Electrocatalytic Nitrogen Reduction Reaction (NRR)*
A Probable Alternative to Haber–Bosch Process (HBP)

Jaydeep Basu and Sanjib Ganguly

Nitrogen is the most abundant gas in the Earth’s atmosphere (nearly 78%). The natural process of its fixation to usable nitrogen species, viz., ammonia, is carried out by certain diazotrophic bacteria containing the enzyme ‘nitrogenase’. This transformation is vital for several biochemical and physicochemical processes on Earth. Thus, the fixation of atmospheric N₂ has always been a topic of interest. Fritz Haber was acknowledged by the Nobel awarding committee in 1918 for finding a solution for the same, and Carl Bosch developed it in industrial scale. Despite this development, the Haber–Bosch process (HBP) has certain shortcomings, particularly the fact that it requires high temperature and pressure, i.e., the process is not clean, unlike that by Nature. In this context, the electrocatalytic community is striving hard to use several types of molecular catalysts to transform the highly unreactive nitrogen to its more useful form, like ammonia, under ambient conditions.

Introduction

Nitrogen is an essential element since it is present in many biomolecules such as amino acids, proteins, nucleotides, nucleic acids, hormones, enzymes, vitamins, etc., [1–3]. Nitrogenous fertilisers are of prime importance for plants’ healthy growth and are, therefore, vital in supporting an ever-growing population on the planet. Even though 78% of the Earth’s atmosphere comprises molecular nitrogen, it is chemically and biologically unusable in this form. Certain diazotrophic microorganisms containing the met-

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alloenzyme nitrogenase can catalyse the synthesis of NH$_3$ from atmospheric nitrogen at ambient conditions [4]. Even though ammonia synthesis is an exothermic reaction, the process consumes 16 equivalents of ATP per N$_2$ molecule (see equation 1). Three distinct types of nitrogenase enzymes with similar features have been isolated, and they differ primarily in their metal-centred catalytic cofactors (co): FeMo–co, FeFe–co and VFe–co. Among these, the FeMo-nitrogenase has been extensively studied and understood. For each dinitrogen molecule being reduced during the process, at least one equivalent dihydrogen is produced via the reduction of H$^+$. It is further understood that the formation of H$_2$ is not a side reaction in the true sense but an inherent phenomenon of catalytic dinitrogen reduction by nitrogenase.

$$N_2 + 8H^+ + 16\text{MgATP} + 8e \rightleftharpoons 2\text{NH}_3 + H_2 + 16\text{MgADP} + 16P_i$$

(1)

Although the conversion of dinitrogen to ammonia is exothermic at standard conditions, the process of fixation of dinitrogen (uncatalyzed) has been found to be extremely difficult. This is attributed to the very strong N≡N triple bond, which is hard to activate owing to the absence of a permanent dipole [5]. Therefore, a significant amount of energy is required to activate dinitrogen, even in the presence of suitable catalysts. It is worth mentioning that ammonia finds extensive utility as an industrial and domestic chemical, as a fertilizer feedstock, chemical precursor, as a future fuel substitute, and as a hydrogen storage molecule. Therefore it is bound to have a considerable influence on the global economy. The Haber–Bosch process (HBP) is still the leading technique for the manufacture of ammonia, and it produces nearly 500 million tons of NH$_3$ per year [7–8].
1. Haber–Bosch Process (HBP)

Fritz Haber\(^1\) was awarded the Nobel Prize in Chemistry in 1918 after filing his patent on the “synthesis of ammonia from its elements” utilizing the idea of high-pressure chemical engineering. Subsequently, Carl Bosch developed it on an industrial scale, for which he was also awarded the Nobel Prize in 1931. The process involves exothermic nitrogen reduction reaction (NRR) by hydrogen in the presence of an iron-based catalyst, generally promoted with K\(_2\)O and Al\(_2\)O\(_3\). It demands a temperature of 300–500°C and a pressure of 150–200 atmosphere to augment the reaction kinetics and swing the reaction equilibrium towards the product side (see equation 2).

\[
\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \Delta H = -45.9 \text{ kJ mol}^{-1} \tag{2}
\]

HBP is still the most economical method for nitrogen fixation, and it has enhanced the manufacture of agricultural fertilisers on an industrial scale, thereby increasing global agricultural productivity to a significant extent in most regions of the world [9]. In his Nobel lecture, Haber clarified that his prime intention for producing ammonia from its elements was the rising demand for food as well as the prerequisite to replace nitrogen lost from fields during the course of harvesting crops. His vision was absolutely correct since the worldwide use of fertiliser nitrogen has increased manifolds over the past one hundred years. Unfortunately, it is also a reality that the manufacture of ammonia was instrumental in synthesising raw material for explosives that can be used in weapons since they require large amounts of reactive nitrogen. It has been suggested that Haber’s discovery had a major impact on both World Wars and the following battles. Nevertheless, the large-scale production of ammonia has enabled the manufacture of several chemical compounds and certain synthetic products, leading to the development of a large variety of industries. However, there are two major shortcomings of HBP for the production of ammonia: (1) for the high-cost of clean hydrogen (H\(_2\)) produced from fossil resources, huge energy inputs are derived from

fossil fuels, but there is a relatively low yield of NH₃ (conversion rates of 10%–15% from dinitrogen) (2) harsh reaction conditions of temperatures and pressures despite using catalysts. Such conditions are derived from high-temperature rapid biomass conversion, but the process is not eco-friendly since a lot of CO₂ is released to the environment.

2. Electrocatalytic Reduction of Nitrogen: A Potential Alternative

Based on the biological nitrogen fixation, it may be envisaged that the conversion of dinitrogen to ammonia may occur upon supplying suitable number of protons and electrons, whereby the thermodynamic driving force may be manipulated by an electrochemical potential. This could lead to ammonia synthesis at room temperature, favouring the equilibrium between ammonia and dinitrogen. An increase in energy consumption (required in HBP) and release of CO₂ can impact global climate change. To mitigate these issues, the electrocatalytic reduction of nitrogen to ammonia may be a potential alternative to HBP. Electrochemical nitrogen reduction reaction (ENRR) to ammonia seems to be more advantageous [10] than HBP in the following ways:

- ENRR is thermodynamically 20% more efficient than HBP.

- ENRR can afford the benefit of rejecting fossil fuels as the source of H₂ and energy by using water as the source of H₂, combined with renewable energy expertise.

- It offers the synthesis of ammonia directly from humidified air (in a carbon-neutral means).

- Requires smaller plant infrastructure that can exploit renewable resources, thereby achieving the goal of de-centralising ammonia production and providing it in remote areas.

There has been some progress in recent years regarding electrocatalytic NRR, but this methodology is indeed challenging. Due to the inherent inertness of N₂, large overpotentials are indispensable for its electrochemical activation. Furthermore, the selectiv-
ity of formation of NH$_3$ is often low when N$_2$ reduction is carried out in aqueous electrolytes since the overpotential for NRR is higher than that required for the competing hydrogen evolution reaction (HER), thereby leading to low Faradaic efficacies [11–12]. In general, four categories of electrochemical cells have been developed to carry out the laboratory-scale study of electrocatalytic NRR, and these include H-type cells, single-chamber cells, half-cells, and flow cells. The electrolytes may be 0.05 M H$_2$SO$_4$ or 0.1 M HCl for acid, 0.1 M phosphate buffer solution (PBS) or 0.1 M Na$_2$SO$_4$ for neutral, and 0.1 M KOH for alkaline solutions. The role of pH and counter-ions in the electrolyte on NRR activity and selectivity is widely investigated. The working electrode may be glassy carbon rotating disk electrodes (GC-RDE), glassy carbon plates, carbon paper electrodes or self-supported electrodes. In the majority of the cases, Ag/AgCl reference electrodes with different KCl filling solutions are used, while Pt or graphite rods may behave as counter electrodes [13].

The performance of ENRR is determined by the detection of ammonia in the sampled electrolyte or acid traps. The technique of analysis of ammonia is of primary importance and needs to be highly selective, accurate, sensitive, and reproducible. The methods include spectrophotometry, ion-selective electrode detection, ion chromatography, fluorescence, and also some commercial test kits [14]. In the spectrophotometric process, indophenol blue method and Nessler’s method are commonly used to detect ammonia formed from nitrogen, owing to their affordability and good sensitivity. The indophenol blue method and the salicylate method appear to be more efficient, owing to their lower detection limit, formation of more stable colour and better reproducibility. It may be noted that spectrophotometric procedures are quite sensitive to pH, temperature, the concentration of the electrolytes, and interference from metal ions.

During ENRR to ammonia (in an aqueous medium), water is oxidized at the anodes, while N$_2$ reduction occurs at the cathodes. In an acidic solution, NH$_3$ is formed from nitrogen by the transport of protons (produced at anodes) via a proton exchange membrane

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to cathodes. On the other hand, under alkaline conditions, N\textsubscript{2} (at the cathode) combines with H\textsubscript{2}O and electrons to produce NH\textsubscript{3} and OH\textsuperscript{–}. The latter is transferred to the anodes through an anion exchange membrane and is finally oxidized to O\textsubscript{2} [15]. N\textsubscript{2}H\textsubscript{2} and N\textsubscript{2}H\textsubscript{4} are usually formed as byproducts [16–18] during the NRR. To avoid the interference of HER in aqueous electrolytes, certain organic solvents like acetonitrile have been tried, and it has been found that NH\textsubscript{3} formation is thermodynamically favoured in acetonitrile with the potential difference of 0.43 V between NH\textsubscript{3} and N\textsubscript{2}H\textsubscript{2} while for NH\textsubscript{3} and N\textsubscript{2}H\textsubscript{4} it is 1.26 V [19]. In fact, reaction kinetics appears to play a significant role in influencing the selectivity towards NH\textsubscript{3}. This, in turn, is further tuned by the use of a suitable catalyst. An effective electrocatalyst for NRR should be able to activate molecular N\textsubscript{2} to produce NH\textsubscript{3} at a low overpotential. It should have high selectivity in ammonia production (formation of side products like H\textsubscript{2}, N\textsubscript{2}H\textsubscript{2} and N\textsubscript{2}H\textsubscript{4} will be less favoured), and must be able to retain its catalytic activity for a long period of time. Certain specific strategies may be employed to suppress the HER during NRR:

(a) Restrict the concentration of protons in the electrolytes. E.g., a solution having higher pH can suppress proton adsorption on surfaces of the catalyst.

(b) Regulate the reaction environments to accelerate NRR other than HER. E.g., diverse temperature conditions in reactions can tune the overpotentials of NRR and HER.

(c) Choose catalysts with specified structures/configurations/morphologies to reduce the possibilities of HER. E.g., confining Fe\textsubscript{2}O\textsubscript{3} on activated charcoal.

(d) Active sites of catalysts may be such that they are more effective for N\textsubscript{2} adsorption and activation rather than proton adsorption. Computational results reveal that Sc, Y, Ti, and Zr are more selective to NRR than HER.

Faradaic efficiency is a measure of the efficiency with which charge/electrons are transferred in the catalytic system, which facilitates
<table>
<thead>
<tr>
<th>Molecular Catalyst</th>
<th>Reaction Conditions</th>
<th>Faradic Efficiency</th>
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<tbody>
<tr>
<td>2(a) Titanocene dichloride</td>
<td>Electrolysed in ionic liquids like tris (pentafluoroethyl) trifluorophosphate or trifluoromethyl sulfonate</td>
<td>1.44%</td>
</tr>
<tr>
<td>2(b) Metal phthalocyanine M = Fe</td>
<td>Fe–Pc was appended to carbon nanotube and electrolysed for 2 hrs in aqueous 0.1 M HCl electrolyte at −0.3 V versus cobaltocene electrode</td>
<td>9.73%</td>
</tr>
<tr>
<td>3(b) Trinuclear Ni complex</td>
<td>Electrolysed using a potential of −2.35 V across a glassy carbon electrode vs Fe/Fe⁺, using a 0.1 M phenol solution in THF as electrolyte</td>
<td>8.10%</td>
</tr>
<tr>
<td>4(b)</td>
<td>Electrolysed in Et₂O at 45°C, at $E = −2.3$ V versus Fe/Fe⁺, using 50 eq. of H [BARF₄] as a proton source (BARF₄ = tetrakis (3,5-bis(trifluoromethyl)phenyl)borate)</td>
<td>25%</td>
</tr>
<tr>
<td>[Mo(HSO₄)(NNH₂)(dppe)₂]HSO₄ (dppe = 1, 2-bis(diphenylphosphino)ethane)</td>
<td>H-type cell, 30 ml THF (distilled over Na) and 0.3 M n-Bu₄NClO₄ in H₂SO₄, Hg cathode</td>
<td>6.6%</td>
</tr>
</tbody>
</table>

**Table 1.** A summary of representative homogeneous catalysts with Faradaic Efficiency for electrochemical NRR.

NRR. It is generally used as a parameter to designate the extent of efficiency of a catalyst for the process. A comparative table with the most effective catalysts with their Faradic efficiencies is provided in *Table 1* [20]. Thus, a good electrocatalyst for NRR should have high Faradaic efficiency and should be able to facilitate the dissociation of N≡N triple bond for larger NH₃ production. The majority of the homogeneous catalysts that have been tried for electrocatalytic NRR are transition metal complexes that may be dissolved in acidic electrolytes and further supplied with electrons at the surface of electrodes (that are themselves inert to

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NRR). In general, the metal centre gets coordinated to molecular N₂ and utilizes the electrons to be transformed to NH₃. The latter is then lost, and the catalyst is converted back to its original conformation. Some of the representative homogeneous transi-
tion metal catalysts for the process are represented in Schemes (1 to 5), and the catalysis follows two types of pathways, viz., associative dissociation and direct dissociation. In the first case, the dissociation of \( \equiv N \) triple bond and hydrogenation at N-centres coincide. These are again of two categories—the distal pathway and the alternating pathway—as depicted in Scheme 6.
Scheme 6. Schematic representation of distal and alternating pathway for electrochemical reduction of \( \text{N}_2 \) to \( \text{NH}_3 \).

3. Conclusion

Modern-day ammonia production is totally reliant on Haber–Bosch process, which has certain shortcomings. In order to overcome them, there is an emerging methodology to synthesize \( \text{NH}_3 \) via electrocatalytic NRR at ambient conditions. The required electricity may be obtained from renewable energy sources such as solar power and wind. Substantial research efforts have been devoted to the synthesis of green \( \text{NH}_3 \) via electrochemical NRR from inexhaustible nitrogen and water, and these include the design of reactors, electrolytes, and electrocatalysts. Although ho-
mogeneous catalysts are ideal for understanding the mechanism of catalysis due to their well-defined structures as well as due to high activity (attributed to efficient mass transfer of reactants, products, and catalysts in the same liquid phase), the difficulty in separating and recovering them limits their practical applications. Despite the structural complexities of heterogeneous catalysts, they are the most widely studied nowadays and are better candidates for electrochemical NRR. With respect to transition metal complexes as catalysts, nitride catalysts have been reported to be more active toward electrochemical NRR, sulphide-, carbide-based catalysts, as well as non-metal-element-doped catalysts, are also potential candidates for the process. Further investigation is needed to understand the role of the electrocatalysts in activating molecular nitrogen. Certain hybrid catalysts, comprising two or more active components, may also display superior efficiency. Perovskites, spinels, Li salts and pyrochlores also have the potential to perform as pertinent catalysts in electrochemical NRR. Although the electrocatalytic community is working hard on it, certain challenges will require a lot of effort to be sorted out:

(a) HER is a competing reaction with NRR, which is a reason for the lower efficiency of NH₃ production. The majority of the electrocatalysts show low N₂ conversion rates, low turnover frequencies, and larger overpotentials.

(b) The Faradaic efficiency for the production of NH₃ in most cases are lesser than 10% while in some, they are below 1%.

(c) The generalized catalytic reaction pathway, primarily the active sites for N₂/H⁺ adsorption or activation, is still not properly understood.

(d) Understanding the stability of catalysts is required to determine their lifetime, and this is currently not properly reported.

(e) Most of the research is performed in laboratories with small samples. Investigation on a larger and economic scale is needed for the development of a promising catalyst for NRR.

Despite enormous challenges, we believe that collective theoretical and experimental approaches to ENRR involving in situ char-
acterization methods, rapid as well as precise measurements of ammonia/ammonium from nitrogen and choice of opposite catalyst will further supplement the progress of more active, more selective, more efficient, and more stable electrocatalysts in the near future.

Suggested Reading

[14] X Cui, C Tang and Q Zhang, A review of electrocatalytic reduction of dini-


Address for Correspondence
Sanjib Ganguly
Email: icsgxav@gmail.com
icsg@sxccal.edu
Jaydeep Basu
Email: jbasujaydeep@gmail.com
St. Xavier's College
(Autonomous)
Kolkata: 700 016.