The runt of ammonia production by N2 reduction: Electrocatalysis in aqueous media

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The Runt of Ammonia Production by N_2 Reduction: Electrocatalysis in Aqueous Media

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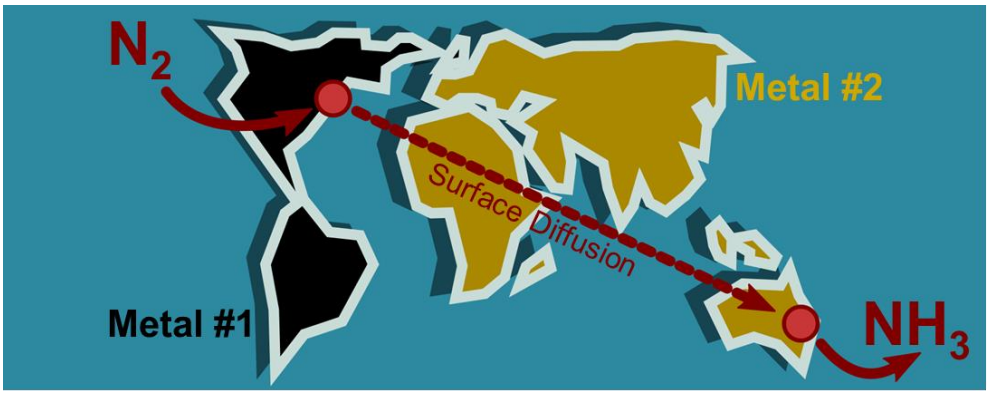
Graphical Abstract



Highlights:

- Design of bifunctional electrocatalysts to break the scaling relationships;
- New interfaces to better control the reactant concentration in the local reaction environment;
- Updated experimental protocols to ease the emergence of new systems/electrocatalysts design.

Abstract: The nitrogen reduction reaction (NRR) in aqueous media is often dismissed, owing to the overwhelming amount of 'false positives' that have been published throughout the past years, and the almost impossible to overcome limitations that have been highlighted, both by rigorous experimental protocols and theoretical findings. Nevertheless, it is here believed that the gate should not be definitively closed on a system that might still hold promises. However, to do so, it is mandatory to rethink the way the NRR systems are designed. Improvements should be done at the electrocatalytic and electrode level, as well as on 'how' the NH_3 generation is ascribed, to ease the barrier of entry for newcomers in the field while putting an end to the propagation and the promotion of electrocatalysts design based on an incorrect assessment of the NH_3 generation.

Key words: Nitrogen Reduction Reaction, Surface Diffusion, Control Experiments, Ionic Liquids, Gas Diffusion Electrode

Introduction: Ammonia is a cornerstone of our society, present and future. It is essential in the fertilizers production chain, therefore being an indispensable tool of a farming industry faced with an ever-growing human population. Furthermore, it is often envisioned as a key alternative for the hydrogen storage and, thus, the entire fuel cell industry. However, its main mean of production remains the Haber-Bosch process, which extreme conditions (200 – 300 × 10^5 Pa, 300 – 500°C), high energy consumption and CO_2 generation [1,2] justify the willingness of the scientific community to investigate potential alternatives. They are inspired in this endeavour by the existence of nitrogenase, an enzymatic structure built around a FeMo complex (-co) able to produce NH_3 from N_2 in ambient conditions (see **Figure 1a**) [3,4]. The latter has been extensively investigated during the past decade, leading to the identification of activity and selectivity defining features, *i.e.*, the ability to control (i) the local reaction environment (LRE) of the FeMo-co (*e.g.*, concentration in protons, nitrogen and oxygen) and (ii) the rate of delivery of the two former to the FeMo-co [1,5,6]. The goal thus became to 'mimic' nitrogenase, while adding advantageous features of other (electro)catalytic systems, *e.g.*, increased active site density, ease of preparation, stability when exposed to O_2, *etc.* The three main alternatives are, nowadays, well identified (see **Figure 1b-d**):

(i) Homogenous catalysis [7];

(ii) Li-mediated electrocatalysis [8–11];

(iii) Electrocatalysis in aqueous media (*e.g.*, nitrogen reduction reaction, NRR);

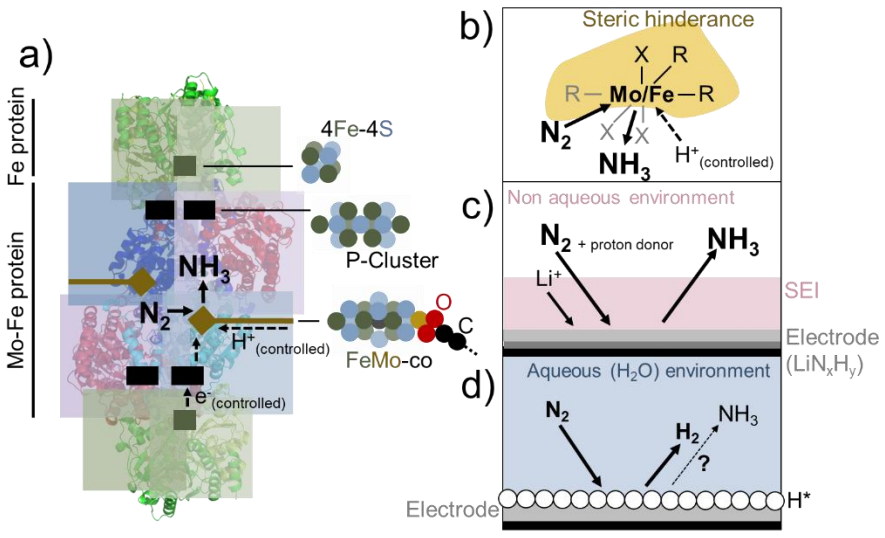


Figure 1. Illustration of the main alternatives to the Haber-Bosch process to reduce N_2 in NH_3, *i.e.*, (a) the nitrogenase enzyme and the clusters of interest (with the FeMo-co including a R-homocitrate group, here illustrated with a dotted line); (b) catalysis for the homogeneous reduction of N_2 on Fe/Mo complexes (the electrons are provided by the Fe/Mo oxidoreduction cycle), taking advantage of 'bulky ligands' to control the environment near

the catalytic site; (c) Li-mediated nitrogen reduction, in non-aqueous environment with a constant plating of Li^+ (→ Li), with the SEI standing for 'solid electrolyte interface' and (d) nitrogen reduction reaction (NRR) in aqueous media, being limited by the preferential adsorption of H* and the low N_2 solubility in aqueous media.

Among those, homogenous catalysis and Li-mediated systems are most often pursued, owing to the shortcomings of the N_2 electroreduction in NH_3 in aqueous environment. Indeed, (i) theoretical calculations evidenced that, in the presence of an aqueous proton source, most electrocatalyst surfaces favour the hydrogen evolution reaction (HER) *vs.* the NRR, resulting in extremely low faradaic efficiencies [12]. Furthermore, albeit the NRR has been extensively studied throughout the past decade, it has been plagued by incorrect assessment of the NH_3 generation, due to (i) the ease of contamination of the reactive system by NH_3 and (ii) the low amount of NH_3 generated by electrochemical means [13–15]. This resulted in a general disbelief in the future of the generation of NH_3 by NRR in aqueous environment, coupled with extremely complex experimental procedures to certify the findings. Here, we shall nevertheless discuss it, and its perspectives. As the two other approaches are not discussed here, any interested reader is encouraged to read the excellent review by Westhead *et al.* [1] on these topics.

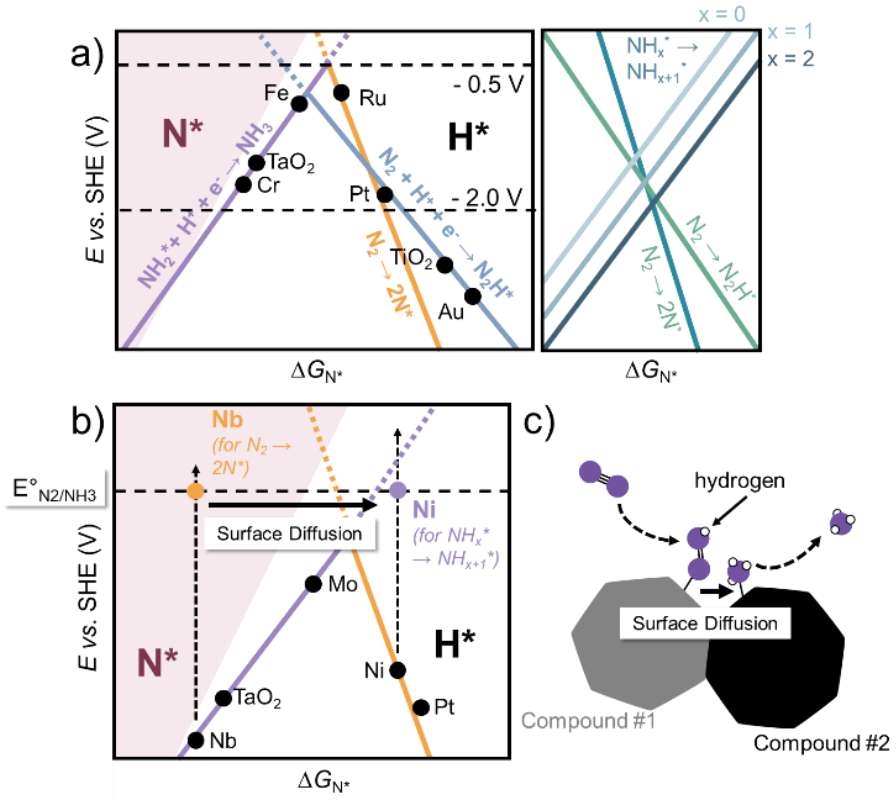


Figure 2. Schematic representation of (a) the 'volcano-plot' relationship between the theoretical potential and the free energy of adsorption of N* (ΔG_{N*}) (in pink, the domain in which N* is more favourable than H*) and the scaling relationship between different intermediate steps of the nitrogen reduction reaction (NRR); (b) a surface-diffusion-based alternative to the NRR, to 'break' the scaling relationships through the replacement of

unfavourable intermediate steps by surface diffusion to a more adequate surface; (c) the surface-diffusion mechanism on a Janus-type nanostructure.

Directions for the nitrogen reduction reaction: The NRR potential has long been seen in the prism of the theoretical calculations of the Gibbs energy of adsorption of N* (ΔG_{N*}) *vs.* the Gibbs energy of adsorption of H*, ΔG_{H*}. This started with the pivotal work of Skúlason *et al.* [12] underlining the potential gap between the NRR equilibrium potential (E = 0.057 V *vs.* SHE) and the highest onset potential achievable on a mono-element surface, at E = *ca.* – 0.5 V *vs.* SHE. Such discrepancy is due to the existence of 'scaling relationships' [16], *i.e.*, the fact that the binding strength of the NRR intermediates are correlated (see **Figure 2a**). They imply that an electrocatalyst surface cannot be optimal for each intermediate step as it cannot bind all intermediates with the 'ideal' binding strength, but should instead be a compromise of 'acceptable' binding strength for all of them. In addition, Skúlason *et al.* also evidenced a favourable adsorption of hydrogen, and subsequent reduction in H_2 *vs.* the NRR, for the overwhelming majority of the elements they investigated [12].

The limitations of theoretical findings – Promising approaches for the NRR were nevertheless underlined by theoretical calculations and modelling, *e.g.*, metal nitrides (operating through a Mars-van Krevelen mechanism), atomically dispersed single or dual atoms, *etc.* [17–19]. Unfortunately, modelling and theoretical calculations were also almost systematically used to explain the NH_3 generation of electrocatalysts published during the last decade. This is an issue, as it is nowadays understood that most of those electrocatalysts were unlikely to be active for the NRR, but that the NH_3 observed came either from environmental pollution or NO_x reduction [13]. The main problem here arise that modelling does not often consider some reactive pathways and critical steps, *e.g.*, the non-electrochemical N_2 dissociation in 2N*. Furthermore, it is often performed in unrealistic conditions, *e.g.*, in vacuum, on model slabs, without a time dimension, *etc.* Thus, it fails to see the hinderances in the LRE (*e.g.*, local pH, cations distribution, *etc*.) and other parameters that contribute to the modification of the reactivity and surface state of the electrocatalyst. As such (i) theoretical calculations and modelling should be carefully used, and never as the sole justification of an electrocatalyst' performance and (ii) substantial time should be invested to develop modelling (and experimental [20]) tools that are able to adequately mimic the NRR' LRE [21–23].

Bifunctional electrocatalysts – Hence, the design of the NRR interface in aqueous environment should be built either from our understanding of the multi-steps nature of its mechanism or of the nitrogenase. Specifically, the aim should be to (i) break the scaling relationships and/or to (ii) control the presence of H* at the reactive interface. It is expected that N* binding energy on an active site is strongly dependent on its local environment. A relevant example is that, for the oxygen reduction reaction (ORR), the OH* binding strength to a platinum atom is correlated to the platinum coordination number and its

distance with its closest neighbours. Modifying those parameters by increasing the structural disorder leads to the emergence of active sites with a near-perfect local environment (*i.e.*, coordination number and distance with its nearest neighbours), therefore being at the apex of the volcano plot [24,25]. But this remains limited by the scaling relationships, and, to go 'beyond', an option that ought to be envisioned is the use of bifunctional electrocatalysts [16], *i.e.*, surfaces where two types of active sites are in close proximity while presenting widely different ΔG_{N*} (arising from various coordination/atomic distance with nearest neighbours, different elements – see **Figure 2b**, *etc*.) and thus being each optimal for different steps of the reaction. The two main questions on those structures would then be (i) what is the minimal dimension of the domain for each type of active site and (ii) will the surface diffusion (SD) of the reactive intermediates be possible? Indeed, an alloy, resulting in an atomic-ranged alternance of each domains, might result in a common, and not two individual ΔG_{N*}, whereas nanoparticules decorating NRR-active supports or Janus-like nanoparticles (**Figure 2c**) might be adequate. The idea of SD to ease the reduction of NRR intermediates arises from the field of alcohols and CO* oxidation. Lebedeva *et al.* [26] observed CO* diffusion from terraces to steps, *i.e.*, toward more favourable oxidation sites. Dubau *et al.* [27,28] then observed an enhanced activity for a mixture of platinum and ruthenium nanoparticles (*vs.* the individual nanoparticles or the alloy) for the methanol oxidation reduction, arguing that the methanol adsorption-dehydrogenation was occurring on platinum, followed by the CO* diffusion to the ruthenium sites, where it was oxidized in CO_2. Here, it is critical to underline that (i) SD is not limited by the N* energy of adsorption (ΔE_{N*}), but by the energy required to move out of an adsorption site to a neighbouring one (*i.e.*, ΔE_{diff}, with $\Delta E_{diff} << \Delta E_{N*}$) and that (ii) SD is fast, even on > 3 nm Pt nanoparticles, for strongly bound CO* [29] (*e.g.* Kobayashi *et al.* [30] estimated a 36 nm^2/s diffusion rate for CO* on Pt nanoparticles of 7 nm). Hence, it would be meaningful to investigate, through microkinetic modelling, if the same can apply to the SD of the NRR intermediates (*e.g.*, N_2H*, N*) from *surfaces on which they are strongly bound* to *surfaces that are adequate for hydrogenation and are weakly binding them.* Using heterogenous surfaces has been touched upon in the NRR field, through the study of vacancies, heteroatoms, single and dual-atoms sites [31,32], *etc.* [33,34] but decorrelating NH_3 generation arising from the NRR and the contamination in these works is extremely difficult [13]. However, albeit the performances themselves can be debated, electrocatalysts such as the gold nanoparticules supported on Fe_3O_4 developed by Zhang *et al.* [35] echoes the concept of a bifunctional electrocatalyst.

Controlling the local reaction environment – A fine tuning of the LRE itself would help in (i) increasing the N_2 concentration and (ii) minimizing the concentration in aqueous proton sources at the reactive interface. Similarly to other reactions in aqueous environment, the solubility of N_2 is extremely low (*i.e.*, *ca.* 0.7 mmol L^{-1} in H_2O at room temperature – RT), this being partly responsible for the almost-inexistent selectivity toward the NRR in aqueous media (see **Figure 3a**). Such phenomenon has been deemed an issue when comprehensively studying electrocatalysts for the ORR, with O_2 as the reactant (*i.e.*, *ca.* 1.2 mmol L^{-1} in H_2O at RT), resulting in the design of 'gas diffusion electrode' (GDE)-cell [36,37], in

which the O_2 is provided to the LRE under gaseous form, through the working electrode (see **Figure 3c**). This substantially decreased the O_2 mass transport related limitations. In the NRR field, this approach was suggested by Kani *et al*. [38], along with optimizing the pH of the solution and the nature of the cation. Lazouski *et al.* [39] also discussed this topic, suggesting the use of carbon or stainless steel cloth in non-aqueous environment for the NRR.

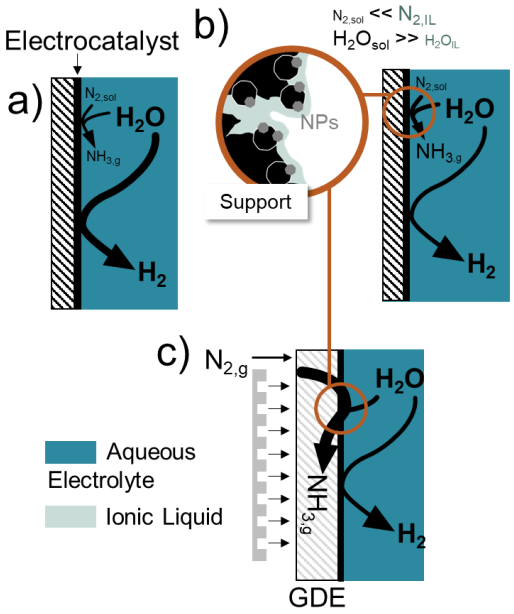


Figure 3. Schematic representation of the different types of interfaces to be envisioned for the nitrogen reduction reaction (NRR): (a) the 'conventional' interface, with aqueous environment and N_2 dissolved in H_2O, leading to a hydrogen evolution reaction (HER) dominated interface; (b) an aqueous interface with the active material encapsulated in ionic liquid (IL), thus tuning the solubility of the reactants at the interface; (c) a 'gas diffusion electrode' design, in which the N_2 is provided under gaseous form directly in the LRE.

Of greater challenge is the control of the concentration of the aqueous proton sources in the LRE. Removing altogether the aqueous electrolyte has been investigated, by using ionic liquids (ILs). An increased selectivity [40,41] was observed at the cost of a low NRR activity, likely induced by a near-inexistent concentration of a proton source in the IL, required for the NRR intermediates hydrogenation. This could be addressed by adding in the electrolyte an alternative, non-aqueous proton source, similarly to the Li-mediated system approach (**Figure 1c**) [39,42,43]. But, if the objective is to maintain a less expensive, aqueous like design, an encapsulation (*vs.* a bulk presence) of the IL should be favoured (see **Figure 3b**). This approach was explored for the ORR by Snyder *et al.* [44] to ease the transport of O_2 in the complex porous network of an active material, or, more recently, by Avid *et al.* [45] to increase the accessibility of the active sites, and would allow a fine tuning of the N_2, and aqueous proton source concentration, in the LRE. Controlling the electron availability, by tuning the conductivity of the electrocatalyst support, should not be overlooked either. Indeed, Singh *et al.* [46] calculated that the HER

would be greatly inhibited by decreasing the electron availability while the NRR activity would remain identical.

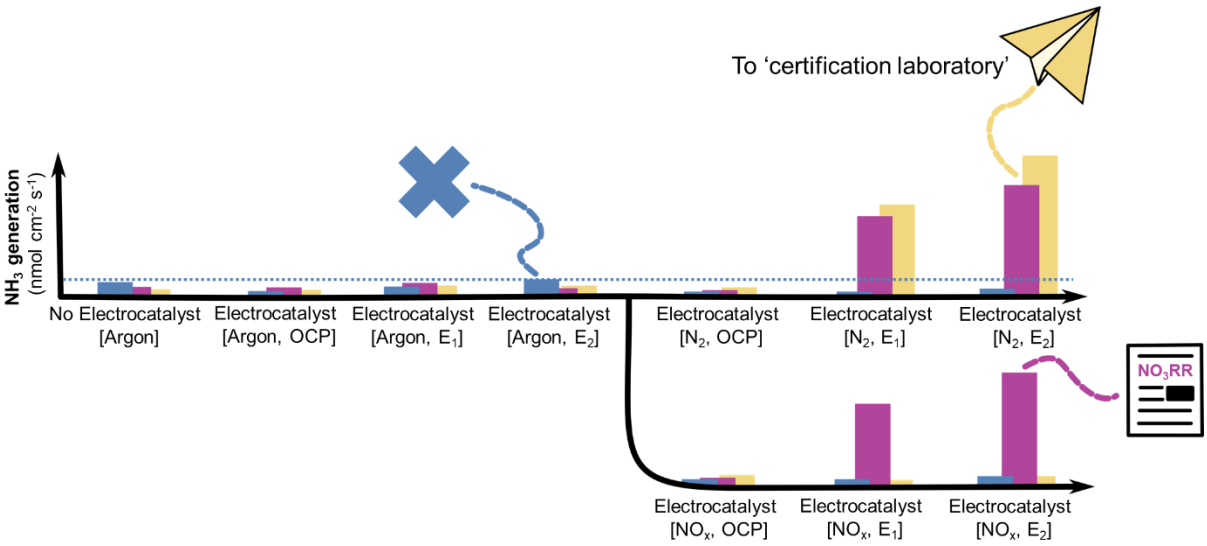


Figure 4. Illustration of different cases of NH_3 detection in a potential NRR system in aqueous environment, using several reference points to rigorously assess any parasitic NH_3, *e.g.*, under Ar, in absence of electrocatalyst (empty), at open-circuit potential and two potential of interest (OCP, E_1, E_2) and at OCP and two potentials of interest under N_2 or in presence of NO_x (*e.g.*, NO_3^-, NO_2, NO): (yellow) a substantial increase of the NH_3 generation is observed at E_1 and E_2 under N_2, and no NH_3 generation is observed in presence of NO_x = promising NRR electrocatalyst; (purple) a substantial increase of the NH_3 generation is observed at E_1 and E_2 under N_2 and NO_x = promising NO_xRR electrocatalyst; (blue) albeit NH_3 'generation' is observed at E_1 and E_2, it is below, or equivalent, to the highest reference point in non-NRR conditions = non-NRR active electrocatalyst.

Easing scientific innovation in the NRR field: The exploration of new directions for the NRR in aqueous environment requires a less tedious characterization process. Indeed, our community became extremely dismissive of new findings, ascribing the performances of any supposed NH_3-generating electrocatalyst to a yet-to-be-identified source of pollution. This resulted in the development of extremely rigorous, yet imperfect, assessment procedures (*e.g.*, including mandatory characterization with $^{15}N_2$. However, without a proper purification, the latter might contain substantial amount of easy-to-reduce $^{15}NO_x$, as evidenced by Dabundo *et al.* [47] in a systematic analysis of the $^{15}N_2$ from different providers, which would render the $^{15}N_2$ characterization meaningless) that did not manage to stop the propagation of false positives while putting a notable barrier of entry to the field (*e.g.*, the purchase of the requested amount of $^{15}N_2$ and/or the development of an adequate gas recirculation and purification system is, based on the author experience, > 10,000 euros), thus greatly limiting the spread of new ideas. Therefore, a less constraining, more collaborative, protocol is here suggested: (i) characterization of new material through a rigorous, multi-reference samples approach in Ar-, N_2- and NO_x- saturated environment (see **Figure 4**), as the promising activity of a given electrocatalyst might simply arises of traces of $^{15}NO_x$ or

$^{14}NO_x$ in the N_2 feed (*e.g.*, Murphy *et al.* [48] recently evidenced that metal-nitrogen-carbon materials, often assessed as promising NRR electrocatalysts, were instead catalysing the NO_x reduction reaction – NO_xRR); (ii) transfer of the promising electrocatalysts to an independent research group that possesses the equipment and the know-how to fully assess the promises of the this electrocatalyst (*e.g.*, similarly to the recent works of Choi and Du *et al.* [13,49–51] to debunk several 'so-called' NRR electrocatalysts) and insure not only its robustness while exposed to more elaborated characterization protocols, but also its reproducibility, along to promoting interactions between different NRR-related fields (electrochemistry, systems, materials design, *etc.*); (iii) if the electrocatalysts validates this first set and second set of characterization, to publish it as an electrocatalyst for the NRR.

Conclusion: The nitrogen reduction reaction in aqueous media is an uphill battle – one that might eventually conclude in the foretold conclusion that this field was always hopeless. However, directions to be explored remain. First, at the scientific level: (i) the use of bifunctional electrocatalysts might allow to go beyond the scaling relationships, enhancing the intrinsic activity for the NRR, whereas (ii) tuning the LRE (*e.g.*, N_2 and aqueous proton sources concentration near the reactive interface) should greatly improve the electrocatalyst' selectivity for the NRR. Both directions might allow the community to generate sufficient amount of NH_3 to be freed of the substantial contribution of contaminants, NO_3RR, *etc.* However, since this goal is yet to be achieved, the means of characterization should also be thought upon. Echoing the message sent by Greenlee *et al.* [15] and Choi *et al.* [13] in 2018 and 2020, respectively, the overwhelming complexity of this field requires to rethink the way we do share our results and interact with our so-called competitors: validating new concepts should be done carefully and with the contribution of research labs with the proper expertise (*i.e.*, the so-called 'certification laboratories' [13]) for each new material; the publication of negative results should be encouraged and valorised [15], to avoid the community losing itself in the wrong direction. This aims to eventually rebuild trust in this domain – and not to see it, yet again, being swept by incorrect findings, and identified, yet again, as the runt of the litter in the future of ammonia generation.

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