy required from renewable resources. It uses nitrogen from the air and protons from the electrolysis of water, so the reagents for this process are also sustainable. Most of the hydrogen, for the large-scale Haber-Bosch process, is obtained from natural gas or coal.¹⁶ However, on a small-scale, it is feasible to provide sufficient energy for the electrolysis of water to hydrogen, from renewable sources, which reduces the carbon footprint of the system.

Patil *et al.*³² report the design for an NFuel unit, by the company Proton Ventures, which produces ammonia at a rate of 120 kg h⁻¹. The research is important, as the designs show that decentralised production of ammonia, powered by renewable energy, is possible but the research is limited by its theoretical nature. From current projects completed by Proton Ventures,³⁰ it seems that the company is focused on designing and building wind powered NFuel units with increasing capacity, with the

aim to provide a sustainable alternative to the Haber-Bosch process. The smallest NFuel unit produces 3 metric tonnes of ammonia per day, which makes the research less relevant to the context of this review. This is because this review is focused on the production of ammonia on a very small scale, for Kenyan farms who may only require 1.2 kg of ammonia per season.

The paper proposes that the unit could be situated next to an existing wind farm but stresses that 'such unit can accompany a solar farm too,' highlighting that this technology can withstand the power fluctuations associated with renewable energy sources. In this way, it would be an ideal system in Kenya, a country with a high average insolation of 5-7 kWh m⁻² for directly south facing solar panels,⁷ and a growing solar industry, for providing electricity for establishments that are off their national grid. The solar energy absorbed by the solar panels, to 3 significant figures, would be 4.83 kWh m⁻², using an average insolation of 6 kWh m⁻² and the Earth's albedo of 0.31.³¹ This is compared to Southampton, where the average insolation varies from 0.67 kWh/m² in December to 5.66 kWh m⁻² in June, for directly south facing solar panels.⁷

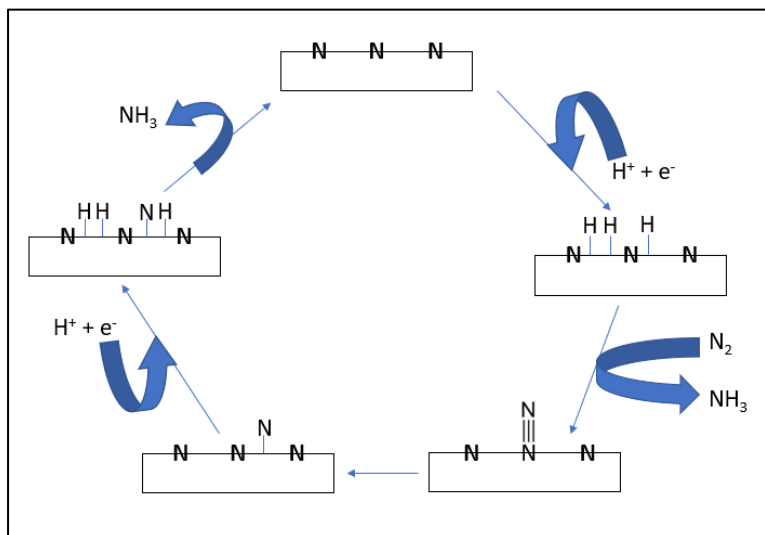
A group of engineers from the West Central Research and Outreach Centre, Minnesota have designed and built a renewable hydrogen and ammonia pilot plant, in Morris Minnesota. The plant produces ammonia at a rate of 2.7 kg h⁻¹, utilising the region's abundant wind supply, via a 1.65 MW wind turbine. The research is particularly interesting, as it is the first local farm-to-coop scale system for fertiliser production. The research paper associated with this project,¹ is relevant because, although it does not discuss the objectives of my project, it has the same overarching aim to 'search for optimized small-scale, distributed ammonia production'. Thus, this technology offers a viable alternative to electrochemical ammonia production. It seems that the rate of production of this plant would be more appropriate for a Kenyan farmer than the other plant envisaged,³² as the mass of ammonia required for an average farm, would be produced in less than an hour, using this system. It would be particularly interesting to ascertain whether it would be possible for solar power to meet its energy consumption.

2.2 A review of the patented Atmonia process

Skúlason *et al.*¹⁵ report a theoretical analysis of pure transition metal electrodes. The results indicated a dissociative mechanism of N₂ reduction, analogous to the Haber-

Bosch process, in the potential region between -1.0 V and -1.5 V, with respect to the standard hydrogen electrode (SHE). They place emphasis on the fact that the HER will compete with the NRR, even in biological systems where the NRR is catalysed by the enzyme nitrogenase. However, they identify the pure transition metal surfaces of Sc, Y, Ti and Zr as promising catalytic surfaces because they bind nitrogen more strongly than hydrogen and, in this way, these catalysts can suppress the HER. The research comprises computational DFT calculations, which saves time and reduces the cost of the overall catalyst design process, by identifying which surfaces have the most potential to be efficient catalysts. However, the theoretical nature of the paper, limits its use for commercial ammonia production, as the scientists cannot report key experimental data, such as the rate of ammonia production.

Later, Skúlason worked, as part of a different research team, on another research project,¹⁶ which aimed to investigate the use of transition metal nitrides, for electrochemical production of ammonia at ambient conditions. They discovered that the most promising transition metal nitrides were the 100 surfaces of VN and ZrN, in their rock salt structures, forming ammonia at -0.51 V and -0.76 V with respect to the SHE,¹⁶ significantly lower than the values reported previously.¹⁵ DFT calculations were made on the presumption that the production of ammonia occurs via a Mars-Van Krevelen mechanism, depicted in scheme 1 below. Transition metal nitrides already have nitrogen atoms incorporated into their structures. In a Mars-Van Krevelen mechanism, the nitrogen atoms in the 1st surface layer of the material, can be directly reduced to ammonia in a gas phase reaction, under a steady flow of hydrogen. The ammonia molecules desorb in the gas phase, leaving a vacancy in the surface layer, which is then replenished by a stream of gaseous nitrogen, to complete the catalytic cycle. If this mechanism is going to be efficient, then the surface must be able to stabilise the N₂ vacancies.



Scheme 1 A schematic illustration of the mechanistic pathway of the Mars-Van Krevelen mechanism, by which N_2 reduction occurs, on the 100 surfaces of VN and ZrN, in their rock salt structures. Adapted from Y. Abghoui, A. L. Garden, J. G. Howalt, T. Vegge and E. Skúlason, *ACS Catal.*, 2016, 6, 635-646.

Focusing on the relative energies of the intermediates, the results of the DFT calculations indicate that for rock salt VN, ZrN and NbN 100 surfaces, it is possible to shift the rate determining step of the NRR, if it proceeds via a Mars-Van Krevelen mechanistic pathway. On pure transition metal surfaces, such as Ru and Fe, the rate determining step is the cleavage of the highly thermodynamically stable N_2 bond.¹⁵ However, if NRR proceeds via a Mars-Van Krevelen pathway, the dissociative chemisorption of the N_2 bond on the surface of the catalyst, to replenish the nitrogen atom vacancies, becomes exothermic. This work forms the basis of the Atmonia process, which was patented by Skúlason, in 2017.² The patent supports the results in the research paper, by emphasising that the formation of the $*NH$, $*NH_2$ intermediates and the NH_3 species, on the surface of the catalyst, are also thermodynamically favourable and thus, this is the dominating factor in enabling the electrochemical production of ammonia at lower overpotentials.

A second patent was granted to Skúlason, in 2019, to reflect further refinements to the Atmonia process.³³ The aim of the work was to illustrate how theoretical evaluation of the promise of metal oxide catalysts for the production of ammonia, using DFT calculations, could improve the Atmonia process. One of the notable catalysts was the 110 surface of rutile NbO_2 , on which it was theoretically possible to synthesise ammonia at electrode potentials in the range -0.4 V to -0.5 V vs SHE. Niobium oxide catalysts have received attention from other scientists, due to the naturally occurring and abundant nature of Nb. Nb_2O_5 had previously been investigated as a catalytic

material for the NRR, in an oxygen defective, nanofiber form, producing ammonia at an electrode voltage of -0.55 V vs RHE,²⁵ which shows that that niobium oxides have the potential to be cost-effective and sustainable catalysts, for electrochemical ammonia production.

The ammonia electrochemical ammonia production units are small, robust and low-cost, which implement a metal nitride catalyst. They would be ideal for the small-scale production of ammonia close to the farm on which the ammonia will be used. The patent is a particularly useful source of information as, in addition to the theoretical basis of the invention, it is realistic about the practicalities of installing the technology on a rural farm. For example, the ammonia can be directly injected into the soil as fertiliser.³³ Over 40% of the nitrogen, present in inorganic fertilisers, is lost in the runoff, which then perturbs water and ecosystems near to the farm.³⁴ In addition to this, ammonia is lost from its liquid form or from solid inorganic fertiliser, in its gaseous form, due to its high volatility. The use of micro-dosing and the application of fertiliser directly to crops, makes the use of fertiliser more cost effective and environmentally sustainable, by preventing the soil from becoming over saturated with fertiliser. However, this requires investment in ammonia storage and injection equipment.

Another approach to consider would be producing solid ammonium nitrate fertiliser, by reacting the produced ammonia with nitric acid, *in-situ*. The production of ammonium nitrate could be difficult, at a smaller community scale, due to security concerns and the added complexity of the process.³⁵ The additional equipment associated with both fertiliser application processes, would be unaffordable for most Kenyan farmers, without financial assistance. Thus, making the technology more financially viable for Kenyan farmers is a possible area for future research.

2.3 A review of the use of nano catalysts

Transition metals, such as Pd and Ru, show high catalytic activity for N₂ reduction and importantly have high electrical conductivity, which is an ideal physical property for a material that is being used as a working electrode. Figure 3 shows a volcano plot for the NRR reaction. It indicates that the Ru 111 surface is a more efficient catalytic material, for NRR, than Pd 111. This is because the ΔG_{ads} for the Ru surface is more

negative, indicating that the adsorbed nitrogen molecule is more thermodynamically stable, on the Ru surface.

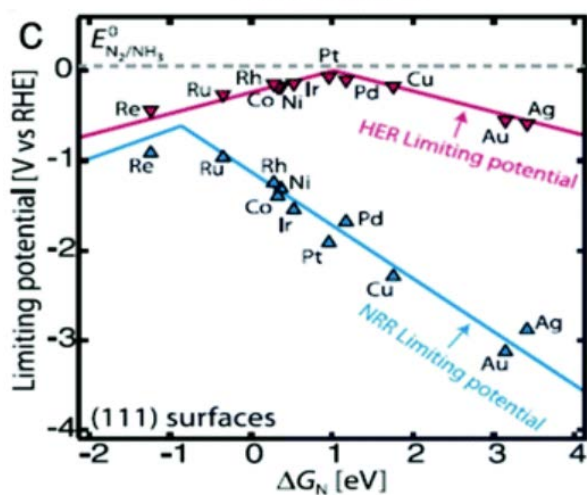


Figure 3 Volcano plot for NRR on metals, with that of HER overlaid for comparison. Adapted from E. Skúlason, T. Bligaard, S. Gudmundsdóttir, F. Studt, J. Rossmeisl, F. Abild-Pederson, T. Vegge, H. Jónsson and J.K. Nørskov, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1235-1245.

Due to the relative scarcity and therefore expense of these metals, the quantity of metal required for each unit cell of the catalytic material, should be kept to a minimum.³⁶ The electrochemical production of ammonia is therefore, an ideal application for nanomaterials, as the greater surface area to volume ratio of nanoparticles, means that a smaller mass of catalytic material can be used, without compromising the catalytic activity. With the advancement of experimental techniques, such as magnetron sputtering, it is possible to synthesise nanoparticles more easily,³⁷ which has encouraged scientists to revisit expensive but highly active catalysts, such as Ru, for ammonia production, as it makes their use more cost effective and environmentally sustainable. All of the papers reviewed in this section, were published in the last two years, clearly indicating that this is an area of cutting-edge research, which brings with it merits and disadvantages. The increased interest and thus work in this field of research is positive but few studies showed focused and rigorous research.^{38,39}

The use of nanoparticles, in proposed catalysts for electrochemical ammonia production, has been widely researched.^{25,38-43} The yields are not commercially viable however, there are several promising areas for further research. Li *et al.*⁴⁰ report a

yield of $2.42 \times 10^{-4} \text{ g h}^{-1} \text{ mg}_{\text{cat}}^{-1}$, which is two orders of magnitude higher than reported with other nano catalysts.^{38,43} The catalyst consisted of a spherical core of Au nanoparticles, surrounded by a shell of 1-2 layers of C (s) atoms with abundant defects. It is postulated that the particularly high FE of 40.5%, at a potential of -0.45 V vs the reversible hydrogen electrode (RHE), could be explained by the increase in active sites for nitrogen reduction, at the site of carbon atom vacancies. The study is limited by only testing the catalyst for an hour whereas other catalysts reported were tested for 12 hours,⁴³ 24 hours,⁴⁰ and 75 hours,³⁹ respectively. These values are not in line with industrial tests, of approximately 1000 hours but they give a more accurate representation of the electrochemical stability, for which the current density is measured against time. The stability of a catalyst is important because, for it to be commercially viable, the rate of ammonia production must be stable for a sufficient length of time.

The experimentation with atomically defective nano catalysts has revealed how defect engineering can be used to promote the nitrogen reduction reaction,^{25,38,42} and thus increase the rate of ammonia production, by providing additional catalytic sites for N₂ reduction. A clear example of this concept is one in which the rate of ammonia production at -0.55 V vs RHE is $0.86 \times 10^{-5} \text{ g h}^{-1} \text{ mg}_{\text{cat}}^{-1}$ for a pristine Nb₂O₅ nanofiber, compared to $4.36 \times 10^{-5} \text{ g h}^{-1} \text{ mg}_{\text{cat}}^{-1}$, for a Nb₂O₅ nanofiber, with oxygen defects.²⁵ Other studies support this idea by describing analogous behaviour with oxygen deficient Ta₂O₅ and CeO₂ nanorods, respectively.^{38,42} The research by Fu *et al.*³⁸ and Han *et al.*²⁵ is of particular value, as DFT simulations are used as part of their research. Fu *et al.*³⁸ show that N₂ is activated in the oxygen vacancy site, between two Ta atoms, thus NRR is promoted by the presence of the vacant sites. Whereas, Han *et al.*²⁵ show that pi back bonding of electrons, from the d orbitals of Nb, into the pi* anti-bonding orbital of N₂, weakens the N₂ bond and is thus an alternative way to activate the N₂ bond, for reduction to ammonia.

Ren *et al.*³⁹ describe a Mo₂C catalyst, on a glassy carbon electrode which served as the working electrode in the experiments. Akin to other studies,^{38,44} the nano molybdenum precursor, is in the form of a nanorod. The experiments were conducted in 0.1 M HCl and a good FE of 8.13% was achieved. It would be interesting to repeat the experiments in LiClO₄, with which the catalyst achieved a FE of 22%, to prove with more certainty that the use of an aprotic solvent suppresses the HER, and thus leads

to a notable FE. Molybdenum is a material of particular interest, as it is a key element in nitrogenases. Nitrogenases are enzymes which catalyse the fixation of nitrogen, in biological systems.¹⁵ It is an example of how scientists can use the optimised biological processes, to influence inorganic catalyst design.

2.4 A review of nitrogen-doped carbon catalysts

Nitrogen doped carbon, as an example of a cost effective catalyst, is explored in many studies.^{26-28,45,46} Nitrogen doped carbon is a highly cost effective material, which makes it particularly applicable to the development of a low-cost, electrochemical ammonia production unit. The maximum rate of ammonia production exhibited by a nitrogen doped carbon catalyst was $0.024 \text{ g h}^{-1} \text{ g}_{\text{cat}}^{-1}$, at a potential of -0.9 V and at ambient conditions. However, at -0.9 V , the maximum FE was only 1.42%,⁴⁵ which shows that this catalyst has poor selectivity for the NRR. Qu *et al.*²⁸ reported the results of experimentation with catalyst materials, including the synthesis of molybdenum carbide, encapsulated in nitrogen doped carbon layers. Surprisingly, the rate of ammonia production, at ambient conditions, was comparable to that shown by nitrogen doped carbon alone. However, perhaps due to the higher catalytic activity of molybdenum compared to carbon, it showed a much higher FE of 25.1%, at a much lower potential of -0.35 V . However, the results cannot be directly compared, as some components of the electrochemical systems are not the same. They use different solvents, at different concentrations: 0.1 mM hydrochloric acid,²⁸ and 0.05 M sulphuric acid.⁴⁵ Although the FE demonstrated by Qu *et al.*²⁸ is impressive, the lack of focus in this study decreases its value. The main body of the report focuses on the NRR, however, the introduction emphasises that the scientists could use the findings for the development of catalysts for related reactions, such as the ORR, which gives the impression of a broad research aim.

The synthesis of an alfalfa-derived nitrogen doped porous carbon catalyst, with a 6.35% nitrogen content by atom, is a particularly interesting research development. The rate of ammonia production was comparable to that shown by nitrogen doped carbon but the Faradaic efficiency reported is almost six times higher, at a lower potential of -0.4 V ,²⁷ which demonstrates the significance of using porous carbon. The use of porous carbon increases the total number of active sites available to a N_2 molecule, and thus increases the efficiency of the NRR, when compared to the use of

non-porous carbon. The pores present in the carbon also increase the efficiency of the reaction, by increasing the rate of diffusion of N_2 gas into the pore and the rate of diffusion of ammonia out of the pore. This study shows that, whilst the research is currently at a very early stage, it is possible to further increase the sustainability of electrochemical ammonia production, by using a catalyst derived from biomass. This research reveals the possibility of producing the catalysts more locally to the farms, on which the electrochemical ammonia production unit would be situated.

2.5 A review of plasma-based catalysts

Non-thermal plasma has been used in experimental designs, for N_2 reduction.⁴⁷⁻⁴⁹ It can be produced by passing an electric current through a substance in its gaseous state. If a molecule absorbs sufficient energy, it may be vibrationally excited and thus activated for a particular reaction. Some molecules absorb enough energy to be ionized and thus eject high energy electrons. In a non-thermal plasma, there is a large thermal energy gradient between the high energy electrons and the remaining ions and neutral molecules, resulting in a system that is not in thermal equilibrium. For the system to return to thermal equilibrium, it is necessary for the electrons to lose this additional energy, through further collisions with other electrons and neutral molecules. This leads to the activation of further neutral molecules, such as N_2 , in the NRR. The use of non-thermal plasma is particularly applicable to this review, as it is revealed that it can play a key role in the activation of the N_2 bond for reduction to ammonia. However, the current energy consumption associated with the production of plasma needs to be considered for it to be a sustainable and cost effective technology.

An interesting trial of a non-catalysed one step synthesis of ammonia from atmospheric air and water has been demonstrated.⁴⁹ However, its strength is limited by a brief 10 minute reaction time, as it is unclear whether the rate of ammonia production will remain stable over reasonable time period. In addition to this, the authors of the paper have only one or two papers published in their name. In this experiment, both N_2 plasma and the air plasma, which contains N_2 molecules, are discharged to atomic nitrogen plasma, using a 6 kV silent electric discharge voltage. They also propose that the use of ultraviolet (UV) irradiation promotes the dissociation of N_2 , in the plasma. This is an advantageous addition to the design, as it is an

alternative way of increasing the rate of dissociation of the very strong N₂ triple bonds, whilst avoiding the use of harsh reaction conditions such as high pressure. However, the paper clearly warns that this could be counterproductive, if the UV irradiation also decomposes the ammonia produced. The production of ammonia occurs at ambient conditions, at the interface between the air plasma gas and the surface of the water phase. The rate of ammonia production of 3.08 mg m⁻² which, based on a 10 minute reaction time, is an ammonia production rate of 18.5 mg m⁻² h⁻¹ (to 3 sf). Initially, this seemed significant, however, it was difficult to compare this rate of production to that of the catalysts explored earlier in the report. This was because the rate of ammonia production was reported in relation to the area of the reaction locus whereas, for the catalytic materials, it was reported in relation to the mass of the catalyst used.

A more recent study,⁴⁷ approaches the use of plasma in a different way, replacing a typical solid electrode with a gaseous plasma electrode but it is emphasised that the role of plasma is to activate the N₂ bond for the NRR. A study published in the journal *Nature Catalysis*⁴⁸ is particularly perceptive in its approach, as it proposes that plasma could be used in conjunction with a catalyst. Again, the plasma would be used to activate the N₂ molecules for reduction and this could enable more abundant and thus cheaper but less active catalysts to be viable for N₂ reduction. This is a significant point because it shows that there is potential for scientists to combine well established knowledge about catalysts and enhance their performance with plasma technology.

Hawtof *et al.*⁴⁷ propose that the activated N₂ molecules, react with a proton in the water vapour layer, at the plasma-liquid interface, to produce an intermediate. The intermediate then dissolves in the liquid water layer, where it is reduced further, to ammonia. The rate of ammonia production demonstrated was 0.44 mg h⁻¹ at a plasma voltage of 500 V, which is an order of magnitude lower than reported previously.⁴⁹ As stated in the title of the paper, a FE of 100% was achieved however, this is somewhat misleading as, after 5 minutes, the FE had decreased to 60%. In a separate test it was shown to be 24.9% after five hours, which is comparable to that reported by Qu *et al.*²⁸ and, in this way, it demonstrates reasonable stability. Haruyama *et al.*⁴⁹ illustrate that ammonia production can be carried out at ambient conditions, with a low power consumption of 5 W h required for the electric discharger and U V lamp. However, it omits the power consumption, associated with generating the plasma. The study by Hawtof *et al.*⁴⁷ is more thorough, successfully highlighting the challenges associated

with using plasma by detailing the power consumption of the experiment, in its entirety. The power consumption is significant, at 2270 kWh, at 2 mA, for 45 min, which is greater than the 9-13 kWh consumption,⁵⁰ of a typical Haber Bosch set up. This illustrates that for plasma to be a commercially viable material in the electrochemical production of ammonia, with consideration of its cost effectiveness and sustainability, further studies should be aimed at refining the production of plasma, to make it more energy efficient. This would make it more feasible to couple the technology with renewable energy sources, so that it could be used sustainably on remote farms.

3. Conclusions and outlook

The aim of this literature review was to identify promising catalysts for the sustainable and cost effective *in-situ* electrochemical production of ammonia, in line with the existing small-scale Haber process and Atmonia's electrochemical ammonia production unit. The research also has a significant social impact, whereby the technology could improve both the food and financial securities of rural farmers in Kenya and Africa as a whole. In the papers analysed, the over-arching theme was the search for promising catalytic materials that could activate the strong N₂ bond for reduction to ammonia, via a dissociative mechanism. Fu *et al.*³⁸ have shown, through DFT calculations, that defect engineering can play an important role in the activation of the N₂ bond but more stringent testing must be carried out to fully realise their stability and durability. Similarly, the role of plasma in the activation of N₂ has been investigated. However, the research highlights the concerns regarding the high energy demand associated with generating the plasma. Therefore, further research must be done to optimise the process, so that it can be more easily paired with renewable technology. Finally, Skúlason *et al.*¹⁵ identified VN and ZrN, as potential catalysts for ammonia production. These catalysts have been used in the commercial, patented Atmonia process, which gives the research additional credibility. More theoretical research should be conducted to identify other catalysts, with which nitrogen reduction occurs via a Mars-Van Krevelen mechanism. To improve the sustainability and cost effectiveness of the process, a particular research focus on non-metal catalysts should be made.

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