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Recent Progress towards the Electrosynthesis of Ammonia from Sustainable Resources

Michael A. Shipman and Mark D. Symes*

WestCHEM, School of Chemistry, University of Glasgow, Glasgow. G12 8QQ, United Kingdom

*Email: mark.symes@glasgow.ac.uk

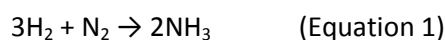
Abstract: Ammonia (NH₃) is a key commodity chemical of vital importance for fertilizers. It is made on an industrial scale *via* the Haber Bosch process, which requires significant infrastructure to be in place such that ammonia is generally made in large, centralized facilities. If ammonia could be produced under less demanding conditions, then there would be the potential for smaller devices to be used to generate ammonia in a decentralized manner for local consumption. Electrochemistry has been proposed as an enabling technology for this purpose as it is relatively simple to scale electrolytic devices to meet almost any level of demand. Moreover, it is possible to envisage electrosynthetic cells where water could be oxidized to produce protons and electrons at the anode which could then be used to reduce and protonate nitrogen to give ammonia at the cathode. If this nitrogen were sourced from the air, then the only required infrastructure for this process would be supplies of water, air and electricity, the latter of which could be provided by renewables. Hence an electrosynthetic cell for ammonia production could allow NH₃ to be generated sustainably in small, low-cost devices requiring only minimal facilities. In this review, we describe recent progress towards such electrosynthetic ammonia production devices, summarizing also some of the seminal literature in the field. Comparison is made between the various different approaches that have been taken, and the key remaining challenges in the electrosynthesis of ammonia are highlighted.

Keywords: Nitrogen reduction, Ammonia synthesis, Electrocatalysis, Electrosynthesis, Sustainable chemistry

1. Introduction

Ammonia is essential for fertilisers in order to feed the World's growing population. Indeed, it is estimated that between a third and half of us would starve to death if ammonia-based fertilisers were not available, and ammonia's industrial-scale synthesis from its elements is arguably the single biggest scientific discovery of the 20th century.¹ In 2014, total worldwide NH₃ production exceeded 140 million tons, and demand for ammonia continues to grow.²

Industrially, ammonia is produced almost exclusively *via* the Haber Bosch process. This process reacts high purity streams of N₂ and H₂ together at high temperatures and pressures (300 – 500 °C and 200 – 300 atm.) over iron or ruthenium-based catalysts, as in Equation 1:



High temperatures are needed in order to off-set the sluggish kinetics of this reaction, however, the thermodynamics of this process favour ammonia decomposition to nitrogen and hydrogen at elevated temperatures and hence the need for high pressure. Including the energy required to obtain the pure feed gases, pressurization and so forth, ammonia synthesis by the Haber Bosch process typically requires an energy input of around 485 kJ mol⁻¹.³ Whilst this is indeed a large amount of energy (especially in comparison to the Natural systems, see below), and therefore methods that reduce this requirement would be welcome, we shall see that this is in fact a very challenging target. Much is made of the inefficiencies of the Haber Bosch process and its requirement for pure H₂ (often obtained from fossil fuels), but currently there is no scalable ammonia synthesis technology that comes close to matching its performance.

Nitrogen reduction to ammonia on a heterogeneous surface can proceed by two broad classes of mechanism: *Associative* and *Dissociative* (see Figure 1). In an associative mechanism, the two nitrogen centres in N_2 remain bound to each other as the molecule is hydrogenated, with NH_3 being released only once the final N-N bond is broken. Hydrogenation in an associative mechanism can then itself be envisaged to occur through two possible pathways. Hydrogenation might occur preferentially on the nitrogen furthest away from the surface (assuming an end-on coordination mode for the N_2 molecule), leading to the release of one equivalent of NH_3 and leaving behind a metal nitrido ($M\equiv N$) unit which will itself be hydrogenated to give a second equivalent of ammonia. This is known as a *distal* associative pathway. The second type of associative mechanism (the *alternating* pathway) calls for each of the two nitrogen centres to undergo single hydrogenation events in turn, until such time as one of the nitrogens is converted into NH_3 and the N-N bond is broken. In a *dissociative* mechanism on the other hand, the $N\equiv N$ bond is broken before any hydrogenation takes place, leaving individual N-atoms on the surface which are converted into NH_3 independently. Current evidence suggests that the Haber Bosch process operates through a dissociative mechanism.

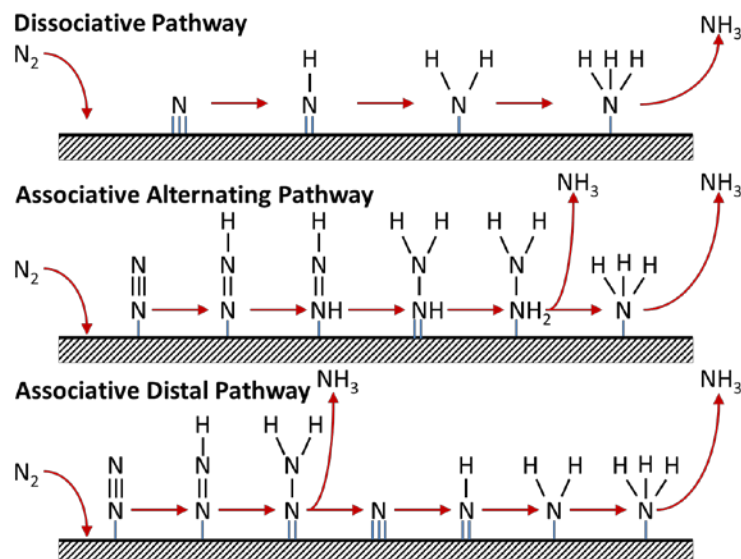
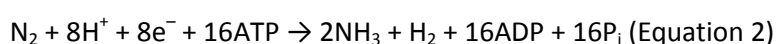


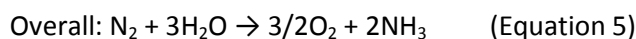
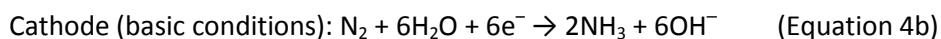
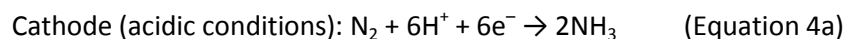
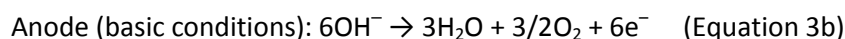
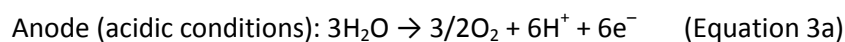
Figure 1. Generic mechanisms for nitrogen reduction to ammonia on heterogeneous catalysts.

In Nature, nitrogen reduction to ammonia is achieved by a class of enzymes called the nitrogenases and presents a very different picture to the Haber Bosch process. The most effective nitrogenases are the FeMo nitrogenases, which consist of two fused iron-sulfur clusters with a carbon atom at their junction and a molybdenum atom in one of the apical positions.^{4,5} It appears that a minimum of 16 equivalents of ATP (adenosine triphosphate) are required in order to reduce one N₂ molecule (Equation 2), meaning that 244 kJ are required per mole of NH₃ produced:⁶



where ADP is adenosine diphosphate and P_i denotes “inorganic phosphate” (a mixture of HPO₄²⁻ and H₂PO₄⁻ ions). The formation of H₂ as a side-product may well be obligatory, and indeed more H₂ than suggested by Equation 2 may be formed, rendering the energetic requirements for ammonia synthesis somewhat greater (depending on how much H₂ is actually produced). In contrast to the Haber Bosch process, the mechanism of formation is believed to be associative (with the N₂ molecule coordinating to a metal centre in the FeMo nitrogenase end-on), although whether hydrogenation proceeds by a distal or an associative pathway is still open to debate.⁷ Regardless of the details of the mechanism operating, however, it is clear that nitrogenase enzymes are able to catalyse the production of ammonia from air and water under very mild conditions (room temperature and pressure, aqueous media) with impressive energy efficiency. Reproducing similar chemistry in a format applicable to industrial-scale production is in many respects the ultimate goal of all nitrogen reduction studies.

Against this backdrop, electrochemistry has emerged as an alternative technology by which to reduce nitrogen to ammonia.⁸ In particular, an electrochemical system that oxidises water in order to obtain protons and electrons for the reduction of nitrogen would be very attractive, as the only inputs required would be N₂ (which could conceivably come from the air), water and electricity (which could conceivably come from renewable sources). The basic equations for such a process can be expressed as:



Hence no fossil fuels would need to be consumed to generate ammonia. Furthermore, by exploiting the inherent flexibility of electrochemical systems, NH_3 production could be carried out at either a small or a large scale as required. It has been estimated that such a system could be up to 20% more energy-efficient than a Haber Bosch process using coal as the hydrogen source, although with today's technology it would remain 30% less efficient than a Haber Bosch process using natural gas as its hydrogen source.⁹

In this review, we shall examine recent progress towards electrochemical systems that produce ammonia by the reduction of nitrogen. We shall look in turn at systems where H_2 , sacrificial reagents and water are used as the proton sources, and we shall also explore systems where air can be used directly as the source of nitrogen. It must be stated at the outset that all the electrochemical systems described herein produce ammonia at much slower rates and much less efficiently than does the Haber Bosch process. However, we hope that by highlighting some of the key advances and remaining challenges in this area that we will inspire the next generation of electrochemists to investigate this fascinating field, which may well have important implications for our food supply and for mitigating climate change in the near future.

2. Electrochemical ammonia production from N_2 and H_2

We shall begin our review by considering the electrosynthesis of ammonia from its elements, which is in some ways the exact electrochemical analogue of the Haber Bosch process. An important milestone in this field was set by Furuya and Yoshida in 1990, who demonstrated the production of ammonia from nitrogen and hydrogen in aqueous solution (1 M KOH) at room temperature using a back-to-back cell configuration.¹⁰ The authors screened 26 different cathode materials. ZnSe was found to be the most efficacious catalyst for N₂ reduction at an applied potential of -1 V vs. RHE, achieving a Faradaic yield for ammonia production of 1.3% whilst producing ammonia at an electrode area-normalized rate of 0.23 mol h⁻¹ m⁻² (see Table 1). Whilst this rate of ammonia formation is impressive in comparison to other electrochemical systems, the Faradaic yield is much less so. This is presumably because at these very negative cell potentials, water reduction to produce hydrogen becomes the dominant cathode reaction (especially given the high relative concentration of H₂O in the aqueous electrolyte employed). As we shall see throughout this review, suppressing the hydrogen evolution side-reaction is possibly the single biggest challenge facing N₂ reduction in the presence of water.

Subsequently, Marnellos and Stoukides managed to reduce the effects of competitive hydrogen evolution by employing a solid-state proton-conducting electrolyte in a cell reactor such as that shown in Figure 2.¹¹ In this design, both the cathode and anode were palladium, in-between which the ceramic H⁺-conductor SrCe_{0.95}Yb_{0.05}O₃ was sandwiched as the electrolyte. Under atmospheric pressure at 570 °C, hydrogen supplied to the anode chamber was dissociated into electrons and protons when modest current densities (around 2 mA cm⁻²) were applied to the cell.

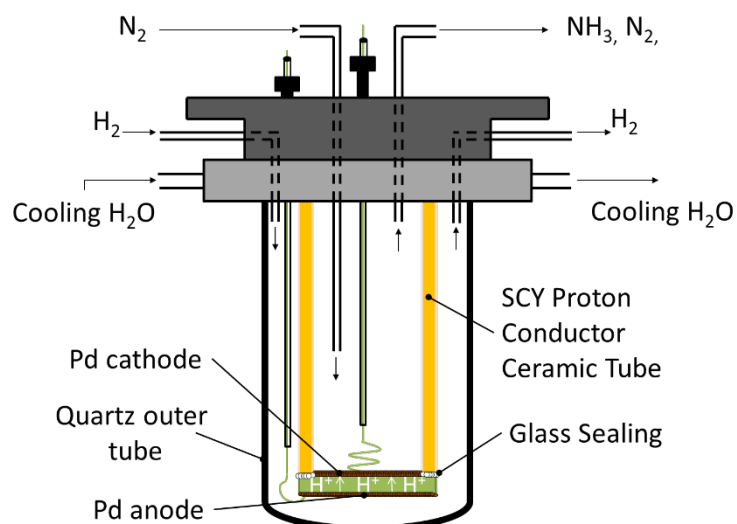


Figure 2. Marnellos and Stoukides' solid-electrolyte ammonia synthesis reactor.¹¹ SCY = Strontia-ceria-ytterbia.

When N_2 was present at the cathode, ammonia was produced according to Equation 4a. In contrast, no ammonia was observed in the absence of an applied bias. At 570 °C, a linear relationship was observed between the rate of ammonia production and the rate of electrochemical hydrogen supply (the latter calculated by dividing the current flowing by $2 \times$ Faraday's constant for the two-electron oxidation of H_2 to protons), whilst the rate of ammonia formation was essentially independent of the partial pressure of N_2 over the range 0.3 to 1.8 kPa. This is in agreement with Equation 1: three times the number of moles of H_2 are required relative to moles of N_2 , and so the rate of supply of H_2 (and hence protons and electrons) is likely to be limiting. Under the conditions probed, at least 78% of the electrochemically-dissociated hydrogen was converted into ammonia detectable in the product stream (*i.e.* the apparent Faradaic yield was at least 78%). The difference from ideal behaviour may be at least partially explained by product ammonia decomposition back to N_2 and H_2 within this high-temperature cell: the authors estimated in a separate experiment that up to 20% of a stream of NH_3 sent through the cell at 570 °C decomposed in this way. A maximum rate of ammonia production of $0.18 \text{ mol h}^{-1} \text{ m}^{-2}$ was obtained, although the authors noted that this rate

was limited in large part by the high ohmic resistance of the proton conductor, which prevented current densities in excess of 2 mA cm^{-2} from being applied.

An interesting extension to this work was described independently by the Stoukides group¹² and by Vayenas and co-workers.¹³ In the system described by the latter authors, a proton-conducting ceramic disc of $\text{CaIn}_{0.1}\text{Zr}_{0.9}\text{O}_{3-\alpha}$ was covered on one side with a layer of silver (to act as a hydrogen oxidation catalyst) and on the other side with a commercial iron-based Haber Bosch catalyst. An external electrical connection was established to allow bias potentials to be supplied and hence facilitate the movement of protons through the ceramic electrolyte (Figure 3). However, unlike the original Stoukides report,¹¹ a mixed N_2/H_2 stream was allowed to access both electrodes. At the anode under an applied bias, this resulted in oxidation of H_2 to protons and electrons at a rate that was measurable by examining the current flowing in the external circuit. However, the rate of ammonia production under these conditions was found to exceed that which could be expected on the basis of the rate of proton delivery to the cathode as given by Equation 4a. Indeed, it was found that for every proton arriving at the cathode, *two* molecules of NH_3 were formed. Clearly then, NH_3 production was not simply occurring in a Faradaic fashion as per Equation 4a, but also catalytically as per Equation 1.

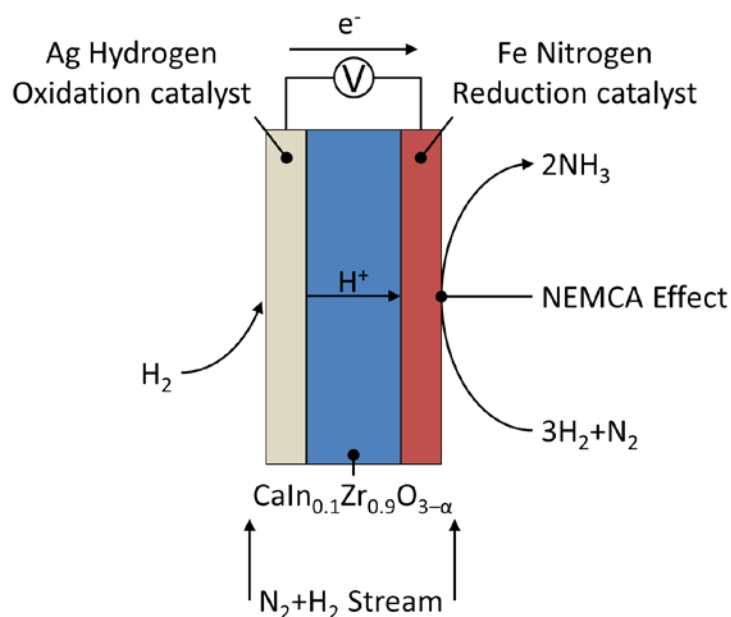
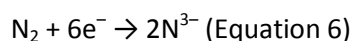


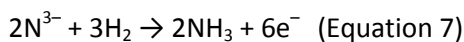
Figure 3. Vayenas' reactor for the electrochemical promotion of the catalytic synthesis of ammonia from its elements.¹³

Importantly, when no bias was applied to the cell (and hence no protons were supplied to the cathode, such that Equation 1 alone was operating in a manner similar to that in the conventional Haber Bosch reactor), the rate of ammonia production decreased by a factor of up to 1300%, depending on the ratio of N₂ to H₂ in the feed gas. The underlying cause of this behaviour is the phenomenon known as *Non-Faradaic Electrochemical Modification of Catalytic Activity* (NEMCA),¹⁴⁻¹⁶ whereby an applied potential can be used to pump ions to or from a catalyst, thus improving its (non-Faradaic) catalytic activity. These results were subsequently re-visited by Stoukides *et al.*, who suggested that the cause of the NEMCA effect in this instance was a lowering of the Fe catalyst work function by the electrochemically-driven influx of protons from the anode, with this lowering of the work function facilitating N₂ chemisorption (generally held to be the rate-determining step) on the Fe catalyst.¹⁷

Molten salt electrolytes have also been explored for the electrosynthesis of NH₃ from its elements. For example, Ito and co-workers reported the electrosynthesis of ammonia in a molten salt eutectic mixture of LiCl-KCl-CsCl at 723 K.¹⁸ A schematic of their experimental set-up¹⁸ is given in Figure 4. Hence nitrogen gas was introduced into the cell through the porous nickel gas diffusion cathode, where it was reduced to nitride according to the equation:



The same group had already established that the electrochemical reduction of nitrogen gas at a nickel cathode in a molten LiCl-KCl system produced nitride ions almost quantitatively according to Equation 6.¹⁹ Meanwhile, the anode reaction during Ito's electrochemical reduction of nitrogen to ammonia as shown in Figure 4 can be described by the equation:



This reaction is also performed over porous nickel. Under continuous operation for 1 h, a Faradaic efficiency for ammonia production of 72% was obtained, with ammonia being synthesised at an electrode area-normalised rate of $0.12 \text{ mol h}^{-1} \text{ m}^{-2}$. The remaining 28% of the charge passed was speculated to be consumed in the non-productive re-oxidation of nitride to nitrogen (Equation 8), which is a possible competing anode reaction.

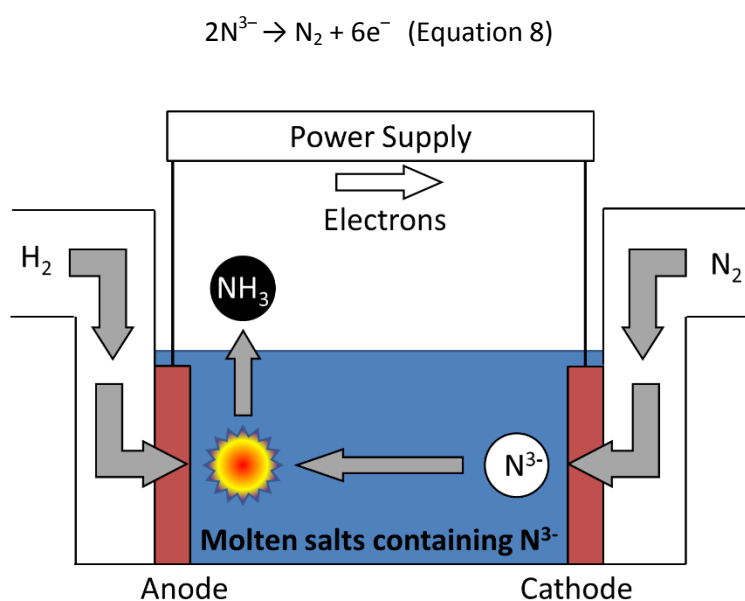


Figure 4. Ito's reactor for the electro-synthesis of ammonia in molten salt eutectics.¹⁸

Recently, the groups of both Ma and Tao have demonstrated increased rates of ammonia formation from nitrogen and hydrogen using more sophisticated ceramic electrode/electrolyte combinations. Ma's cell consisted of a $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\alpha}$ cathode, a porous nickel-based anode and an interstitial membrane of $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3-\alpha}$ as the solid-state electrolyte.²⁰ Under an applied current of 2 mA cm^{-2} at $530 \text{ }^\circ\text{C}$, a maximum rate of ammonia production of $0.15 \text{ mol h}^{-1} \text{ m}^{-2}$ was obtained with a Faradaic efficiency of H_2 conversion to NH_3 of 60%. Meanwhile, Tao and co-workers assembled a

cell that used a composite samarium-doped cerium / ternary carbonate (Li_2CO_3 - Na_2CO_3 - K_2CO_3) electrolyte with a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3.5}$ - $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2.6}$ composite cathode and a nickel oxide / samarium-doped cerium anode.²¹ The optimum rate of ammonia production of $0.19 \text{ mol h}^{-1} \text{ m}^{-2}$ was achieved at a cell bias of 0.8 V and a temperature of 450 °C. An overall electrical energy efficiency of 7700 kJ mol^{-1} of NH_3 produced has been estimated for this system by Hetterscheid and co-workers,⁶ which is an energy requirement around 15 times greater than that required by a Haber Bosch-type system even before the costs of obtaining H_2 for this electrosynthesis are considered. This in many ways indicates the scale of the challenge facing electrocatalytic methods of nitrogen reduction if they are ever to approach the efficiency of existing routes to NH_3 production.

As noted above, lower temperature devices reduce the extent of ammonia decomposition back to N_2 and H_2 . With this in mind, Liu and co-workers investigated the electrosynthesis of ammonia from nitrogen and hydrogen at atmospheric pressure and relatively low temperatures (up to 100 °C) in a cell containing a SmBaCuNiO_x nitrogen reduction cathode, a $\text{Ni-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2.6}$ ceramic pellet anode and using Nafion as the electrolyte.²² Nafion is used widely in numerous electrochemical devices such as hydrogen-oxygen fuel cells and proton-exchange membrane electrolyzers,²³ is physically very flexible, is produced on a large scale, and has excellent chemical and mechanical stability. An optimal rate of ammonia production of $0.31 \text{ mol h}^{-1} \text{ m}^{-2}$ was obtained from this cell at a temperature of 80 °C and a bias across the cell of 2.5 V. On account of the known practicality of Nafion in commercial electrochemical devices, cells such as this have great potential as the basis of low-temperature ammonia electrosynthesis platforms, provided the rate and efficiency of ammonia production can be kept acceptably high.

Finally in this section, Wessling and co-workers have recently used Rh and Ru catalysts on Ti felt supports as catalysts for the production of ammonia from N_2 and H_2 in aqueous acidic electrolyte. Ru was found to be the more desirable catalyst of the two, on account of its superior catalysis of ammonia production (a rate for NH_3 generation of $0.0043 \text{ mol h}^{-1} \text{ m}^{-2}$ was measured), its lower cost,

and because it is easier to plate onto the robust Ti support than Rh.²⁴ However, no Faradaic yields for ammonia production were quoted and we may speculate that significant H₂ evolution may have occurred, on account of precious metals such as Ru and Rh being good proton reduction catalysts. These results, and others from Section 2, are summarized in Table 1.

Table 1: Examples of systems that generate ammonia electrochemically from its elements with selected metrics and conditions. A “-” indicates that this data is not given in the source reference.

Entry	Electrolyte	Optimal Temperature (°C)	Optimal rate of NH ₃ production (mol h ⁻¹ m ⁻²)	Faradaic yield for NH ₃	Reference
1	1 M KOH	25	0.23	1.3%	10
2	SrCe _{0.95} Yb _{0.05} O ₃	570	0.18	>78%	11
3	LiCl-KCl-CsCl	450	0.12	72%	18
4	BaCe _{0.85} Y _{0.15} O _{3-α}	530	0.15	60%	20
5	Sm-doped Ce / (Li ₂ CO ₃ - Na ₂ CO ₃ - K ₂ CO ₃)	450	0.19	-	21
6	Nafion	80	0.31	-	22
7	0.5 M H ₂ SO ₄	30	0.0043	-	24

3. Electrochemical ammonia production using sacrificial proton donors

An alternative to the use of H₂ as a source of protons and electrons for N₂ hydrogenation is to use sacrificial reactants that are destroyed as they are oxidised. Whilst this is probably even less sustainable than a fossil fuel-fed Haber Bosch reactor, the use of sacrificial reagents that can be easily handled and added to the reduction reaction in specific amounts has historically allowed useful insights into the mechanism of NH₃ electrosynthesis to be gained. We shall briefly survey a few of the more seminal works in this area in this Section, before moving on to discuss the electrosynthesis of ammonia using water as the proton source in Section 4.

Perhaps the most important work in which sacrificial reagents were used in the electroreduction of N₂ to ammonia was performed in the mid-1980s by Pickett and Talarmin.²⁵ Building on Chatt's discovery that *cis*-[W(N₂)₂(PMe₂Ph)₄] reacts with protons to produce two equivalents of ammonia,²⁶ the authors reasoned that electroreduction of analogous tungsten complexes in the presence of nitrogen and a suitable proton source would lead to ammonia formation. Accordingly the authors reacted *trans*-[W(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂] with *p*-toluenesulfonic acid, and then performed controlled potential electrolysis on the resulting adduct in a THF-based electrolyte at a mercury electrode. As mercury is a very poor hydrogen evolution electrocatalyst, competing hydrogen evolution was thus kept to a minimum, allowing both NH₃ and hydrazine to be detected after electrolysis. Although a catalytic cycle was not possible with this system, it proved to be the first example of the electroreduction of nitrogen to ammonia at a well-defined, molecular and mononuclear complex by successive electron and proton transfers, with important implications for the study of both natural and artificial nitrogen reduction platforms. This approach was subsequently extended by Becker and Avraham to a range of other W and Mo complexes.²⁷

At around the same time as Pickett's study, Shilov, Strelets and co-workers reported a series of molybdenum complexes that mediated the electroreduction of nitrogen to ammonia at a mercury cathode.^{28,29} The reactions were conducted in basic methanolic solutions, suggesting that methanol was a sacrificial reagent providing the necessary protons. However, due to the amorphous nature of

the catalytic species and a lack of certainty over the optimal composition, firm conclusions on the nature of the most active catalyst from this system could not be obtained. Indeed, subsequent work by some of the same authors identified two possible catalysts: one containing Mo alone and one containing both Mo and Mg salts.³⁰

An alternative approach was taken by Sakata and co-workers, who hypothesized that the spontaneous reaction of lithium metal with nitrogen could be exploited to generate lithium nitrides, which could in turn be reacted with proton donors to give ammonia at room temperature (see Figure 5).³¹ Hence the authors reduced lithium salts in a mixed THF/ethanol solvent medium at very cathodic potentials (-4 V vs. Ag/AgCl), in the hope that lithium metal species would deposit on the cathode.

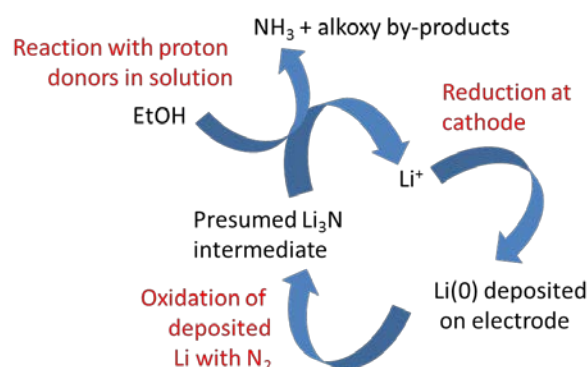


Figure 5. The putative cycle for Li-mediated electrosynthesis of ammonia as proposed by Sakata.³¹

Sakata's team explored numerous cathode materials for this reaction, and found that silver and titanium gave the best Faradaic yields for ammonia production under 1 atm. of N_2 (8.4 and 8.2% respectively). Electrodes such as copper displayed poorer efficiencies for NH_3 production due to their higher efficacy for hydrogen evolution under these conditions.³² Moreover, metals that readily form alloys with lithium (such as tin, lead and aluminium) were also found to give poor conversion efficiencies to ammonia, which lends credence to the proposed cycle in Figure 5: the lithium metal must be deposited on the electrode surface (and not alloyed with it) in order to form the nitride

intermediate. This intermediate then reacts with the ethanol in solution to produce ammonia. When ethanol was omitted, only traces of ammonia were produced, supporting the conclusion that ethanol is the source of protons for this reaction. The authors did not detect any hydrazine production with this system, which they suggested was evidence that the mechanism was *via* Li_3N species (*i.e.* implying a dissociative mechanism in which the $\text{N}\equiv\text{N}$ bond was broken before the formation of any N-H bonds). Intriguingly, the team were even able to use air as the nitrogen source, reporting a Faradaic yield of 3.7% for NH_3 production from air (1 atm.) and ethanol on a silver cathode. The reduced Faradaic efficiency in air compared to pure N_2 is presumably due to reaction of oxygen with the $\text{Li}(0)$ deposits to give lithium oxides in a wasteful side-reaction.

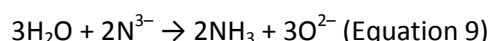
More recently than the examples given above, Köleli and Röpke reported the electroreduction of nitrogen to ammonia at polyaniline-decorated electrodes.³³ Hence polyaniline films were first deposited onto platinum supports from solutions of aniline in 0.5 M H_2SO_4 . These films were then transferred to a cell suitable for electrolyses at elevated pressures. In an electrolyte of methanol/ LiClO_4 containing 0.03 M H_2SO_4 as a proton source, reduction at -0.12 V vs. NHE under 50 atm. of nitrogen gave an optimum Faradaic yield for ammonia production of 16%. The efficiency for conversion to ammonia under 1 atm. of nitrogen was only 1.3%, which the authors attributed to the lower concentration of N_2 in solution at lower pressures. If the acid was omitted from the electrolyte, no ammonia was produced. However, if concentrations greater than 0.03 M were used, competitive hydrogen evolution prevented any ammonia from being generated. A subsequent study of the same materials as cathodes for the electrochemical reduction of N_2 in an all-aqueous system (0.1 M Li_2SO_4 / 0.03 M H_2SO_4) also produced ammonia, although no Faradaic yield or rate were quoted.³⁴ These results were intriguing in suggesting that metals catalysts are not essential for N_2 electroreduction to ammonia, of which we shall see another example in Section 4.2.

4. Electrochemical ammonia production using water as the proton source

As mentioned in the Introduction, water is a ubiquitous and sustainable source of protons and electrons for nitrogen hydrogenation to ammonia. Electrochemical systems employing water in this fashion have (in theory at least) the advantage of being able to oxidise water to O₂, protons and electrons at the anode and then feed these protons and electrons to N₂ at the cathode, co-generating O₂ and NH₃ in the same device (see Equations 3-5). In practice, reducing N₂ at the cathode in preference to forming H₂ from these protons and electrons is extremely challenging. However, some progress has been made in this regard in recent years, and we shall examine a cross-section of the key literature in this field in Section 4. This Section is further sub-divided into those cells that operate above 100 °C (and hence employ water vapour as the proton source, Section 4.1) and those operating at temperatures below 100 °C (and therefore using liquid water, Section 4.2). The key data from Sections 4.1 and 4.2 are summarised in Table 2.

4.1 Ammonia electrosynthesis using water as the proton source at temperatures above 100 °C

Based on their results showing nitride formation by reduction of N₂ in molten salt eutectics,¹⁹ the Ito group have also demonstrated the electrosynthesis of ammonia from water vapour and nitrogen at 300 °C.³⁵ The system was operated on a batch-type basis. Initially, Li₃N was added to the LiCl-KCl-CsCl eutectic as a nitride source, without the application of any bias. Water vapour was supplied to the melt in the form of a stream of wet argon, with the conversion of this water to ammonia being essentially quantitative. This was hypothesised to leave behind O²⁻ ions in the eutectic according to the equation:

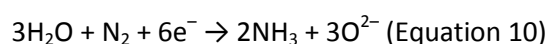


The cell was then placed under a nitrogen atmosphere and a bias of 2.9 V (vs. Li⁺/Li) applied to the glassy carbon anode. This led to the removal of the O²⁻ ions from the melt as both O₂ and CO₂ (the

latter by reaction with the electrode under anodic bias), whilst N_2 was reduced to N^{3-} at the counter electrode. Once all the O^{2-} ions had been removed from the melt in this way (and the electrolyte replenished with nitride ions), water vapour was again passed through the eutectic to generate NH_3 and the cycle was repeated. An overall Faradaic yield for ammonia production of 23% was reported, with the remaining charge suggested to be consumed in the non-productive re-oxidation of nitride to N_2 (as in Equation 8), or in the reduction of any unreacted water to hydrogen. The rate of ammonia production was dominated by the time required for electrolysis (around 1 hour, compared to the $\text{H}_2\text{O}/\text{Ar}$ bubbling step which took only 30 seconds) and was found to be $0.72 \text{ mol h}^{-1} \text{ m}^{-2}$. Some of the same authors later showed that substitution of the glassy carbon anode for boron doped diamond allowed the O^{2-} ions to be removed from solution exclusively as O_2 (which would therefore be more environmentally sustainable in any large scale process), with initial Faradaic yields for this process as high as 80%.³⁶ However, these yields again fell off on account of nitride re-oxidation to nitrogen. The electrical energy consumption for this process has been calculated as 3100 kJ mol^{-1} of ammonia produced,⁶ making this system around six times less efficient overall than the Haber Bosch process. In terms of efficiency and overall rate of NH_3 production, this represents a high-water mark for NH_3 electrosynthesis from N_2 and H_2O . The Ito group have also demonstrated that ammonia can be produced by an analogous process, but using HCl as the proton donor.³⁷ In this case, the nitride reacts with bubbled HCl gas to produce ammonia and chloride ions. These chloride ions can then be removed from the melt electrolytically as Cl_2 .

Stoukides has also extended his solid-state reactor approach (see Figure 2) to the electrosynthesis of ammonia from nitrogen and steam using cells containing both proton-conducting and O^{2-} -conducting electrolytes.³⁸ In the proton-conducting device, a $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ membrane was employed as the electrolyte, onto which a Pd anode and a commercial Ru/MgO ammonia synthesis catalyst cathode were deposited. As the electrical conductivity of the Ru/MgO catalyst was low, a thin layer of Ag was deposited on the electrolyte in-between the ceramic and the Ru/MgO. At 650°C , a stream of wet helium gas was fed to the anode side of the cell. The H_2O in this feed was

oxidised at cell voltages of 2 V to give oxygen, protons and electrons. These protons travelled through the membrane to the cathode compartment, where reduction of N₂ occurred to give NH₃. An optimum rate of NH₃ production of around 1.4 × 10⁻⁵ mol h⁻¹ m⁻² was reported. A very similar rate was obtained in an analogous cell based on the O²⁻-conductor yttria-stabilized-zirconia. In this cell, the anode was Ag and the cathode was again Ru/MgO. Both nitrogen and steam were supplied to the cathode chamber where the following reduction occurred:



The O²⁻ ions then migrated through the membrane to the anode where they were oxidised to O₂. Optimal performance was again reached at 650 °C with a 2 V bias across the cell. The poor rates of ammonia production in both configurations were attributed to the low electrical conductivity of the Ru/MgO catalyst, and the tendency for parasitic hydrogen evolution to occur on the Ag film that was deposited on the electrolyte membrane to mitigate this lack of conductivity. Nevertheless, this work gave the first examples of ammonia synthesis from N₂ and H₂O (as opposed to N₂ and H₂) in cells using solid-state electrolytes. For a short review focusing specifically on solid state ammonia production methods, the reader is directed to Reference 39.

In a similar vein, Amar *et al.* reported the electrosynthesis of ammonia from wet nitrogen in a mixed metal oxide / carbonate salt electrolyte cell where O²⁻ ions were again the charge carriers.⁴⁰ A calcium-gadolinium-doped-ceria (Ce_{0.8}Gd_{0.18}Ca_{0.02}O_{2-δ}) perovskite-based oxide was used throughout the device as a support for the anode, cathode and electrolyte. The nitrogen reduction cathode consisted of La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-δ} and the anode was Sm_{0.5}Sr_{0.5}CoO_{3-δ}. In-between these catalysts, the separating membrane was impregnated with a ternary carbonate (Li₂CO₃- Na₂CO₃- K₂CO₃) electrolyte as a conductor for O²⁻ ions. At 375 °C and an applied bias of 1.4 V across the cell, ammonia was formed at a rate of 0.014 mol h⁻¹ m⁻² with a Faradaic efficiency of 3.9%. The same group have also reported the direct synthesis of ammonia from wet air (as opposed to wet N₂) in a single chamber reactor that generates NH₃ at a rate of 0.004 mol h⁻¹ m⁻² and with a peak Faradaic

yield for ammonia of over 5%.⁴¹ The cell employed a tri-layer design, where both the anode and cathode catalysts were $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ supported on a composite $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ matrix. In-between these catalyst layers, the supporting matrix was again impregnated with a ternary carbonate (Li_2CO_3 - Na_2CO_3 - K_2CO_3) electrolyte as a conductor for O^{2-} ions. The optimal yields of ammonia stated above were achieved at 400 °C and 1.4 V bias across the cell.

Yoo and co-workers compared the rates of ammonia formation from steam and nitrogen in all-solid state cells that used $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ as the proton-conducting electrolyte (selected due to its high chemical stability) and three different catalysts: Ag, Pt and the mixed oxide $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$.⁴² Three different cells were thus constructed, where the anode and cathode catalysts were both the same in the respective cells. The cell using Pt anode and cathode catalysts displayed negligible NH_3 production, possibly on account of Pt being an excellent hydrogen evolution electrocatalyst and therefore performing this reaction in preference to nitrogen reduction. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ was found to be the most effective catalyst over short timespans (the rate of NH_3 production at 550 °C was $0.0031 \text{ mol h}^{-1} \text{ m}^{-2}$ with a Faradaic yield of 0.33%), but this performance could not be sustained due to delamination of the electrocatalyst from the solid electrolyte. Silver was therefore the preferred catalyst as it exhibited greater stability under operation (see Table 2).

Exciting recent work in this area has been performed by Licht *et al.*, who have examined the electrosynthesis of ammonia from air and steam in a molten salt electrolyte at modest temperatures (200 – 250 °C).⁴³ These comparatively low temperatures were made possible by using a 1:1 NaOH-KOH eutectic. A schematic of the cell set-up is given in Figure 6.

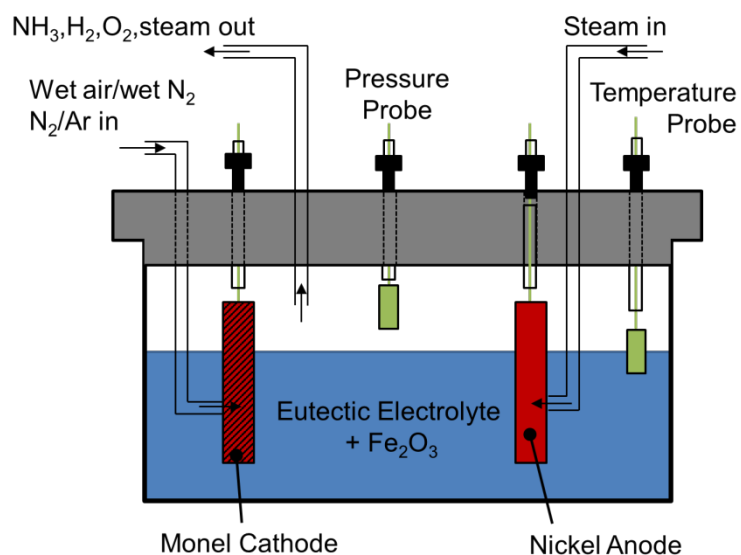
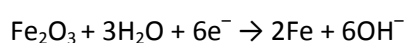


Figure 6. Licht's reactor for the electro-synthesis of ammonia from air and water in a low-temperature eutectic.⁴³

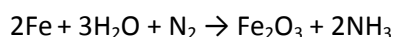
Under a cell bias of 1.2 V at 200 °C (giving a total current density of 2 mA cm⁻²), nitrogen was introduced into the electrolyte through a porous Monel (Ni-Cu alloy) cathode, whilst water vapour was supplied to the nickel anode. When finely divided Fe₂O₃ (of diameter 20 – 40 nm) was added to the electrolyte under these conditions, ammonia was produced at a rate of 0.086 mol h⁻¹ m⁻² and a maximal Faradaic efficiency of 35%. This is the highest Faradaic yield for electrolytic ammonia production using water as the proton source yet reported (see Table 2) and crucially this yield was not significantly affected by replacing the N₂ feed with air. However, using the methods of Hetterscheid and co-workers,⁶ the overall efficiency of this system is still sub-optimal, requiring around 1000 kJ per mole of NH₃ that is produced (at a current density of 2 mA cm⁻²). The remaining electrons not used in ammonia production were consumed in hydrogen production. The rate of ammonia production was found to increase with increasing cell potential (and hence increasing current density), being 0.24 mol h⁻¹ m⁻² at 25 mA cm⁻² and 0.36 mol h⁻¹ m⁻² at 200 mA cm⁻². However, the Faradaic yield for ammonia decreased with increasing cell potential as competitive hydrogen evolution became more and more dominant. The energy efficiency for ammonia

production also decreased for the same reason. Subsequently, Li and Licht were able to prevent any hydrogen formation and increase the Faradaic yield of NH₃ to 71% by operating at even lower current densities (0.7 mA cm⁻², produced at cell voltages ~1 V), although the overall rate of production of ammonia was naturally much slower at these low biases.⁴⁴

The Licht group have also gone some way towards establishing the mechanism of this N₂ reduction reaction. For example, in the absence of Fe₂O₃ nanoparticles, no ammonia is formed regardless of cell potential or the nature of the feed gases, implying a strict requirement for the iron catalyst. Moreover, in a reaction medium containing Fe₂O₃ nanoparticles but with no applied bias, no ammonia is formed whether N₂ and water vapour or N₂ and H₂ are supplied to the cell. This implies that the iron oxide is not simply functioning as a catalyst for the thermodynamically-downhill formation of NH₃ from N₂ and H₂ (whether the H₂ is fed to the cell directly, or produced electrolytically by the reduction of water vapour).⁴³ Instead, it seems that electron transfer from the cathode to the Fe₂O₃ nanoparticles is a necessary step in the mechanism, in support of which the authors found that Fe metal powder reacts with nitrogen and water to produce ammonia at a rate which increases with decreasing particle size. Hence the authors suggested the following key steps in the nitrogen reduction mechanism:⁴⁴



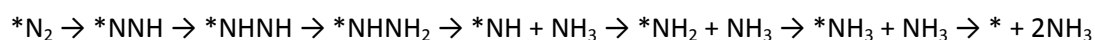
(Reduction of iron oxide nanoparticles at the cathode)



(Chemical reduction of N₂ to ammonia at Fe particles in the electrolyte)

A computational modelling study on this system has been described recently, in which density functional theory was used to evaluate the various pathways for NH₃ formation on hematite.⁴⁵ It was found that an associative mechanism is more energetically favourable, proceeding first by adsorption of N₂ to the surface (indicated as *N₂), and then proceeding through sequential coupled

electron and proton transfers from the electrode and electrolyte respectively (a Heyrovsky mechanism) according to the scheme:



where * is a surface binding site. Of these steps, the initial formation of *NNH (*i.e.* the first proton-coupled-electron transfer to adsorbed nitrogen) was found to be the most difficult, requiring around 1.14 eV in order for the proton transfer to be spontaneous. This agrees well with the cell biases (~1.2 V) that were found to be required experimentally by Licht *et al.*⁴³ The authors of this computational study went on to suggest that hematite itself could be used as a cathode material in such cells in future, in place of the nickel-based materials used in Licht's original reports.

4.2 Ammonia electrosynthesis using water as the proton source at temperatures below 100 °C

The use of temperatures below 100 °C, in conjunction with using water and air as the reactants for ammonia synthesis has long been seen as something of a Holy Grail in the field, as these conditions approach those under which the nitrogenases operate. In this subsection, we will briefly review some of the classical electrochemical literature in this area, before moving on to some current examples of devices that produce NH₃ under these very mild conditions.

In the late 1960s, van Tamelen and Seeley reported that the reduction of titanium isopropoxide species under an N₂ atmosphere at an aluminium cathode gave rise to ammonia upon subsequent hydrolysis of the electrolyte solution with aqueous sodium hydroxide.⁴⁶ Yields of ammonia of up to 600% (based on the amount of titanium complex present) were reported. This quite possibly constitutes the earliest claim of electrocatalytic ammonia production from N₂ using water as the ultimate proton source. However, as the aluminium cathode is consumed during this process (by

conversion first to aluminium nitride and then likely becoming Al_2O_3 upon hydrolysis, according to the authors), the overall process does not lend itself to large-scale production.

Subsequently, a mixed $\text{Ti}(\text{OH})_3$ -Mo(III) system produced by the electroreduction of MoCl_5 and TiCl_4 in sodium methylate at a mercury pool electrode was reported by Gorodyskii *et al.* to mediate the reduction of nitrogen to ammonia when poised at -1.9 V vs. SCE (the standard calomel electrode).⁴⁷

The authors noted that addition of up to 3% water into the electrolyte was necessary in order to obtain any NH_3 , which suggested that water was the ultimate source of protons in this synthesis.

In 1983, Sclafani and co-workers moved into purely aqueous electrolytes and reported the electroreduction of nitrogen to ammonia in 6 M KOH solution at an iron cathode.⁴⁸ At 45 °C, a peak rate of ammonia electrosynthesis of 0.5 μmol per hour was obtained at a potential of -1.07 V vs. SCE, with a Faradaic yield of around 1%. Lowering the temperature to 25 °C was found to lower the rate of NH_3 formation, but had little effect on the Faradaic yield. In contrast, applying reduction potentials more cathodic than -1.07 V vs. SCE led to a significant reduction in the overall Faradaic yield for ammonia production, which was attributed to increased competitive absorption of hydrogen rather than nitrogen on the electrode, and hence an increased level of undesired H_2 evolution.

At the turn of the century, Kordali *et al.* employed a solid polymer electrolyte cell containing both a Nafion membrane and a liquid electrolyte (2 M KOH) in order to produce ammonia from nitrogen and water at temperatures in the range 20 – 100 °C (see Figure 7).⁴⁹ The cathode was formed from Ru electrodeposited on carbon felt and the anode was Pt. Optimal performance was obtained at 90 °C, at which the rate of ammonia production was 7.2×10^{-4} mol h^{-1} m^{-2} and the Faradaic yield for ammonia approached 1%. As in previous attempts to produce ammonia in aqueous solution, the efficiency of the process was severely hampered by hydrogen evolution at the cathode occurring in preference to nitrogen reduction. This prevented efforts to improve the rate of production by using more cathodic reduction potentials: the rate of ammonia production was actually found to decrease

with more cathodic potentials (much as in the study by Sclafani⁴⁸) as hydrogen production became more and more dominant.

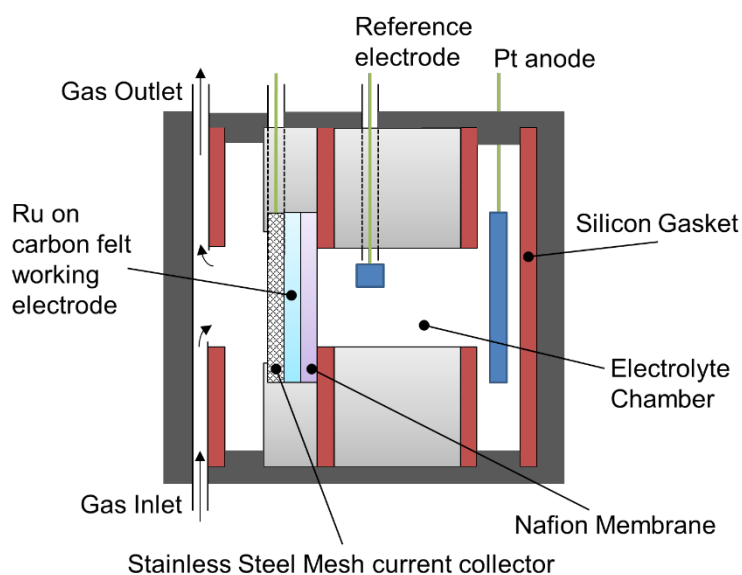


Figure 7. The Nafion/liquid electrolyte ammonia synthesis cell reported by Kordali et al.⁴⁹

Non-metal catalysts have also been reported to be capable of N_2 reduction to ammonia using water as the ultimate proton and electron source. To this end, Pospíšil and co-workers used C_{60} encapsulated in γ -cyclodextrin as an electron relay for ammonia electrosynthesis in 0.1 M KCl at 60 °C,⁵⁰ building on earlier work showing that C_{60} was able to mediate the photochemical reduction of N_2 to NH_3 in the presence of chemical reductants.⁵¹ In Pospíšil's electrochemical system, potentials of -1.2 V vs. Ag/AgCl were applied using a mercury pool cathode, which reduced the C_{60} - γ -cyclodextrin complexes by two electrons in two successive one-electron steps. This reduced relay species was then postulated to react with N_2 to produce N_2H_2 , which was then reduced to ammonia either by direct electron transfers from the electrode or by electron transfers from other reduced relay complexes.⁵² The use of the cyclodextrin was critical in ensuring that the C_{60} species were sufficiently water-soluble for this chemistry to occur. Moreover, as mercury has a very large overpotential requirement for the hydrogen evolution reaction, competitive formation of H_2 during

reduction was minimised. This work shows some parallels with Köleli's earlier reports of N_2 reduction on polyaniline cathodes^{33,34} in suggesting that ammonia electrosynthesis is possible in metal-free systems.

More recently, Lan *et al.* have reported the direct synthesis of ammonia from air and water in a back-to-back membrane electrode assembly-type cell using a Nafion electrolyte and Pt/C as both the anode and cathode (see Figure 8).⁵³ At 25 °C and a cell bias of 1.8 V, the maximal rate of ammonia production using air as the nitrogen source was measured as being $0.04 \text{ mol h}^{-1} \text{ m}^{-2}$ (up to $0.126 \text{ mol h}^{-1} \text{ m}^{-2}$ was possible when pure N_2 was used in place of air). The Faradaic yield for ammonia production from air was around 0.5%, largely on account of competing hydrogen evolution from the aqueous reaction medium (Pt/C is an excellent hydrogen evolution electrocatalyst). The same authors subsequently improved the Faradaic efficiency of this system to 0.8% by moving to an operating temperature of 80 °C and a cell bias of 1.2 V.⁵⁴

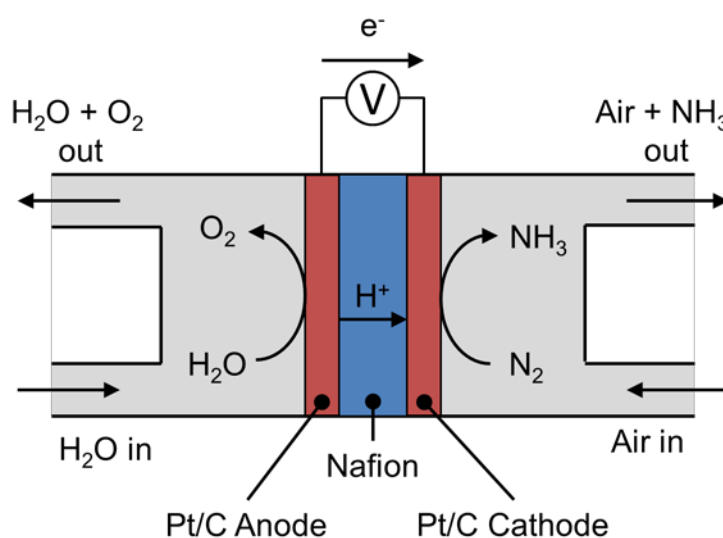


Figure 8. The back-to-back membrane-electrolyte-assembly cell for ammonia synthesis reported by Lan *et al.*⁵³

Table 2: Examples of systems that generate ammonia electrochemically using water as the proton source, together with selected metrics and conditions. A “-” indicates that this data is not given in the source reference. Cell biases are given as absolute voltages applied across the cell (two-electrode configuration) unless noted otherwise. ^a Reference vs. Li⁺/Li. ^b With Ag as the electrode material. ^c At a current density of 2 mA cm⁻². ^d Reference vs. Ag/AgCl.

Entry	Electrolyte	Cell Bias (V)	Optimal Temperature (°C)	Nitrogen source	Optimal rate of NH ₃ production (mol h ⁻¹ m ⁻²)	Faradaic yield for NH ₃ (%)	Reference
1	LiCl-KCl-CsCl	2.9	300	N ₂	0.72	23	35
2	SrCe _{0.95} Yb _{0.05} O _{3-α}	2	650	N ₂	1.4 × 10 ⁻⁵	-	38
3	Ce _{0.8} Gd _{0.18} Ca _{0.02} O _{2-δ} / Li ₂ CO ₃ - Na ₂ CO ₃ - K ₂ CO ₃	1.4	375	N ₂	0.014	3.9	40
4	Ce _{0.8} Gd _{0.2} O _{2-δ} / Li ₂ CO ₃ - Na ₂ CO ₃ - K ₂ CO ₃	1.4	400	Air	0.004	5.3	41
5	BaZr _{0.8} Y _{0.2} O _{3-δ}	0.8	550	N ₂	0.0018	0.46 ^b	42
6	NaOH / KOH	1.2	200	Air	0.0864	35 ^c	43
7	2 M KOH	1 ^d	90	N ₂	7.2 × 10 ⁻⁴	0.9	49
8	Nafion	1.8	25	N ₂	0.126	0.7	53
9	Nafion	1.8	25	Air	0.040	0.5	53
10	Nafion	1.2	80	Air	0.034	0.83	54

5. Recent Theoretical Insights into Electrocatalytic Nitrogen Reduction

The foregoing discussion describes approaches towards the electrosynthesis of NH_3 driven largely by experiment and chemical intuition. Within the last four or five years however, there has been increased interest in electrocatalytic N_2 reduction from a theoretical standpoint. These studies are often interested in suggesting materials on which the reduction of water or protons might be suppressed, in favour of the reduction of N_2 to ammonia in aqueous media. As this is perhaps the biggest single challenge within the whole subject area of “The Electrosynthesis of Ammonia from Sustainable Resources” it is pertinent here to review some of the key findings of these modelling studies and how they might influence future approaches to electrochemical ammonia production.

In a landmark paper in 2012, Skúlason *et al.* undertook a theoretical analysis of the electrochemical formation of ammonia on pure transition metal electrodes and calculated trends in the expected catalytic activity at various applied bias potentials.⁵⁵ Volcano diagrams were created showing the most active surfaces, with Mo, Fe, Rh, and Ru predicted to be the most active for NH_3 generation. However, these same surfaces were also predicted to be more effective at promoting hydrogen formation than N_2 reduction. In order to circumvent excessive competing hydrogen evolution, the authors suggested that the surfaces of the early transition metals (*e.g.* Sc, Y, Ti, and Zr) should be examined as nitrogen reduction electrocatalysts. These early transition metals bind N-adatoms more strongly than they bind H-adatoms. Hence in a dissociative mechanism (where nitrogen and hydrogen atoms do not react until the $\text{N}\equiv\text{N}$ and H-H bonds have been broken) these surfaces should be covered to a significant degree in N-adatoms. Protons from the electrolyte would then add directly to these adsorbed nitrogen centres in a Heyrovsky-type reaction, forming ammonia (rather than H_2 , which by contrast would occur by a combination of electrolyte protons with adsorbed hydrogen). Potentials of between -1 and -1.5 V (vs. NHE) were suggested for this ammonia-producing process on the early transition metals. These findings were also held to account for the generally poor rates of ammonia production compared to hydrogen production in much of the

existing literature: according to this analysis, the commonly used Ru and Pt electrodes would be covered with adsorbed hydrogen at negative bias, preventing nitrogen from accessing the surface in order to bind and become reduced. Hence it was suggested to use metals such as Sc, Y, Ti, and Zr such that N-adatoms would bind more strongly than H-adatoms, and thus favour NH_3 formation over H_2 formation. To our knowledge, however, no experimental verification (or refutation) of these predictions has yet been reported.

An alternative strategy to disfavour competitive hydrogen evolution would be to consider using cathodes other than the pure metals. In this regard, recent modelling of metal nitrides as cathodes for nitrogen reduction suggests that ZrN and VN would form ammonia at potentials of -0.76 V and -0.51 V (vs. NHE) respectively: potentials at which these nitrides would not be covered in adsorbed H-atoms.⁵⁶ NbN and CrN may also act in a similar fashion.⁵⁷ As yet, it would again seem that no such nitride materials have been tested experimentally as cathodes for nitrogen electroreduction, and so it would be very interesting to see if they performed as anticipated in real-world situations. It would also be very useful if the same kind of theoretical investigations that have been performed on these simple nitrides could be extended to binary nitrides. Species such as $\text{Co}_3\text{Mo}_3\text{N}$ are amongst the most active catalysts for ammonia synthesis,⁵⁸ and their catalytic properties under conventional Haber Bosch conditions have recently been modelled.⁵⁹ A thorough investigation of their electrocatalytic properties, both from a theoretical and an experimental viewpoint, seems warranted.

5. Conclusions

In this review, we have examined some of the seminal literature describing the electrosynthesis of ammonia from commonly available feedstocks. Systems that use purified H_2 and N_2 tend to display the highest Faradaic yields and conversion rates, but by using the same starting materials as the Haber Bosch process they surrender a key potential advantage of an electrochemical approach: the ability to generate protons *in situ* from sources other than fossil fuels. Water is an obvious candidate

for this latter purpose, and it is encouraging that systems where water and nitrogen are used as the starting materials for generating ammonia have been reported. Even more encouragingly, there are now examples of systems where air and water can be used as the feedstocks. This opens up the possibility that ammonia synthesis devices could be scaled down to sizes suitable for decentralized production, where the only requirements would be supplies of water, air and electricity. Fertiliser production could therefore become a more democratic process, and ammonia might even find utility as a carbon-neutral fuel produced at a local scale using renewable power.⁶⁰

The challenges facing this vision are still enormous, however. In any system where water is present, suppression of competing hydrogen evolution will be crucial. This is the single biggest reason behind the low Faradaic yields reported for ammonia synthesis from water-fed devices. Heterogeneous catalysts that bind nitrogen atoms to their surfaces more strongly than they bind hydrogen atoms may reduce hydrogen evolution, but this seems likely to require employing catalysts that are not optimal for the nitrogen reduction reaction itself, such as the early transition metals.⁵⁵ Then again, given the thermodynamics of the nitrogen hydrogenation reaction, low temperature devices are to be favoured in order to prevent the wasteful decomposition of NH_3 into H_2 and N_2 . The precise balance in temperature necessary in order to minimise the required cell potentials and maintain suitable rates for N_2 reduction on the one hand and to reduce NH_3 decomposition on the other will vary depending on the design of system in question and the materials from which the cell is constructed. Systems operating using water vapour inputs at temperatures between 100 and 300 °C may well prove to be the most effective in this regard.

Assuming that hydrogen production can be completely suppressed by selective catalysts and optimal operating conditions, what are the prospects for electrochemical ammonia-producing cells displacing the Haber Bosch process as the chief means of generating NH_3 in the near future? According to the calculations of Skúlason *et al.*,⁵⁵ no catalytic activity is expected above -0.5 V vs. NHE for NH_3 production on pure transition metal surfaces, equivalent to an energy input of 288 kJ

mol^{-1} .⁶ It is possible that more efficient catalysis could be achieved with composite or molecular catalysts, and in this regard we note that Schrock,⁶¹ Peters,⁶² Nishibayashi⁶³ and others⁶⁴ have all reported molecular systems which yield ammonia upon reduction in the presence of a proton source (we also note that although these systems have yet to be driven electrochemically, there remains the prospect that they could be). In terms of pure transition metal surfaces, the value of 288 kJ mol^{-1} of ammonia produced quoted above is already greater than the minimum required by the nitrogenase enzymes and leaves little scope for significantly improving on the efficiency of Haber Bosch process. Thus it seems that although there are several reasons as to why we might wish to investigate electrochemical alternatives to the Haber Bosch process (*e.g.* the ability to work at both large and small scales, with minimal infrastructure and using only sustainable, widely available resources), increased overall efficiency is unlikely to be a driver of innovation in this area. One thing, however, is almost certainly true. As a prominent electrochemist in his day,⁶⁵ Haber would have approved of the ongoing search to find an efficient route to the electrosynthesis of ammonia.

6. Acknowledgments

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