

## Review Article

# Electrifying the nitrogen cycle: An electrochemical endeavor

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## Abstract

The advent of the Haber–Bosch (HB) process has made accessible all forms of nitrogenous derivatives (ammonia, nitrates, nitrites, and amines), revolutionizing the chemical industry. However, the depleting natural resources and growing environmental concerns demand a shift toward an energy-abated and environment-friendly alternative to the HB process, hence the shift in the recent research focus. The electrochemical reduction pathway offers one of the most alluring prospects as a carbon-free, environment-friendly, energy-abated alternative to the HB process. In this context, we provide a holistic overview of the electrochemical pathways for nitrogen fixation into its activated forms and categorically discuss the energetical and technological challenges that researchers encounter, simultaneously highlighting commendable contributions in the field. We also propose research targets that can serve as a benchmark to measure progress toward the practical realization of the electrochemical nitrogen reduction reaction.

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Ammonia synthesis, Electrochemical nitrogen-reduction reaction, Electrocatalysis, Nitrogen oxidation reaction, Nitrate reduction.

## Introduction

The quest for an amicable solution to the food crisis pre-World War I era culminated in the discovery of the now

celebrated ‘Haber–Bosch’ (HB) process [1]. Today, we face a similar predicament: global energy and environmental crisis, which demands a shift toward a sustainable and environment-friendly energy future. In this context, N<sub>2</sub> fixation into NH<sub>3</sub> and HNO<sub>3</sub> plays an instrumental role. With a combined global production of 200 million metric tons, these two chemicals serve as feedstock in various industrial chemical processes [2]. Besides, ammonia’s versatile applications in transport, power generation, and distributed energy storage systems make it a forerunner among candidates for sustainable fuel of the future [3,4]; however, to realize this future, a carbon-free, energy-abated synthesis route as an alternate to the Haber–Bosch process has become the focus of research attention.

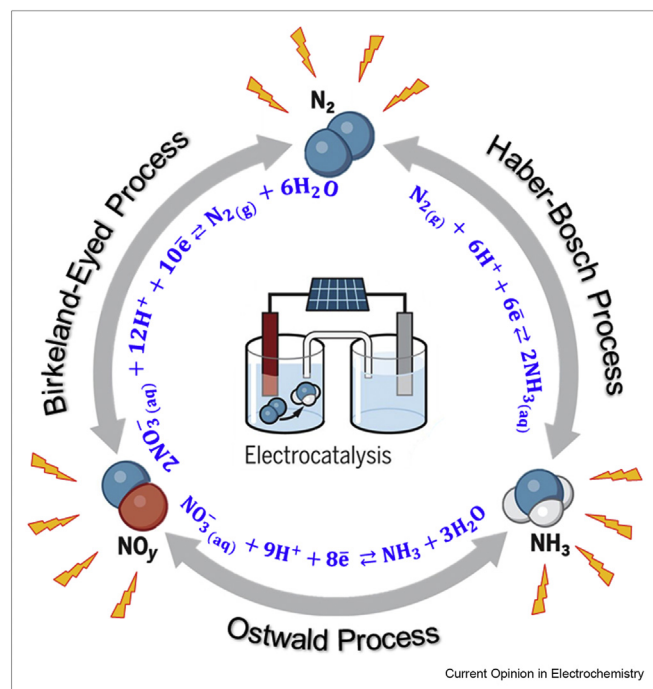
Among the possible alternates, the most enticing one is the direct electrochemical nitrogen reduction reaction (eNRR) to ammonia in aqueous electrolytes. Despite being fraught with challenges like modest faradaic efficiency (FE), low yields, and a competing hydrogen evolution reaction (HER), it remains popularly studied. Alternately, lithium-mediated redox systems for eNRR have also met with some success; however, their prospects are blemished by the high energy consumption, strong reducing potentials, and instability of the electrodes/electrolytes [5]. Other non-eNRR approaches, like the mechanochemical [6] and chemical looping [7] approaches, have also emerged as possible alternatives to the HB process; however, their practical prospects have yet to be thoroughly investigated.

In this context, we provide a holistic overview of the eNRR field and categorically discuss the energetical and technological challenges that eNRR researchers encounter, simultaneously highlighting commendable contributions in the area. We also propose research targets that can serve as a benchmark to measure progress toward the practical realization of eNRR.

## Energy analysis of the nitrogen cycle

The HB process is the *de facto* process used to stimulate the ‘Nitrogen Cycle’ artificially. Produced NH<sub>3</sub> is also a feedstock in the Ostwald Process to synthesize HNO<sub>3</sub>, a mainstay of the modern chemical industry (see [Figure 1](#)). Environmental residues of both NH<sub>3</sub> and NO<sub>3</sub><sup>−</sup>, are subsequently converted back to N<sub>2</sub> via various

Figure 1



The electrochemical pathway for 'Nitrogen Cycle' in parallel with the industrial processes for nitrogen fixation. Adapted from Ref. [2]. Reprinted with permission from AAAS.

bacteria-based wastewater treatment technologies. The HB process relies on the steam-methane reforming (SMR) process for hydrogen ( $\text{H}_2$ ) feedstock, indirectly making it one of the most carbon-intensive processes worldwide, contributing  $\sim 1\%$  of global greenhouse gas emissions. Moreover, the SMR process accounts for  $\sim 75\%$  of the total energy consumption of the HB process ( $30.5 \text{ MJ kg}^{-1} \text{NH}_3$ ) [3] and is at best  $\sim 66\%$  efficient [8] (see Figure 2a). Sourcing  $\text{H}_2$  from solar-powered water electrolysis followed by the HB process (see Figure 2b) is conceptually the cleanest option; however, the low conversion efficiency of solar-to-power results in an increase in the primary energy input: from  $16.4 \text{ MJ kg}^{-1} \text{NH}_3$  for SMR to  $236.7 \text{ MJ kg}^{-1} \text{NH}_3$  for solar energy [3]. Moreover, it eventually leads to a higher production cost because of the increased capital investment for solar-energy harvesting. Alternatively, direct synthesis of  $\text{NH}_3$  via water as feedstock offers small thermodynamic profitability of  $32.9 \text{ kJ mol}^{-1} \text{N}_2$  [2], in contrast to the two-stage water splitting process, followed by the HB process.

However, a direct electrochemical pathway to  $\text{NH}_3$  in aqueous electrolytes can further simplify the process and eliminate the need for an independent  $\text{H}_2$  production unit (see Figure 2d–e). Although this eNRR process is thermodynamically favorable and can circumvent the HB process, an optimized electrocatalyst with significant

ammonia yield and FE still eludes scientists. A modest FE of 15% for  $\text{N}_2$  conversion to  $\text{NH}_3$  requires  $614.6 \text{ MJ kg}^{-1} \text{NH}_3$ , which is more than double that for an electrochemically sourced  $\text{H}_2$  scenario. While considering an ambitious assumption of a high FE of 50%, the scheme can significantly lower the primary energy requirements to  $190.5 \text{ MJ kg}^{-1} \text{NH}_3$ . A possible advancement in the photocatalytic conversion of  $\text{N}_2$  to  $\text{NH}_3$  can further simplify the process by eliminating the need for an electrocatalytic step. At just 10% solar-to-chemical conversion (SCC) efficiency, the energy requirement would stand at  $208.3 \text{ MJ kg}^{-1} \text{NH}_3$ ; however, current technology remains less than 1% SCC efficient (see Figure 2c).

Similarly,  $\text{HNO}_3$  production relies heavily on the HB process, and the subsequent Ostwald process is another energy-demanding transformation process. Interestingly, direct oxidative fixation of  $\text{N}_2$  is also thermodynamically feasible, with  $\text{N}_2$  oxidation to aqueous  $\text{HNO}_3$  requiring only  $87.7 \text{ kJ mol}^{-1} \text{N}_2$ , thus eliminating the need for  $\text{NH}_3$  as an intermediate. The equilibrium constant and Gibbs free energy for this oxidation reaction is favorable enough for spontaneous reaction in the atmosphere; luckily, the reaction proceeds very slowly under ambient conditions without a catalyst. Electrochemical nitrogen oxidation reaction (NOR) to produce nitrate remains seldom investigated, but an exciting avenue worth consideration.

Interestingly, the electrochemical pathway for  $\text{N}_2$  to  $\text{NH}_3$  ( $+0.09 \text{ V}_{\text{RHE}}$ ) [9] and  $\text{NO}_3$  to  $\text{N}_2$  ( $+1.17 \text{ V}_{\text{SHE}}$ ) [10] are both thermodynamically feasible (see Figure 1), along with the transformation of  $\text{NO}_3$  to  $\text{NH}_3$  ( $-0.12 \text{ V}_{\text{SHE}}$ ) [10]. The latter is also facile and has been demonstrated to proceed with high efficiency and selectivity ( $>80\%$ ) [11]. The electrochemical nitrogen cycle is a very lucrative and versatile alternative to the currently available energy-intensive processes.

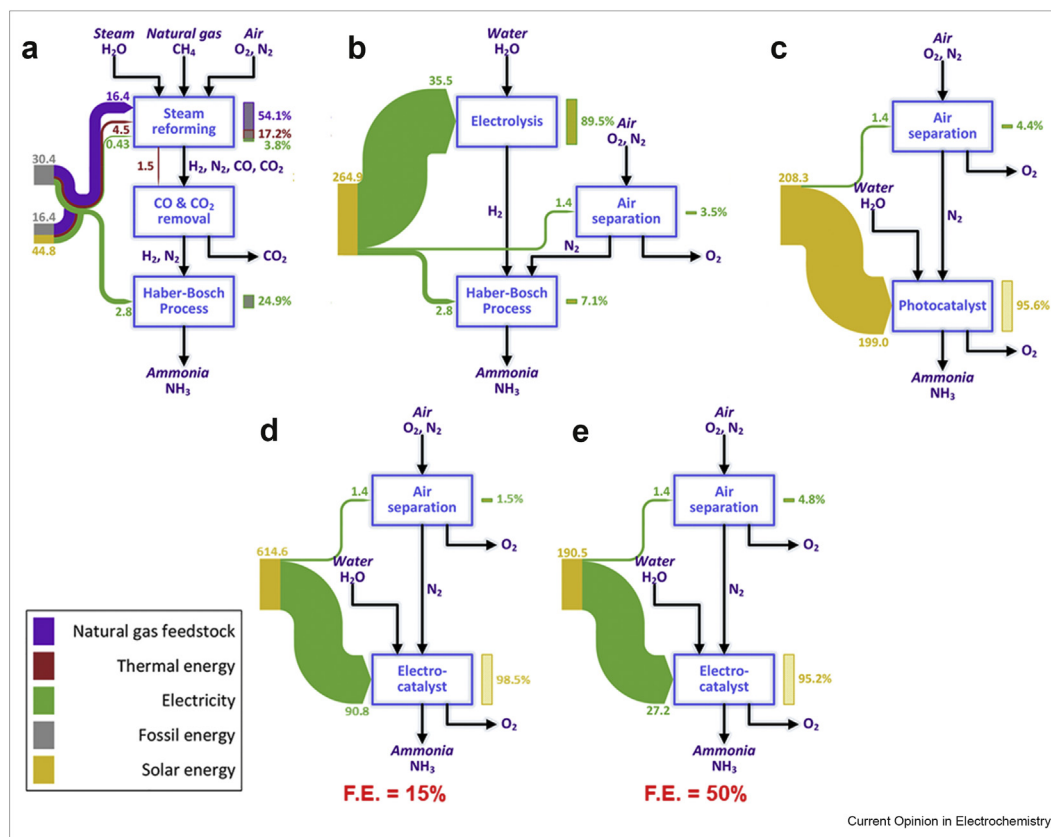
## Fixing nitrogen – the nitrogen cycle

The electrochemical 'Nitrogen Cycle' offers two distinct pathways to ammonia synthesis: A *direct* reduction of  $\text{N}_2$  to  $\text{NH}_3$  and an *indirect* pathway to  $\text{NH}_3$  (see Figure 1). For the purpose herein, we consider the *direct pathway* as a direct protonation of the  $\text{N}_2$  molecule over a catalytic substrate, whereas the *indirect pathway* is achieved via a mediator, which can be either oxidation-derived ( $\text{NO}_x$ ) or reduction-derived ( $\text{N}^x$ ) species. Here we discuss the recent efforts made in both these routes mentioned above.

### Direct pathway

The *direct pathway* to  $\text{NH}_3$  is currently the most intensely pursued research avenue. Various catalyst modes have been investigated in this pursuit, including electrocatalysts, photocatalysts, enzymatic, heterogeneous and

Figure 2



Energy-efficiency analysis of different ammonia production systems. **(a)** Conventional Haber–Bosch strategy. **(b)** Renewable hydrogen production and air separation combined with traditional Haber–Bosch reactor system. **(c)** Photocatalytic strategy. **(d, e)** Electrocatalytic strategy at modest and high efficiency. The width of each stream on the left of each block and the numbers represent energy flow (MJ kg<sup>-1</sup> NH<sub>3</sub>). The height of each column on the right of each block represents the share of total energy input. Adapted from Ref. [3], Copyright 2018, with permission from Elsevier.

homogeneous catalysts. However, the scope of our discussion here is limited to electrocatalysts. The direct eNRR to NH<sub>3</sub> can be further subclassified based on the type of electrolytes: aqueous and nonaqueous.

#### Aqueous electrolytes

Several comprehensive reviews [12–15] can acquaint readers with the wide variety of catalysts that have been reported as *promising* for eNRR. However, despite garnering such intense research fervor, eNRR in aqueous electrolytes has become an increasingly contentious topic, especially in recent years. Notwithstanding the commendable efforts that have truly advanced the field, the lack of robust controls to limit the ominous presence of NO<sub>x</sub> species in electrolytes, catalysts, and gas feeds, as delineated by several researchers [16–18], oppugn the true source of the reported NH<sub>3</sub> production.

The faradaic efficiency of catalysts in aqueous electrolytes has ranged from as high as 97% [19] to as low as 0.05% [20]; however, NH<sub>3</sub> production rates have seldom crossed the 10 nmol s<sup>-1</sup> cm<sup>-2</sup> threshold, which without

robust controls in place is barely discernible from background levels of N-containing contaminants and too low to qualify for practical consideration. The best efficiency performances are often with extremely low current densities, further underpinning the impracticality of these catalysts.

#### Nonaqueous electrolytes

Despite not being as popular, nonaqueous electrolytes may have arguably fared somewhat better than their aqueous counterpart [21]. Electrolytes like organic amines, nitriles, ethers, carbonates, and ionic liquids tend to have a higher affinity for dissolved N<sub>2</sub> (~1–2 orders-of-magnitude greater than water [22]) and, the limited proton supply favors eNRR over the formidable HER. Faradaic efficiency as high as 60% in ionic liquids [23] and up to 17% in ethylenediamine [24] have been reported.

Nevertheless, these nonaqueous electrolytes have yet to overcome the challenges of electrolyte stability, recyclability, and scalability to compete with the status quo. Moreover, these electrolytes (especially nonionic organic

solvents) have high intrinsic resistance ( $\sim 900\text{--}1600\ \Omega$ ) [25], which needs to be overcome before any electrochemical ion transport can be realized. Therefore, large overpotentials are necessary for the operation of these systems, making the process energy-intensive.

#### Indirect pathway

A path less frequently traversed by researchers but may arguably have fared better than the *direct* pathway. This approach can be split into two key stages: the transformation of  $\text{N}_2$  into a reactive intermediate (e.g., nitrate, nitrite, nitride, etc.) followed by its direct reduction to ammonia. Although a Li-mediated nitride-based pathway has been the focus of research lately; however, a nitrate-mediated pathway as an alternative also warrants consideration since the latter's transformation to  $\text{NH}_3$  is demonstrably facile.

#### Nitride mediated pathway

Among possible nitride-mediated pathways, recently revived interest in Li-enabled mediation has rekindled hopes of finding a plausible alternative to the HB process. Proposed in the early 1930s by Fichter et al. [26] and furthered by Tsuneto et al. [27,28] in the early 1990s, the Li-mediated process involves electroreduction of  $\text{Li}^+$  to metallic Li; the spontaneous reaction of Li with  $\text{N}_2$  resulting in  $\text{Li}_3\text{N}$ ; and subsequent hydrolysis of  $\text{Li}_3\text{N}$  to form  $\text{NH}_3$ . The process has been demonstrated in both ambient [29] and high-temperature systems [30,31]. More recently, the field has been advanced by notable contributions from Lazouski et al. [29,32], McEnaney et al. [33], and Andersen et al. [5,21], providing valuable mechanistic insights and strategies (e.g., potential cycling) to improve the stability and efficiency of the system. Similarly, McPherson et al. [34] re-investigated the molten chloride systems and demonstrated lithium hydride as a catalytic mediator (instead of  $\text{Li}_3\text{N}$  reported in earlier studies [35]) to improve the overall performance.

#### Nitrate mediated

Interestingly, before the advent of the HB process, the only available commercial process that could fix nitrogen was the Birkeland–Eyde (BE) process, which involved direct oxidation of  $\text{N}_2$  to produce  $\text{HNO}_3$  using a high-temperature plasma. However, the cheap ammonia from the HB process made the Ostwald process more feasible than the energy-intensive BE process, rendering it obsolete.

Wang and colleagues [36] recently proposed two electrochemical strategies to synthesize  $\text{HNO}_3$  and  $\text{NH}_3$ : (I) direct electrocatalytic oxidation of  $\text{N}_2$  to  $\text{HNO}_3$  and (II) reduction of  $\text{NO}_3^-$  (from wastewater) to ammonia. They reported an efficiency of  $\sim 1.23\%$  for ‘Strategy I’ and a 33% selectivity for  $\text{NH}_3$  in ‘Strategy II’, where  $\text{Co}_3\text{O}_4$  nanorod arrays were used as the working electrode. In a follow-up study, Han and colleagues [37]

further investigated the NOR on tensile-strained palladium porous nanosheets (Pd-PNS) and observed that the strained-catalyst outperformed its unstrained counterpart with an efficiency of 2.5% and 1.9%, respectively. Alternatively, a thermally assisted photocatalytic conversion of air was also reported by Yu and colleagues [38] for the synthesis of NO from the air, albeit at extremely low quantum efficiency (0.31%) and production rate ( $0.16\ \text{mmol g}^{-1}\ \text{h}^{-1}$ ). Another interesting study by Dai et al. [39] also demonstrated NOR on  $\text{ZnFe}_x\text{Co}_{2-x}\text{O}_4$  spinel oxides with a maximum efficiency of 10% and production rates as high as  $130\ \mu\text{mol h}^{-1}\ \text{gMO}^{-1}$ .

‘Strategy II’ is a much more facile process, and multiple studies have reported efficiencies and selectivity  $>80\%$  for  $\text{NO}_3^-$  reduction to  $\text{NH}_3$  [40–42]. ‘Strategy I’ has not attracted much research attention until more recently and warrants more investigation given its potential to compete with the HB process. Notwithstanding the potential of this avenue, extreme caution must be exercised to ensure that the observed  $\text{NO}_x$  species are genuine electrocatalytic oxidation products rather than the adventitious presence of N-contaminants.

### Energetical and technical challenges

Despite the enticing prospects, eNRR research remains fraught with challenges that need to be addressed before any meaningful progress can be achieved. These challenges include but are not limited to; identifying and eliminating false positives, mechanistic understanding of eNRR, selectivity, FE & EE, catalyst/electrode stability, the solubility of  $\text{N}_2$ , and scalability, to name a few [43,44]. Herein we briefly highlight a few of the more critical challenges.

#### Avoiding false positives

The most daunting challenge in the eNRR field is avoiding ‘false positives’. The ominous presence of N-containing reactive species [16–18,45–47] has been intensely studied, and adequate remedial strategies have been proposed in updated protocols [17,21]. Strict adherence to these protocols is imperative to avoid false positives. As a good practice, all components of the experimental setup should be investigated in isolation for their possible contribution to  $\text{NO}_x$  to prevent false positives.

#### Mechanistic understanding

A clear understanding of the underlying mechanism can help researchers design active catalysts that can stabilize the formation of reaction intermediates and their subsequent removal from the catalyst surface. However, a lack of mechanistic understanding in this early stage of eNRR has greatly limited the field's development. Several efforts toward elucidating the intricate workings of eNRR using in-situ techniques [48–53] have been reported;



however, possible interference from N-containing contaminations in these reports cannot be completely ruled out. The lack of controls to limit NO<sub>x</sub> contaminants leave room for an alternate, more facile NORR reaction, which also happens to share the same intermediates as those in eNRR, possibly misleading researchers.

Theoretical modeling has also played an instrumental role in providing an educated direction for advancing the design of highly active and selective eNRR catalysts. Traditionally, researchers have used DFT calculations to calculate energetics of possible reaction pathways and thereby identify the rate-determining intermediates; however, a more detailed investigation into the charge transfer mechanism behind the activation of the N<sub>2</sub> molecule and intermediates may perhaps provide critical insights instrumental from a design perspective [54]. For further reading, readers are directed to seminal works [55–58] in the field.

#### Faradaic and energy efficiency

The most difficult challenge is identifying and designing an appropriate catalyst that is efficient and selective for eNRR to NH<sub>3</sub>. On average, an efficiency of ~15% has been achieved, with some reporting efficiencies beyond 50% [19]. Modulating the three-phase interphase at the electrode has shown promising efficiency enhancement (up to 97%), however, at the expense of low production rates [19,59,60]. If significant ammonia production can be achieved in aqueous systems despite the competing HER, the H<sub>2</sub> byproduct can be separated in a subsequent stage and utilized as an input for other applications. EE has not been explicitly reported for aqueous eNRR systems; however, for nonaqueous Li-mediated eNRR, a maximum EE of only ~7% has been reported [5].

#### Defining milestones

Even with the intense efforts advancing eNRR research, the ultimate goal of having a system that can compete with the HB process remains elusive. The performance targets set by the US Department of Energy (DOE)'s ARPA-E REFUEL [8] program remain ambitious. While these targets will eventually need to be achieved to make eNRR technology practical and competitive as an

alternative to the HB process, a roadmap that delineates *reasonable* milestones is imperative to gauge progress. We propose a two-tier approach, where Tier-I research targets serve as a qualifier for plausibly practical systems, and Tier-II milestones serve as targets that eventually aim to bring the eNRR technology at par with the HB process (see Table 1).

#### Faradaic efficiency

A few studies have proclaimed efficiencies beyond 50% for aqueous eNRR, but their reproducibility has remained doubtful. The target efficiency of 90% for eNRR set by Soloveichik [8] is exceptionally challenging. On the contrary, the average FE achieved thus far is ~15.2% (with a standard deviation of 15.7%, based on a sample of 68 reports), well below the target. A reproducible FE of at least 30–50% can be considered as an excellent Tier-I classifier to filter out highly promising catalysts, in our humble opinion. As evidenced by the energy analysis, a 50% efficiency for the electrocatalytic systems can still be feasible given that electricity is sourced from cheap renewable avenues.

#### Ammonia production rates

The production rates reported to date remained well below 10 nmol s<sup>-1</sup> cm<sup>-2</sup> and most (>95%) without proper prepurification controls to limit NO<sub>x</sub> contaminants, while those that do cross the threshold have not been reproducible [17]. The 10 nmol s<sup>-1</sup> cm<sup>-2</sup> threshold, suggested by Simonov *et al.* as 'highly plausible and promising', is still within the possible background levels of N-containing contaminants. However, with robust prepurification controls, this can serve as a reasonable tier-I milestone, whereas a Tier-II production of 1000 nmol s<sup>-1</sup> cm<sup>-2</sup>, as suggested by Grigorii Soloveichik [8], should be the eventual goal. Alternatively, absolute ammonia production (e.g., in grams or moles), well beyond the absolute cumulative background levels, can also serve as concrete evidence for scale-up potential. Employing higher catalyst loadings on electrodes with higher surface areas or bigger electrochemical cells altogether can also help in this regard; however, an abundance of caution remains essential to limit the background levels of ammonia contamination.

Table 1

#### Milestones for eNRR research.

Performance metric	Tier I	Tier II	REFUEL program [8]
Faradaic efficiency	30–50%	>70%	>90%
Ammonia production rates	>10 nmol s <sup>-1</sup> cm <sup>-2</sup>	>100 nmol s <sup>-1</sup> cm <sup>-2</sup>	>1000 nmol s <sup>-1</sup> cm <sup>-2</sup>
Energy efficiency	>10%	>40%	>60%

### Energy efficiency

The most overlooked aspect in eNRR research is evaluating the EE of these systems, partly because only the half-cell reactions are being investigated in these experiments. Only two studies on Li-mediated eNRR have reported EE, with the highest at 7%. Still far from the 60% target set by the REFUEL program. For Tier-I, a 10% EE target would be sufficient to demonstrate the system's plausibility; however, for practical applications, at least 40% EE is imperative to warrant further pursuit toward commercialization.

### Conclusion and perspectives

Direct N<sub>2</sub> fixation into activated species remains as challenging a feat as it was a century ago. Nevertheless, with advanced technological tools to aid us, the realization of this feat is not impossible. However, a prudent approach must be adopted to realize this ultimate goal. Most importantly, extreme caution must be exercised when evaluating the performance of any prospective catalyst. Literature is replete with rigorous experimental protocols, and the same has been repeatedly emphasized for their importance, yet there are instances where these have been lacking. Strict adherence to protocols must be made a prerequisite for any future endeavors to qualify as reliable. Reliability and reproducibility should be the hallmark of quality research and should be incentivized over quantity. Other nonaqueous eNRR approaches must also be investigated in parallel and thoroughly reassessed before ruling out their prospects. We have confidence that by addressing these technological and energetical challenges with perseverance, the research targets outlined in our discussion can eventually be realized.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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