

Review Article

A Review on Advances in Electrocatalytic N₂ Reduction to Ammonia

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Abstract

Ammonia is one of the most important industrial chemicals which is prepared by the traditional Haber–Bosch process. Haber–Bosch process is an expensive process requiring higher temperature, pressure, and a lot of energy. Electrocatalytic nitrogen reduction reactions (NRR) have gained a lot of interest as the alternate method for the production of ammonia. For obtaining a higher yield, higher Faradic efficiency (FE), inhibition of side reactions e.g., hydrogen evolution reaction (HER), and reducing the production cost for ammonia by NRR, selection of appropriate catalysts, cell layout, and electrolyte selection are important controlling parameters for the NRR. Non-metallic catalysts are preferred over noble metallic catalysts due to their lower cost, more resources, and characteristic d-orbital electron but have the issue of low selectivity due to the higher HER. The selectivity for the NRR can be improved by employing the catalysts with higher absorption of N₂. PEM-type cells and the back-to-back cells are used to inhibit the HER. Apart from these factors, NRR is also dependent on other factors to obtain better experimental results e.g., no nitrides, removing the ammonia from contaminants sites, and controlling the experiment time.

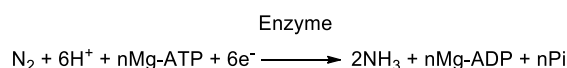
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Introduction

Ammonia (NH₃), the 2nd most popular chemical in industrial production, is primarily utilized in the manufacture of pharmaceuticals products, synthetic fibers, and fertilizers, as well as for energy conversion[1, 2]. NH₃ is a good storage medium for hydrogen gas since it has 17.6 percent hydrogen by mass and requires just 9–10 bar pressure at air temperature to remain in the liquid state, allowing it to be kept in low-pressure vessels[3, 4]. More importantly, NH₃ is the exclusive carbon-free energy carrier that emits no CO₂ during the ultimate breakdown, allowing it to be employed in the future and can replace hydrogen in the energy economy. Instead, NH₃ is currently manufactured mostly using the Haber–Bosch process, which converts N₂ to NH₃ in coal-based or natural gas-based ammonia facilities[5]. This ammonia synthesis process requires a lot of energy, high temperatures (300–550 °C), high pressures (200–350 atm) during the reaction, and a lot of H₂, absorbing 1–2% of the world's annual fossil energy output and creating 300 metric tons of CO₂[6, 7].

As a result, discovering alternate NH₃ synthesis technologies to substitute the energy-intensive Haber–Bosch process is worthwhile. Under mild reaction conditions, NH₃ production is a natural process in which an enzyme is used (nitrogenase enzyme) and the presence of H₂O, electrons, and atmospheric N₂[8, 9].

To transmit electrons to the nitrogenase enzymes, adenosine triphosphate (ATP) molecules must be hydrolyzed, followed by a progressive reduction of nitrogen gas (N₂) to NH₃, as shown in the below equation[10]



This process is efficient when it comes to energy, with Mo-nitrogenase achieving 70% electron efficiency[11]. The energy efficiency of the natural process for the manufacture of ammonia using enzymes and by Haber–Bosch process is 0.38 MJ/mol [12] and 0.48 MJ/mol[13] respectively.

Yet, the industrial applicability of this natural process is severely limited due to the occurrence of an ultralow reaction rate. To provide artificial controls, transition metal complexes (Mo, Fe, etc) are used as catalysts for electrochemical reduction of nitrogen [14–16]. However, due to the complexities of the reactions and problems with catalyst stability, this approach has

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several flaws that limit its use on a broad scale [17]. One major worry is the significant energy usage required for functioning at ambient pressure. For the nitrogen reduction, lithium is used as a reducing agent and utilizes approximately 2.73 MJ/mol and this amount is much higher than the natural nitrogen fixation and Haber-Bosch process both [18].

Natural reduction of nitrogen has also sparked interest in employing electrochemical technology to convert N₂ to NH₃ (reduction) in the absence of enzyme (nitrogenase) and ATP, using homogeneous catalysts, adequate voltage, H₂O, electrons, and N₂ [19-23]. When compared to the Haber-Bosch process, this technology can save over 20 percent on energy and be driven by clean and renewable energy sources [24].

The first study on electro-catalytic reduction of Nitrogen was published in 1969 by van Tamelen *et al.* investigated N₂ reduction in a Ti-Al combination [25]. Their research demonstrated that in nichrome cathodes, N₂ is fixed by Ti (II) to establish an adduct, which is then reduced to NH₃ by liberating titanium nitrogen species under the influence of aluminumisopropoxide in the electrolyte. The anode made of aluminum has been involved in the NH₃ synthesis process and has been hydrolyzed to generate Al₂O₃, limiting its commercial production. From 1970 to 2015, only a few investigations with various electrocatalytic devices under low-temperature settings were described later [26, 27]. In 1983, Sclafani *et al.* presented an electrochemical cell with an iron (Fe) cathode for conversion of N₂ to NH₃ (reduction) at 1 atm and low temperature, with a maximum rate of 0.5 x 10⁻⁶ mol/ h at 1.07 V versus saturated calomel electrode and an NH₃ Faradaic efficiency of roughly 1% [28]. After that, in 1989, Furuya *et al.* developed an electrode based on iron and phthalocyanine for the reduction of nitrogen, reaching a 0.11 % NH₃-Faradaic efficiency in potassium hydroxide electrolyte for 10 minutes [29].

This research also revealed that iron-phthalocyanine species are unstable, with catalytic activity and selectivity rapidly decreasing after 10 minutes of electrolysis. Kordali *et al.* presented a solid polymer electrolyte cell with a Nafion membrane and a 2M potassium hydroxide aqueous electrolyte employing Ru cathode made by electrochemical deposition at the beginning of the 2nd century. At 90 °C, an ammonia production rate of 7.2 x 10⁻⁴ mol/ h m² was attained, with a Faradaic efficiency of around 1% [26]. Since 2016, there has been increased interest in improving Faradaic efficiency for ammonia synthesis at 25 °C temperature. Faradaic efficiency values varied from >1 to several tens of percent have been reached employing some sort of controls in a series of articles published in the last three years [26, 30, 31]. The recent advancements in greater Faradaic efficiency have been amazing, and it is vital to update the summary to have a better grasp of the progress.

The proposed perspective techniques for the selectivity issues in electrocatalytic nitrogen reduction

reaction (NRR) should be thoroughly investigated, as this would help to propel the science forward. I outline contemporary solutions utilized to address the selectivity difficulties for NRR from the perspectives of catalyst design, cell layout, electrolyte selection, and other factors in this paper. Furthermore, because this is a new field, standardization of research methodologies is critical to assure investigational rigor

NRR catalysts

Noble-metal catalysts

Because of the fierce hydrogen evolution reaction and the complex reaction process, several parameters influence the NRR's performance and selectivity, including the catalyst's intrinsic activity, reaction potentials, electrolyte, and reactor design. The key technique for improving NRR performance is the rational design of a catalyst with improved conductivity and robust N₂ adsorption [32, 33]. Noble metal catalysts have outstanding catalytic capabilities and are commonly utilised in electrochemical reactions because of their high electrical conductivity, large active surface area, empty d-orbitals, and can adsorb and stabilise reactants. This is anticipated in the field of nitrogen reduction due to the outstanding activity of noble metal materials for oxygen and hydrogen, and there have been many publications on the application of precious metals for the NRR, such as Pt [34], Ru [32, 35], Rh [36], Pd [32], and so on.

These catalysts cannot be utilised as a parameter for identifying the activities of NRR catalysts are due to the intricacy of the nitrogen reaction mechanism and the interaction of side reactions, but they nevertheless have good reactivity and selectivity when compared to non-noble metal catalysts.

Gold (Au) is regarded as one of the noble and precious metal catalysts, and numerous research studies on Au catalysts with outstanding N₂ selectivity and activity have been published [41]. Yan and colleagues used a seeded growth approach to create tetra-hexahedral Au nanorods (THH-Au-NRs), which were encompassed by the step 730 surface constituted of (210) and (310) sub-facets. With a high NH₃ yield rate of 1.648 X10⁻⁶ g/hcm² and N₂H₄ generation of 0.102 X 10⁻⁶ g/ hcm² at -0.2 V (versus RHE) in 0.1 M KOH, the THH-Au-NRs show expected NRR performance [42, 43].

Table 1. Table elaborates some of the precious metal catalysts that have been described

Catalyst	NH ₃ yield	FE (%)	Potential (RHE)	Ref
Au-Ti ₃ C ₂	30 x 10 ⁻⁶ g/h mg	18	-0.2 V	[37]
Ag ₂ O-Au	2.13 x 10 ⁻⁶ g/ h cm ²	23	-0.4V	[38]
AuHNCs	3.7 x 10 ⁻⁶ g/h cm ²	36	0.4V	[39]
Pd/C	4.5 x 10 ⁻⁶ g/h mg	8.2	0.1V	[32]
pAu-NF	9.4 x 10 ⁻⁶ g/h cm ²	13.4	-0.2V	[40]

Furthermore, DFT calculations show that the NRR occurs on the gold surface and that the process follows the alternating hydrating routes, which is compatible with the N₂H₄ observed. The selectivity of THH-Au-NRs, on the other hand, is insufficient to meet the needs of practical applications, which could be due to the structure being harmful to mass transfer and the possibility of residual surfactant covering the active sites [44]. To increase conductivity and Au site distribution, Wang et al. used a micelle-assisted electrodeposition approach to deposit Au uniformly on Ni foam (pAu/NF) and generate a self-supporting porous gold (pAu) film [40]. Nanopores with a diameter of 59.5 nm may uniformly permeate the Au film with a thickness of 400 nm. The pAu/NF demonstrated exceptional NRR performance with a superior NH₃ generation rate of 9.42 x 10⁻⁶ g/h cm² and a FE as high as 13.36 percent at -0.2 V (RHE) in 0.1 M Na₂SO₄ under ambient circumstances, owing to the interconnected porous architectures and rich Au active sites.

Furthermore, the absence of N₂H₄ is encouraging, leading the author to hypothesize on a distant associative pathway for the NRR across the pAu/NF interface. This not only shows that the N₂ on the Au site has been entirely converted to ammonia, but it also shows that the NRR process can be regulated by altering the catalyst structure and active site density. There is already proved that if the surface of the catalyst selectively adsorbs N₂ instead of proton (H⁺) in an aqueous electrolyte, it will expedite nitrogen reduction [34], so Liu et al. used Ti₃C₂ as a template, and gold (Au) nanoparticles are firmly anchored (Au/Ti₃C₂) using an ultrasonic reduction process [45]. The Au/Ti₃C₂ mimics spider web predation by creating high-energy adsorption with nitrogen on the surface, reducing the triple bond strength and destabilising H₂NNH₂ via an alternate mechanism.

Non-noble-metal catalysts

Despite significant progress in precious metal NRR catalyst research, their widespread use is limited due to very few resources, high costs, and inadequate selectivity for N₂ [46]. Transition-metal catalysts have become ideal alternatives for noble-metal catalysts due to their more resources, low cost, and characteristic d-orbital electrons [47, 48]. In addition, the natural biological nitrogen fixation uses enzymes with Fe-Mo as active sites to accomplish the reduction of nitrogen to ammonia under moderate conditions [49, 50].

Table 2. Some non-noble metal catalysts for nitrogen reduction reaction are listed below in the table

Catalyst	NH ₃ yield	FE	Potential (RHE)	Ref.
MoS ₂	4.9 x 10 ⁻⁶ g/h cm ²	1.2 %	-0.5V	[44]
FeS/MoS ₂ /CFC	70 x 10 ⁻⁶ g/h cm ²	3 %	-0.5V	[51]
Fe ₂ O ₃ nanorods	16 x 10 ⁻⁶ g/h mg	1 %	-0.8V	[52]

The electrochemistry (EN) of iron and molybdenum catalysts has been lucubrated due to their crucial role in natural nitrogen fixation. Through DFT simulations, Sun et al. demonstrated that the Mo-C bond can lessen the difficulties of releasing NH₃ from the Mo surface. This proposes a method for improving the NRR of transition metal catalysts by including non-metal atoms with high EN [53]. Sun and colleagues produced MoS₂ based on theoretical predictions and employed it for the NRR in ambient surroundings for the first time. The MoS₂ shows a positive NRR efficiency in both neutral (NH₃ yield rate: 8.08 x 10⁻¹¹ mol/ s⁻¹ cm⁻¹, FE is 1.17 percent) and acidic (NH₃ yield rate: 8.48 x 10⁻¹¹ mol/ scm², FE: 0.096 percent) environments, because to its luxuriant Molybdenum sites (Active) and uniform sheet structure [44]. This work successfully exploited a Mo-based catalyst for nitrogen reduction and pioneered the use of transition metal sulfides in NH₃ synthesis. However, because of the high adsorption capacity of molybdenum for N₂, it's challenging to desorb it and release the NH₃. Strong hydrogen evolution reaction (HER) competition exists on the surface of MoS₂, resulting in a very low Faradaic efficiency, and DFT simulations confirm that the edge of MoS₂ appears to be the active site toward the HER [43, 44].

Inspired by the nitrogenase enzyme, Sun et al. developed a catalytic electrode with a carbon fibre cloth (CFC) covered in iron sulfide-dotted (FeS) MoS₂ nanosheets (FeS@MoS₂ /CFC) [54]. The FE in neutral electrolyte reached 2.96 percent because of CFC's strong electrical conductivity and abundance of FeS and MoS₂ active sites. FeS@MoS₂/CFC produced a greater NH₃ yield rate (8.75 x 10⁻⁶ g/h cm²) in acid electrolyte than in neutral electrolyte, but with significantly lower selectivity due to the high HER in the acidic electrolyte. This demonstrates that in the NRR, a catalyst's selectivity for N₂ is regulated not only by the catalyst's inherent features, but also by the reaction circumstances, such as the electrolyte and potentials.

Strategy to improve the NRR

Nitrogen is kinetically inert due to the significant N₂ triple bond energy of 945 kJ mol⁻¹ [55], and the substantially high potential prerequisite for the NRR causes intense HER competition on the catalyst surface; hence, ammonia's FE is very poor. The most difficult aspect of synthesising ammonia is developing a good catalyst that can lower the activation energy barriers of inert reactants while also inhibiting the HER reaction on the catalyst surface. The electrocatalytic synthesis of NH₃ is a complex system, and the most important elements impacting the rate of NH₃ generation, which include electrode materials, are equally complicated.

Reactor configuration

For the conversion of N₂ to NH₃, the reactor configuration is critical. Back-to-back cells, polymer

electrolyte membrane (PEM)-type cells, H-type cells, and single chamber cells are the four primary types of reactor configurations[56]. The liquid electrolyte is commonly filled into the H-type cell (Figure 7c) and single chamber cell (Figure 7d). Because of the architecture of these sorts of reactor topologies,

immediate interaction between the electrode and the liquid electrolyte occurs; as a result, the high HER and NRR at the catalyst surface compete with one another, resulting in reduced Faradaic values of ammonia formation.

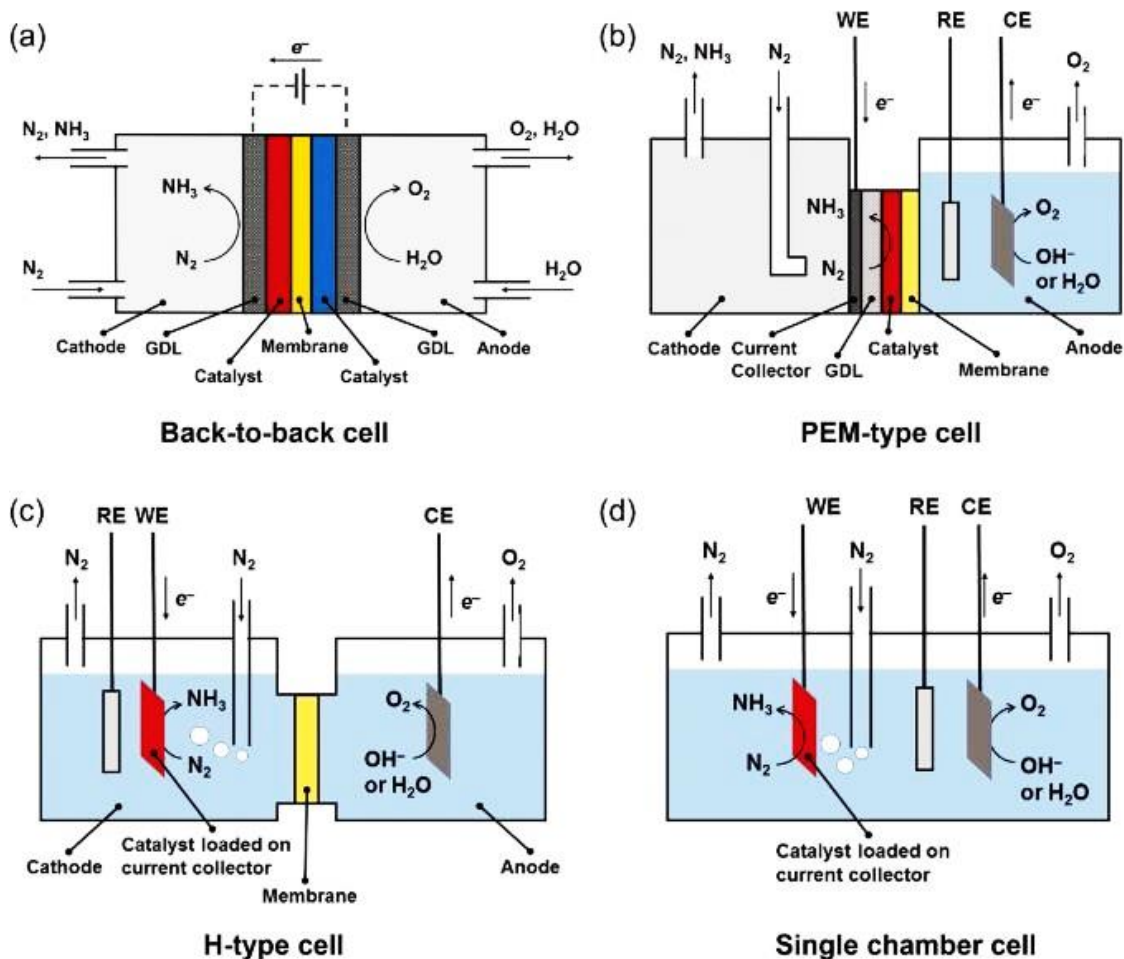


Figure 1. This schematic view shows 4 different reactors used for electrocatalytic reduction of nitrogen. Copyright 2018. Wiley[56].

In the back-to-back cell (Figure 7a), a dense membrane separates the two gas diffusion electrodes, and Nafion membranes are commonly utilised due to their capacity to conduct electricity. The PEM-type cell's cathodic chamber (Figure 7b) receives N₂ gas, and the NH₃ gas produced is dispersed in the acidic electrolyte. The anode of a PEM-type cell is filled with a liquid electrolyte that electrolyzes water from the anode to give protons to the cathode, unlike a back-to-back cell. The cathode has no direct interaction with the electrolyte, as indicated in the above Figure 1, and hence the PEM-type cell and the back-to-back cell can suppress HER. Under ambient settings, the H-type cell is the most researched form of reactor design, and the discussion that follows is mostly focused on the H-type cell. Qiu *et al.* confirm that the Nafion membranes are ineffective for N₂ reduction reactions because it permits NH₃ to pass through while also trapping NH₃ to some extent[57].

The choice of electrolyte

The H-type cell has been widely researched with acidic, alkaline, and neutral electrolytes. In different electrolytes, the reaction between the cathode and the anode is not the same, even though the total reaction is the same. The OH⁻ generated by the cathode is transferred to the anode via an anion exchange membrane and oxidised to O₂ in an alkaline electrolyte. Protons produced from the anode are transferred to the cathode via the proton exchange membrane (PEM) to make ammonia in an acidic electrolyte. Furthermore, different electrolytes affect pH, therefore choosing the right electrolyte is critical for the NRR. Due to proton usage on the catalyst surface, the pH of the near electrode differs significantly from the pH of the solution throughout the reaction, and this substantial pH difference impacts the rate of ammonia synthesis as well as the FE of NH₃. According to Yan *et*

al., the current density in the alkaline electrolyte will drop, while the current density in the acidic electrolyte would increase[58].

When the pH is low, the HER competes with the NRR the most, and the NRR process is repressed. This is because ammonia production necessitates a high overpotential, which is advantageous to the HER. Yan *et al.* research show that by decreasing the transport of protons to the catalyst surface, the HER on the surface of the electrocatalyst may be inhibited, enhancing the selectivity for the NRR[58]. Adding K⁺ cations to the electrolyte improves the selectivity of the catalyst for the NRR. At K⁺ cation concentration of 0.2 to 1.0 mol/L, the Faradaic efficiency rises from 6.3 percent to 22.5 percent, while the current density rises from 4.4 x 10⁻² mA/cm² to 9.1 x 10⁻² mA/cm². Furthermore, different pH levels block the HER in different ways, and the HER can be decreased by lowering H⁺ concentrations in weakly acidic and alkaline electrolytes.

Enhancing the NRR by repressing the hydrogen evolution reaction

Because of the existence of the HER, a high number of protons are created from the decomposed H₂O, and the HER becomes the primary reaction step, resulting in poor NRR performance for all electrocatalysts in an aqueous solution. Even though many of the studies have a good NRR and high Faradaic efficiency, most of them do not examine the absorption energy from the catalyst's surface to explain why the NRR is higher. According to Norskov *et al.* when the produced H₂ or NH₃ is desorbed, the re-vacuum active center can be occupied by H (from the recombination of H⁺ and an e) or N₂[59].

The HER will take up the primary location from a thermodynamic and kinetic viewpoint until sufficient electrons and protons are surrounding the active core, and the NRR will be suppressed. Theoretically, if the quantity of protons around the active center is kept under control and there is enough N₂, N₂ will be absorbed by the active center, effectively inhibiting the HER. Higher temperatures are better for the NRR, according to Liu *et al.* The reaction potential of synthetic ammonia decreases with increasing temperature when water is utilised as a reactant. The reaction potential of synthetic ammonia increases as the temperature rises as the water boils.

Rational design of the catalyst

Nrskov *et al.* demonstrated in 2012 that the transition metals Sc, Y, Ti, and Zr may convert N₂ to NH₃ via the dissociative process without producing too much H₂. A good material with improved nitrogen adsorption should be chosen or the material should be adjusted to make it more selective for the NRR to get a higher FE percentage for the NRR rather than the HER. Tao and coworkers performed density functional theory simulations in 2018 to show that Ru sites with oxygen

vacancies are advantageous for N₂ adsorption[42]. It's worth mentioning that Tao also mentioned that the addition of ZrO₂ enhanced Faraday efficiency, which he attributed to ZrO₂'s inhibitory action on the HER, which agrees with Nrskov's calculations.

Protocol of the electrochemical test

Because ammonia is extremely water-soluble and is present in the atmosphere, the test circumstances necessitate a very well-regulated test environment to ensure reliable findings. This is especially important to consider when evaluating the influence of all minor experimental circumstances on the outcomes. The flowing environment, gases adsorbed on the instrument's walls or materials, and all sources of water contaminated during the test are all potential sources of contamination. Previous research has used stringent control procedures to reveal probable contamination sources. Wang *et al.* used 3 beakers filled with 50 mL of HCl and positioned them in different parts of the lab for 12 hours. Surprisingly, the three beakers' solutions had varying degrees of contamination. NO_x, especially nitrogen-containing anions, have a significant influence on the experimental environment, resulting in orders of magnitude variations. Human breathing and even gloves used in experimental activities might contaminate the experimental environment[32, 60]. Many other potential contaminants haven't been reported, but it's clear that we need to institute tight experimental standards and environmental control in the NRR test environment right once.

We should improve the experimental settings to acquire accurate experimental results and minimize the impact of contamination sources on the outcomes.

- 1) Verify that all designs, supplied N₂, and all solutions have been filtered. Even a small amount of nitride can have a big impact on the outcome of an experiment. Because the NRR experimental findings are time-sensitive and must be completed within a few hours, we should experiment with a closed or stable setting.
- 2) Nitrogen-containing materials and the Nafion membrane employed in the experiment have been shown to have a significant impact on the results[61]. To circuit control measurement be done before each test. Observations of Ar control should be made before and after each nitrogen reduction test at each test potential to evaluate the impact of factors such as the material, reactor setup, and environment.
- 3) Detecting as produced ammonia can be done in a variety of ways. For each test, a very sensitive product detection method should be employed to ensure accurate measurements. Currently, Nessler's reagent and indophenol blue[62] are the most widely used measurement procedures.
- 4) The time-dependent NRR is highly susceptible to contamination sources, and the procedures

provided in earlier studies do not eliminate all impacts.

Regrettably, even if the contamination source is strictly controlled, the test findings may not be correct. As a result, additional verification is required to show that

all synthesized ammonia should be produced from the nitrogen given. As a result, a ¹⁵N isotope label must be quantified. To guarantee the correctness and rationale of the experiment in Figure 10, we advise that rigorous control trials be conducted.

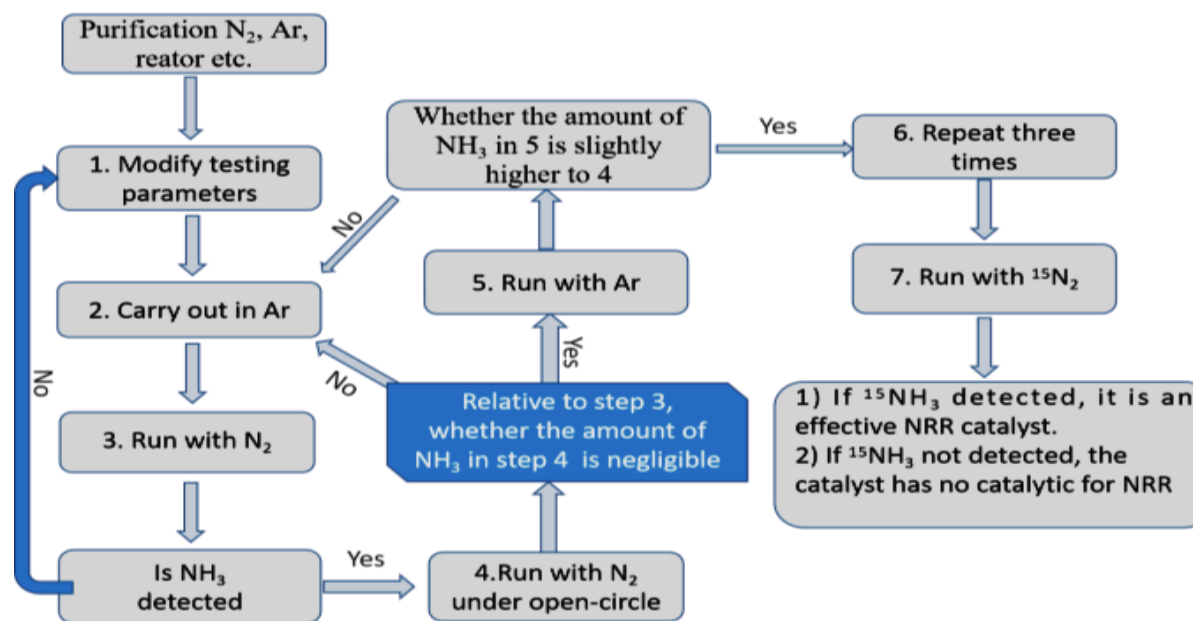


Figure 2. Flowsheet diagram of steps in nitrogen reduction reaction measurement.

Conclusion and Future work

The Haber–Bosch method has had a century-long impact on the globe as one of the greatest technologies. However, because of the Haber–Bosch process's significant energy consumption, electrochemical ammonia synthesis has gained significant attention due to its environmentally friendly nature. Although considerable advances have been made in recent years, electrocatalytic ammonia synthesis still faces obstacles such as selectivity and efficiency of energy due to the competing HER, which cannot be overlooked in the NR process.

Furthermore, to the above-mentioned optimization of the reaction apparatus, more work must be done to enhance the corresponding experimental conditions, which includes the optimization of the electrode, the electrolyte, and the catalyst itself, to improve the catalytic performance and Faraday efficiency. Simultaneously, future research should concentrate on fully comprehending the nitrogen reduction mechanism, enhancing yield rates, and reducing inefficiencies.

For the nitrogen reduction reaction, precision and reliability of measurement data are also key problems. Recent studies on NRR are discussed in this review, and many intriguing outcomes have been reported. Despite this, NRR still confronts several challenges:

1) More research is needed to combine experimental results with theoretical calculations to elucidate

the catalytic mechanism and thereby guide catalyst design. At the same time, more sophisticated characterization approaches are needed to show the catalyst structure at the atomic level. Advanced characterization approaches can give a better platform for understanding the structure-property link and the evolution of active centers in the catalytic process.

- 2) Selectivity is critical for increasing Faraday efficiency, which is required to inhibit HER. Furthermore, we must improve the solubility of N₂ in the electrolyte, necessitating the development of novel highly N₂ soluble electrolyte solutions.
- 3) The NRR study is still in its early stages, and several issues need to be addressed. The most pressing concerns are how to minimise environmental damage, standardise experimental methodologies, and improve the current ammonia detection method. Detection approaches that are both very efficient and easy should be developed. Most significantly, due to its high cost, isotope N¹⁵ should be easily recycled.
- 4) Noble metal catalysts have a greater yield among the currently known catalysts, but their FE is lower than that of non-noble metal catalysts.

Despite having a lower yield than precious metal catalysts, non-precious metal catalysts have a better Faraday efficiency. The non-precious metal catalyst

Fe_{SA}-N-C has a Faraday efficiency of 56.55 percent. If non-precious metal catalysts can be improved to increase yield while maintaining their high Faraday efficiency, it could help in the creation of future NRR catalysts.

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