

Overcoming Chemical Inertness under Ambient Conditions: A Critical View on Recent Developments in Ammonia Synthesis via Electrochemical N₂ Reduction by Asking Five Questions

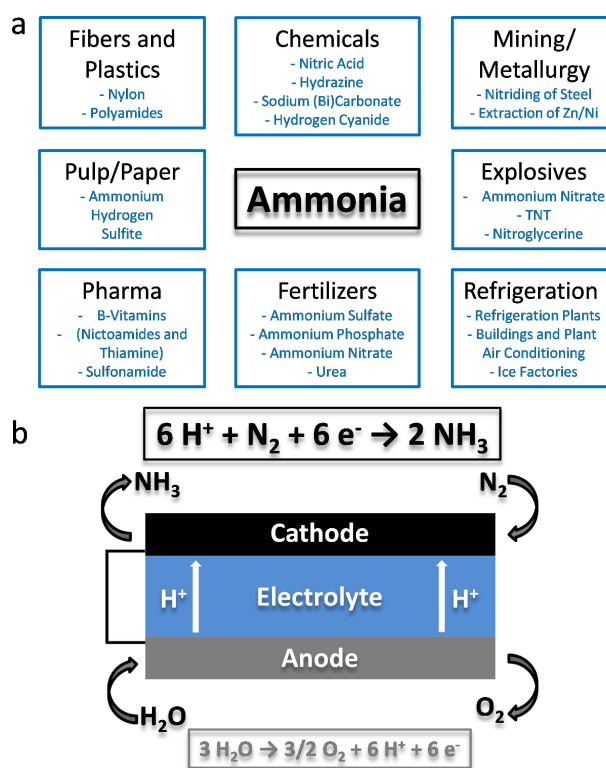
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Ammonia (NH₃) synthesis by the electrochemical N₂ reduction reaction (NRR) is increasingly studied and proposed as an alternative process to overcome the disadvantages of Haber-Bosch synthesis by a more energy-efficient, carbon-free, delocalized, and sustainable process. An ever-increasing number of scientists are working on the improvement of the faradaic efficiency (FE) and NH₃ production rate by developing novel catalysts, electrolyte concepts, and/or by contributing theoretical studies. The present Minireview provides a critical view on the interplay of different crucial aspects in NRR from

the electrolyte, over the mechanism of catalytic activation of N₂, to the full electrochemical cell. Five critical questions are asked, discussed, and answered, each coupled with a summary of recent developments in the respective field. This article is not supposed to be a complete summary of recent research about NRR but provides a rather critical personal view on the field. It is the major aim to give an overview over crucial influences on different length scales to shine light on the sweet spots into which room for revolutionary instead of incremental improvements may exist.

1. Is There a Real Need for an Alternative Ammonia Production Route

Ammonia (NH₃) is one of the most important commodity chemicals used in industry and agriculture.^[1] It plays a major role for the production of agricultural fertilizers and other nitrogen-containing compounds like nitrates, amines, and nitric acid (Figure 1a). Ammonia is thus one major reason for the explosion of the world population after the industrial revolution.^[2] In the last years, this molecule also became increasingly attractive as a chemical energy carrier.^[3] In the early 20th century, it has been realized that the earth-abundant chemically useful nitrogen deposits in form of Chilean saltpetre would not be enough to satisfy future demands for chemically usable nitrogen-containing compounds. Whilst ammonia can be metabolized by most organisms, N₂ is a very non-reactive molecule with a dissociation enthalpy of the N≡N triple bond of ~945 kJ/mol, a negative electron affinity, and high ionization energy.^[4] N₂ is metabolically by far less useful than other nitrogen-containing species. Only a few microorganisms known as diazotrophs can fix N₂ by using enzymes called



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Figure 1. a) The use of ammonia as a commodity chemical. b) Operating principle of an electrochemical NRR cell.

nitrogenases.^[5] However, biological nitrogen fixation has a low space-time yield and did not become an option for large-scale synthesis of chemically useful nitrogen-containing compounds. In consequence, an industrial process for artificial synthesis of

chemically useful nitrogen compounds from dinitrogen (i.e., for “artificial nitrogen fixation”) was needed. For about 100 years, NH_3 is mainly produced from N_2 and H_2 in their elemental forms by the Haber-Bosch (H-B) process under energy-intensive conditions at high temperature (350–550 °C) and high pressure (150–350 atm), most often with iron-based catalysts. The world population could increase significantly after this process has been brought to scale. The high temperature is needed to achieve reasonable reaction rates whereas the high pressure is necessary to counterbalance the thermodynamically unfavorable chemical equilibrium of the exothermic reaction at high temperature. In addition, steam reforming of fossil natural gas is the major route to supply H_2 for the synthesis gas mixture, resulting in large energy consumption and CO_2 release.^[6] Due to the need for steam reforming and the energy required for heating and compression, NH_3 synthesis is responsible for ~2% of the world energy consumption and ~1% of the greenhouse gas emissions (~1.87 tons of carbon dioxide are produced per ton of NH_3).^[7] 20–40 GJ are needed to produce 1 t of NH_3 .^[7b] A further problematic aspect that is sometimes overlooked is the very localized character of NH_3 production.^[7a] H-B plants are huge facilities with large capacity to decrease production costs. Ammonia and fertilizers produced must be transported over long distances to the final consumers. An obvious consequence is that farmers in inner Africa have to pay more than twice as much for fertilizer than farmers in Europe have to.^[8] This problem would remain if H_2 from electrochemical water splitting would be used. Taking these facts into consideration, a more sustainable and carbon-free process for NH_3 production from N_2 is urgently needed to replace or complement Haber-Bosch synthesis. The electrochemical N_2 reduction reaction (NRR) is a promising candidate for that from more than one perspective (Figure 1b).^[1a,6a,9,10] Such a process combines electrochemical water splitting and ammonia production into one and the same electrochemical cell in a process according to $3\text{H}_2\text{O} + \text{N}_2 \rightarrow 2\text{NH}_3 + 3/2\text{O}_2$. H_2 production by water splitting still has a high energy demand but it has no carbon footprint if renewable electricity is used. Excess electrical energy could be directly stored into chemical energy in the form of a useful commodity chemical. Such a “power-to-ammonia process” enables the sustainable and decentralized production of NH_3 . Ammonia and

thus fertilizer could be generated under ambient conditions wherever electricity from renewable sources is available and would not have to be transported over long distances anymore.

Date back to the history, the first electrochemical NRR experiment was carried out by Humphrey Davy in 1807,^[11] although it was unreproducible.^[12] Due to the lack of techniques to detect NH_3 and the lack of understanding about the reaction mechanism, electrochemical NRR developed slowly. Unlike as in electrochemical CO_2 reduction with many different products (due to different possible valence states of carbon atoms and various products resulting from C–C coupling),^[13] there are mainly two possible reduction products for NRR, namely NH_3 and N_2H_4 . The latter is much more difficult to be obtained. As a side note, it should be mentioned that in the literature about catalyst and process development for NRR it is often checked that no hydrazine is formed. This is of course important to make sure that the calculated efficiency for NH_3 production is correct but as a follow-up product of NH_3 , N_2H_4 is not at all a useless and possibly an even more valuable product of NRR than NH_3 . Theoretically, if sufficiently high potential is applied to overcome the corresponding reaction overpotential, N_2 can be converted to NH_3 on the surface of any electron conducting material. In recent years, significant efforts have been made in the development of catalytic materials for NRR.^[14] However, the faradaic efficiency (FE) and NH_3 production rate still remain limited. The big challenges for NRR are the competition from hydrogen evolution reaction (HER) especially in aqueous electrolyte and the inertness of $\text{N}\equiv\text{N}$ bond.^[15] The fundamental role of an NRR catalyst is to promote the activation of N_2 molecules. In the past few decades, many scientists have been devoted to study electrochemical NRR by using advanced equipment, designing new catalysts and to understand mechanisms of this complex 6-electron transfer reaction from DFT calculations.^[16] Although some progress has been achieved, there are still a couple of major obstacles for improving the performance of electrochemical NRR in order to establish it as an alternative to the Haber-Bosch process on scale.

The answer to the first question is definitely “yes” and it is the major aim of this short review article to discuss and respond to four additional fundamental questions about the process of NRR. At first, mechanistic aspects will be discussed because the



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targeted development and real improvement of catalysts will always require (from the one viewpoint), or lead to (from the other viewpoint) a profound understanding about the reaction mechanism. In the following, the two most important compounds in a NRR setup which are the electrolytes and the electrocatalysts will be in focus. The article closes with a rather general view on the question where the largest room for improvement for the efficiency of NRR in the future can be seen.

2. Are the Individual Steps and the Overall Process of Electrochemical NRR Fully Understood Yet

Understanding the mechanisms and activation barriers involved into (electro)catalytic reactions can help scientists to develop strategies to tailor the catalysts and improve the overall processes. In view of the large number of recently reported materials with catalytic activity for NRR, the above question cannot be simply answered with “yes” or “no”. For the surface of a metallic catalyst like iron, cobalt or ruthenium, models are rather established and calculations close to reality can indeed be applied to get a realistic image about catalytic mechanisms. For other reactions, like the activation of dinitrogen on the oxygen vacancies of transition metal oxides, it is more difficult to draw accurate conclusions, most likely because it is often complicated to develop a reliable structure model for such N₂ activation sites. Proper consideration of the applied electric potential on the electrocatalysts and the similar presence of the electrolyte remain other critical problems. In conclusion, although many efforts have been carried out to understand the mechanisms behind NRR, the question has to be answered with “no – but for some catalytic systems it is understood better than for others” from our point of view.

In the following chapter, we will give a brief overview over the existing knowledge the process of electrochemical NRR including adsorption, activation, and the final hydrogenation of N₂. Proposed strategies for controlling and improving each individual step are also introduced and discussed with a special focus on unconventional approaches.

2.1. N₂ Adsorption on the Catalyst Surface

As the first step in NRR, N₂ molecules which are dissolved in the electrolyte adsorb on the catalysts surface. Therefore, catalysts which can supply a high density of N₂ adsorption sites with sufficient strength, are promising for enhanced NRR performance as the surface coverage (at given surface area) will determine the number of N₂ molecules converted per time and by that the space-time-yield of NRR. For that reason, nanostructured catalysts are intensely followed in order to achieve large specific surface area (SSA),^[17] such as porous carbon-based materials, which can adsorb a large amount of N₂.^[18] It is worth noting that spikes of the surface of materials also can be

employed to increase reagent concentration near the tips of electrodes.^[19] Some transition metals (Ti, Y and Zr) exhibit strong N₂ adsorption ability,^[20] but those metal surfaces can be easily oxidized.

In this context, it is important to notice that the adsorbed amount of nitrogen depends on the local concentration as well. In addition to the strategy to increase the density of N₂ adsorption sites, the increase of the N₂ concentration near the active sites is possibly an even more promising way to achieve high NH₃ production rates and FEs. For example, different from the low solubility of N₂ gas in water-based electrolytes (0.66 mmol L⁻¹), fluorinated ionic liquid as electrolytes usually exhibits significantly higher solubility toward N₂, which can largely improve the FE.^[21] Structural changes that occur in such ionic liquids under the presence of an electric potential and/or when they are confined in a nanopore can possibly lead to further enhancement of their N₂ solubility.^[22] Another advantage of this approach is the by far less pronounced HER side reaction because much less water is present as compared to aqueous electrolytes. In addition, the high electrochemical stability window of ionic liquids allows to apply higher electric potentials which can be an additional “regulation screw” to achieve higher NH₃ production rates.

From a more materials scientific point of view, the catalyst can also be designed in such a way that the interaction between water and the surface where NRR is supposed to occur is minimized. Such “surface engineering techniques” can as well help to increase the N₂ concentration near the electrode. For example, Hiang Kwee Lee et al. provided a new strategy for catalysts design by coating a metal-organic framework (MOF) layer over the NRR electrocatalyst (Figure 2a).^[23] Due to the hydrophobic structure and gas-concentrating ability of ZIF, a remarkable NRR selectivity of around 90% can be achieved (Figure 2b). Using a comparable approach, Jianyun Zheng et al. designed a unique aerophilic-hydrophilic heterostructure by using poly(tetrafluoroethylene) porous framework (PTFE) on the Ti layer coated on an Si surface where Au was then highly dispersed (Au-PTFE/TS) (Figure 2c).^[24] This catalyst architecture exhibits a more hydrophobic and aerophilic surface thus providing strong interaction with N₂ gas. Therefore, at the gas-liquid-solid interface, N₂ concentration can be largely increased and HER is suppressed. Under photoelectrochemical conditions (Figure 2d), a high NH₃ production rate of 18.9 mg cm⁻² h⁻¹ with a faradic efficiency of 37.8% at -0.2 V versus a reversible hydrogen electrode (RHE) can be achieved (Figure 2e).

2.2. The Catalytic Activation of N₂

The change of the electron density and electron density distribution in a N₂ molecule during adsorption on a catalyst surface leads to its activation. Considering the extremely strong N≡N bond with high bond energy of 962 kJ mol⁻¹ and high first bond cleavage energy of 410 kJ mol⁻¹, it is not surprising that N₂ molecules usually show chemical inertness.^[16b,25] The first protonation of N₂ is endothermic. Therefore, N₂ activation plays a key role in N₂ fixation, which has been demonstrated in

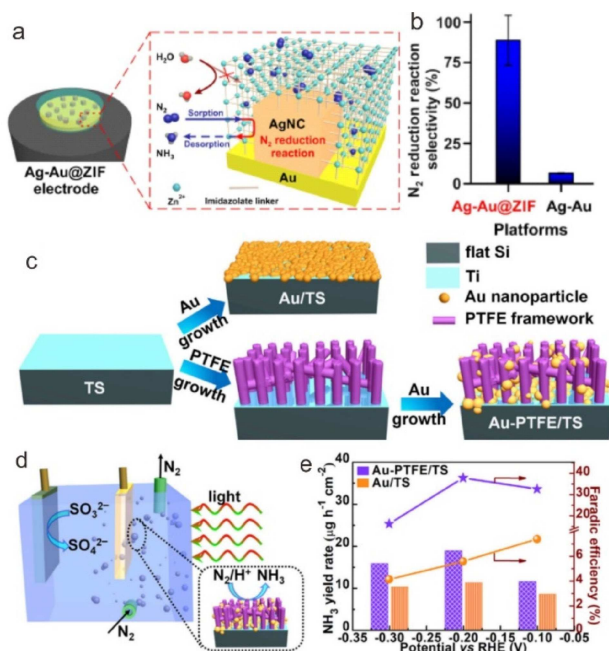


Figure 2. a) The concept of a Ag-Au@ZIF core-shell catalyst design with the ZIF as water repellent and N₂ molecular concentrator for subsequent application in electrochemical NRR to ammonia (inset). The HCl-treated Ag nanocube is denoted as AgNC. b) Comparison of NRR selectivity in the presence and absence of ZIF encapsulation. a,b) Reproduced with permission from Ref. [23]; Copyright (2018) The Authors. c) Illustration of the fabrication procedure of Au/TS and Au-PTFE/TS. d) Schematic of the PEC cell under 1 sun illumination in 0.05 M H₂SO₄ electrolyte with 0.05 M Na₂SO₃. e) Yield rate of NH₃ and faradic efficiency on Au/TS and Au-PTFE/TS at each given potential for 4 h. c–e) Reproduced with permission from Ref. [24]; Copyright (2019) Elsevier.

both homogeneous and heterogeneous electrochemical NRR. As a general rule, it can be assumed that the higher adsorption enthalpy on the catalyst surface is, the easier becomes the chemical conversion. The first strategy to improve N₂ activation is to enhance the electron donation and back-donation effect between the catalyst and N₂. For example, Yuchen Hao et al. synthesized Bi nanoparticles as NRR catalysts and found that Bi 6p bands and the N_{ads} (the N atom directly bonded to the surface) 2p orbitals can overlap both below and above the Fermi level, which can help to activate N₂ molecules.^[26] Different types of surfaces, vacancies, or defects have been reported to be active for N₂ activation, such as oxygen vacancies in oxides, nitrogen vacancies in nitrides, and surface defects on metals as all of them can enhance the charge transfer between catalyst and the adsorbed N₂.^[27] Several other chemical types of sites for N₂ activation have also been studied, which will be discussed in detail in the fourth chapter.

Lithium-mediation is another way for N₂ activation at room temperature and pressure as lithium can react directly with N₂ to form Li₃N and NH₃ can be formed after hydrolysis of Li₃N (Figure 3a).^[28] This strategy can avoid the competition from hydrogen evolution reaction, as N₂ activation and hydrogenation processes are separated, but with complicated procedures. In addition to above strategies towards improved catalyst design, plasma can also be used to active N₂ by generating

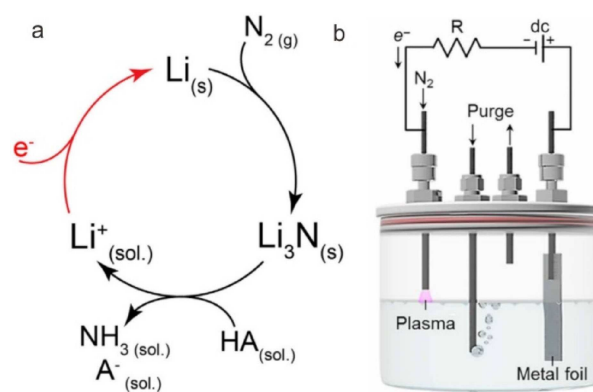


Figure 3. a) The chemistry involved in lithium-mediated nitrogen reduction to ammonia. Compound subscripts denote phases: (s) is solid, (g) is gas, (sol.) is dissolved phase. Reproduced with permission from Ref. [28a]; Copyright (2019) Elsevier. b) The plasma electrolytic system operated by a dc power supply and galvanostatically controlled using a resistor (R) in series. Reproduced with permission from Ref. [29b]; Copyright (2017) Royal Society of Chemistry.

highly energetic electrons, which can also overcome the high pressure and temperature needed for the Haber-Bosch process, but equipment to produce plasma is required.^[29] Ryan Hawtof et al. reported a hybrid electrolytic system of a gaseous plasma electrode without any material surface (Figure 3b) and the FE for NH₃ can be achieved to 100% from N₂ and H₂O at ambient temperature and pressure.^[29b]

2.3. The Hydrogenation of N₂ to NH₃

N₂ hydrogenation can be achieved with the help of protons from water and electrons from the external circuit. Thus, it can be described as a proton-coupled electron transfer (PCET) process according to the following equation:^[30]



Two types of generalized reaction pathways are known for N₂ hydrogenation on heterogeneous catalysts which are denoted as the associative and dissociative mechanism (Figure 4).^[31b] They can be distinguished by the sequence of N≡N bond breaking.^[31] In particular, the N≡N bond breaks before the hydrogenation of N₂ in dissociative mechanism, while it is cleaved with the first release of NH₃ molecule in associative mechanism. Assuming an end-on coordination mode for the N₂, the associative mechanism can be further divided into distal pathway and alternating pathway according to the different hydrogenation steps. In the alternating pathway, the two N atoms undergo hydrogenation at the same time and NH₃ is released one by one as the product. Notably, N₂H₄ could also be formed in this pathway. On the contrary, in the distal pathway, the N atom which is not directly bonded to the catalyst surface is hydrogenated at first and forms one NH₃ molecule with the break of N≡N bond before the hydrogenation of another N atom near the surface. In the dissociative mechanism, the N≡N

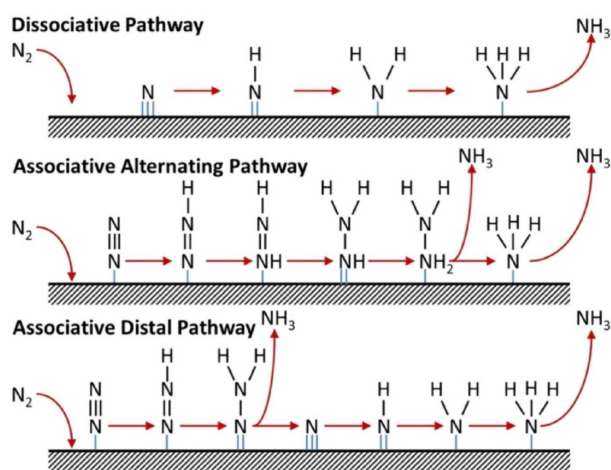


Figure 4. Possible reaction mechanisms for the NRR to form NH_3 . Reproduced with permission from Ref. [31b]; Copyright (2017) Elsevier.

bond is cleaved at first resulting in two adsorbed N atoms on the surface, which then undergo hydrogenation process separately to produce two NH_3 molecules. Although the individual steps involved in N_2 hydrogenation can simply be summed up and these mechanistic models are generally accepted, they appear to be oversimplified. The catalytic processes under real NRR working conditions can be assumed to be much more complicated in the presence of electrolyte and under consideration of energetic barriers for electron transfer (i.e., overpotential) as well as the usually energetically heterogeneous surface of a catalyst.

As mentioned above, NH_3 synthesis from NRR is a multi-electron transfer process, and many different intermediates are formed during the reaction.^[32] For that reason, linear scale relations for binding energies between them have to be considered. For example, Joseph H. Montoya et al. used DFT calculations to study $^*\text{N}_2\text{H}$ and $^*\text{NH}_2$ (* signifies an active site on the surface) as two key intermediates on the surface of transitional metals with associative mechanism and found that NH_3 synthesis is severely limited by the linear scaling between the energetics of them, which can contribute to undesirable NRR performance.^[16c]

Strikingly, some metal nitrides can also catalyze NRR through a Mars-van-Krevelen mechanism.^[33] In this case, the catalytic reaction starts with the hydrogenation of N atom on the surface of the nitride and release of the first NH_3 molecule. In consequence, a nitrogen vacancy is formed, which can be filled by a N_2 molecule from the electrolyte. However, the deactivation of catalysts during the reaction is a serious problem, when the adsorbed N_2 cannot be activated or when the formed nitrogen vacancy is filled with another atom. Both mechanisms will be influenced as well by the local concentration of nitrogen. Experimentally, Xuan Yang et al. used $^{15}\text{N}_2$ as the feeding gas and a catalyst with a composition of $\text{VN}_{0.7}\text{O}_{0.45}$ and found both $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ as products, verifying the Mars-van Krevelen mechanism (Figure 5).^[34] Besides, possible instability was also indicated by theoretical calculations and

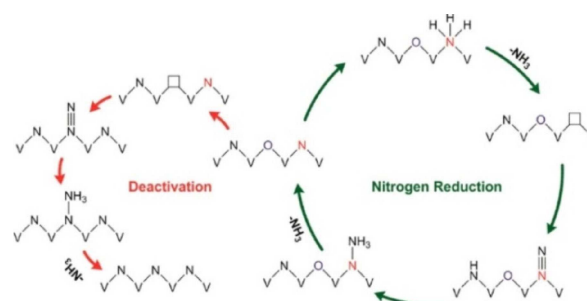


Figure 5. Proposed reaction pathway for nitrogen reduction on the surface of $\text{VN}_{0.7}\text{O}_{0.45}$ via a Mars-van Krevelen mechanism (right) and the catalyst deactivation mechanism (left). Reproduced with permission from Ref. [34]; Copyright (2018) American Chemical Society.

X-ray absorption spectroscopy through the decrease of the content of surface oxygen atoms.

3. How Important is the Role of the Electrolyte in NRR

Solvents usually have a dramatic influence on catalytic reactions in solution. Especially PCET-based processes can be controlled by the physical and chemical properties of liquid electrolytes.^[35] In principle, the optimum electrolyte should have desirable ionic conductivity, be inert and stable under the applied reaction conditions and also promote different reaction steps as mentioned above. It is difficult to match these goals into one and the same electrolyte and much efforts have been devoted to the fine management of electrolytes which already gives the answer that the role of the electrolyte is absolutely crucial in NRR.^[36] However, the role of the electrolyte remains largely underestimated as research in the field of NRR is dominated by catalyst development. The literature of the last years is however showing that some of the most outstanding examples for FEs and ammonia production rates involve unconventional electrolyte solutions such as ionic liquids or high temperature molten salts.^[1a,21a] Unfortunately, it seems that catalysts and electrolytes as the two most important parts in NRR are often considered as being isolated from each other and examples such as the above described Ag-Au@ZIF core-shell catalyst design to control their interface remain rare. However, the interplay between both compounds is absolutely crucial especially when the physico-chemical changes of the electrolyte under the nanoconfinement of the often-porous catalysts and the formation of an electric double layer in presence of an electric potential are considered. For instance, the solubility of nitrogen and thus its local concentration on the catalyst surface will not only change with nitrogen solubility in the bulk electrolyte but also in the presence and absence of an electric charge in the electrode, that is, the presence or absence of an electric double-layer.^[37] For those reasons, the electrolyte can be seen as extremely important for the NRR performance of a given catalyst and vice versa. Catalyst and electrolyte should always be considered and

optimized together and cannot be seen as being isolated from each other. In the following chapter, we will give a short overview over water-based- and liquid salt-based systems as the main electrolytes used in electrochemical NRR. Different electrolytes exhibit different NRR performance, and their corresponding advantages as well as disadvantages will be discussed.

3.1. Water-Based Electrolytes in NRR

Water-based (“aqueous”) solutions of ions are the most commonly used electrolytes for different electrochemical reactions due to their low price, easy operability, and diversity of modification. According to the pH value, they can be classified into acidic, basic, and neutral electrolytes. Because NRR is based on the conversion of N_2 with protons and electrons and due to the HER as the main competitor, the pH of the electrolyte of course plays a crucial role in this reaction. Jun Wang et al. studied Pd-catalyzed electrochemical NRR by using 0.05 M H_2SO_4 (pH = 1.2), 0.1 M Phosphate-buffered saline (PBS) (pH = 7.2), and 0.1 M NaOH (pH = 12.9) as electrolyte, respectively.^[38] At a potential of -0.05 V vs. RHE, a Pd/C catalyst exhibits a NH_3 production rate of $4.9 \mu g mg^{-1}_{Pd} h^{-1}$ in PBS, which is around two times of that in H_2SO_4 and NaOH electrolyte solution, while the FE in PBS (2.4%) is much higher than in the other two electrolytes (less than 0.1%) as well (Figure 6a). Electrochemical impedance spectra demonstrated that the improved NRR performance in PBS solution can be attributed to the retarded HER caused by the higher barrier of mass and charge transfer.

In addition, a recent study has shown that the addition of potassium and other alkali metal cations into aqueous electrolytes could also promote electrochemical NRR.^[26] Firstly, high

concentration of K^+ in the electrolyte can limit the proton transfer from the bulk solution to the electrode surface by blocking the adsorption sites. This can suppress HER (Figure 6b). It is further proposed that surface-adsorbed K^+ can stabilize the reaction intermediates such as $*NNH$. Therefore, FE of NH_3 increases with higher K^+ concentration within the range of concentrations investigated (Figure 6c).

3.2. Alternative Electrolyte Concepts for NRR

Other electrolytes have also been studied, including ionic liquids (ILs), molten salts and solid electrolytes. The development of those electrolytes can overcome some disadvantages of aqueous-based electrolytes, such as the low solubility of N_2 and low ion conductivity. For example, some ionic liquids (ILs) with high N_2 solubility under ambient conditions, which can increase the N_2 concentration near the catalyst surface by as much as 20 times as compared to water on a volumetric basis, have been shown to be promising electrolytes.^[39] As an additional advantage, the limited amount of water in ILs could also suppress HER. The strong local electric fields generated in an IL double-layer on the electrode surface may even contribute to catalytic activation of N_2 . For example, Fengling Zhou et al. reported the use of 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate ($[C_4mpyr][eFAP]$) and trihexyl (tetradecyl) phosphonium tris(pentafluoroethyl) trifluorophosphate ($[P_{6,6,6,14}][eFAP]$) with high N_2 solubility ($0.20 mg g^{-1}$ and $0.28 mg g^{-1}$ respectively) as IL-based electrolytes in electrochemical NRR.^[40] DFT calculations were applied to calculate the adsorption states between N_2 and different ions and found that stronger interaction with ions with charge-delocalization ability will result in the stronger adsorption of more N_2 molecules.

Molten inorganic salts with alkali-metal based cations were found to be suitable electrolytes as well.^[41] For example, Stuart Licht et al. reported the use of NaOH/KOH as electrolyte with a molar ratio of 1:1, where a mixture of air and water steam was introduced to form NH_3 . With a suspension of nano- Fe_2O_3 as catalysts, NH_3 can be produced with a desirable coulombic efficiency of 35% at 1.2 V under an applied current of $2 mA cm^{-2}$ at $200^\circ C$.^[1a] This concept provides a new electrochemical pathway to produce NH_3 by using water as proton sources in one pot without a separator.

Solid state electrolytes have also been studied for the application in electrochemical NRR (e.g. ceramic proton conducting materials).^[42] Compared with other electrolytes, solid state electrolytes can be used under high temperature with excellent ion conductivity,^[43] which can largely promote the reaction kinetic and obtain high NH_3 production rate.^[44] This electrolyte concept can lead to higher stability and easier separation of formed ammonia. As one example, Skodra et al. used $SrCe_{0.95}Yb_{0.05}O_3$ as solid electrolyte.^[45] In the electrolysis, H_2O vapor was employed to provide protons, which were transported to the cathode through a proton conductor disk and then reacted with N_2 to obtain NH_3 in the temperature range of $450\text{--}700^\circ C$.

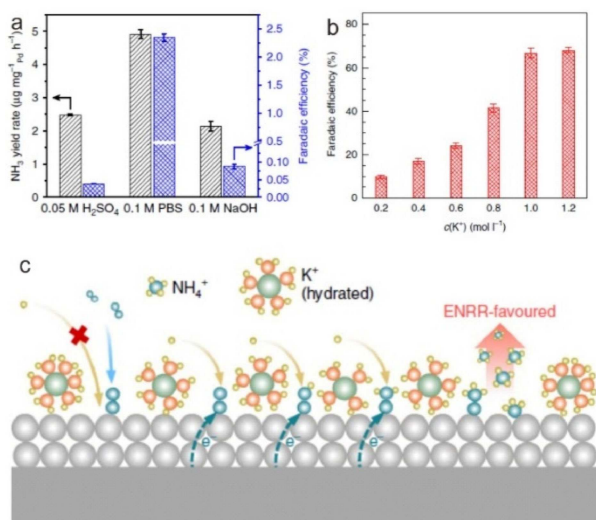


Figure 6. a) NH_3 yield rates and faradaic efficiencies of Pd/C in three different electrolytes. Reproduced with permission from Ref. [38]; Copyright (2018) The Authors. b) FE of NH_3 versus $c(K^+)$. c) Schematic explanation for the hindrance of proton transfer to the catalyst surfaces by K^+ . b,c) Reproduced with permission from Ref. [26]; Copyright (2019) Springer Nature.

4. Can Catalyst Design Alone make NRR a Competitive Process

Above mentioned electrolytes can modify the local environment for the NRR. Designing catalysts with desirable composition and structure can further modulate the secondary local environment, which has recently become a key research area. Over the past few decades, researchers have been devoted to design different catalysts based on both experimental and theoretical studies, including bio-inspired catalysts, homogeneous catalysts and heterogeneous catalysts.^[14b,16b,25,46] Different catalytically active sites for activation of N₂ have been reported and the catalyst is presumably the most crucial part of the NRR process. However, due to the interplay between catalyst, mass and electron transfer, electrolyte and electrode design, catalyst development alone will not be able to make NRR a process that will be competitive to Haber-Bosch synthesis when it comes to scale. The interplay between these fields is crucial and they have to be optimized together. The catalyst is, however, naturally the starting point and it is thus not surprising that research is mainly focusing on the point where the nitrogen is finally activated and ammonia is formed. Many catalyst structures for NRR have been published recently, often coupled with theoretical calculations to get an understanding for the nitrogen activation mechanism. In this section, some recently reported NRR catalysts with different composition and structure will be introduced.

4.1. Catalysts with Different Chemical Composition

4.1.1. Metal-Based Catalysts

Metal-based catalysts have been widely studied in electrochemical NRR in recent years. They can be mainly classified into metals and their alloys, metal oxides, metal nitrides, metal carbides and many others.^[47] In general, most transition metals or some p-electron metals with incompletely filled orbitals can donate or accept electrons, which makes them candidates for N₂ activation.^[16b,26] For nanostructured metals it should always be considered that their surface exhibits different facets and that the energetics of N₂ adsorption and activation (as also the energetics of ammonia binding) will differ on these different facets. For example, Qing Jiang's group synthesized a series of Au catalysts with various textures (Au nanorods, Au sub-nanoclusters and others) and studied their application in N₂ fixation (Figure 7).^[48] It has been demonstrated that Au materials with high-index sites, low-coordination sites, and amorphous structure seem to be favorable for N₂ fixation.

Besides, Jun Wang et al. investigated the role of Pd in NRR by using Pd/C catalysts. Different from the large overpotential required for other metal catalysts, Pd/C can achieve N₂ electroreduction at positive potential of 0.1 V vs. RHE with only a smaller overpotential of 56 mV with a FE of 8.2% and NH₃ production rate of 4.5 $\mu\text{g mg}^{-1}$.^[38] DFT calculations indicated that this good performance is caused by the balanced HER

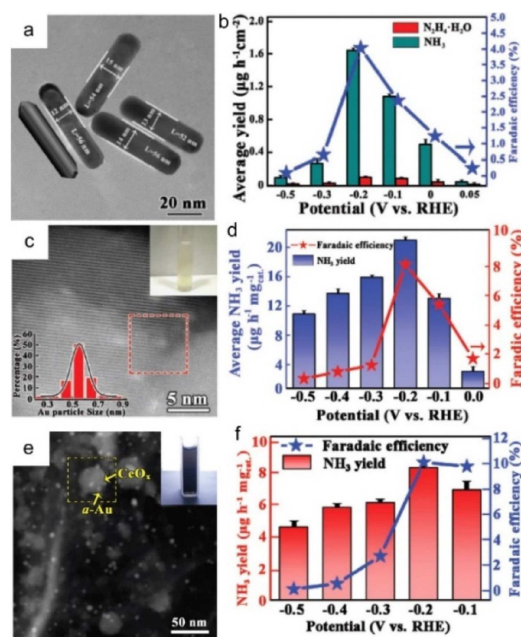


Figure 7. TEM images of a) Au nanorods, c) Au sub-nanoclusters and e) Au/CeO_x-rGO. Yield rate and FE of NH₃ at each given potential for b) Au nanorods, d) Au sub-nanoclusters and f) Au/CeO_x-rGO. Reproduced with permission from Ref. [48]; Copyright (2017) Wiley-VCH.

activity of Pd, and the formed α -palladium hydride on the catalyst surface, which can lower the free energy barrier of N₂ hydrogenation to ^{*}N₂H. Besides, doping Cu to Pd can modulate its electronic structure and with that the interaction with nitrogen, leading to desirable NRR performance for Pd_{0.2}Cu_{0.8}/rGO (reduced graphene oxide) composites.^[49] Hui Cheng et al. also indicated that Mo₂C can be potential electrocatalysts for NRR due to their unique electronic structure and rich N₂ adsorption and activation sites.^[50]

4.1.2. Non-Metal-Based Catalysts

Considering cost and stability of NRR catalysts, non-metal-based compounds have emerged as promising alternatives.^[51] For example, carbon-based materials usually have large surface area to provide more active sites and controllable and/or hierarchical porosity to ensure enhanced gas adsorption and mass transfer ability as well.^[52] Doping heteroatoms (e.g., B, N, F, P, S, etc.) into pure carbons can also modify their electron density distribution and thus catalytic performance.^[53] Yanming Liu et al. reported N-doped carbon in electrochemical NRR and elucidated that pyridinic and pyrrolic N species can promote N₂ reduction.^[17] In addition, due to the similar valence electron structure to nitrogen, orthorhombic black phosphorus was also demonstrated as efficient metal-free electrocatalyst for NRR with a high NH₃ yield rate of 31.37 $\mu\text{g h}^{-1} \text{mg}^{-1} \text{cat}$. (Figure 8a).^[54] DFT calculations showed that high electron densities on the zigzag and diff-zigzag edges of black phosphorous are favorable to adsorb and activate N₂ molecules (Figure 8b). Boron nano-

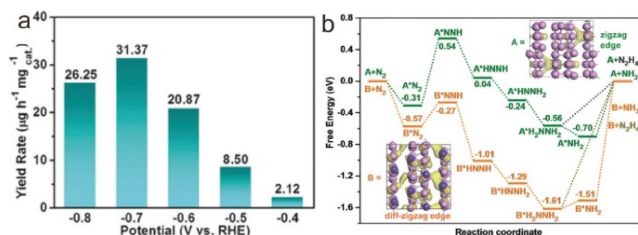


Figure 8. a) NH₃ yield rate at various potentials for black phosphorus. b) DFT-calculated reaction pathways and the corresponding energy changes for the NRR on the active sites of zigzag-edge and diff-zigzag-edge. Reproduced with permission from Ref. [54]; Copyright (2019) Wiley-VCH.

sheets have also been studied as NRR electrocatalysts, and their catalytic activity can be attributed to defects such as oxidized and H-deactivated B atoms.^[55] B and N co-doped carbons with highly porous structures were synthesized with desirable NRR performance. Doped heteroatoms can successfully construct B–N bonds and possible Frustrated Lewis pairs (FLPs) from unsaturated B and N atoms, which can provide active sites for N₂ reduction.^[53d]

4.2. Catalysts with Different Structure

4.2.1. Vacancies or Defects

Introducing vacancies or defects into electrocatalysts can result in physicochemical properties which are suitable to enhance their electrocatalytic performance due to the modulated electronic structure.^[56] For instance, Chade Lv et al. synthesized Bi₄V₂O₁₁/CeO₂ hybrid catalysts (Figure 9a), into which Bi₄V₂O₁₁ was amorphous with rich defects and oxygen vacancies (OVs), while CeO₂ can also help to promote charge transfer.^[27b] Thus, this unique structure showed

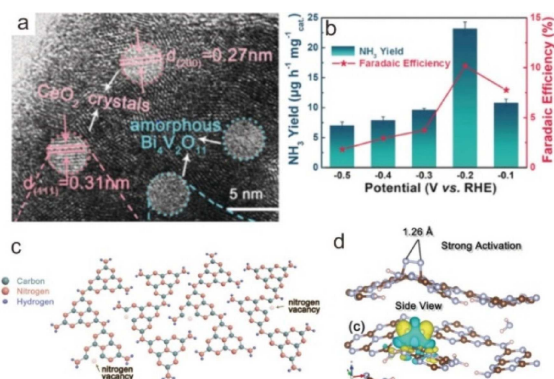


Figure 9. a) High-resolution TEM image of Bi₄V₂O₁₁/CeO₂ materials. b) NH₃ yield rate and FE for Bi₄V₂O₁₁/CeO₂ hybrid catalysts at various potentials. Reproduced with permission from Ref. [27b]; Copyright (2018) Wiley-VCH. c) Schematic illustration of NV engineered polymeric carbon nitride. d) The charge density difference of the N₂-adsorbed PCN with nitrogen vacancy; the yellow and blue isosurfaces represent charge accumulation and depletion in the space, respectively. Reproduced with permission from Ref. [15]; Copyright (2018) Wiley-VCH.

remarkable electrocatalytic NRR performance with a FE of 10.16% and NH₃ production rate of 23.21 mg h⁻¹ mg⁻¹ cat. (Figure 9b). Recently, it has also been demonstrated that the doping of carbon atoms into OVs can even improve the NRR performance through both experimental results and DFT calculations.^[57] Si-Jia Li et al. also designed amorphous Au/CeO_x/rGO hybrid materials with abundant unsaturated coordination sites in Au which act as active sites for NRR.^[58] Like oxygen vacancies, nitrogen vacancies (NVs) in N-doped carbons can also be active for NRR. Chade Lv et al. reported the synthesis of polymeric carbon nitride (PCN) with NVs (Figure 9c) and found that N₂ can adsorb on PCN in a dinuclear end-on coordinated mode, and that as-adsorbed N₂ can be further activated by the electron back-donation from adjacent carbon atoms.^[15] Therefore, the N≡N triple bond is intensively weakened as indicated by the increase in bond length from 1.0975 Å (in free N₂) to 1.26 Å (Figure 9d).

4.2.2. Edges or Corners

Edges or corners are specific sites in nanostructured materials, which have special adsorption characteristics and may thus influence their catalytic properties.^[59] For example, Yang Song reported the synthesis of N-doped carbon nanospikes with sharp structure on the corner, and this tip can largely enhance the electronic field to promote NRR.^[60] Besides, Laiquan Li et al. synthesized a 2D mosaic bismuth nanosheet (Bi NS) with sufficient exposure of edge sites.^[47e] Bi atoms on the edge sites can promote the delocalization of Bi p-electrons, which is beneficial for the adsorption and activation of N₂. A decent FE of 10.46 ± 1.45% and NH₃ production rates of 13.23 µg mg_{cat.}⁻¹ h⁻¹ could be achieved. In addition, Yaru Luo et al. firstly used DFT calculations to predict different catalytic sites in MXenes, including: middle Ti atoms, lateral Ti atoms, C atoms, and O atoms (Figure 10a and b), and found that the edge planes with exposed middle Ti sites are most active for NRR and can retard HER as well.^[61] These theoretical findings were supplemented by experimental investigations. In detail, small MXene sheets (300 ± 50 nm) on stainless steel mesh (SSM) with a higher density of exposed middle Ti sites in the edge planes can exhibited higher FE and NH₃ production rates than large MXene sheets (1.35 ± 0.3 µm) on SSM (Figure 10c). Besides, MXenes sheets aligned vertically on metal hosts of FeOOH sheets exhibited better performance than randomly ordered small or large MXene sheets due to the higher amount of active edge sites (Figure 10d).

4.2.3. Single-Atom-Based Surface

Single-atom catalysts (SACs) for electrochemical NRR have also attracted significant interest due to their unique properties, and often outstanding catalytic performance.^[47f,62] Nature often uses this single-site principle and the corresponding strong local electric fields in enzymes for the activation and storage of small molecules which researchers like to try to

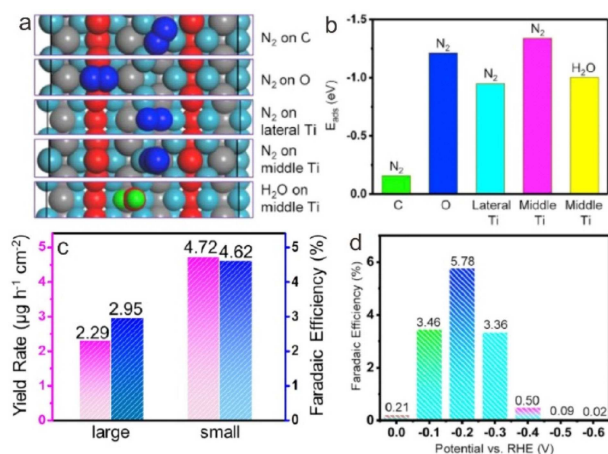


Figure 10. a) Optimized structures of MXene. The gray, red, sky blue, green, and blue balls represent C, O, Ti, H, and N, respectively. b) Adsorption energy (E_{ads}) values for N_2 on various atomic sites of MXene and H_2O on the middle Ti atomic site. c) FE and NH_3 yield rate of large and small MXene nanosheets on SSM. d) FE and NH_3 yield rate of MXene/FeOOH at various potentials. Reproduced with permission from Ref. [61]; Copyright (2019) Elsevier.

mimic in order to enhance the properties of their catalysts. In addition, SACs offer the advantage that every atom or ion can possibly act as a catalytically active center which is minimizing the use of metal. This can be seen as an approach of closing the gap between homogeneous and heterogeneous catalysis. For example, Mengfan Wang et al. reported the synthesis of Fe SACs supported on N-doped carbons as NRR catalysts.^[62d] Interestingly, the NRR onset potential can be shifted to 0.193 V (Figure 11a), which effectively inhibits HER and enhances the FE of NH_3 production to 56.55% as well (Figure 11b) with 0.1 M KOH as electrolyte. The corresponding reaction mechanism was further studied by molec-

ular dynamics simulations and DFT calculations. The results indicate that a large amount of N_2 molecules can be attracted by Fe single sites with a small energy barrier, which results in a decreased N_2 adsorption energy. This could further provide energy for the following hydrogenation steps. In addition, Hengcong Tao et al. synthesized Ru SACs on N-doped porous carbon with the addition of ZrO_2 , and the excellent NRR performance with the FE of 21% (Figure 11c) and NH_3 formation rate of $3.665 \text{ mg}_{\text{NH}_3} \text{ h}^{-1} \text{ mg}^{-1}_{\text{Ru}}$ (Figure 11d) can be achieved with a small overpotential of 0.17 V.^[62b] Recently, our group also reported the synthesis of Au single atoms (AuSAs) by using N-doped porous carbon as supports (NDPCs) derived from controlled condensation of a molecular precursor, by which gold atoms in a positive oxidation state can be stabilized on the surface of NDPCs (Figure 12a and b).^[63] At a potential of -0.2 V vs. reversible hydrogen electrode (RHE), a stable NH_3 yield of $2.32 \text{ } \mu\text{g h}^{-1} \text{ cm}^{-2}$ is produced at a Faradaic efficiency (FE) of 12.3% with a desirable stability as well (Figure 12c and d).

5. Where is the Room for Revolutionary Improvement of NRR

Electrochemical NRR for sure offers great potential to be an alternative and complement to the traditional Haber-Bosch process. Until now, great efforts have been made in catalyst development, mechanistic studies, electrolytes and in other subfields. It is our belief that the necessary significant improvements for the energy efficiency, selectivity, and space-time yield of NH_3 production with NRR will hardly be achievable with research on advanced catalyst design alone. A comparable trend as in the field of electrochemical energy

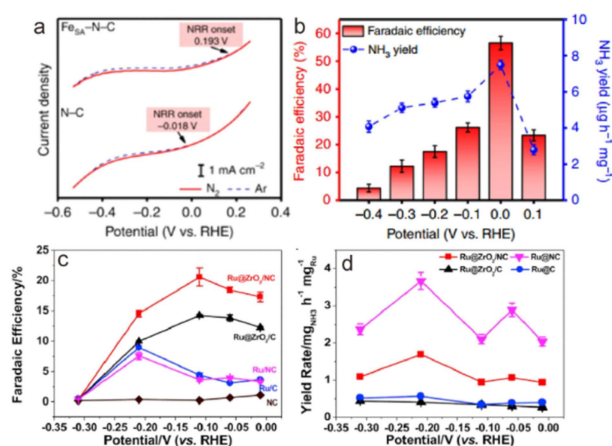


Figure 11. a) Linear sweep voltammograms of single-atom dispersed Fe-N-C ($\text{Fe}_{\text{SA}}\text{-N-C}$) and N-doped carbon (N-C) in Ar-saturated (dashed line) or N_2 -saturated (solid line) 0.1 M KOH solution with a scan rate of 50 mV s^{-1} . b) FE and mass-normalized yield rates of NH_3 at each given potential of $\text{Fe}_{\text{SA}}\text{-N-C}$. Reproduced with permission from Ref. [62d]; Copyright (2019) The Authors. c) The FE of NH_3 over NC, Ru@NC, Ru@C, Ru@ZrO₂/NC, and Ru@ZrO₂/C at various applied potentials. d) NH_3 yield rates of Ru@NC, Ru@C, Ru@ZrO₂/NC, and Ru@ZrO₂/C. Reproduced with permission from Ref. [62b]; Copyright (2019) Elsevier.

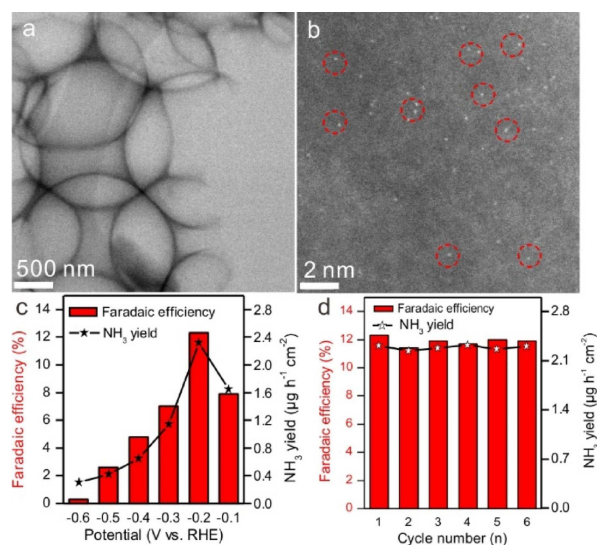


Figure 12. a) Representative TEM image and b) High-magnification HAADF-STEM image of AuSAs-NDPCs. Faradaic efficiency and yield rate of NH_3 of c) at each given potential and d) during the recycling test. Reproduced with permission from Ref. [63]; Copyright (2018) Wiley-VCH.

storage where research on advanced electrolyte concepts for a given electrode material to achieve novel mechanisms of energy storage is often carried out can be foreseen for NRR as well. Research in the related electrocatalytic CO₂ reduction field is currently also undergoing a transition from the catalyst aspect to device design as a whole. Catalyst, electrode construction, and electrolyte have to be investigated together and cannot be seen as being isolated. Taking this into consideration, there is a lot of room for improvement in NRR if synthetic design of advanced and sustainable catalytic materials is wisely combined with novel electrolyte concepts and electrode architecture. The way in which the NRR catalysts are most often evaluated (supported on carbon paper) leads to low areal current which is far away from how a real world process would look like. Free-standing electrodes can be a solution for that. In this context it is also of utmost importance to find ways to couple NRR with a value adding oxidation process on the anode side in a full cell. This could for example be the oxidation of biomass instead of the established oxygen evolution reaction. Furthermore, the removal of formed ammonia from the electrolyte may be more complicated than separation from a gas mixture in to the H-B process. This issue has to be solved by intelligent device engineering. In most reports in the current literature is reported that the NRR catalysts can be stable operated for a couple of hours but then stop working. This is likely caused by the blocking of nitrogen activations sites by the much stronger adsorbing NH₃ or ammonium ions and in consequence, the catalytic activity has to be reactivated by heating of the electrodes after such a cycle. From the academic point of view, we see the following, rigorous challenges which future research will have to focus on: a) Detailed NRR mechanisms have to be illuminated by using advanced in-situ techniques to track the reaction process and thus to check and supplement the findings from DFT calculations which most often neglect the presence of electrolyte. b) NRR selectivity and activity should be improved by searching more efficient NRR electrocatalysts always in combination with tailoring of reaction conditions (electrolyte, temperature, pH value, N₂ flow rate, mass loading on the electrode etc.). c) To efficiently promote the development of electrochemical NRR, critical experimental standards should be established and complied.^[16a,64] For example, Ib Chorkendorff et. al demonstrated that ¹⁵N₂ labeling experiments are necessary to clarify the origin of the N species in the NH₃ product and quantify the reliable value for the NH₃ yield.^[64]

We are sure that there is still plenty of room for improvement of NRR if the above issues are carefully considered and addressed. Due to the ever-increasing demand for NH₃ and its follow-up products, the rise of the CO₂ level in the atmosphere, and the increasing production of renewable electricity, the time to establish NRR as an alternative to the Haber-Bosch process on scale has come but a lot of research, new ideas/unconventional solutions, and engineering efforts are still needed to make it a competitive solution.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: N₂ reduction · ammonia synthesis · catalysis · catalyses · electrolytes

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