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Sustainable Nitrogen Activation – Are We There Yet?

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DOI: 10.1039/D3FD00087G

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Abstract

The activation of dinitrogen as a fundamental step in reactions to produce nitrogen compounds, including ammonia and nitrates, has a cornerstone role in chemistry. Bringing together research from disparate fields where this can be achieved sustainably, this Faraday Discussion seeks to build connections between approaches that can stimulate further advances. In this paper we set out to provide an overview of these different approaches and their commonalities. We explore experimental aspects including the positive role of increasing nitrogen pressure in some fields, as well as offering perspectives on when $^{15}\text{N}_2$ experiments might, and might not, be necessary. Deconstructing the nitrogen reduction reaction, we attempt to provide a common framework of energetic scales within which all of the different approaches and their components can be understood. On sustainability, we argue that although green ammonia produced from a green- H_2 fed Haber-Bosch process seems to fit the bill, there remain many real-world contexts in which other, sustainable, approaches to this vital reaction are urgently needed.

1. Introduction

Nitrogen is a fundamental component of all life on our planet. Earth's atmosphere contains about 4×10^{15} tonnes of N_2 , of which about 4×10^6 tonnes (or about 0.1 ppm) is transformed into a variety of other nitrogen compounds per year; about half of this due to anthropogenic activities and the remainder due to natural processes. Its key role in human food supply has necessitated rapid development, over the last 100 years, of the Haber-Bosch process by which atmospheric N_2 is reduced to ammonia and thence to various forms of fertiliser. Unfortunately, this process relies on fossil fuels as both a source of energy and H_2 , the by-product being fossil-origin CO_2 . This creates an unfortunate nexus between global food supply and climate change. Over the last decade or more this has generated substantial interest in alternate approaches to converting atmospheric N_2 to nitrogen compounds using renewable energy to break this nexus. The multistep reduction of N_2 to ammonia appears to be a relatively straightforward process in thermodynamic terms, with an E^0 of the $\frac{1}{2}\text{N}_2 + 3\text{e}^- + 3\text{H}^+ \rightleftharpoons \text{NH}_3$ half-reaction just slightly above that of the reversible hydrogen electrode ($\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2$). However, the first step in any such nitrogen reduction process is inevitably difficult due to the stability of the N_2 triple bond requiring significant energy input to activate the molecule for further reaction. As such, N_2 activation has become a key area of scientific investigation and this timely Faraday Discussion focusses precisely on this topic.

Figure 1 attempts to summarise the approaches that are being investigated towards N_2 activation and conversion. From the perspective of oxidation states, we split these reactions into two distinct groups, those that are reductive in nature and those that are oxidative. The reductive processes have many elements in common in the sense that all involve transfer of an energetic electron from a source such as an electrode, a reducing agent, or the conduction band of a photoexcited semiconductor. Proton transfer from a suitable carrier is likely strongly coupled to each electron transfer, although the activation of N_2 on $Li(s)$ to form Li_3N is an interesting example where a metal ion, in this case Li^+ , takes the place of the proton in the initial stages.

Included in the chemical processes are those that form C-N, P-N and similar compounds in which the reaction might not be considered fully reductive or oxidative, but nonetheless some degree of electron transfer to or from the N occurs and is likely a key feature of the activation process. An example would include the reaction of simple carbenes with N_2 .¹

The oxidative processes in many cases involve an activated or partially reduced “O” species. Notably, a number of the potential pathways in the oxidative direction, for example direct electrochemical oxidation, are not yet well established, potentially due to difficulties in the initial activation step. These are shown in light grey colours in Figure 1.

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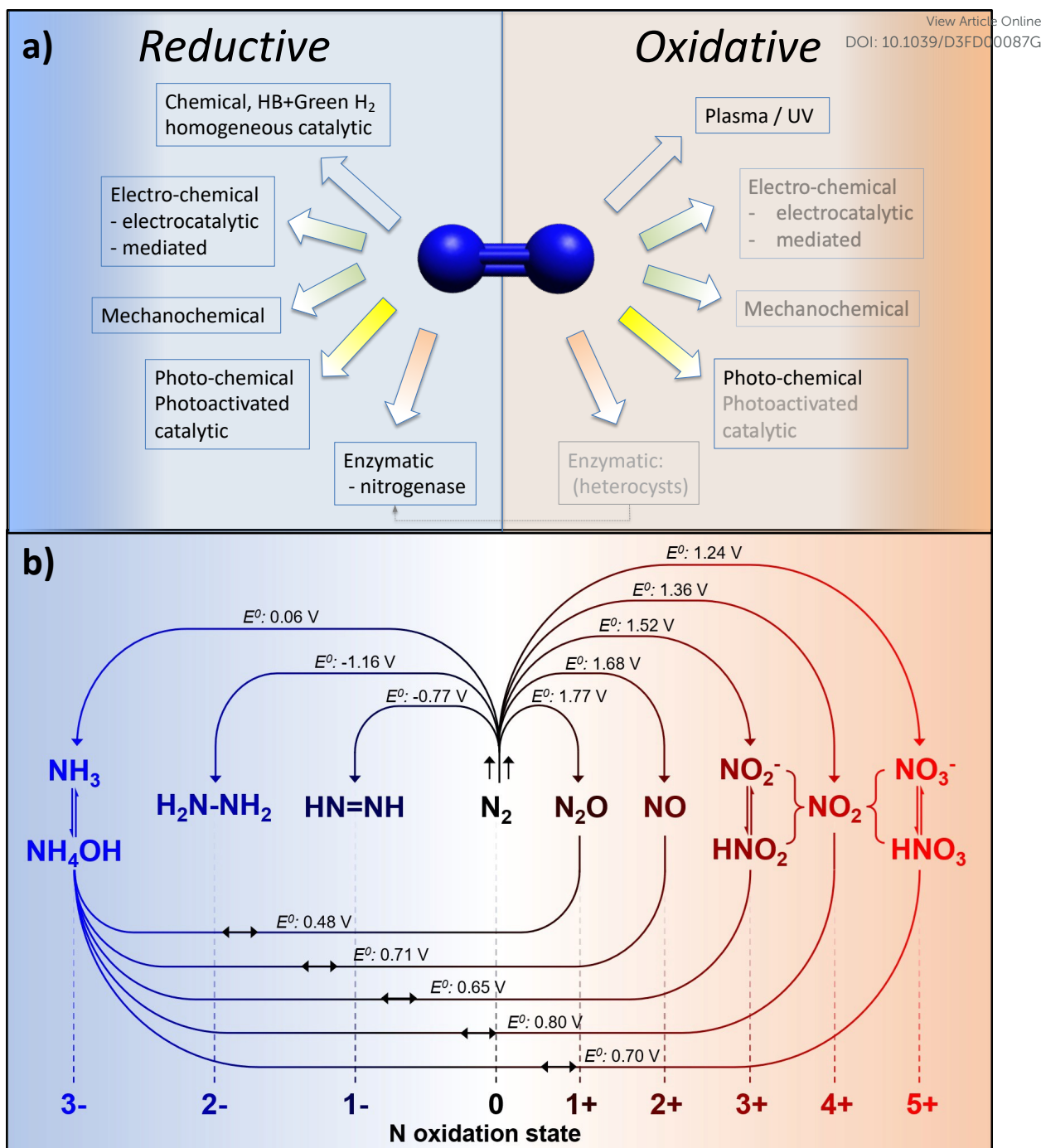


Figure 1. a) Overview of approaches to N₂ activation; (b) Oxidation states of nitrogen and their corresponding standard reduction potentials (E^0 at 298.15 K) for the various interconversions shown.

This distinction underlines the amazing, almost unparalleled amongst the elements, range of oxidation states of N that are possible, the majority of which are of practical significance in both industrial chemistry as well as the biosphere. Figure 1b provides a summary of these oxidation states and the processes by which they can be interconverted. As an aside it is worth mentioning the value of the Pourbaix diagrams in understanding the inter-relationship of these various compounds as a function of pH in aqueous solutions.² These diagrams are readily

available in Pourbaix's original treatise, or can be calculated for various different concentrations and temperatures/pressures in available software packages.³

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The wide range of viable N₂ activation process summarised in Figure 1a are well represented in this Faraday Discussion, including the heterogeneous catalytic and chemical looping routes,⁴⁻¹² as well as the enzymatic,¹³⁻¹⁵ electro/photocatalytic,¹⁶⁻²² mechano-catalytic,²³ homogeneous catalytic,^{22, 24} mediated¹⁷ and plasma-based²⁵ approaches. In the present article we attempt to provide some perspectives on this broad field. Our goal is not to provide a review, several examples of which are available.^{26, 27} Rather, and consistent with the goals of the Faraday Discussion itself, we attempt draw together some common themes and understandings from the disparate fields that focus on sustainable N₂ activation in such a way that researchers can understand and benefit from each other's methods, perspectives and concepts.

2. Green-H₂ + Haber-Bosch = Green Ammonia. Do we need anything else?

Water electrolysis, based on renewable energy input to produce hydrogen and oxygen, is a technology that has developed rapidly in recent years. Along with electrocatalysts based on earth abundant elements and material-efficient electrolyser designs, the renewables origin of this H₂, justifiably allow it to be labelled "green-H₂". Using such green-H₂ as an input to the Haber-Bosch process, in place of the steam-methane reformed H₂, allows in principle the production of green-ammonia and this concept has gained substantial traction in the industry. Demonstration sites are being developed in a number of locations globally. Given the likely rapid development of green ammonia produced in this fashion, a key question worth considering is: why bother, technologically, with any other approach to green-ammonia or green-nitrate production? A purely scientific answer to this question is simply that an understanding of such an important mechanism as N₂ activation by any means will always be of high fundamental interest.

An important answer also emerges at the practical level from the farming community. Recent global events have generated severe price shocks and supply disruptions such that the timely supply of fertilisers to farms globally has become much more fraught than any other time in the last 50 years or more. The concept of highly distributed production of ammonia and fertiliser compounds has generated strong interest as a result. Production at the large farm, or local farming community, level through cooperatives, would insulate regions from such global events. Green-H₂ + Haber-Bosch scaled downwards to the tonnes per day level becomes significantly less efficient and more capital intensive than the large, 1000's of tonnes per day plants that are the mainstay of today's industry. Globally, ammonia production is also concentrated at a relatively small number of sites; this creates significant 'sovereign risk' in countries and regions that are substantially reliant on imported fertilisers. For these reasons, practical interest in alternate sustainable routes to fertilisers is intense and the activities of academic groups, PhD students and funding agencies towards this end are well justified.

3. The challenge of limited N₂ solubility – putting Henry's Law to work

Many of the ambient temperature approaches to N₂ activation in Figure 1 share one challenge in common – limited N₂ solubility in aqueous or other reaction solvents. At only 0.6 mmol N₂ per L, at 1 atm N₂ pressure, water is especially troublesome as a solvent in this regard. Some of the non-aqueous solvents are slightly better, at 4 – 5 mM, but these are still very low values

in a chemical reaction. The problem is that in any context where the reduction of H_2O or H^+ to H_2 is a competing reaction, their concentration high compared to N_2 strongly favours hydrogen production. Altering the pH is not necessarily an answer as the thermodynamics of the two processes parallel one another as a function of pH, as easily observed in the very useful Pourbaix diagram for N_2 . Equally, given a large excess of H^+ , surface kinetics will usually favour high coverage of reduced H species and thence H_2 production.

However, it is possible to tip this balance of H^+ vs. N_2 somewhat in favour of the latter *via* Henry's Law. Over limited pressure ranges this is a simple linear dependence:

$$c(\text{N}_2) = k_{\text{H}} P(\text{N}_2)$$

where $P(\text{N}_2)$ is the partial pressure of N_2 applied, k_{H} is the Henry's Law constant for N_2 in the medium involved and $c(\text{N}_2)$ is the concentration of N_2 in solution at equilibrium that we seek to increase.

The value of this has been demonstrated very clearly in the work from our group (Figure S11 of ref.²⁸ and Figure 3D of ref.²⁹) where the effect of pressure on the Li-mediated N_2 reaction was investigated between 1 and 20 bar. In both cases, the ammonia production yield rate and faradaic efficiency (FE) of the nitrogen reduction reaction (NRR) increased with pressure over the first 10 bar (ie a 10-fold increase in N_2 concentration). Thereafter, both metrics became somewhat independent of pressure and notably the FE approaches closely to 100% in this region of pressure and the yield rates reach distinctly practical levels. This provides a clear demonstration of the possibility of a continuous and selective electrochemical N_2 reduction process. One could note that the 1 bar metrics in these experiments could have been rated as rather disappointing and might have discouraged further research!

The pressure dependence observed here also provides some direct mechanistic insights. Since rate appears to be linear in $c(\text{N}_2)$ up to 10 bar, and since $\text{N}_2(\text{g})$ itself is presumably only involved in the surface adsorption step, it is clear that this is limiting at low (*i.e.* ambient) pressures. However, above 10 bar in these experiments, other steps in the process become limiting, indicating that N_2 is now in excess and other steps, for example N_2 activation, electron transfer or proton transfer, are limiting. Each of these can be manipulated *via* (semi-)independent experimental parameters.

It is important for us to note that the safety aspects of dealing with equipment at elevated pressures must be taken very seriously. We recommend that multiple layers of shielding/protection be continuously provided around cells and gas lines in operation. We have recently shared the design of our Li-mediated electrochemical N_2 reduction cell;²⁸ a minor clarification on a safety aspect of the design is included in the Supplementary Information herewith.

4. **Other practical challenges in N_2 chemistry**

A common issue across a number of the approaches to nitrogen activation summarised in Figure 1 is the problem of unambiguously proving that the process has actually taken place, as opposed to the reduction or oxidation of some N-containing contaminant that is intrinsic to the experimental setup. This problem tends to be a challenge for the lower yielding approaches, for example when the amounts of ammonia produced are in the region of 1 - 10 μmol s or less; the detection techniques are thoroughly capable of detecting such amounts, but the source of the N may not be the supplied N_2 at these levels. The issue is that nitrogen chemistry presents a rich diversity of oxidation states ranging from -3 to +5 (Figure 1b) and the kinetics of their

transformation into NH_3 or NO_3^- is much more facile than that of N_2 , in many cases because they are mono-N compounds and the troublesome N_2 activation event is not involved. View Article Online
DOI: 10.1039/D3FD00087G

This challenge has been well recognised in the photo- and bio-chemical approaches to nitrogen fixation for decades, but is only more recently (and reluctantly) recognised by the electrochemists. $^{15}\text{N}_2$ studies provide well understood confirmatory evidence, though they provide *necessary* proof but not *sufficient* proof. The latter point simply suggests that if the contaminants that are present in the N_2 gas supply are also present as ^{15}N -species in the $^{15}\text{N}_2$ supply then the $^{15}\text{N}_2$ results can be expected to be similarly false. In our view a long-running, fixed gas-volume experiment is a straightforward approach to providing confirmatory evidence of N_2 activation and should always be done before incurring the cost of $^{15}\text{N}_2$ experiments. Particularly important is the use of only a known, fixed and no larger than necessary volume of N_2 in the experiment (Figure 2). A very common outcome of experiments with the fixed nitrogen volume is significant deceleration of the reaction as compared to tests under flowing gas conditions and eventual cessation of the reaction well before any significant amount of N_2 could be consumed. In other words, large volumes of bubbling gas *before* or *during* the experiment should be avoided. Significant reports of aqueous electrochemical N_2 reduction to ammonia have been refuted, the false positive results being likely due to this issue.

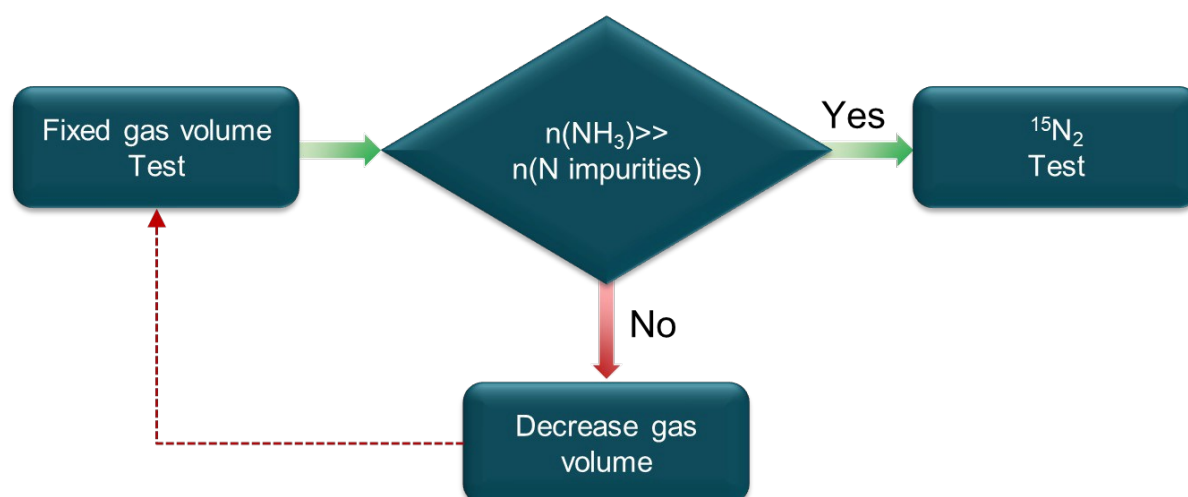


Figure 2. Recommended protocol to avoid false positives from $^{14}\text{N}_2$ and $^{15}\text{N}_2$ activation experiments. The value of $n(\text{N-impurities})$ should be calculated on the basis of a worst-case scenario from the stated or measured (whichever is worst) purity of the gas supplies. If the stated/measured level of a contaminant is below the limit of detection (LOD), the value of the LOD should be used for the calculation.

These fixed gas volume experiments should be designed on the basis of the preliminary results and a worst-case assumption about the level of impurities that might be present in the gas supply. An example of analysing the impurities in the gas supplies ($^{14}\text{N}_2$ and $^{15}\text{N}_2$) comparing their possible impact on the measured results can be seen in Table S3 of ref.²⁹ The calculated quantity of N_2 gas in the headspace of the cell is usually sufficient excess for days or even months of run time at the yield rates in the type of experiments involved. For example, at 1 atm partial pressure and 298 K, 1 mL of N_2 gas contains approximately 8×10^{-5} mol of N, while *ca* 10 mL of an N_2 -saturated aqueous solution under these conditions contains *ca* 1×10^{-5} of dissolved N. Taken together, this amount of N would be sufficient to sustain over 1 day of N_2 conversion at a respectable rate of $1 \text{ nmol}_\text{N} \text{ s}^{-1}$, which is notably higher than the rates reported

in the vast majority of recent publications. Until significant depletion of N_2 is achieved, the total yield of a target product should increase linearly in time if all is well. A tendency to trend towards a constant value of total yield, *i.e.* unexpectedly fast deceleration of the process before a significant amount of N_2 has been consumed, is a sign of impurities being the main actors, or of catalyst poisoning, neither of which is a good outcome or indicative of any value in proceeding to $^{15}N_2$ tests. An often-quoted reason for not attempting longer running experiments is the potential for consumption of ammonia at the anode due to increasing amounts of produced into the electrolyte. This hypothesis should be tested by adding appropriately small amounts of ammonia at the beginning of a control experiment to demonstrate its consumption.

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5. *Understanding N_2 Activation via Quantum-level Calculations*

Given the multistep aspect of both N_2 reduction and oxidation it can be extremely difficult to experimentally unpack the fundamental aspects of the nitrogen activation event from the other steps in the process. Significant progress in this respect is emerging in the enzymatic approaches reported at this Faraday Discussion. In other approaches it is often fruitful to employ density functional theory (DFT) calculations of possible reaction pathways to reveal more detail than can be gleaned from experimental studies, and also initially screen and investigate catalyst options that are not immediately straightforward to test experimentally.³⁰

The Li-mediated nitrogen reduction reaction mentioned above, which involves formation of a Li_3N intermediate, is a good example, where deconvoluting the mechanism is experimentally challenging, though is an ongoing focus of attention in several groups. That the activation and reduction to N^{3-} is not a simple electrocatalytic process is relatively obvious from the fact that the reaction does not occur readily in the absence of the Li^+ ions in the electrolyte and that its chemical equivalent ($3Li(s) + 0.5N_2 \rightleftharpoons Li_3N$) is very well known and spontaneous. Therefore, focus turns to a hypothesis involving (i) electrodeposition of $Li(s)$ and (ii) subsequent N_2 absorption and activation on the $Li(s)$. A DFT investigation of the latter step (Figure 3) reveals that an activation barrier is observed, despite the highly energetic surface that $Li(s)$ represents. Adsorption to form the adsorbed $*N_2$ state is spontaneous, to the extent of approximately 0.8 eV. This is just sufficient (with thermal energy) to overcome the subsequent activation step to a transition state where the N-N bond distance is stretched by approximately a factor of two. DFT studies such as these clearly provide mechanistic insights that are difficult to achieve experimentally, potentially revealing steps that are rate limiting.

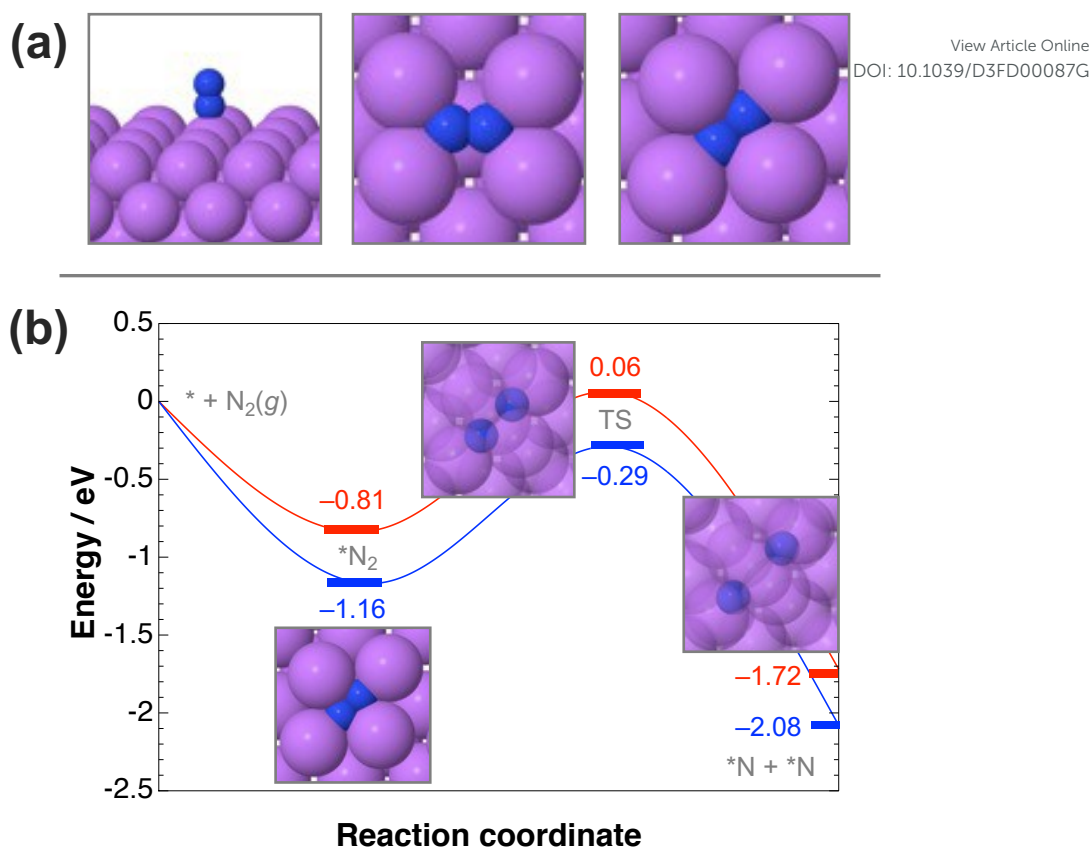


Figure 3. (a) Structures of the end-on and two side-on adsorption modes of N₂ on a (001) surface of bcc Li surface. Binding electronic energies are -0.29 , -0.31 , and -1.16 eV, while binding free energies are 0.22 , 0.15 , and -0.66 eV, respectively, indicating that only the latter side-on mode provides spontaneous adsorption; N \equiv N distances are elongated from 1.12 , to 1.13 , 1.24 , and 1.27 Å, respectively, indicating that the greater the N \equiv N distance elongation, the greater the exergonicity of the N₂ adsorption. (b) Energy profiles for N₂ splitting on the Li surface (electronic and free energy profiles are in blue and red, respectively). Activation electronic barrier to the transition state (TS) is 0.87 eV. The N–N distances in the TS is 2.03 Å and in the completely dissociated state has increased to 3.16 Å; inset images show the top view of the structures at each step.

6. Common Activity Scales – A Unifying Picture

The goal of the present Faraday Discussion is to bring together researchers from the quite different fields of nitrogen activation, as broadly summarised in Figure 1. One of the challenges in doing so is finding common terminologies and conceptual frameworks such that similarities and vital differences in the mechanisms involved can be understood. Towards this end, we have attempted to reduce the different processes to a common picture within which the role and chemical activity can be compared. Chemical activities might then be compared using familiar energy scales.

Such an activity scale diagram is shown in Figure 4. This focusses on the reductive processes only, as the extra detail introduced by dealing with the oxidative reactions, while possible, only adds complexity. In narrative terms we could describe the process (black text in Figure 4) as follows: N₂ (gaseous or dissolved) binds to a substrate (surface, molecular species or enzyme) and becomes activated (bond lengthened, electron orbitals distorted) by interaction with the

substrate, electron transfer occurs (from the substrate, or a molecular reducing agent, or an electrochemical circuit), proton transfer from a proton carrier (solvent, molecular proton carrier, adsorbed H atoms) occurs at the same time (Concerted Proton Electron Transfer) or shortly thereafter (Proton Coupled Electron Transfer), further electron and proton transfers occur and at some (any) point in this sequence the N atoms become separated from one another (dissociation). The result is a fully formed NH_3 molecule which must then spontaneously detach from the substrate (desorption). The dissociative mechanism of the Haber-Bosch reaction is a variant of this in which the electron and proton transfers occur simultaneously *via* surface H atoms.

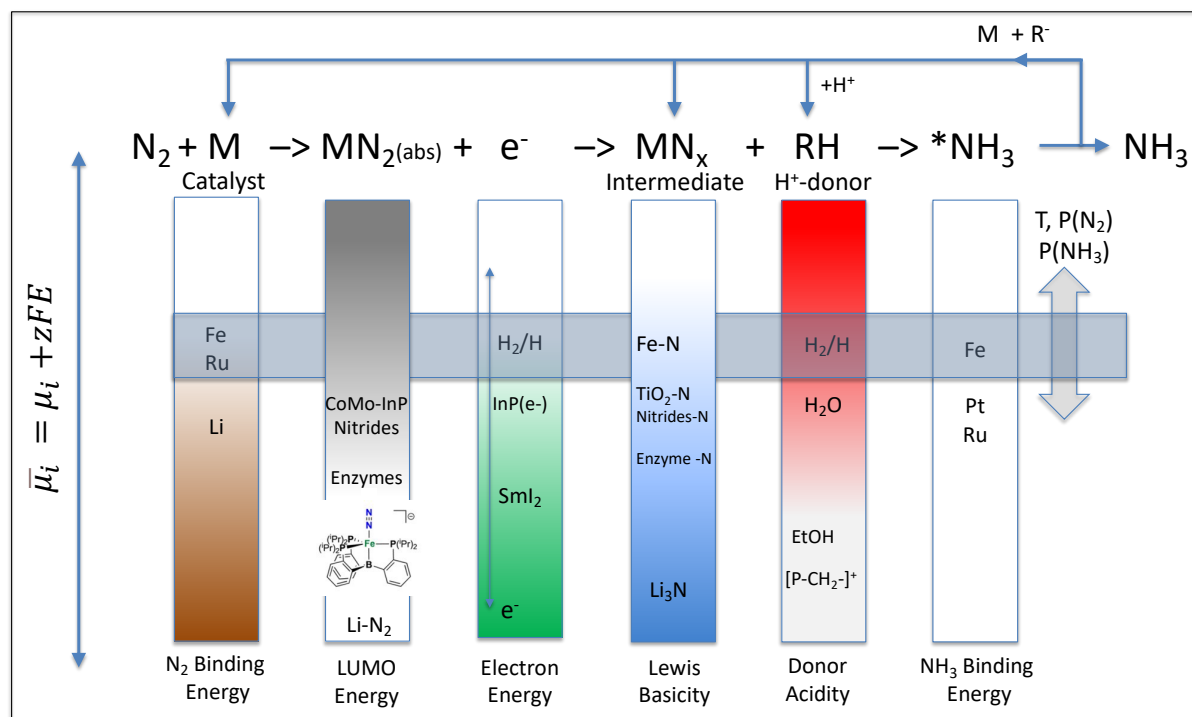


Figure 4. Steps in a generalised N_2 reduction process to ammonia and the energy scales that can be used to describe and rank the reactivity of the various species in the mechanism. The vertical colour-coded scales (lower to higher values are shown as white to colour gradients) indicates: *brown* – the N_2 binding energy on various substrates; *grey* – an electron acceptor (LUMO energy) of the bound N (the Fe-centred structure is an example of a homogeneous catalyst discussed by Peters²²); *green* – the incoming electron energy (InP(e⁻) is the photoexcited electron in for example an InP semiconductor¹⁹); *blue* – proton acceptor activity (most generally Lewis basicity) of the reduced N species; *red* – the proton donor acidity (EtOH and $[\text{P-CH}_2]^-$ being examples of weak and very weak acids used in some NRR work); *yellow* – the binding energy of the NH_3 produced. The horizontal grey band indicates the role of temperature and pressure in some of these steps, as is important in the Haber-Bosch process.

Figure 4 then prompts us to describe the various participants in this process on some common energy scale that combines both electrochemical and chemical energy changes. The electrochemical potential $\bar{\mu}_i$ is suitable as it incorporates both chemical, μ_i , and electrochemical potentials via $\bar{\mu}_i = \mu_i + zFE$ where z is the charge of the species i , F is the Faraday's constant and E is the electric potential. The latter is a well understood scale which is directly controllable experimentally by setting a desired electric potential on an electrode. The other scales are less easily quantified but are at least qualitatively familiar. The binding energy of N_2 to the substrate

can be measured in some circumstances and calculated in others. The electron accepting ability of the bound species MN_2 could be characterised *via* its lowest unoccupied molecular orbital (LUMO) energy, to which the electron energy (redox potential) needs to be tuned to facilitate an electron transfer. Beyond an external electrical circuit, the source of this electron can be the substrate itself if already reduced (for example Li(s)) or a chemical reducing agent such as SmI_2 or a photoexcited electron in the conduction band of a semiconductor; in each of these cases the electron energy is determined by the redox properties of the material. The reduced species can then be considered as a Lewis base and the proton donor as a Lewis (Brønsted) acid; leaving these characterisations in terms of Lewis rather than Brønsted acid/base properties reminds us to be aware of other possible actors in these processes, such as Li^+ as a Lewis acid. Finally, the detachment of the NH_3 from the surface involves its binding energy; where this step is not spontaneous, accumulation of NH_3 causes poisoning, as discussed by Aslan et al.¹¹

The direct chemical and chemical looping mechanisms facilitated by H_2 can be placed on the diagram on the basis of the redox potential of H_2 . Notably since both reactants are gaseous in this case, there is considerable scope to manipulate the activities involved *via* temperature and pressure, as is the case in the optimised Haber-Bosch cycle conditions.

With these various scales in mind our goal is that a broad community of researchers can readily understand the roles of the various actors in the process, for example the SmI_2 reducing agent in the work of Hegg et al.²⁴ or the phosphonium proton source in the work of Suryanto et al.²⁹

7. On Sustainability

It is important to conclude these comments with a focus on sustainability given its prominence as a feature of the Faraday Discussion. Sustainability is certainly the key challenge for N_2 activation and conversion to useful products, as it must be for all major chemical processes in the future. The Haber-Bosch technology that current-day science is endeavouring to improve upon is fundamentally flawed on sustainability grounds because of its reliance on the fossil fuel sourced H_2 . In historical fairness to Haber, Bosch and others at the time, it is worth noting that “sustainable” in the context of the early 20th century meant finding a process that could replace the dwindling supplies of natural fertilisers to feed a rapidly growing global population; the role of CO_2 emissions from fossil fuel use was only just being recognised. In the context of the 2020s, and beyond, sustainability must indicate (i) an ability to re-use or re-extract all non-abundant elements and (ii) the lack of any by-products that are harmful or long lasting in the environment (*e.g.* N_2O). Given that the N_2 activation processes we are considering here are likely to become an important part of global energy technology, the quantities of materials involved could become enormous and the task of ensuring sustainability correspondingly vital.

Addressing these challenges must become a micro-challenge for us all in every research project and publication. For example, in the catalytic and chemical looping approaches to N_2 activation, compounds containing metals other than Fe, Al, Ca, Na and Mg are arguably non-abundant when employed at scale and their use in novel catalytic materials should be accompanied by a consideration of how they can be made completely sustainable. That is, how might a catalyst be recycled or the components re-separated at end of life so that the element is not lost to the environment (*i.e.* to landfill, or into the oceans as dilute aqueous waste)? Long effective lifetime does not make it more acceptable to consider sending the material to waste; rather we should see it as justifying a higher potential recycling cost.

Similar end of life separation and recycling issues will challenge the electrochemical, plasma and photochemical approaches to N₂ activation. The loss or degradation of cell, electrode, solvent or electrolyte components will likely be one aspect of end of life for these materials, requiring complex processes to separate any degraded products from the reusable components. The ultimate fate of the degraded products then needs to be considered.

Traditional life cycle assessment (LCA) in this regard may not be a useful approach in all cases. The tendency is for the LCA software tools to draw in, or link to, existing LCA's for related materials, for example a solvent needed for extraction of a by-product; this amounts to looking at future challenges through the limited lens of today's chemical technologies. Instead, we believe it is appropriate here to imagine that the magnitude of the potential applications will drive the required innovation in sustainability, whenever we can envisage it to be practically possible (*i.e.* using only abundant elements and renewable energy). A recent example of "the practical visionary" approach can be found in our analysis of the sustainable aspects of thermal energy storage materials.³¹ It is where we *cannot* envisage such sustainable solutions (*e.g.* in the use of fluorinated solvents) that we must be wary.

The same must be said of the role our anthropogenic nitrogen activation processes will play in the global nitrogen cycle in the future. It is imperative that humankind, led by the science community, must learn from the mistakes we have made in overloading the planetary carbon-cycle and ensure that we do not repeat those mistakes with the planetary nitrogen cycle. The rate of anthropogenic generation of fixed nitrogen compounds already almost equals the natural processes and the ultimate fate of the additional N-compounds is not completely understood, partly because of long half-lives of compounds such as N₂O in the oceans.³² Hence, as we contemplate a massively greater rate of production of fixed nitrogen compounds it is imperative that the combustion of ammonia fuel, in particular, *must* achieve very high levels of NO_x mitigation.

8. Sustainable Nitrogen Activation – Looking forward

The Faraday Discussion has provided a broad overview of the available mechanisms for N₂ activation and conversion to nitrogen compounds; notably most of these are reductive mechanisms. Not prominent in our discussion was the electrochemical nitrogen oxidation reaction (eNOR) which is a particularly tantalising option that unfortunately has never been fully demonstrated and established. It has the potential to allow the sustainable production of nitrates at scale, under practical conditions, using renewable energy sources to achieve the oxidation. In principle, the oxidation should be spontaneous versus an oxygen reduction reaction, but the activation process is likely to require substantial energy input depending on the electrocatalyst that can be deployed. Various strategies have been proposed for selecting eNOR catalysts. These include choosing transition metal-based catalysts which form strong metal-N bonds due to the coexistence of empty and occupied d-orbitals.^{33,34} Another approach involves selecting transition metal-based catalysts based on DFT calculations that present the lowest energy barrier.³⁵ Other strategies include promoting the eNOR *via* the activation of a mediating compound, in particular radicals.³⁶

While the eNOR offers promise as a sustainable method for nitrate production, significant challenges remain. As aqueous media are ideal for this reaction by virtue of the desired product, competition from the parasitic oxygen evolution reaction (OER) is a challenge. From the nitrogen Pourbaix diagram it is evident that selective oxidation of dinitrogen to nitrate is

thermodynamically viable in neutral to basic conditions.³⁶ As pH increases, the gap in the thermodynamic potential between the eNOR and the OER increases in favour of nitrogen oxidation. As such, working in mildly alkaline media could be a viable strategy to improve selectivity. Progress in this area remains uncertain due to the issues with impurities and false positive results discussed above; nonetheless, it remains an important goal in N₂ activation. An interesting variation that remains little investigated is photo-electrochemical NOR, which could make use of the ability of a photogenerated species to facilitate the reaction of N₂ absorbed on an attached surface.

On more familiar territory than the eNOR, it is clear that there is much yet to be explored in all of the areas of N₂ activation discussed here. From novel Haber-Bosch catalyst structures and strategies, and new materials that can support a chemical looping approach, to further developments in electrochemical, photochemical and mechanochemical N₂ reduction, there are huge opportunities for significant developments. In all of these areas, advanced computational techniques have an important role to play, including DFT studies of reaction pathways, molecular dynamics simulations of reaction dynamics, reaction kinetics modelling, as well as macro scale simulations of the role of flow dynamics in innovative reactor designs. The key point in all of these, both in terms of justifying the need and also in designing the investigation, is that N₂ activation and conversion is a competitive process in many cases with other process such as hydrogen generation. It is thought provoking to note that, despite approximately one billion years of evolution, the natural processes in plants that are the origin of the majority of the non-industrial fixed nitrogen in the biosphere, still produce H₂ alongside reduced nitrogen compounds. Of course, this H₂ release is part of the enzymatic mechanism; nonetheless nature has never managed to find a way to avoid it and be more efficient with its energy source.

Returning to computational studies, our view is that a “big data” based machine-learning approach to utilising the information that flows from these calculations could be pivotal in supporting further developments. The computational screening approach to sifting through the critical properties of alloys and mixed metal compounds is developing, though the outcome tends to be focussed on one or more key questions the researcher identifies in advance. One wonders if progress could be significantly facilitated by a ready means of global-sharing such computations into a machine-learning database (hence the reference to big data above) for all to probe with AI type tools. The powerful, everyday tool that the crystal structure and XRD powder pattern databases have become is an excellent 20th century example of such databasing. Similarly, the Human Genome project of the 1990's illustrates how progress can be made on a mammoth task by data sharing and international cooperation.

Whether it be targeted towards sustainable farming or the even bigger goal of sustainable energy, nitrogen activation clearly has a vital role to play in the coming decades and we commend researchers to heighten their endeavours to this end, remembering always to keep reliability of results and genuine sustainability of the new technologies in sharp focus.

9. Acknowledgments

L.M.A. is a Ramón y Cajal fellow (ref. RYC2021-030994-I) and thanks MCIN/AEI and NextGenerationEU/PRTR for support and the KAUST Supercomputer Laboratory (KSL) for providing the computational resources (Shaheen II). DRM and ANS are grateful for funding from the Australian Research Council through Discovery Project DP200101491 and ANS for funding through DP200101878 and Future Fellowship FT200100317.

10. References

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