Electrochemical Reduction of Nitrogen to Ammonia: Progress, Challenges and Future Outlook

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Abstract

Ammonia is an important chemical used in the production of fertilizers. The electrochemical reduction of nitrogen (NRR) to synthesize ammonia has emerged to be a potential alternative approach. Here, we provide a short opinion of the current progress and challenges of nitrogen reduction reaction from the recent literatures. Different types of electrocatalysts with their performances and design principles are briefly outlined. However, most of the electrocatalysts showed unsatisfactory catalytic performance for NRR due to various factors such as the competing side reactions and the large thermodynamic energy barrier. Hence, the concept of conducting NRR should be re-evaluated. We provide our opinion on the future possible outlook on how to improve the NRR performance. Alternative external energy input should be coupled with the electrochemical reduction of nitrogen to help with the activation of nitrogen to ammonia. Some possible energy input could be the use of cold plasma and Surface Plasmon Resonance.

Introduction

Ammonia (NH_3) has been widely used in pharmaceutical, chemical industries and the production of fertilizers. [1, 2] Over the years, ammonia is quickly gaining recognition as a potential energy carrier and a source of clean fuel for the shipping industry due to its attractive energy density, ease of storage and poor flammability.[3, 4] For a century since the discovery of man-made ammonia, the predominant synthesis method of ammonia production remains to be the Haber-Bosch process which is a great concern despite its evolution because it consumes large volumes of hydrogen and nitrogen gases as raw materials and combine them together under high temperatures and pressures ranging from 300°C to 500°C and 200 atm to 300 atm, respectively. [1, 2] To support this process, statistics have shown that more than 95% of the global hydrogen is produced by reforming fossil fuels and approximately 50% of this hydrogen produced is used for ammonia production. [5-9] These means of obtaining hydrogen are detrimental to the environment as significant amounts of carbon dioxide are constantly released into the atmosphere, worsening the global warming phenomena. The Haber-Bosch process is stated to contribute approximately 3% of greenhouse emission. [1, 2] As a result of the growing demand for ammonia, there is a need to develop less energy-intensive approach to produce green ammonia. The term “green ammonia” refers to ammonia that is produced using a process that is fully renewable and carbon-free. [10] Here, the electrochemical synthesis of ammonia through nitrogen fixation, Nitrogen Reduction Reaction (NRR), is an example of such process where the hydrogen source is derived from water electrolysis, powered by renewable electricity. [10]

In some works, the hydrogen source can be derived from water since water is a rich source of protons. Moreover, the proton transfer process can be adjusted using different aqueous electrolytes to improve the performance capabilities. This method is more advantageous as 90% of carbon dioxide emission caused by the reforming of fossil fuels to obtain hydrogen for the Haber-Bosch process may be avoided.[10] NRR has become a great interest to many researchers because it can produce green ammonia and its efficiency heavily relies on the selection of suitable catalysts with high activity and selectivity for nitrogen reduction. This allows for the whole synthesis process to be able to occur at less severe operating conditions, possibly at ambient conditions. [11] In addition, the entire process may be driven by renewable electricity, eradicating the use of fossil fuels for this purpose. [12] However, most of the investigated electrocatalysts to date displayed low faradaic efficiencies and yield rates of ammonia. The poor performance is mainly attributed to the non-polarization traits and strong binding energy of the N≡N triple bond (940.95 kJ/mol) of the nitrogen molecule, which makes it extremely hard to cleave and thus severely hinders the reaction kinetics of NRR under ambient conditions. [12, 13] In addition, the strong competition of the side reaction on the surface of the electrocatalyst, Hydrogen Evolution Reaction (HER), tends to consume the protons and limit the rate of NRR. [14, 15]

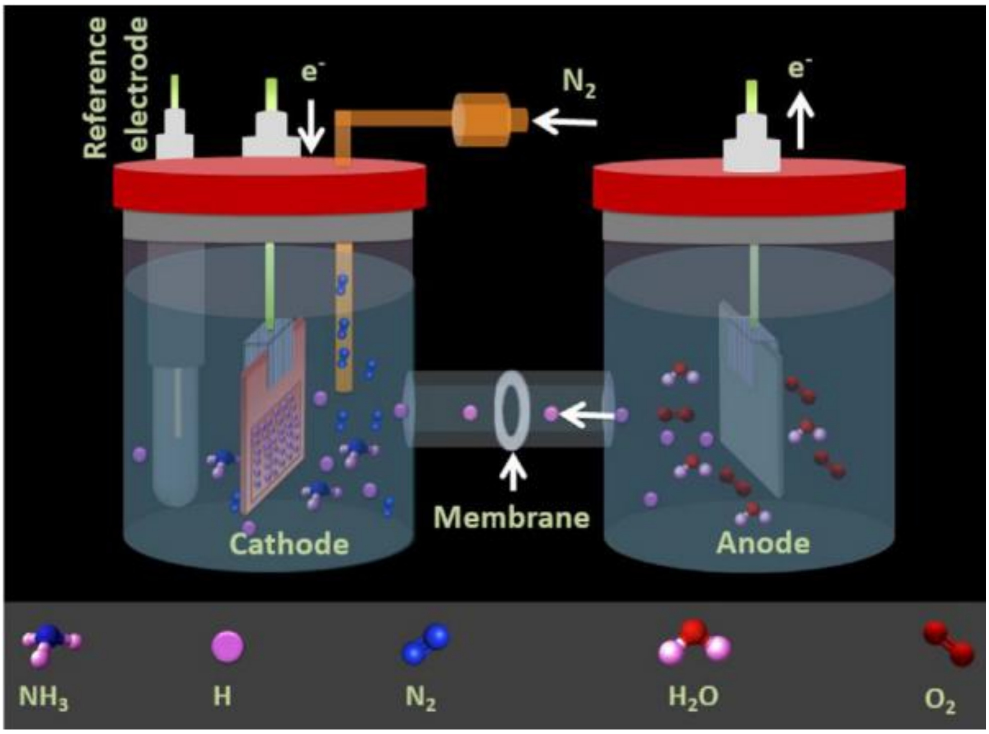

Figure 1. Illustration model for the electrochemical N_2 fixation. Figure reprinted (adapted) with permission from Elsevier, reference 16, Copyright 2018, Elsevier Nano Energy Volume 49. [16]

Overview of experimental methods and limitations

The electrochemical reduction of nitrogen measurements is typically carried out in the H-cell. (Figure 1) The post-test electrolyte would be collected from the cathode chamber and then subjected to ammonia quantification tests such as UV-spectrometry or Ion Chromatography tests. The key limitation of these tests is that the amount of ammonia produced are usually in very minute concentration and may not be fully attributed to NRR. Ammonia contamination is common during testing procedures due to the possibility of background ammonia being produced from the unstable Nitrogen-containing species. This may lead to inaccurate quantification of actual produced ammonia concentration and thus contribute huge errors to the experimental data. Hence, more stringent control experiments with Argon control and quantitative ^{15}N isotope experiments (e.g mass spectrometry and NMR spectroscopy) should be employed to quantify the impact of NO_x contamination on the ammonia yield as the NO_x contamination in the nitrogen gas source is not observable and is hard to remove through background subtraction. By using NMR spectroscopy to detect $^{15}N_2$ reduction, it may be possible to determine the origin of the produced ammonia and improve the accuracy of ammonia quantification. [17, 18] It is suggested that ^{15}N isotopic labelling experiments, using ^{1}H NMR spectras may be used to verify the origin of ammonia produced quantitatively and qualitatively. [19] However, one should take precautions as the ^{15}N source may not be of high purity and may contain ^{15}N ammonia and NO_x. [19, 20]

Interesting Findings

Generally, noble-metal catalysts are favored as electrocatalysts over the other classes of materials owing to their great stability and high abundance of catalytic active sites. However, these metals are very expensive, which limits their commercial use.[21, 22] Hence, Earth-abundant metals and even non-metals are being extensively sought out as electrocatalysts for NRR. To date, a plethora of materials were crafted and experimented with in a bid to attain good NRR performance in terms of Faradaic Efficiency and yield rates. For this review, only electrocatalysts with reasonable Faradaic efficiencies are evaluated instead as we believe that the direction of research for NRR should be headed for the use of inexpensive materials with great performance to achieve industrial scalability and economic viability. Through these mentioned published works, it is worth noting that the Faradaic Efficiency can be significantly improved by tuning the electronic structure of the electrocatalyst's surface to enhance the interaction between nitrogen molecule and electrocatalyst, and subsequently allow for activation of nitrogen molecule.

Ruthenium (Ru) is known to be one of the best noble-metal candidates and there have been extensive research done on Ru-based electrocatalysts. [23] Geng and his co-workers distributed Ru single atoms on nitrogen-doped carbon (Ru SAs/N-C) and used them as electrocatalyst for NRR. [24] Due to the strong interaction between the nitrogen molecule and Ru SAs/N-C, this boosted the adsorption capability for nitrogen and achieved Faradaic efficiency of 29.6% and ammonia yield rate of 120.9 ug/h.mg$_{cat}$ at -0.2V vs RHE, which was the highest rate in its time and encouraged the development of single atom catalysts for NRR. [24]

Some very interesting works on the use of transition metal catalysts for NRR have also been reported due to the attractive qualities such as abundance in nature, lower costs and the unique d-orbital electrons. [22] Niobium dioxide nanoparticles were tested for NRR application and displayed a high Faradaic Efficiency of 32% at -0.6V vs RHE. [25] In this work, Niobium being a transition metal, where the Nb^{4+} cation is claimed to provide the empty d-orbital which can accept and back-donate electrons with the π orbitals of Nitrogen and therefore allow for strong adsorption of Nitrogen and activation of the N≡N triple bond. [25] Molybdenum-based catalysts were also explored for NRR due to Molybdenum having been part of the biological nitrogen fixation process which could potentially convert nitrogen into ammonia under ambient conditions. [23] Molybdenum is stated to have strong adsorption capacity for Nitrogen molecules and Qu with his co-workers developed Nitrogen-doped carbon shells-coated Oxygen-doped Molybdenum Carbide nanoparticles for NRR, which achieved a Faradaic efficiency of 25.1% and yield rate of 22.5 ug/h.mg$_{cat}$ at -0.35V vs RHE. [26] This was achieved by the tuning of electronic structure to suppress the competing side reaction HER and improve the electron transfer process for NRR. While employing nitrogen-doped catalysts for NRR, we advise to take precautionary measures regarding the nitrogen source as the ammonia can be produced from the existing nitrogen from the catalyst itself.

The use of Bismuth Nanocrystals (BiNCs) which is a semiconductor, have also attained great experimental results. In this work, the group presented a strategy to collectively use BiNCs and potassium cations in the catalytic system because Bismuth is said to have better intrinsic NRR activity due to the good interaction between the Bismuth 6p band and the nitrogen 2p orbitals and Potassium cations can help stabilize the key NRR intermediates and control proton transfer to boost selectivity towards ammonia. [27] Hence, a high faradaic efficiency of 66% and yield rate of 3.4 mg/h.mg$_{cat.}$ which is the best NRR performance achieved thus far. [27] In another work, Bismuth-based material with occupied orbitals as well as vacant orbitals ($Bi_4O_5I_2$ (V_O-$Bi_4O_5I_2$-OH)) at the Bi atom was introduced for NRR. [28] This design could achieve a unique electronic surface structure which was specially done to mimic "π back-donation" behaviour like the d-block element electrocatalysts. As a result of this rational design, a Faradaic Efficiency of 32.4% was achieved, which is much higher than most of the prior reports that employed p-block elements as electrocatalyst. [28]

Recommendation for Future work

Despite substantial research efforts, satisfactory NRR performance has yet been achieved and the absolute yield is still not high enough to compete with the current industrial level of production. Due to the extremely high thermodynamic energy barrier, it is exceptionally challenging to effectively activate the nitrogen molecule and reduce it into ammonia at a suitable voltage under ambient conditions before substantial HER occurs, regardless of the catalyst material chosen. In this regard, we believe that the concept of conducting NRR to synthesize ammonia should be re-evaluated. We thereby suggest breaking the green ammonia synthesis system into 2 parts, which includes the activation of nitrogen using external energy input before NRR to form green ammonia.

Extra energy input may be necessary to activate the nitrogen molecule into a more reactive intermediate form such as nitrite or nitrate, and these intermediates are highly soluble in water and can be reduced more readily to ammonia. With the N-O bonds having a lower dissociation energy of only 204 kJ mol^{-1}, it is easier to transform nitrate in aqueous solution into harmless or high- value products such as ammonia. [29, 30] To date, many works published for nitrates reduction have demonstrated high faradaic efficiencies with some works presenting FE values exceeding 90%. [31] This coupled system could potentially yield more green ammonia and be scaled up for decentralized green ammonia synthesis.

One of such external energy inputs to activate nitrogen by breaking the N≡N triple bond could be derived from plasma processes. Over the years, various types of plasmas have been investigated for ammonia synthesis. [32] Cold plasma has the potential to create NO_x species while maintaining lower reaction temperature. The theoretical limit of energy consumption (5.56×10^{-2} kW h mol^{-1} NO_x^-) of this method is 2.5 times lesser than that for the Haber-Bosch process (0.4 kW h mol^{-1} NH_3), thus increasing the overall energy efficiency. [33]

Recently, researchers reported nitrogen activation into NO_x^- species using cold plasma and NO_x^- species conversion into ammonia via electrocatalytic reduction using surface born-rich core-shell nickel boride electrocatalyst. This work has achieved closed to 100% Faradaic Efficiency due to the increase in activity, selectivity and stability of the system. [34] Moreover, Copper-based material was also used as catalyst in the hybrid system with plasma-activated nitrogen due to its stability and ability to suppress HER. The hybrid system consisting of Copper Nanowires was revealed to achieve Faradaic efficiency of ~100%. [33]

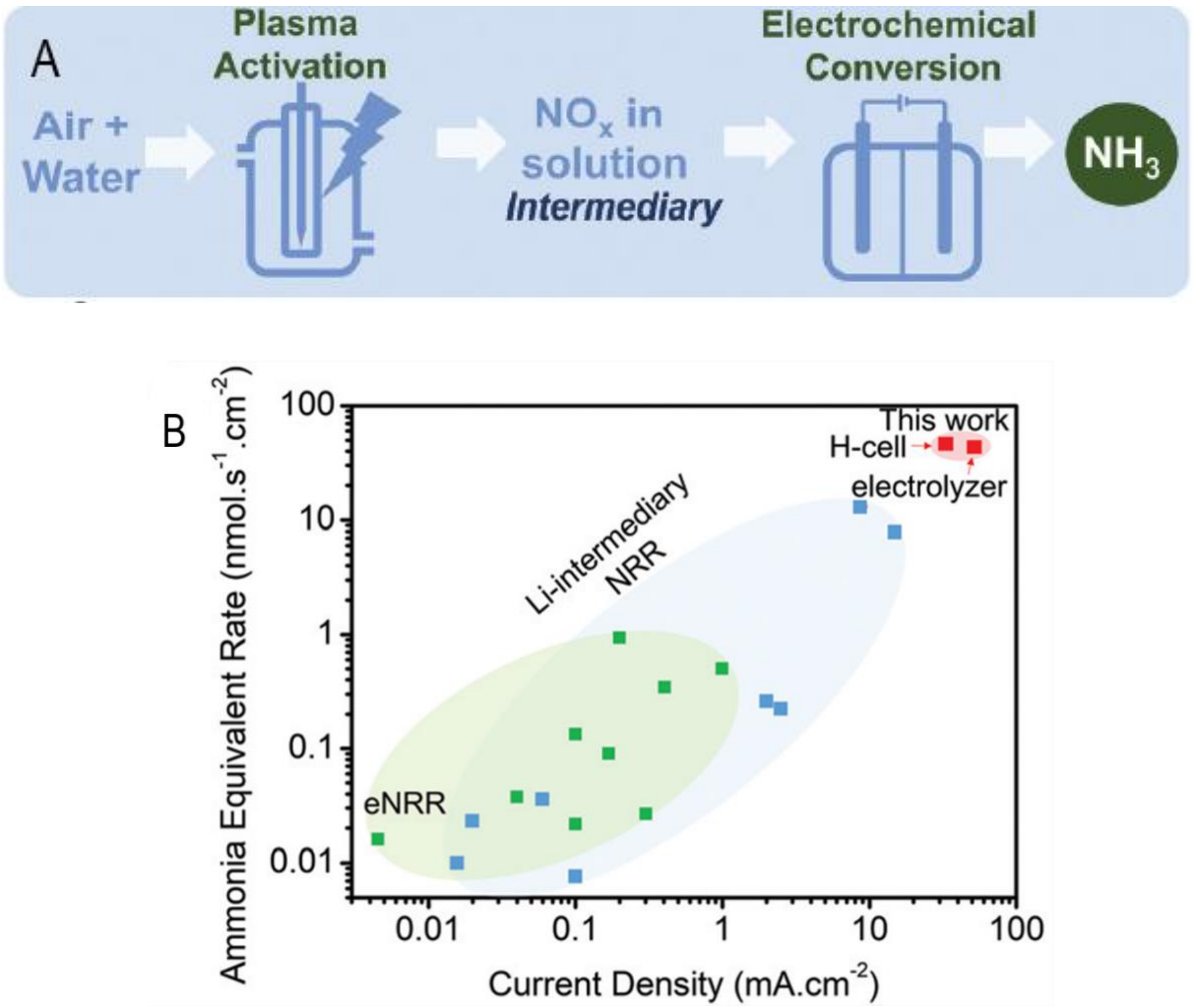

Figure 2. A) Illustration of the hybrid plasma-electrochemical technology for the synthesis of green ammonia. B) Graphical comparison of ammonia production rates between the plasma-catalyst system (red) and NRR without plasma assistance. The ammonia production rates are significantly higher with plasma assistance.[33] Figures adapted with permission from reference 33, Copyright 2008 Royal Society of Chemistry, Energy & Environmental Science.

The application of cold plasma to the electrocatalytic system for NRR could allow us to manipulate the reaction energetics and cause vibrational excitations in nitrogen which may lower the dissociation barriers for efficient green ammonia synthesis. [35] However, the major limitations of this method are the high costs and the need for better electrocatalysts and electrolytes, which currently renders inadequate ammonia yield to compete with existing haber-bosch process. [36, 37]

Another example of energy input could be the use of localised Surface Plasmon Resonance (LSPR) to devise plasmon-induced ammonia synthesis. Noble metal nanoparticles, especially gold and silver, have strong optical field enhancement which results in strong scattering and absorption of light. [38] There are a few notable works on SPR for ammonia synthesis: the creation of Os-Au composite nanoparticles, [39] and $AuRu_x$ nanocatalyst [40]. In both catalytic systems, the surface plasmonic energy of Au were suggested to be transferred to the adjacent catalytically active Os and Ru metals directly. The system was then used for NRR with the addition of visible light irradiation as external energy input to activate nitrogen through dissociative mechanism. [39] Hence, the use of light irradiation as external energy input coupled with the knowledge of SPR could potentially help to aid in NRR under ambient conditions. While employing this method, more research should be done to investigate the optimal SPR sufficient for nitrogen activation.

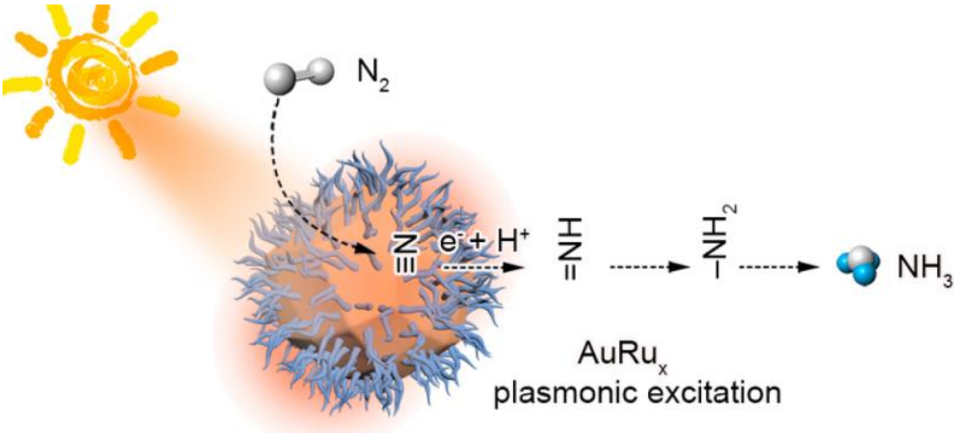

Figure 3. Schematic illustration of surface plasmon-induced NRR for ammonia synthesis using $AuRu_x$ electrocatalyst. [40] Reprinted (adapted) with permission from reference 39. Copyright 2019 American Chemical Society.

While non-thermal plasma-assisted NRR and plasmon-induced NRR can possibly become alternatives to the Haber-Bosch process for its energy-saving green ammonia synthesis capabilities, the conversion and efficiency of these processes still require improvement to scale up for industrial use. We strongly encourage researchers in this field to consider other potential external energy input alternatives such as renewable energy to induce plasma, all of which can potentially activate nitrogen molecules under ambient conditions to facilitate effective NRR with better energy efficiencies.

Acknowledgement

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