

Johnson Matthey's international journal of research exploring science and technology in industrial applications

\*\*\*\*\*Accepted Manuscript\*\*\*\*\*

## This article is an accepted manuscript

It has been peer reviewed and accepted for publication but has not yet been copyedited, house styled, proofread or typeset. The final published version may contain differences as a result of the above procedures

It will be published in the April 2024 issue of *Johnson Matthey Technology Review*

Please visit the website <https://technology.matthey.com/> for Open Access to the article and the full issue once published

## Editorial team

**Editor** Sara Coles

**Editorial Assistant** Yasmin Stephens

**Senior Information Officer** Elisabeth Riley

Johnson Matthey Technology Review

Johnson Matthey Plc

Orchard Road

Royston

SG8 5HE

UK

**Tel** +44 (0)1763 253 000

**Email** [tech.review@matthey.com](mailto:tech.review@matthey.com)



# Advancements in Green Ammonia Production and Utilisation Technologies

John Humphreys<sup>a</sup> and Shanwen Tao<sup>a,b,\*</sup>

<sup>a</sup> School of Engineering, University of Warwick, Coventry CV4 7AL, UK

<sup>b</sup> Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia

\* Corresponding author, E-mail: [s.tao.1@warwick.ac.uk](mailto:s.tao.1@warwick.ac.uk)

<Article history>

PEER REVIEWED

Received 25th June 2023; Revised 14th September 2023; Accepted 14th September 2023; Online 14th September 2023

<end of article history>

## Abstract

Green ammonia, produced through renewable energy-powered electrochemical and thermal processes, is emerging as a promising candidate to replace fossil fuel-based ammonia in the fertilizer, transportation, and energy sectors. This paper provides an overview of the production methods, utilisation methods, and technological advancements for green ammonia. The electrochemical production and Haber-Bosch with renewable hydrogen and energy, are discussed in detail highlighting recent material advances. Green ammonia utilisation methods are discussed with direct use cases such as ammonia combustion and direct ammonia fuel cells examined. Green ammonia's potential as a carbon-free hydrogen carrier is also discussed in regards to ammonia cracking for effective hydrogen recovery. This paper concludes that green ammonia has the potential to play a significant role in the transition to a sustainable energy system and offers new opportunities for the fertilizer, transportation, and energy industries.

## Introduction

Ammonia is one of the world's most produced chemicals due to its versatile nature with a large range of applications, including as a fertiliser for agriculture, in the production of chemicals such as plastics and pharmaceuticals, and as a refrigerant in industrial cooling systems [1-3]. Out of these its use as a fertiliser dominates its current application with 70% of globally produced ammonia used for this, contributing to the production of around 45% of the world's food [1, 4]. Recently, there has been discussion of ammonia's use as a fuel for applications such as transportation due to its enhanced energy density compared to other carbon free chemical fuels such as hydrogen. The volumetric energy density of liquid ammonia is 3.50 kWh L<sup>-1</sup> which is much higher than 2.36 kWh L<sup>-1</sup> for liquid hydrogen makes green ammonia a promising fuel for marine applications [5-7]. Ammonia is a liquid at only slightly elevated pressure (~8 bar at 20 °C) making transportation and storage much more manageable than hydrogen which requires significantly higher pressures (~ 700 bar) and is more prone to leakages and storage container embrittlement. Despite its many applications, traditional ammonia production

through the Haber-Bosch process (typically operating at intensive conditions between 10 and 20 MPa and 400 to 500 °C)[8, 9] is heavily reliant on fossil fuels and emits large amounts of greenhouse gases accounting of 2% of all global CO<sub>2</sub> emissions [2, 10, 11] with roughly 1.9 tons of CO<sub>2</sub> emitted per ton of ammonia produced [12]. Despite ammonia production for nitrogen and hydrogen being an exothermic process, with nearly 100% theoretical conversion at room temperature, the rate of reaction at this temperature is exceptionally low because the activity of the catalysts is not high enough. This requires high operating temperatures in order to achieve a suitable rate of reaction which in turn requires high pressures to achieve a reasonable conversion. As such extensive research has been undertaken over the last 100 year to lower these energy intensive operating conditions with this focusing on the development of new catalysts that will allow the process to operate at reduced temperature and pressure. The production of the required feed, hydrogen and nitrogen, also produces significant emissions, with hydrogen being produced through the steam reforming of methane which has CO<sub>2</sub> as a by-product [13]. Despite efforts being made to reduce the CO<sub>2</sub> emissions from this process through technologies such as carbon capture, it is not carbon neutral [14]. Green ammonia has the potential to produce ammonia with zero greenhouse gas emissions by utilising renewable energy such as solar, hydro and wind along with hydrogen produced from the electrochemical splitting of water in electrolyzers and the separation of nitrogen from air. If green ammonia is to be truly carbon neutral, then all parts of the process must be powered through the renewable technologies mentioned. Therefore, at this time small scale localised green ammonia is more appealing than replacing the large-scale Haber-Bosch processes, with these small synthesis facilities located near current renewable energy production sources in order to store surplus electricity [9]. Green ammonia also has the potential to be used as a fuel in certain cases, especially those that are targeting zero emissions [15]. The landscape of green ammonia can be seen in Figure 1 which highlights generation, synthesis and use.

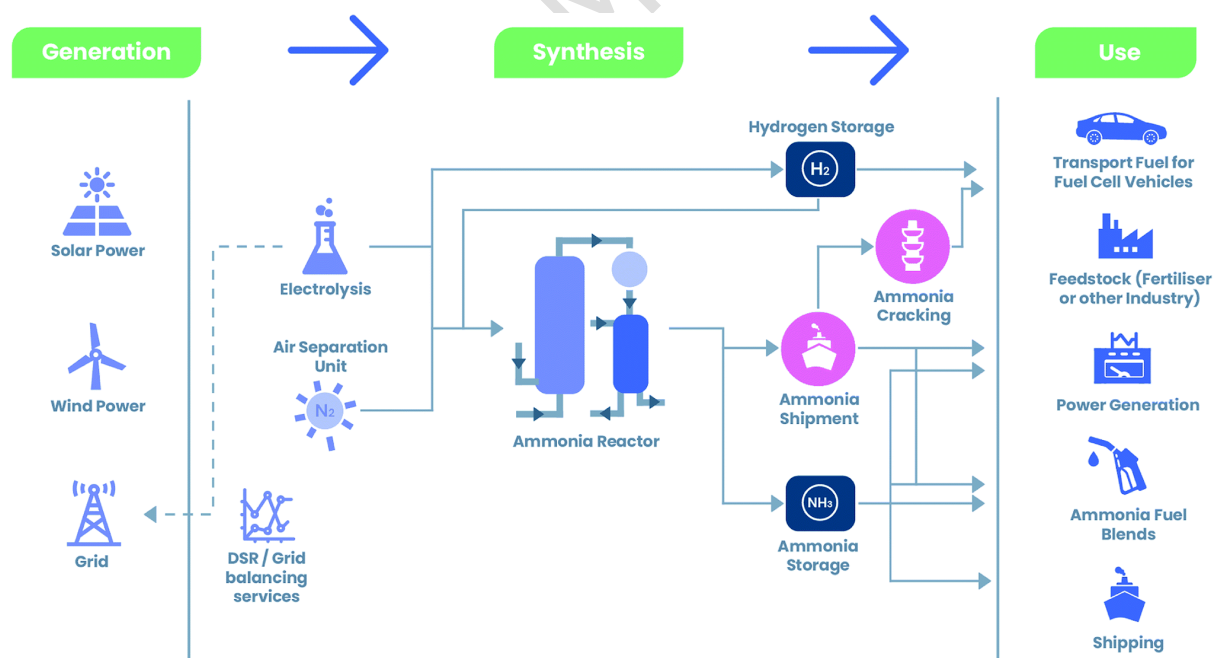


Fig. 1 The Green Ammonia Landscape [16]

In this review, we will look at the whole lifecycle, examining the latest advances in the catalysts suitable for conventional green ammonia synthesis, the electrochemical synthesis of ammonia, ammonia's use as a means of hydrogen storage and its cracking back to hydrogen and nitrogen, as well as its direct use in ammonia combustion and direct ammonia fuel cells. By highlighting current research challenges and advances for

both ammonia synthesis and use we aim to provide an overview of the complete current state of green ammonia with a particular focus to its use as a fuel.

## Green Haber Bosch Process

Currently the most common method of ammonia production is the large-scale Haber-Bosch process taking place at intensive reaction conditions with the ammonia converter operating at temperature of between 400 and 500 °C and pressures over 10 MPa [8]. As such this process is extremely energy intensive, using 2 % of the world's total energy production [1]. Green ammonia produced through this process proposes to operate using entirely renewable electricity from sources such as solar, wind, and hydro. However, in order to feasibly operate an ammonia production plant through renewables, the scale of the plant must be drastically decreased. These small-scale localised ammonia production plants can be located at the renewable source, converting excess energy into ammonia. In order to ensure true carbon neutrality of the green ammonia the hydrogen feed must come from clean hydrogen, mainly green hydrogen produced through the electrochemical splitting of water in electrolyzers. Effective catalyst development is the main focus for green ammonia synthesis for a number of reasons, including;

1. Lowering reactor conditions, by achieving improved reaction rates at more mild temperatures and pressures the energy efficiency of the process can improve to a level where the operation on solely renewables is viable.
2. The conversion of nitrogen and hydrogen to ammonia is exothermic, therefore the high temperature required for a reasonable rate limits the overall conversion with most current Haber Bosch plants achieving ~20% conversion per pass [8]. By lowering temperature, the total conversion per pass will also improve.
3. Design considerations on the system are intensive due to the harsh conditions required. By lowering these the barriers to the deployment of small-scale localised ammonia plants would be reduced.
4. Current feed purities of the reactant gases is very demanding due to most catalysts poor tolerance to oxygen and oxygenate impurities [17]. This is a particular problem for green hydrogen produced from water which will contain trace amounts of oxygen and moisture [18]. By developing more oxygenate tolerant catalysts, the need for energy intensive purification processes can be removed.

Catalyst design has been a significant area of investigation for the conversion of hydrogen and nitrogen to ammonia over the last 100 years and has led to the award of three Nobel prizes [19]. It is evident that the success of localised green ammonia is directly linked to advances in the current catalyst technology, as such this section will provide an overview of the current state of this technology.

Fused-iron catalysts are the most studied and developed class of ammonia synthesis catalysts, with the vast majority of ammonia synthesis plants worldwide employing fused iron catalysts [20-25]. In order to achieve the desired characteristics such as catalyst stability, structural integrity, and activity these iron catalysts utilise a range of promoters. Conventional promoters include  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ , and  $\text{SiO}_2$  [26, 27] and can achieve ammonia conversions between 15-20% per converter pass (425 °C, 15 MPa) [8]. Improving the promoter materials has been the focus of iron-based ammonia synthesis catalyst development over the recent years. Wang et al [28] have demonstrated the promotion effect of lithium hydride on iron reporting excellent activity at temperatures as low as 300 °C. Hydride promoters were further investigated by Gao et al [29], not only were impressive results noted when  $\text{BaH}_2$  was employed for conventional ammonia synthesis, but by employing a chemical looping synthesis method where the feed hydrogen and nitrogen are looped rather than fed together exceptional results at low temperature and ambient pressure were obtained. Despite these

promising results, the practical application of these catalysts is limited due to their complicated synthesis method and low tolerance to oxygen and moisture.

Both samarium doped cerium oxides and oxynitrides as promoters for iron-based ammonia synthesis catalysts was recently reported by our group [18, 30]. In this work we noted the beneficial effects these promoters have on the catalyst activity through the presence of anion vacancies (oxygen vacancies for the oxide support and both oxygen and nitrogen vacancies for the oxynitride support) along with the strong metal support interaction (SMSI) effect. However, the key benefit of these promoter materials is the significant resistance to oxygenate impurities they provide. When 150 ppm of known  $O_2$  was injected into the gas stream the oxynitride catalyst maintained 70 % of its activity while the oxide catalyst maintained 47.4 %. This is in contrast to industrially used Wustite and magnetite which have retentions of 26.4 % and 7.6% respectively [30].

The lifetime of commercially available fused iron catalysts is normally 10 years, after which they lose activity. Due to the large-scale nature of ammonia synthesis this leads to thousands of tons of spent catalyst being produced each year [8]. Therefore, the desire to recycle this spent catalyst is high, especially considering the value of promoter materials such as  $CoO$ ,  $CaO$ , and  $K_2O$ ; however, currently most spent catalyst is discarded as waste. The obvious use for this catalyst would be to regenerate it so it can be reused in the ammonia synthesis process; however, this has some limitations. For the industrial magnetite catalyst, the  $Fe^{2+}/Fe^{3+}$  ratio must be carefully controlled which is difficult to achieve through reoxidation of the metallic spent catalyst [8]. This reoxidation process is also significantly higher costing than using new cheap natural magnetite. With the increased use of Wustite based catalysts the recycling process becomes more appealing as the waste metallic catalyst can be mixed with natural magnetite to form the  $Fe_{1-x}O$  catalyst with a much greater control of the  $Fe^{2+}/Fe^{3+}$  ratio [8].

After iron, ruthenium is the second most common ammonia synthesis catalyst and has been used industrially in the Kellogg advanced ammonia process [8]. Due to its cost, when employed as a catalyst ruthenium is supported on a range of materials with a total ruthenium weight content in the final catalyst between 2 and 10%. These support materials are the key area of development for ruthenium catalysts, with specifically designed promotion effects introduced to improve activity. Recent highlights include the core-shell  $Ru/Ba-Ca(NH_2)_2$  which achieved excellent activity by providing enhanced electronic promotion through its structure as well as improved resistance to hydrogen poisoning, in which hydrogen blocks surface sites needed for nitrogen dissociation [31]. Inorganic electride materials have proven to be excellent supports for ruthenium catalysts, with excellent low pressure and temperature results reported by Inoue et al [32] for a  $C12A7:e^{-1}$  electride, discovering the promotion effect of these materials towards ammonia synthesis. Lu et al [33] recently reported a water stable electride  $Y_5Si_3$  based ruthenium catalyst, again with an excellent rate of ammonia production at low temperature and ambient pressure.

Other ammonia synthesis catalysts include cobalt and nickel-based catalysts, however, due to their lower performance than ruthenium-based catalysts, and increased cost compared to iron-based catalysts they receive comparably less interest. For comparison both cobalt and nickel are three orders of magnitude cheaper than ruthenium weight for weight, with cobalt around twice that of nickel. However, iron is two orders of magnitude cheaper than either of these. Recently, nickel has gained interest as it has been shown to perform better towards the chemical looping process than the equivalent iron catalyst by Gao et al [29]. Therefore, nickel catalysts may find their niche in this new process.

As such it can be seen that significant progress has been made towards tackling the challenges listed above. By working to address the remaining limitations of these catalysts such as high cost compared to the conventional fused iron catalyst and the less than desirable stability of some of these catalysts we can move towards the possibility of small scale localised green ammonia production from renewable energy sources.

Table 1 Highlighted Advances in Haber-Bosch Ammonia Synthesis Catalysts

Catalyst	Promotor	Reactor temperature (°C)	Reactor pressure (MPa)	Weight hourly space velocity (WHSV) (mL g <sup>-1</sup> h <sup>-1</sup> )	NH <sub>3</sub> synthesis rate (mmol g <sup>-1</sup> h <sup>-1</sup> )	Ref.
Industrial Hematite/Wüstite based catalyst	10wt% (Al <sub>2</sub> O <sub>3</sub> , K <sub>2</sub> O, MgO, CaO, SiO <sub>2</sub> )	400	9		260	[34]
Industrial Magnetite based catalyst		450	1	16,000	5.8	[35]
Industrial Wüstite based catalyst		450	0.9	36,000	16	[31]
5wt%Ru clusters/La <sub>2</sub> O <sub>3</sub>		400	1	24,000	32.14	[36]
(5wt%Ba-Co)40% - MgO-La <sub>2</sub> O <sub>3</sub>		400	9	140,000	249.41	[37]
10wt% Co/MgO-Nd <sub>2</sub> O <sub>3</sub> (Mg/Nd=10)		400	6.3	140,000	39	[38]
5wt%Ru/Y <sub>2</sub> O <sub>3</sub> -P		400	1	24,000	21.12	[39]
20% Fe-BaH <sub>2</sub> (chemical looping synthesis)		300	0.1	60,000	1.703	[29]
Fe-5LiH		300	1	60,000	4.840	[28]
80% Fe/Ce <sub>0.8</sub> Sm <sub>0.2</sub> O <sub>2-δ</sub>		450	1	16,000	8.7	[30]
BaCs-RuC (N <sub>2</sub> )	Ru:Ba:Cs 1:0.05:0.2	400	9.5		287.647	[40]

10wt%Ru/Ba -Ca(NH <sub>2</sub> ) <sub>2</sub>	Ba (3 at%)	360	0.9	36,000	60.4	[31]
10wt%Ru/Y <sub>5</sub> Si <sub>3</sub> NP		340	0.1	36,000	4.448	[33]
(Co-Ce) <sub>T</sub> /C	0.071 mmol g <sub>(C+Co)</sub> <sup>-1</sup> Ce,  0.89 mmol g <sub>(C+Co)</sub> <sup>-1</sup> B a	400	9	155,555	452.390	[41]
50%Ni-LiH (chemical looping)		300	0.1	60,000	1.533	[29]
80 wt%Fe- 20 wt%Ce <sub>0.5</sub> Sm <sub>0</sub> .5O <sub>2-x</sub> N <sub>y</sub>		450	1	16,000	9.3	[18]

## Electrochemical Ammonia Synthesis

Green ammonia synthesis detailed in this review so far has been concerned with improving the Haber-Bosch process for small scale green ammonia production. However, ammonia can also be generated in an electrochemical cell for nitrogen and water. This process does not rely on the intensive conditions required for the Haber-Bosch process and can produce ammonia at ambient temperature and pressure. As such, this process has the potential to revolutionise the ammonia production industry. In the electrochemical cell nitrogen is fed to the cathode where the nitrogen reduction reaction takes place while water is fed to anode and oxidised to oxygen [42-45]. Although we have highlighted the direct use of water which removes the need to generate hydrogen either through electrolysis of the heavily polluting steam reforming process, the electrochemical synthesis of ammonia can also run using nitrogen and hydrogen working on a similar principle where hydrogen is fed to the anode instead of water. The cathode nitrogen reduction reaction (NRR), anode oxygen evolution reaction (OER) are shown below. When a proton-conducting electrolyte is used in the electrochemical cells for ammonia synthesis, the overall reaction is shown below [42, 45].



As well as the reduced reaction conditions and direct use of water without the need for hydrogen this process is also highly flexible and can be easily scaled further increasing its potential allowing it to adapt to its specific use case. As can be seen from the wide range of scales renewable projects are operating at, this makes this technology a potential excellent fit. Despite this, the technology is still at the early stages of development with advances required to improve the efficiency and selectivity while advances in both the cathode and anode catalysts are required to reach the high synthesis rate, low cost and high durability required for use at scale [43]. If these

challenges can be overcome, electrochemical ammonia synthesis could become a promising alternative to the Haber-Bosch process for ammonia production. In this review recent reported advances in this process will be examined with the results highlighted in table 2

Recently exceptional electrochemical ammonia production rates have been reported with near 100 % faradaic efficiency by Du et al [46] utilising a LiNTf<sub>2</sub> electrocatalyst. Their rate is around 2 orders of magnitude greater than those previously reported due to an interrelation between lithium-mediated nitrogen reduction reaction and the physicochemical properties of the electrode-electrolyte interface. However, it should be noted that instead of water or hydrogen gas, ethanol was used as the proton carrier thereby making this currently economically unfeasible for real production. As such the findings of this work will have to be applied to a system using either water or hydrogen as the proton source in order to prove commercially viable. Similarly, Li et al [47] reported an exceptional rate for electrochemical ammonia synthesis of  $2.5 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$  using an LiBF<sub>4</sub> electrocatalyst. Again, this was utilising ethanol as the proton source limiting its application. None the less these electrocatalysts have the potential to achieve significant ammonia production from nitrogen and water if they can be applied to such systems.

For electrochemical nitrogen reduction from either water or hydrogen, respectable rates and faradaic efficiencies have been reported for low-cost iron based electrocatalysts. These electrocatalysts have the benefit of moving away from precious metals commonly found in electrochemical devices which will be required if the technology is required to be operated at scale, especially when compared to the scale of the conventional Haber Bosch process. Reaction rates in the order of magnitude of  $1 \times 10^{-6} \text{ mol cm}^{-2} \text{ h}^{-1}$  are common for these electrocatalysts such as the Fe<sub>2</sub>O<sub>3</sub> (oxygen vacancy) electrocatalysts reported in table 2 that produced ammonia from nitrogen and water at a rate of  $1.05 \times 10^{-6} \text{ mol h}^{-1} \text{ cm}^{-2}$  [48]. Despite this its reported faradaic efficiency is rather low at 6.63%, other iron based electrocatalysts have increased this to around 20% but their reported activity is lower [49]. Despite this, their low cost and ability to produce ammonia directly from nitrogen and water makes them promising electrocatalysts.

Table 2 Highlighted Advances in Electrochemical Ammonia Synthesis

Catalyst	NH <sub>3</sub> synthesis rate (mol h <sup>-1</sup> cm <sup>-2</sup> )	Faradic Efficiency	Electrolyte	Ref.
Fe <sub>2</sub> O <sub>3</sub> (oxygen vacancy)	$1.05 \times 10^{-6}$	6.63 %	0.1 M KOH	[48]
Fe-SnO <sub>2</sub>	$4.86 \times 10^{-6} \text{ mol h}^{-1} \text{ mg}_{\text{cat}}^{-1}$ (no loading per area given)	20.4 %	0.1 M HCl	[49]
LaCoO <sub>3</sub>	$2.73 \times 10^{-7}$	7.6 %	0.1 M Na <sub>2</sub> SO <sub>4</sub>	[50]
Fe-TiO <sub>2</sub>	$1.50 \times 10^{-7}$	25.6 %	0.5 M LiClO <sub>4</sub>	[51]
Ni wire	$5.40 \times 10^{-4}$	98 %	LiNTf <sub>2</sub> (ethanol hydrogen source)	[46]
Ni <sub>1</sub> Cu-SAA (nitrate)	$3.27 \times 10^{-4}$	100 %	0.5 M K <sub>2</sub> SO <sub>4</sub>	[52]



nitrogen source)				
Porous Cu	$9.00 \times 10^{-3}$	71%	LiBF <sub>4</sub> (ethanol hydrogen source)	[47]
ECOF coated boron-doped carbon	$3.89 \times 10^{-6}$	54.54 %		[53]
NCNT@MIL-101(Fe)	$1.03 \times 10^{-7}$	25.15 %	0.05 M H <sub>2</sub> SO <sub>4</sub>	[54]
CuAg-PS alloy	$2.26 \times 10^{-6}$	12.72 %	0.05 M H <sub>2</sub> SO <sub>4</sub>	[55]
Cuboctahedron Pd	$4.50 \times 10^{-7}$	35 %	0.1 M NaOH	[56]

## Ammonia Cracking

Ammonia cracking is the process of decomposing ammonia into its constituent elements, nitrogen and hydrogen, through the application of heat. This is the reverse of the ammonia synthesis reaction and is endothermic, therefore requires high temperatures to get close to 100 % conversion, normally between 600 and 800 °C [57, 58]. Through this ammonia can effectively be used as a medium of hydrogen storage, producing hydrogen for use in fuel cells. This process is also utilised to produce high purity nitrogen for application where the amount of oxygen present in air separated nitrogen is too high. In order to achieve high conversions at lower temperatures, a catalyst is employed, mainly nickel, ruthenium, iron or cobalt [58]. If ammonia is to be utilised as an effective storage medium for hydrogen then effective catalysts are required to lower the operating temperature, and therefore the energy consumption of this process. Recent advances in ammonia cracking catalysts are highlighted in the table below.

When ruthenium is employed as an ammonia cracking catalyst excellent conversion can be achieved at low temperatures with Pinzón et al [59] reporting near 100 % conversion (99.3%) at 400 °C with a Ru/SiC catalyst utilising the porous nature of the support and low catalyst reduction temperature to obtain this stable active catalyst. When caesium was used to promote a Ru/CeO<sub>2</sub> catalyst a conversion of 80 % was achieved at 300 °C reporting that the Cs formed anchor sites for their Ru particles aiding in forming small well dispersed Ru particles [60]. It was also found to increase the number of strong basic sites. Strong basic sites have been reported to reduce the amount of competitive adsorption of H<sub>2</sub> and re-hydrogenation of NH<sub>x</sub>, leading to a higher overall reaction rate as the reverse reactions are suppressed and catalyst sites are free for the ammonia decomposition reaction [61].

However, as with ammonia synthesis catalysts the expensive nature of ruthenium makes it unattractive for ammonia cracking. Although commercial ruthenium-based ammonia cracking catalysts are available, if the scale of this process is to increase with ammonia being utilised as an ammonia carrier, then cheaper alternatives will be required.

Despite showing moderate activity for ammonia synthesis, the low binding energy of Ni means that it struggles to break the nitrogen triple bond, a key requirement in ammonia synthesis [9]. However, for ammonia cracking this is not required thereby making Ni a promising alternative to Ru based cracking catalysts. Although not able to match the high conversion at low temperatures that Ru catalysts can achieve, Ni based catalyst can achieve good conversion at moderate temperatures in the range of 500 °C to 550 °C.

Since these Ni based catalysts will have a much lower cost than their Ru alternatives this increase in temperature is a reasonable trade off. Ogasawara et al [62] reported 91.2 % conversion at 500 °C using a Ni/CaNH-HS catalyst through a NH<sup>2-</sup> vacancy mediated Mars-van Krevelen mechanism in which this vacancy activated the ammonia to form NH and NH<sub>2</sub> intermediate species while the Ni was found to regenerate these vacancies. Ni/Ba-Al-O was found to convert ammonia with a conversion of 95 % at 550 °C by Im et al [63] noting that the strong basic properties weakened hydrogen adsorption thereby alleviating hydrogen inhibition of the catalyst.

Alongside the conventional thermal ammonia decomposition catalysts discussed above, plasma ammonia decomposition has gained attraction as a method to decompose ammonia non thermally [64, 65] or to achieve high conversion at elevated temperature either on its own or through a combination with high performing conventional thermal catalysts [66, 67]. Akiyama et al [65] examined non thermal plasma ammonia decomposition at atmospheric pressure using a feed gas mixture of 4.87% NH<sub>3</sub> in N<sub>2</sub> in a dielectric barrier discharge reactor. A range of different materials were used for the inner electrode (Ag, Al, Cu, Fe, and Ti) with these showing no catalytic activity towards ammonia decomposition. Ammonia decomposition was seen to be solely dependent on power supplied and was linear over the range 0 – 50 W with full conversion at 50 W [65]. The synergistic effect of combined plasma and catalytic decomposition was further examined by Wang et al utilising a commercial Fe-based catalyst in a dielectric barrier discharge reactor at 410 °C. When the reactor was operated without catalyst the conversion was only 7.8%, decreasing to 7.4% when the reactor was operated thermally with the catalyst. However, when the plasma and catalysts were combined a conversion of 99.9% was reported at 500 °C [66].

While this new technology is promising in its ability to deliver NH<sub>3</sub> conversion at low temperatures, the amount of electric energy required to convert a relatively small amount of NH<sub>3</sub> or low conversion means that further development is still required.

Table 3 Highlighted Advances in Ammonia Decomposition Catalysts

Catalyst	Reactor temperature (°C)	NH <sub>3</sub> Conversion	Weight hourly space velocity (WHSV) (mL g <sup>-1</sup> h <sup>-1</sup> )	Ref.
10wt%Ni/Y <sub>2</sub> O <sub>3</sub>	550	87 %	6,000	[68]
40wt%Ni/BaZrO <sub>3</sub>	550	94 %	6,000	[69]
K-CoNi alloy-MgO-CeO <sub>2</sub> -SrO (Ni60wt%)	450	97.7 %	6,000	[70]

2.5Ru/10 C-rGO	400	96 %	150,000 (5% NH <sub>3</sub> in Ar)	[71]
35Co/BHA	500	87.2 %	30,000	[72]
(SA-600A)/RuCl <sub>3</sub> .nH <sub>2</sub> O/LiOH·H <sub>2</sub> O (40:5:3)	490	99.9 %	1,250	[73]
Ru/La <sub>0.33</sub> Ce <sub>0.67</sub>	400	91.9 %	6,000	[74]
Cs/Ru–CeO <sub>2</sub>	300	80 %	2,000	[60]
Ru/SiC	400	99.3 %	60,000 (5% NH <sub>3</sub> )	[59]
Fe-CNFs/mica	600	98.9 %	6,500	[75]
Ni/CaNH-HS	500	91.2 %	15,000	[62]
Ni/Ba–Al–O	550	95 %	6,000	[63]

## Ammonia Combustion

The direct use of ammonia in internal combustion engines has attracted attention due to its high energy density when compared to other carbon free fuels [76]. Compared to conventional fuels used in internal combustion engines, ammonia releases significantly less harmful emission with no carbon emissions released. However, the combustion can release nitrogen oxides (NO<sub>x</sub>) which are harmful pollutants that contribute to smog and acid rain [76]. This problem is currently being tackled through the development of technologies such as selective catalytic reduction (SCR) to reduce NO<sub>x</sub> emissions [77]. In this review we will be examining these current developments in solving this key problem for ammonia combustion while looking at the best use cases for this technology.

When combusted the following reactions take place



In order to remove the produced NO<sub>x</sub>, the products can be catalytically reduced using ammonia through the following reaction.



Due to the release of  $\text{NO}_x$  from other industrial processes, catalysts based on Cu containing chabazite (CHA) structured Zeolites and  $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$  are available for commercial applications and can be applied to the ammonia combustion processes [77]. Current research into SCR catalysts involves increasing the working temperature window with a particular focus on lower the temperature requirement, increasing the metal resistance and improving catalyst stability. Recently Han et al [77] provided an extensive review of the current SCR catalysts. When operating at low temperature 100 % NO conversion was achieved by a Mn-Ce/ $\text{TiO}_2$  catalyst operating at 150 °C by Jin et al [78], however this conversion dropped to 60 % after  $\text{SO}_2$  was introduced, which is commonly found in flue gases. However, when used to treat the products of ammonia combustion this may prove not to be an issue as  $\text{SO}_2$  is not expected to be present. At 240 °C, Cu-Fe-W-Ti oxide was reported by Ma et al [79] to achieve 100 % conversion even in the presence of  $\text{SO}_2$ .

Different ammonia combustion technologies were reviewed by Chiong et al [80] in which spark ignition (SI), compression ignition (CI), and gas turbines were examined. For spark ignition it was reported that hydrogen is the most common additive, obtained either through a separate feed of integrated ammonia cracking. When blended with a mass fraction of 10% hydrogen in ammonia, performances in line with neat gasoline can be obtained for SI engines [80, 81]. They also reported that for CI engines, retarding the ammonia injections time can substantially reduce NO emissions, however, this has the adverse effect of increasing unburnt ammonia emissions [80, 82]. For gas turbines partially premixed combustion was examined, which incorporates the benefits of both premixed and non premixed combustion which can extend the lean blow-off limit while retaining flame stability with low NO emissions [80, 83, 84].

## Direct Ammonia Fuel Cells

Direct Ammonia Fuel Cells (DAFCs) are a type of fuel cell that directly uses ammonia as the fuel to generate electricity. These fuel cells are an attractive technology when ammonia is utilised as a means for hydrogen storage as they forgo the need for the energy intensive ammonia cracking that would be required for a hydrogen fuel cell [15, 85-87]. Like hydrogen fuel cells there is a wide range of ammonia fuel cells that follow the same design principles as their hydrogen counterparts, these include, proton exchange membrane fuel cells (PEMFCs), both proton and oxide ion conduction solid oxide fuel cells (SOFC-H and SOFC-O), Alkaline ammonia fuel cells (AAFCs), and alkaline membrane based fuel cells (AMFCs) [15]. Figure 2 shows the operation of both a SOFC-O and SOFC-H, despite large differences in operating temperature and materials, the mechanism shown for SOFC-H is a good representation of all proton conducting ammonia fuel cells.

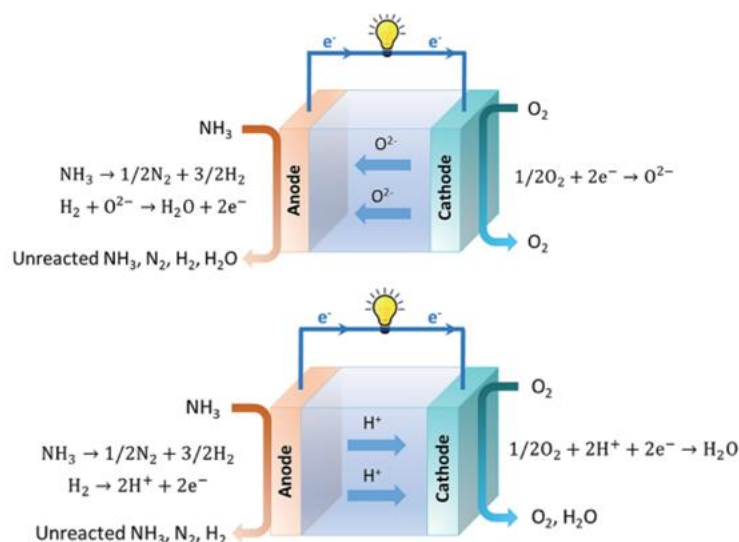


Fig. 2 Schematic Illustrations of both ammonia fed SOFC-O and SOFC-H [15]

High power density was recently reported by Zhong et al [88] for an oxide conducting solid oxide fuel cell using ammonia. By using a  $\text{Pr}_2\text{Zr}_2\text{O}_7$  (PZO) cathode, NiO- Yttria stabilised Zirconia (YSZ) anode and YSZ electrolyte they achieved a power density of  $1220 \text{ mW/cm}^2$  at  $800 \text{ }^\circ\text{C}$ . This strong electrochemical performance was attributed to the high conductivity, fast oxygen transport, and matched thermal expansion coefficient of the PZO cathode [88]. For proton conducting solid oxide fuel cells good performance was obtained by Pan et al [89] with a power density of  $1078 \text{ mW cm}^{-2}$  obtained at  $700 \text{ }^\circ\text{C}$ . To achieve this they employed a  $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$  (PBSCF) as the cathode while  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}$  (BZCYyb) was employed as the electrolyte and Ni-BZCYyb as the anode. They also reported that for nickel based anodes, deterioration of the anode can occur through undesirable ammonia nickel interactions [89]. To limit this, they protected the anode with a layer of catalytic iron to effectively decompose the ammonia, limiting its contact with nickel, leading to a reported increase in activity and durability.

Our group recently reported an efficient noble metal free cathode for an anion exchange membrane direct ammonia fuel cell [90]. A maximum current density of  $379 \text{ mA cm}^{-2}$  was achieved with air as the oxidant at a temperature of  $100 \text{ }^\circ\text{C}$ . The  $\text{LaCr}_{0.25}\text{Fe}_{0.25}\text{Co}_{0.5}\text{O}_{3-\delta}$  on carbon cathode used to obtain these results showed similar performance to Pt on carbon when used in a direct ammonia fuel cell under similar conditions [90]. This noble metal free oxide catalyst has the potential to dramatically lower the cost of low temperature direct ammonia fuel cells which conventionally rely on platinum group metals. For low temperature DAFCs, a remarkable power density of  $314 \text{ mW cm}^{-2}$  has been achieved at  $90 \text{ }^\circ\text{C}$  when pure  $\text{O}_2$  was used as the oxidant [91].

Despite this, there are still significant challenges to overcome for the widespread application of direct ammonia fuel cells. Ammonia fed SOFCs are currently the most promising of these with numerous advantages to hydrogen fuel cells including; higher volumetric power density, higher mechanical stability, high thermal shock resistance and no sealing issues [15]. However, the rate of ammonia conversion is slow requiring the use of a suitable catalyst, this is further exasperated through the high operating temperature which requires long start-up and cool down period, limiting their use to applications that have long run times. At high temperature, the steam present at the anode also becomes a concern for the formation of  $\text{NO}_x$ . For alkaline membrane direct ammonia fuel cells, commercialisation is still a way off with improvements required in both performance and stability [15]. As the conventional polymeric based alkaline membrane is not chemically compatible with  $\text{CO}_2$  in air, the power density of DAFcs

based on polymeric alkaline membrane electrolyte will be significantly reduced when pure 'free' air is used as oxidant at cathode. Therefore it is desired to develop stable and conductive OH<sup>-</sup> ionic conducting materials for low temperature fuel cells, particularly low temperature DAFCs. Therefore, in order to improve AMFCs new low-cost cathode and anode materials must be development with good ammonia binding strength and low onset potential in order to achieve the required power densities.

Unlike hydrogen, storage of ammonia is not an issue, the low temperature DAFCs have short start-up time, is particularly useful in long distance transportation such as buses, long-haul lorries, trains, planes and vessels.

Table 4 Highlighted Advances in Direct Ammonia Fuel Cells

Catalyst	Electrolyte	Temperature (°C)	Current density (mA cm <sup>-2</sup> )	Power density (mW cm <sup>-2</sup> )	Ref.
Pt nanoparticle	1 M NH <sub>3</sub> + 1 M KOH	Room Temperature	≈58		[92]
Pt/Ir/MWCNT nanoparticle	0.1 M NH <sub>3</sub> + 0.1 M KOH	22	≈0.23		[93]
NiCu/C	1 M KOH + 0.5 M NH <sub>3</sub>	Room Temperature	110.4		[94]
2.2 mg <sub>PGM</sub> cm <sup>-2</sup> PtIr(50 wt%)/C(50 wt%)	PiperION-A20-HCO <sub>3</sub> TP-85	100	379	34	[90]
Ni-YSZ//SYO (0.1)-60YSZ	YSZ	800	100	1210	[95]
NiO-YSZ//PZO	YSZ	800		1220	[88]
Ni-SDC//BSCF	SDC	650	2500	1190	[96]
Ni-BZCYYb//PBSCF	BZCYYb	700		1078	[89]
2 mg <sub>PGM</sub> cm <sup>-2</sup> / Acta 4020 1 mg cm <sup>-2</sup>	HEM (PAP-TP)	80	500	135	[87]
2 mg <sub>PGM</sub> cm <sup>-2</sup> / PGM-free	HEM (unspecified)	100		450	[97]
CDN/C //MnO <sub>2</sub> /C	CPPO-PVA-based membrane electrolyte	Room Temperature		16	[98]
Ni <sub>4</sub> Cu <sub>5</sub> Fe <sub>1</sub> /C	0.1 M KOH solution	80		8.9	[99]

## Conclusions

In this paper green ammonia has been examined as a potential energy carrier, looking at effective methods of green ammonia synthesis along with the different ways it can be utilised. The need for low temperature, highly resistant catalysts that can operate at low pressure in order to operate the Haber Bosch process at low scale running on renewables was examined along with recent developments in the electrochemical synthesis of green ammonia and what advances are required for commercialisation. Ammonia utilisation was examined either directly in ammonia combustion engines or direct ammonia fuel cells. For ammonia combustion the reduction of harmful NO<sub>x</sub> emission is the key consideration in order to make the technology viable with a range of methods for achieving this, including, selective catalytic reduction. For direct ammonia fuel cells, the need for key advances in stable and conduction alkaline membrane, low-cost anode and cathode materials was identified in order to unlock the benefits associated with this technology when compared to hydrogen fuel cells. Recent advances in ammonia cracking were examined in order to recover hydrogen at the user end, noting that in order to improve the energy cost of this process, effective catalysts to lower the temperature was required, with 400 °C conversion only possible with expensive ruthenium catalysts. It can be seen that by examining these technologies from a materials perspective side by side that a lot of overlap is present. Suitable ammonia cracking catalysts can be employed in direct ammonia fuels cells to help with ammonia decomposition, effective Haber Bosch catalysts can be integrated into the cell for electrochemical ammonia synthesis. By examining the recent best performing materials in each of these fields we aim to provide a jumping off point for new research that can learn from advances in these other adjacent processes in order to make green ammonia a valuable clean energy carrier.

## References

1. Sara Budinis, A.G., Peter Levi, Hana Mandová, Tiffany Vass. , *Ammonia Technology Roadmap*. 2021, IEA: <https://www.iea.org/reports/ammonia-technology-roadmap>.
2. Lan, R., J.T.S. Irvine, and S.W. Tao, *Ammonia and related chemicals as potential indirect hydrogen storage materials*. International Journal of Hydrogen Energy, 2012. **37**(2): p. 1482-1494.
3. Smart, K., *Review of Recent Progress in Green Ammonia Synthesis: Decarbonisation of fertiliser and fuels via green synthesis*. Johnson Matthey Technology Review, 2022. **66**(3): p. 230-244.
4. Brightling, J., *Ammonia and the fertiliser industry: The development of ammonia at Billingham*. Johnson Matthey Technology Review, 2018. **62**(1): p. 32-47.
5. Salmon, N. and R. Banares-Alcántara, *Green ammonia as a spatial energy vector: a review*. Sustainable Energy & Fuels, 2021. **5**(11): p. 2814-2839.
6. Ayvali, T., S.E. Tsang, and T. Van Vrijaldenhoven, *The position of ammonia in decarbonising maritime industry: an overview and perspectives: Part II: costs, safety and environmental performance and the future prospects for ammonia in shipping*. Johnson Matthey Technology Review, 2021. **65**(2): p. 291-300.
7. Tsang, S., T. Ayvali, and T. Van Vrijaldenhoven, *The Position of Ammonia in Decarbonising Maritime Industry: An Overview and Perspectives: Part I: Technological advantages and the momentum towards ammonia-propelled shipping*. Johnson Matthey technology review, 2021. **65**(2): p. 275-290.
8. Liu, H., *Ammonia Synthesis Catalysts Innovation and Practice*. Vol. 1. 2013: World Scientific Publishing Co and Chemical industry press. 871.

9. Humphreys, J., R. Lan, and S. Tao, *Development and Recent Progress on Ammonia Synthesis Catalysts for Haber–Bosch Process*. Advanced Energy and Sustainability Research, 2021. **2**(1): p. 2000043.
10. Erisman, J.W., et al., *How a century of ammonia synthesis changed the world*. Nature Geosci, 2008. **1**(10): p. 636-639.
11. MacFarlane, D.R., et al., *A Roadmap to the Ammonia Economy*. Joule, 2020. **4**(6): p. 1186-1205.
12. Ronduda, H., et al., *Co supported on Mg–La mixed oxides as an efficient catalyst for ammonia synthesis*. International Journal of Hydrogen Energy, 2022. **47**(84): p. 35689-35700.
13. Song, C., *Introduction to Hydrogen and Syngas Production and Purification Technologies*, in *Hydrogen and Syngas Production and Purification Technologies*. 2009. p. 1-13.
14. Howarth, R.W. and M.Z. Jacobson, *How green is blue hydrogen?* Energy Science & Engineering, 2021. **9**(10): p. 1676-1687.
15. Jeerh, G., M. Zhang, and S. Tao, *Recent progress in ammonia fuel cells and their potential applications*. Journal of Materials Chemistry A, 2021. **9**(2): p. 727-752.
16. Technology. *The Green Ammonia Landscape*. 2023 07/04/2023]; Available from: <https://www.eneuseenergy.com/technology/>.
17. Fastrup, B. and H. Nygård Nielsen, *On the influence of oxygen on iron catalysts during ammonia synthesis and catalyst characterization*. Catalysis Letters, 1992. **14**(2): p. 233-239.
18. Humphreys, J., et al., *Cation doped cerium oxynitride with anion vacancies for Fe-based catalyst with improved activity and oxygenate tolerance for efficient synthesis of ammonia*. Applied Catalysis B: Environmental, 2021. **285**: p. 119843.
19. Liu, H., *Ammonia synthesis catalyst 100 years: Practice, enlightenment and challenge*. Chinese Journal of Catalysis, 2014. **35**(10): p. 1619-1640.
20. Stepan, O. and B. Stverak, *Influence of ionizing radiation on catalytic activity of iron catalysts for ammonia synthesis* Collection of Czechoslovak Chemical Communications, 1971. **36**(6): p. 2358-&.
21. Boudart, M. and Khammoum.Sb, *Ammonia synthesis on supported iron catalysts* Abstracts of Papers of the American Chemical Society, 1972. **164**(AUG-S): p. 15.
22. Zubritsk.Di, et al., *Thermal-stability of complex iron and molybdenum cyanides and their catalytic activity in ammonia synthesis* Zhurnal Prikladnoi Khimii, 1973. **46**(2): p. 329-332.
23. Berengar.Mg, et al., *Electron work function and catalytic activity of ammonia-synthesis melted iron catalysts promoted by oxides of scandium and rare-earth elements* Doklady Akademii Nauk Ssr, 1974. **214**(3): p. 601-604.
24. Badik, V.S., et al., *Activity and thermal-stability of precipitated iron catalysts for ammonia-synthesis, promoted with uranium oxides* Journal of Applied Chemistry of the Ussr, 1974. **47**(10): p. 2239-2241.
25. Dvornik, O.S., O.A. Streltsov, and V.L. Chernobrivets, *Effect of bivalent and trivalent iron in non-reduced catalysts of ammonia-synthesis on their catalytic properties under higher pressures* Ukrainskii Khimicheskii Zhurnal, 1975. **41**(5): p. 544-545.
26. Bridger, G.L., et al., *Production and performance of ammonia-synthesis catalyst* Chemical Engineering Progress, 1947. **43**(6): p. 291-302.
27. Yu, X.J., et al., *A novel fused iron catalyst for ammonia synthesis promoted with rare earth gangue*. Journal of Rare Earths, 2008. **26**(5): p. 711-716.
28. Wang, P., et al., *The Formation of Surface Lithium–Iron Ternary Hydride and its Function on Catalytic Ammonia Synthesis at Low Temperatures*. Angewandte Chemie International Edition, 2017. **56**(30): p. 8716-8720.
29. Gao, W., et al., *Production of ammonia via a chemical looping process based on metal imides as nitrogen carriers*. Nature Energy, 2018. **3**(12): p. 1067-1075.
30. Humphreys, J., et al., *Improved stability and activity of Fe-based catalysts through strong metal support interactions due to extrinsic oxygen vacancies in Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2-δ</sub> for the*



- efficient synthesis of ammonia*. Journal of Materials Chemistry A, 2020. **8**(32): p. 16676-16689.
31. Kitano, M., et al., *Self-organized Ruthenium–Barium Core–Shell Nanoparticles on a Mesoporous Calcium Amide Matrix for Efficient Low-Temperature Ammonia Synthesis*. Angewandte Chemie International Edition, 2018. **57**(10): p. 2648-2652.
  32. Kitano, M., et al., *Ammonia synthesis using a stable electride as an electron donor and reversible hydrogen store*. Nature Chemistry, 2012. **4**(11): p. 934-940.
  33. Lu, Y., et al., *Synthesis of Rare-Earth-Based Metallic Electride Nanoparticles and Their Catalytic Applications to Selective Hydrogenation and Ammonia Synthesis*. ACS Catalysis, 2018. **8**(12): p. 11054-11058.
  34. Ronduda, H., et al., *Kinetic studies of ammonia synthesis over a barium-promoted cobalt catalyst supported on magnesium–lanthanum mixed oxide*. Journal of the Taiwan Institute of Chemical Engineers, 2020. **114**: p. 241-248.
  35. Humphreys, J., et al., *Improved stability and activity of Fe-based catalysts through strong metal support interactions due to extrinsic oxygen vacancies in Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2-δ</sub> for the efficient synthesis of ammonia*. Journal of Materials Chemistry A, 2020.
  36. Zhang, X., et al., *The role of lanthanum hydride species in La<sub>2</sub>O<sub>3</sub> supported Ru cluster catalyst for ammonia synthesis*. Journal of Catalysis, 2023. **417**: p. 382-395.
  37. Ronduda, H., et al., *Co nanoparticles supported on mixed magnesium–lanthanum oxides: effect of calcium and barium addition on ammonia synthesis catalyst performance*. RSC Advances, 2023. **13**(7): p. 4787-4802.
  38. Ronduda, H., et al., *Ammonia synthesis using Co catalysts supported on MgO–Nd<sub>2</sub>O<sub>3</sub> mixed oxide systems: Effect of support composition*. Surfaces and Interfaces, 2023. **36**: p. 102530.
  39. Feng, J., et al., *Ru nanoparticles on Y<sub>2</sub>O<sub>3</sub> with enhanced metal–support interactions for efficient ammonia synthesis*. Catalysis Science & Technology, 2023. **13**(3): p. 844-853.
  40. Luz, I., et al., *MOF-derived nanostructured catalysts for low-temperature ammonia synthesis*. Catalysis Science & Technology, 2020. **10**(1): p. 105-112.
  41. Karolewska, M., et al., *Ammonia synthesis over a Ba and Ce-promoted carbon-supported cobalt catalyst. Effect of the cerium addition and preparation procedure*. Journal of Catalysis, 2013. **303**: p. 130-134.
  42. Shen, H., et al., *Electrochemical ammonia synthesis: Mechanistic understanding and catalyst design*. Chem, 2021. **7**(7): p. 1708-1754.
  43. Jiao, F. and B. Xu, *Electrochemical Ammonia Synthesis and Ammonia Fuel Cells*. Advanced Materials, 2019. **31**(31): p. 1805173.
  44. Zhao, R., et al., *Recent progress in the electrochemical ammonia synthesis under ambient conditions*. EnergyChem, 2019. **1**(2): p. 100011
  45. Amar, I.A., et al., *Solid-state electrochemical synthesis of ammonia: a review*. Journal of Solid State Electrochemistry, 2011. **15**(9): p. 1845-1860.
  46. Du, H.-L., et al., *Electroreduction of nitrogen with almost 100% current-to-ammonia efficiency*. Nature, 2022. **609**(7928): p. 722-727.
  47. Li, S., et al., *Electrosynthesis of ammonia with high selectivity and high rates via engineering of the solid-electrolyte interphase*. Joule, 2022. **6**(9): p. 2083-2101.
  48. Zhang, C., et al., *Oxygen vacancy-engineered Fe<sub>2</sub>O<sub>3</sub> nanocubes via a task-specific ionic liquid for electrocatalytic N<sub>2</sub> fixation*. Chemical Communications, 2019. **55**(51): p. 7370-7373.
  49. Zhang, L., et al., *A Janus Fe-SnO<sub>2</sub> Catalyst that Enables Bifunctional Electrochemical Nitrogen Fixation*. Angewandte Chemie International Edition, 2020. **59**(27): p. 10888-10893.
  50. Liu, Y., et al., *Enhanced N<sub>2</sub> Electroreduction over LaCoO<sub>3</sub> by Introducing Oxygen Vacancies*. ACS Catalysis, 2020. **10**(2): p. 1077-1085.
  51. Wu, T., et al., *Greatly Improving Electrochemical N<sub>2</sub> Reduction over TiO<sub>2</sub> Nanoparticles by Iron Doping*. Angewandte Chemie International Edition, 2019. **58**(51): p. 18449-18453.

52. Cai, J., et al., *Electrocatalytic nitrate-to-ammonia conversion with ~100% Faradaic efficiency via single-atom alloying*. Applied Catalysis B: Environmental, 2022. **316**: p. 121683.
53. Liu, S., et al., *Proton-filtering covalent organic frameworks with superior nitrogen penetration flux promote ambient ammonia synthesis*. Nature Catalysis, 2021. **4**(4): p. 322-331.
54. Lv, Y., et al., *Nitrogen reduction through confined electro-catalysis with carbon nanotube inserted metal-organic frameworks*. Journal of Materials Chemistry A, 2021. **9**(3): p. 1480-1486.
55. Wei, Z., et al., *Phase-separated CuAg alloy interfacial stress induced Cu defects for efficient N<sub>2</sub> activation and electrocatalytic reduction*. Applied Catalysis B: Environmental, 2023. **320**: p. 121915.
56. Lim, J., et al., *Structure Sensitivity of Pd Facets for Enhanced Electrochemical Nitrate Reduction to Ammonia*. ACS Catalysis, 2021. **11**(12): p. 7568-7577.
57. Schüth, F., et al., *Ammonia as a possible element in an energy infrastructure: catalysts for ammonia decomposition*. Energy & Environmental Science, 2012. **5**(4): p. 6278-6289.
58. Lamb, K.E., M.D. Dolan, and D.F. Kennedy, *Ammonia for hydrogen storage; A review of catalytic ammonia decomposition and hydrogen separation and purification*. International Journal of Hydrogen Energy, 2019. **44**(7): p. 3580-3593.
59. Pinzón, M., et al., *Hydrogen production by ammonia decomposition over ruthenium supported on SiC catalyst*. Journal of Industrial and Engineering Chemistry, 2021. **94**: p. 326-335.
60. Furusawa, T., et al., *Development of a Cs-Ru/CeO<sub>2</sub> Spherical Catalyst Prepared by Impregnation and Washing Processes for Low-Temperature Decomposition of NH<sub>3</sub>: Characterization and Kinetic Analysis Results*. Industrial & Engineering Chemistry Research, 2020. **59**(41): p. 18460-18470.
61. Sayas, S., et al., *High pressure ammonia decomposition on Ru-K/CaO catalysts*. Catalysis Science & Technology, 2020. **10**(15): p. 5027-5035.
62. Ogasawara, K., et al., *Ammonia Decomposition over CaNH-Supported Ni Catalysts via an NH<sub>2</sub>-Vacancy-Mediated Mars-van Krevelen Mechanism*. ACS Catalysis, 2021. **11**(17): p. 11005-11015.
63. Im, Y., et al., *Ammonia decomposition over nickel catalysts supported on alkaline earth metal aluminate for H<sub>2</sub> production*. International Journal of Hydrogen Energy, 2020. **45**(51): p. 26979-26988.
64. Andersen, J.A., et al., *Plasma-catalytic ammonia decomposition using a packed-bed dielectric barrier discharge reactor*. International Journal of Hydrogen Energy, 2022. **47**(75): p. 32081-32091.
65. Akiyama, M., et al., *Ammonia decomposition to clean hydrogen using non-thermal atmospheric-pressure plasma*. International Journal of Hydrogen Energy, 2018. **43**(31): p. 14493-14497.
66. Wang, L., et al., *Plasma driven ammonia decomposition on a Fe-catalyst: eliminating surface nitrogen poisoning*. Chemical Communications, 2013. **49**(36): p. 3787-3789.
67. Wang, L., et al., *Highly Dispersed Co Nanoparticles Prepared by an Improved Method for Plasma-Driven NH<sub>3</sub> Decomposition to Produce H<sub>2</sub>*. Catalysts, 2019. **9**(2): p. 107.
68. Okura, K., et al., *Ammonia Decomposition over Nickel Catalysts Supported on Rare-Earth Oxides for the On-Site Generation of Hydrogen*. ChemCatChem, 2016. **8**(18): p. 2988-2995.
69. Okura, K., et al., *Ammonia decomposition over Ni catalysts supported on perovskite-type oxides for the on-site generation of hydrogen*. RSC Advances, 2018. **8**(56): p. 32102-32110.
70. Tabassum, H., et al., *Hydrogen generation via ammonia decomposition on highly efficient and stable Ru-free catalysts: approaching complete conversion at 450 °C*. Energy & Environmental Science, 2022. **15**(10): p. 4190-4200.

71. Pinzón, M., et al., *New catalysts based on reduced graphene oxide for hydrogen production from ammonia decomposition*. *Sustainable Chemistry and Pharmacy*, 2022. **25**: p. 100615.
72. Li, G., et al., *Production of hydrogen by ammonia decomposition over supported Co<sub>3</sub>O<sub>4</sub> catalysts*. *Catalysis Today*, 2022. **402**: p. 45-51.
73. El-Shafie, M., S. Kambara, and Y. Hayakawa, *Development of zeolite-based catalyst for enhancement hydrogen production from ammonia decomposition*. *Catalysis Today*, 2022. **397-399**: p. 103-112.
74. Le, T.A., et al., *Ru-supported lanthania-ceria composite as an efficient catalyst for CO<sub>x</sub>-free H<sub>2</sub> production from ammonia decomposition*. *Applied Catalysis B: Environmental*, 2021. **285**: p. 119831.
75. Duan, X., et al., *Tuning the size and shape of Fe nanoparticles on carbon nanofibers for catalytic ammonia decomposition*. *Applied Catalysis B: Environmental*, 2011. **101**(3): p. 189-196.
76. Erdemir, D. and I. Dincer, *A perspective on the use of ammonia as a clean fuel: Challenges and solutions*. *International Journal of Energy Research*, 2021. **45**(4): p. 4827-4834.
77. Han, L., et al., *Selective Catalytic Reduction of NO<sub>x</sub> with NH<sub>3</sub> by Using Novel Catalysts: State of the Art and Future Prospects*. *Chemical Reviews*, 2019. **119**(19): p. 10916-10976.
78. Jin, R., et al., *The role of cerium in the improved SO<sub>2</sub> tolerance for NO reduction with NH<sub>3</sub> over Mn-Ce/TiO<sub>2</sub> catalyst at low temperature*. *Applied Catalysis B: Environmental*, 2014. **148-149**: p. 582-588.
79. Ma, S., et al., *Effect of W on the acidity and redox performance of the Cu<sub>0.02</sub>Fe<sub>0.2</sub>W<sub>a</sub>TiO<sub>x</sub> (a = 0.01, 0.02, 0.03) catalysts for NH<sub>3</sub>-SCR of NO*. *Applied Catalysis B: Environmental*, 2019. **248**: p. 226-238.
80. Chiong, M.-C., et al., *Advancements of combustion technologies in the ammonia-fuelled engines*. *Energy Conversion and Management*, 2021. **244**: p. 114460.
81. Lhuillier, C., et al., *Experimental investigation on ammonia combustion behavior in a spark-ignition engine by means of laminar and turbulent expanding flames*. *Proceedings of the Combustion Institute*, 2021. **38**(4): p. 5859-5868.
82. Lamas Galdo, M.I., L. Castro-Santos, and C.G. Rodriguez Vidal, *Numerical Analysis of NO<sub>x</sub> Reduction Using Ammonia Injection and Comparison with Water Injection*. *Journal of Marine Science and Engineering*, 2020. **8**(2): p. 109.
83. Franco, M.C., et al., *Characteristics of NH<sub>3</sub>/H<sub>2</sub>/air flames in a combustor fired by a swirl and bluff-body stabilized burner*. *Proceedings of the Combustion Institute*, 2021. **38**(4): p. 5129-5138.
84. Zhu, X., et al., *NO and OH\* emission characteristics of very-lean to stoichiometric ammonia-hydrogen-air swirl flames*. *Proceedings of the Combustion Institute*, 2021. **38**(4): p. 5155-5162.
85. Abbasi, R., et al., *Low-temperature direct ammonia fuel cells: Recent developments and remaining challenges*. *Current Opinion in Electrochemistry*, 2020. **21**: p. 335-344.
86. Lan, R. and S.W. Tao, *Direct ammonia alkaline anion-exchange membrane fuel cells*. *Electrochemical and Solid-State Letters*, 2010. **13**(8): p. B83-B86.
87. Zhao, Y., et al., *An Efficient Direct Ammonia Fuel Cell for Affordable Carbon-Neutral Transportation*. *Joule*, 2019. **3**(10): p. 2472-2484.
88. Zhong, F., et al., *Defect-induced pyrochlore Pr<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> cathode rich in oxygen vacancies for direct ammonia solid oxide fuel cells*. *Journal of Power Sources*, 2022. **520**: p. 230847.
89. Pan, Y., et al., *A high-performance and durable direct NH<sub>3</sub> tubular protonic ceramic fuel cell integrated with an internal catalyst layer*. *Applied Catalysis B: Environmental*, 2022. **306**: p. 121071.
90. Jeerh, G., et al., *Perovskite oxide LaCr<sub>0.25</sub>Fe<sub>0.25</sub>Co<sub>0.5</sub>O<sub>3-δ</sub> as an efficient non-noble cathode for direct ammonia fuel cells*. *Applied Catalysis B: Environmental*, 2022. **319**: p. 121919.

91. Li, Y., et al., *High-performance ammonia oxidation catalysts for anion-exchange membrane direct ammonia fuel cells*. *Energy & Environmental Science*, 2021. **14**(3): p. 1449-1460.
92. Hanada, N., et al., *Electrolysis of ammonia in aqueous solution by platinum nanoparticles supported on carbon nanotube film electrode*. *Electrochimica Acta*, 2020. **341**: p. 136027.
93. Morita, S., et al., *Electrochemical oxidation of ammonia by multi-wall-carbon-nanotube-supported Pt shell-Ir core nanoparticles synthesized by an improved Cu short circuit deposition method*. *Journal of Electroanalytical Chemistry*, 2016. **762**: p. 29-36.
94. Zhang, H., et al., *An ammonia electrolytic cell with NiCu/C as anode catalyst for hydrogen production*. *Energy Procedia*, 2017. **142**: p. 1539-1544.
95. Zhong, F., et al., *Tuning defect nonequilibrium of brownmillerite  $Sr_{1+x}Y_2-xO_{4+\delta}$  for rich-oxygen-vacancy direct ammonia solid oxide fuel cells cathode*. *Journal of Power Sources*, 2022. **524**: p. 231078.
96. Meng, G., et al., *Comparative study on the performance of a SDC-based SOFC fueled by ammonia and hydrogen*. *Journal of Power Sources*, 2007. **173**(1): p. 189-193.
97. Gottesfeld, S., *The Direct Ammonia Fuel Cell and a Common Pattern of Electrocatalytic Processes*. *Journal of The Electrochemical Society*, 2018. **165**(15): p. J3405.
98. Lan, R. and S. Tao, *Direct Ammonia Alkaline Anion-Exchange Membrane Fuel Cells*. *Electrochemical and Solid-State Letters*, 2010. **13**(8): p. B83.
99. Zhang, M., et al., *A symmetric direct ammonia fuel cell using ternary NiCuFe alloy embedded in a carbon network as electrodes*. *Journal of Materials Chemistry A*, 2022. **10**(36): p. 18701-18713.