

## Electrochemical nitrogen oxide formation from ammonia and dinitrogen

Jungbacker, Peter; Kortlever, Ruud; Mulder, Fokko M.

**DOI**

[10.1039/d5gc05480j](https://doi.org/10.1039/d5gc05480j)

**Publication date**

2025

**Document Version**

Final published version

**Published in**

Green Chemistry

**Citation (APA)**

Jungbacker, P., Kortlever, R., & Mulder, F. M. (2025). Electrochemical nitrogen oxide formation from ammonia and dinitrogen. *Green Chemistry*. <https://doi.org/10.1039/d5gc05480j>

**Important note**

To cite this publication, please use the final published version (if applicable).  
Please check the document version above.

**Copyright**

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

**Takedown policy**

Please contact us and provide details if you believe this document breaches copyrights.  
We will remove access to the work immediately and investigate your claim.



Cite this: DOI: 10.1039/d5gc05480j

## Electrochemical nitrogen oxide formation from ammonia and dinitrogen

Peter Jungbacker, <sup>a</sup> Ruud Kortlever <sup>b</sup> and Fokko M. Mulder <sup>\*a</sup>

Synthetic fertilizers are required to sustain the increasing human population. Out of the many different types of fertilizers, ammonium nitrate is the most widely used type. Currently, both nitrate and ammonia are produced *via* energy-intensive processes, requiring high temperatures and pressures. Therefore, to make the production of the necessary fertilizers more sustainable, alternative production methods are required. One of those potential routes is electrochemical synthesis. While the electrochemical reduction of dinitrogen to ammonia has been investigated thoroughly, the synthesis of nitrate has not received as much attention. In this review, we review two different routes for the electrochemical synthesis of nitrate, starting from either molecular nitrogen or ammonia. We show that the reaction conditions can significantly alter the selectivity of ammonia oxidation. Consequently, this means that a catalyst currently tailored for oxidising ammonia to dinitrogen could potentially be used for ammonia oxidation to nitrate. Meanwhile, the direct electrochemical oxidation of molecular nitrogen suffers from false positives due to contaminations, similar to electrochemical nitrogen reduction. The current published results still lack proper control experiments, making the outcomes for now unreliable. In conclusion, for dinitrogen oxidation research, we suggest rigorous testing procedures to exclude false positive results.

Received 15th October 2025,  
 Accepted 25th November 2025  
 DOI: 10.1039/d5gc05480j  
[rsc.li/greenchem](http://rsc.li/greenchem)

### Green foundation

1. Here, the electrochemical production of  $\text{NO}_x$  is discussed from the emerging field of direct electrochemical di-nitrogen oxidation. This perspective provides guidance in the di-nitrogen electrochemical activation field.
2. Nitrogen oxides are used intensively as fertilisers and chemical feedstocks. They may also provide an alternative pathway to enable electrochemical synthesis of ammonia from  $\text{NO}_x$  as a future large-scale carbon free energy storage technology. Both nitrogen chemistries belong to the largest chemical commodities.
3. Current low yields are reported in this emerging field, enhancing the sensitivity to impurities. This can lead to false positive results, for instance, from unanticipated ammonia oxidation to nitrite and nitrate, instead of the expected di-nitrogen. We argue that it is essential to develop test protocols, which were earlier also found necessary in the associated direct di-nitrogen reduction to ammonia.

## Introduction

The human population is ever increasing. To enable sufficient global food production, artificial fertilizers are necessary.<sup>1</sup> Without the use of these fertilizers, only ~50% of the current population could be sustained. This highlights the importance of these fertilizers. Out of the many different types of fertilizers, N-based fertilizers are the most applied, and over the past 50 years, their use has significantly increased.<sup>2</sup> Furthermore, this trend is expected to continue due to the increasing population. We need fertilizers to feed the world, but we are producing enough, so where does the problem lie? The problem lies in the

fossil feedstock used to make these fertilizers, as these nitrogen-containing fertilizers are produced from grey ammonia, of which the production is expected to become replaced by green, and  $\text{CO}_2$  emission-free alternatives in the coming decades.

Conventionally, ammonia is produced *via* the Haber–Bosch process. In this process,  $\text{N}_2$  and  $\text{H}_2$  gases are passed over Fe or Ru-based catalysts at high pressures and high temperatures. These reaction conditions are around 450–500 °C and 150–200 atm.<sup>2</sup> Additionally, part of ammonia is further converted into nitric acid *via* the Ostwald process. This is another process requiring high temperatures and pressures. Both processes are most often performed in large-scale centralized plants.<sup>3</sup> Collectively, these two processes use ~12% of the energy consumed by the chemical industry. In addition to the large energy consumption, these processes have a large carbon footprint. These emissions are mainly the result of hydrogen production for the Haber–Bosch process, as the hydrogen is currently pro-

<sup>a</sup>Materials for Energy Conversion and Storage (MECS), Delft University of Technology, 2629 HZ Delft, The Netherlands. E-mail: f.m.mulder@tudelft.nl

<sup>b</sup>Large-Scale Energy Storage, Process & Energy, Faculty of Mechanical Engineering, Delft University of Technology, Leeghwaterstraat 39, 2628 CB Delft, The Netherlands

duced by steam methane reforming. In this process, methane is used as a hydrogen source and CO<sub>2</sub> is the major side product.

Therefore, if we continue the way things are, we can continue to feed the world. However, this will also have a major negative impact on the environment. Thus, we need to find alternatives that are more sustainable and fit in a new renewable-based energy economy. These renewables such as solar power and wind power produce electricity in a distributed and intermittent manner. The simplest alternative may be electrolytic green hydrogen production and then centrally performing the large scale Haber–Bosch process to produce NH<sub>3</sub>, and subsequently converting that to nitrates in the Ostwald process.<sup>4–6</sup> However, alternative processes may also be considered, which can be applied in a more distributed manner on varying scales fitting to the more distributed and intermittent generation of renewables. Two promising alternatives are enzymatic and electrochemical processes. The enzymatic pathway is promising, since nature can produce ammonia and nitrate at ambient temperature and pressure.<sup>7,8</sup> However, on an industrial scale, enzymatic processes are often not viable. This is due to the high cost of coenzymes or the difficulty of isolation of the products without losing the bacteria.<sup>9,10</sup> Because of this, electrochemical conversion is considered the most promising alternative and can be operated on different scales, from small to large, and potentially intermittently. Similar to the enzymatic pathway, electrochemical conversion can be performed at ambient temperature and pressure.<sup>11,12</sup> Furthermore, the process could potentially be operated in aqueous electrolytes, making it environmentally benign. Finally, these alternatives have no intrinsic carbon emissions.

Here, we discuss the current state of the electrochemical synthesis of nitrate by electrochemical oxidation of NH<sub>3</sub> and N<sub>2</sub>. We will focus on this process specifically, since the nitrogen reduction reaction to NH<sub>3</sub> has already been studied extensively at this point.<sup>13–15</sup> Specifically, we address the current state of the electrochemical nitric acid synthesis starting from NH<sub>3</sub> or N<sub>2</sub> and discuss published literature studies in comparison with each other. Moreover, we will highlight the current state of the art with respect to catalysts for the process and highlight the current challenges that are yet to be overcome and give directions to overcome these challenges.

First, we will discuss the electrochemical ammonia oxidation reaction (AOR). This reaction has been extensively investigated over the last 20 years. However, most of the research was aimed at removing ammonia contaminations from waste and groundwater.<sup>16–19</sup> Therefore, the desired product of this reaction has been environmentally benign nitrogen gas. When noble metals, such as Pt, are used for ammonia oxidation, dinitrogen is the main product.<sup>20,21</sup> However, when nitrates are the intended products, converting ammonia to dinitrogen is a loss, since a molecule with ‘active’ nitrogen is converted into the almost inert nitrogen molecule.

When looking at the Pourbaix diagram of nitrogen in Fig. 1, we can see that the reaction thermodynamically can take place inside the stable potential regime of water, given between the dotted lines for the OER and HER. This means that the electrochemical oxidation of ammonia to nitrate in aqueous electro-

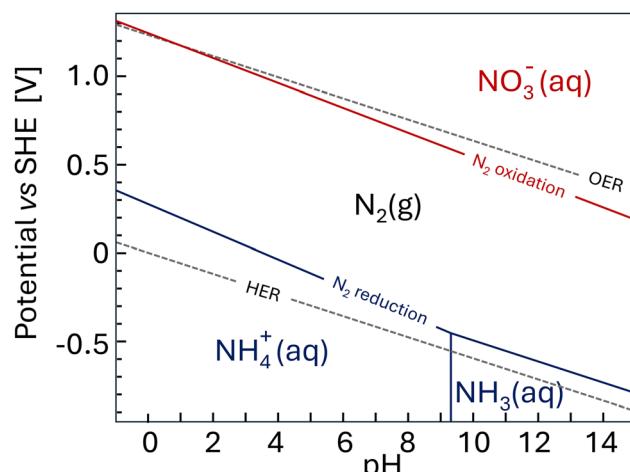
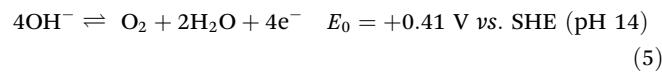
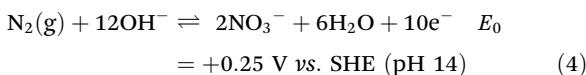
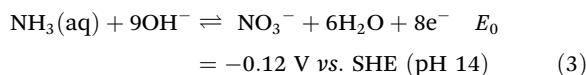
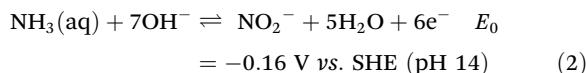
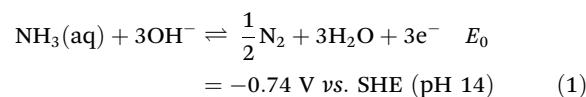


Fig. 1 Pourbaix diagram of nitrogen, showing the stable species of nitrogen at different pH values and potentials calculated from ref. 22.

lytes is not restricted by thermodynamics and can potentially occur without oxygen evolution as a side reaction. Being able to use water means that one does not have to use more expensive electrolytes, such as ionic liquids.

The Pourbaix diagram illustrates the thermodynamically most stable compounds in the pH-potential landscape. However, that does not mean that, for instance, nitrite or nitrates cannot form at the potentials intermediate to the N<sub>2</sub> reduction and oxidation lines. The equations below give possible half reactions of ammonia and the relevant potentials deduced from  $\Delta G$ , the Gibbs free energy of the products at the nitrogen oxidation working electrode and the hydrogen evolution counter electrode at the RHE, minus that of the respective input species. The obtained working electrode potential *vs.* the RHE was then calculated *vs.* the SHE using the pH. The potential indicated that nitrite and nitrate could be formed below the N<sub>2</sub> oxidation line shown in Fig. 1 and the potential shown in eqn (4). These potentials are also all below the (competing) oxygen evolution reaction (OER) shown in eqn (5).



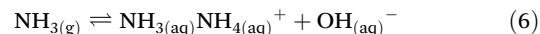
Unlike the ammonia oxidation reaction, the dinitrogen oxidation reactions (NORs) such as in eqn (4) have barely been

explored. This possible route to nitrate has only recently received attention from researchers. To the best of our knowledge, the first paper on this subject was published no earlier than 2019.<sup>11</sup> Since then, there have been some additional publications investigating this reaction; however, this reaction still has significantly fewer published studies than both the ammonia oxidation and nitrogen reduction reactions. This is correlated to the fact that this reaction is significantly more challenging than ammonia oxidation. To convert dinitrogen to nitrate, the triple bond in dinitrogen needs to be activated,<sup>23</sup> which requires a significant amount of energy. Its potential shown in eqn (4) is also higher than that of the AOR (eqn (1)–(3)) and therefore closer but still below the competing OER potential. In addition, there will be overpotentials for the NOR and OER of the intermediate oxidation steps that will determine the selectivity to which reaction prevails at which overpotential. Lowering the applied potential towards the OER equilibrium potential should, however, see relatively larger reductions in the OER yield (if present) than in the NOR yield when one would have a good NOR catalyst and sufficient sensitivity to measure the product  $\text{NO}_x$ . Furthermore, the challenging dinitrogen activation may cause the nitrogen oxidation research development to resemble the situation in nitrogen reduction reaction research. The electrochemical nitrogen reduction reaction has been a field of interest for quite some time. This is reflected by the large number of papers published on this specific reaction. However, more recently, highly cited papers have been retracted due to faulty results.<sup>24</sup> Unfortunately, this seems to be a common occurrence within the field of  $\text{N}_2$  activation research.<sup>25,26</sup> The published results either suffer from very low reaction rates or the results are irreproducible and faulty. These faulty results mainly come from these low ammonia yields, which makes the contamination sources of nitrogen-containing species become important, leading to false positives for the reduction of nitrogen. Therefore, we are aware that, when investigating the nitrogen oxidation reaction, we may encounter similar sluggish  $\text{N}_2$  activation reaction rates and therefore a similar sensitivity to contamination problems as in nitrogen reduction studies.

### Electrocatalysts for dinitrogen and ammonia electro-oxidation in aqueous electrolytes

The materials available that are stable at oxidizing potentials in a water-based electrolyte are limited, and their choice depends on the pH of the electrolyte. In an acidic electrolyte, the only relatively active and stable options available for the oxygen evolution reaction (OER) are  $\text{IrO}_2$ -based catalysts with possibly  $\text{RuO}_2$  additives and  $\text{TiO}_2$  substrates.<sup>27,28</sup> In alkaline media, non-noble metals such as Ni, Fe and Co provide stable oxyhydroxide surfaces such as  $\text{NiOOH}$  and  $(\text{Ni}, \text{T})\text{OOH}$ , with T = Fe and/or Co. Most research for nitrogen and ammonia oxidation to date has focused on the use of alkaline or close to neutral electrolytes, which could thus potentially also use such non-noble catalysts as well as noble catalysts. Also, the basic pH of ammonium hydroxide solutions promotes the use of

alkaline systems since the equilibrium below lies to the  $\text{NH}_3\text{(aq)}$  side in eqn (6).<sup>29</sup>



Here, it is indicated that the gas phase ammonia ( $\text{NH}_{3\text{(g)}}$ ), dissolved ammonia ( $\text{NH}_{3\text{(aq)}}$ ) and ammonium ion ( $\text{NH}_4^+$ ) equilibria depend on the pH. For a pH higher than 11, the equilibrium is completely shifted to the left side of the equation. The relevant equilibrium to be considered is then between ammonia in the gas phase ( $\text{NH}_{3\text{(g)}}$ ) and dissolved ammonia ( $\text{NH}_{3\text{(aq)}}$ ).

### Ammonia oxidation reaction (AOR) at alkaline pH

Research on the electrochemical ammonia oxidation reaction (AOR) to nitrite and nitrate can be split into two groups based on the investigated electrode materials. The first materials we will discuss are nickel-based catalysts for the AOR. An overview of the reported nickel-based materials for ammonia oxidation is given in Table 1. These results indicate that nickel is an interesting material for the electrochemical oxidation of ammonia. Furthermore, the results show that slightly changing reaction parameters can have a major influence on the selectivity. Out of these results, we highlight one of the publications, which is a study published by Medvedev *et al.*<sup>1</sup> Therein, they demonstrate an efficient route towards  $\text{NH}_4\text{NO}_3$ -based fertilizers *via*  $\text{Ni}(\text{OH})_2$ -catalysed electrochemical oxidation of ammonia. They examine how operating conditions affect the AOR product distribution and show that, under optimized conditions, a concentrated ammonia solution can be efficiently converted into  $\text{NH}_4\text{NO}_3$  with up to 72% faradaic efficiencies and up to 98% ammonia removal.

In addition to these high conversions, Medvedev *et al.* also performed various experiments to gain mechanistic insight into the AOR.<sup>1</sup> During these experiments, they found that the oxidation of ammonia to nitrite might occur spontaneously on their charged  $\text{Ni}(\text{OH})_2$  electrode. To prove this hypothesis, they charged the  $\text{Ni}(\text{OH})_2$  electrode by passing a constant current of 50 mA  $\text{cm}^{-2}$  through the anode for 20 min. During this charging,  $\text{Ni}(\text{OH})_2$  was oxidized to  $\text{NiOOH}$  in the reaction given in eqn (7).<sup>30</sup>



The oxidation reaction of  $\text{Ni}(\text{OH})_2$  takes place with a standard equilibrium potential of +0.49 V *vs.* SHE during charging. The charged electrode is subsequently removed from the cell and submerged in a 0.1 M NaOH solution containing 0.2 M  $\text{NH}_3$ . The reactions were performed at different temperatures, and the products were analyzed by ion chromatography (IC). For all temperatures, only the formation of nitrite was observed, while the formation rate was found to be temperature dependent. The increased rate can be understood not only as a kinetic effect of faster catalysis at higher  $T$ , but also as a faster  $\text{H}^+$  and  $\text{e}^-$  charge transport from within the charged  $\text{NiOOH}/\text{Ni}(\text{OH})_2$  electrode towards its surface. Following these results, they tried the same procedure but replaced the ammonia with nitrite. However, no



**Table 1** Reported ammonia oxidation reaction (AOR) performance of several Ni-based electrocatalysts

| Anode                                       | <i>E</i> or <i>J</i>  | pH                | Electrolyte  | Results   | Ref. |
|---|---|-------------------|--|---|------|
| $\text{Ni(OH)}_2/\text{NF}^a$               | 1.6 V <sub>RHE</sub> ( $\sim 6$ mA cm $^{-2}$ ) <sup>b</sup>    | 11.3 <sup>c</sup> | 0.2 M $\text{NH}_3$ + 0.1 M $\text{Na}_2\text{SO}_4$   | FE <sub>(<math>\text{N}_2</math>)</sub> 51%   | 1    |
| $\text{Ni(OH)}_2/\text{NF}^a$               | 1.9 V <sub>RHE</sub> ( $\sim 30.5$ mA cm $^{-2}$ ) <sup>b</sup> | 11.5 <sup>c</sup> | 0.3 M $\text{NH}_3$ + 0.1 M $\text{K}_2\text{SO}_4$    | FE <sub>(<math>\text{NO}_3^-</math>)</sub> 72% <sup>d</sup>   | 1    |
| $\text{Ni(OH)}_2/\text{NF}^a$               | 1.6 V <sub>RHE</sub> ( $\sim 10$ mA cm $^{-2}$ ) <sup>b</sup>   | 13 <sup>c</sup>   | 0.2 M $\text{NH}_3$ + 0.1 M $\text{NaOH}$              | FE <sub>(<math>\text{NO}_2^-</math>)</sub> 58%  | 1    |
| $\text{Ni}_{0.8}\text{Pd}_{0.2}$            | 20 mA cm $^{-2}$  | 10.5              | 0.2 M $\text{NH}_4\text{NO}_3$ + 1 M $\text{NaNO}_3$   | FE <sub>(<math>\text{N}_2</math>)</sub> 38.7%   | 33   |
| NF <sup>a</sup>                             | 0.7 V <sub>Hg/HgO</sub>   | 11                | 20 ppm $\text{NH}_3$ + 0.1 M $\text{Na}_2\text{SO}_4$  | FE <sub>(<math>\text{N}_2</math>)</sub> 50%   | 34   |
| NF <sup>a</sup>                             | 0.85 V <sub>Hg/HgO</sub>  | 11                | 20 ppm $\text{NH}_3$ + 0.1 M $\text{Na}_2\text{SO}_4$  | FE <sub>(<math>\text{NO}_3^-</math>)</sub> 10%  | 34   |
| Activated Ni                                | 20 mA cm $^{-2}$  | 11                | 50 mM $\text{NH}_4\text{ClO}_4$ + 1 M $\text{NaClO}_4$ | No FE are given<br>3 : 1 $\text{N}_2 : \text{NO}_3^-$ ratio   | 35   |
| $\text{Ni}_2\text{P}/\text{NF}^a$           | 15 mA <sup>e</sup>  | 13                | 1000 ppm $\text{NH}_3$ + 0.1 M KOH                     | Up to 50% CE without specification<br>( $\text{N}_2$ major; $\text{NO}_2^-$ , $\text{NO}_3^-$ ~1 : 1) | 36   |
| $\text{Ni}_{x}\text{Cu}_{1-x}(\text{OH})_2$ | 1.53 V <sub>RHE</sub>   | 13                | 1 mM $\text{NH}_3$ + 0.1 M KOH                         | >80% FE of $\text{NO}_2^-$ minor oxidation of $\text{NH}_3$ was observed without applied voltage      | 37   |
| CNT-Ni <sup>f</sup>                         | 1.5 V <sub>RHE</sub>  | 11                | 130 ppm $\text{NH}_3$ + 10 mM $\text{Na}_2\text{SO}_4$ | No FE are given<br>~14 : 1 $\text{N}_2 : \text{NO}_3^-$ ratio   | 38   |
| CNS-Ni <sup>g</sup>                         | 1.5 V <sub>RHE</sub>  | 11                | 130 ppm $\text{NH}_3$ + 10 mM $\text{Na}_2\text{SO}_4$ | No FE are given<br>~16 : 1 $\text{N}_2 : \text{NO}_3^-$ ratio   | 38   |
| NiO NPs <sup>h</sup>                        | 30 mA cm $^{-2}$  | 9                 | 200 mM $\text{NH}_4\text{OH}$ + 100 mM $\text{NaNO}_3$ | No FE are given ( $\text{N}_2$ major; $\text{NO}_2^-$ , $\text{NO}_3^-$ ~1 : 2)                       | 39   |
| NiO NPs <sup>h</sup> /NF <sup>a</sup>       | 2 mA cm $^{-2}$   | 9                 | 100 ppm $\text{NH}_3$ + 0.1 M $\text{Na}_2\text{SO}_4$ | 80% removal; 90% $\text{N}_2$ selectivity   | 40   |
| $\text{NiCoO}_x$ NPs <sup>h</sup> /Ni       | 2 mA cm $^{-2}$   | 9                 | 130 ppm $\text{NH}_3$ + 0.1 M $\text{Na}_2\text{SO}_4$ | 98% removal; 80% $\text{NO}_3^-$ selectivity  | 40   |

<sup>a</sup> NF is nickel foam. <sup>b</sup> Average current density in the first two hours of electrolysis. <sup>c</sup> Initial pH of the electrolyte. <sup>d</sup> Total FE at the end of 52 h electrolysis. <sup>e</sup> Current is reported instead of current density. <sup>f</sup> CNT denotes a carbon nanotube. <sup>g</sup> CNS denotes a carbon nanosphere. <sup>h</sup> NPs denotes nanoparticles.

higher oxidation products were observed in this case. This further proved their conclusion that the oxidation of ammonia to nitrite occurs spontaneously as soon as the NiOOH is present in the charged  $\text{Ni(OH)}_2/\text{NiOOH}$  electrode, while the oxidation to nitrate occurs purely electrochemically. The relatively high concentration of 0.2 M  $\text{NH}_3$  also introduces a non-negligible  $\text{NH}_3(\text{g})$  vapour pressure,<sup>31</sup> which also means that application of  $\text{NH}_3$  pressure above the liquid increases the  $\text{NH}_3$  concentration near the catalyst surface, which will enable higher limiting currents for the oxidation reaction. However, at higher currents, the  $\text{OH}^-$  consumption will decrease the local pH and increase the required potentials shown in eqn (2) and (3) accordingly. Applying higher pH by using higher NaOH or (KOH) concentration can counteract that; however, then increased  $\text{NH}_3$  pressure needs to be applied to keep the  $\text{NH}_3(\text{aq.})$  concentration high.<sup>31</sup>

Special care needs to be taken when working at low ppm-scale  $\text{NH}_3$  concentrations: while all of these results seem very promising, there is unfortunately a lack of control experiments. Even though a significant amount of reaction parameters were varied, there is no report of the reaction being run without the  $\text{NH}_3$  reactant. Nor is there any mention of the accumulation of  $\text{NO}_x$  when the experiment is run without applying any external current/voltage. This means that the possibility exists that the measured low concentration products are in part also the result of contaminations, rather than reaction products. For instance,  $\text{NO}_x$  from the air or catalyst precursors can be captured in the alkaline electrolyte as well. To prove beyond a shadow of doubt that these are not contaminations, further control experiments are required.

Copper-based materials are another promising option for ammonia oxidation electrocatalyst as the work of Johnston *et al.*

illustrates.<sup>32</sup> In this work, they investigate the viability of copper as a catalyst for the AOR, despite the fact that copper is prone to electrodissolution by ammonia under alkaline conditions. In their study, they demonstrate that the issue of Cu dissolution and complexation of copper ions with ammonia can be mitigated by fine-tuning both the pH and operating potential.<sup>32</sup> Furthermore, they claim that changing these parameters could even lead to a highly selective AOR to either nitrite or nitrate.

Moreover, they found that the AOR follows two main pathways on copper electrodes. The first is a heterogeneous pathway, of which  $\text{NO}_3^-$  is the main product. The second is a homogeneous mediated reaction pathway, where the primary product is  $\text{NO}_2^-$ . The mediator of the second pathway is  $[\text{Cu}(\text{OH})_4]^-$ , where the copper cycles between the +2 and +3 oxidation states. The best overall yield was obtained at 2.0 V<sub>RHE</sub> in 0.11 M KOH, giving a selectivity of 25% FE for  $\text{NO}_3^-$  and 42% FE for  $\text{NO}_2^-$ .<sup>32</sup> These results indicated that the homogeneous pathway is the more prevalent of the two.

The second study highlighting the potential of copper as an electrocatalyst is by Huang *et al.*<sup>41</sup> They tested three different CuO-based samples, *i.e.*, oxygen vacancy ( $V_o$ ) rich, oxygen vacancy poor and oxygen vacancy free CuO. All these catalysts were tested in the electrochemical oxidation of ammonia and the products were measured by the online MS analysis of gas products. Out of the three tested catalysts,  $V_o$ -poor CuO seemed the most promising catalyst for the purpose. This material had the highest selectivity towards nitrite as a product, which is a known intermediate in the current industrial synthesis of nitric acid. They reported a FE of 72.2% toward nitrite for their catalyst.<sup>41</sup>

It may be noted that catalysts for the reverse reaction of  $\text{NO}_x$  to  $\text{NH}_3$  are based on copper and its alloys.<sup>12,29,42</sup>



Therefore, further leads to copper-based catalysts may be deduced from  $\text{NO}_x$  reduction studies, assuming that good catalysts would be able to catalyse both the back and forward reactions.

### Mechanism of the ammonia oxidation reaction

In order to understand the difference in selectivity obtained, even with the same catalyst, a clear understanding of the mechanism needs to be obtained. The interest in the mechanism is not only present for the oxidation to value added  $\text{NO}_x$  products but can also be seen in the field of wastewater treatment.<sup>34</sup> In this field, Kapalka *et al.* investigated the electrochemical behavior of ammonia at a Ni/Ni(OH)<sub>2</sub> electrode. They observed that increasing the ammonia concentration led to an increase of the oxidation peak for the Ni(II)/Ni(III) redox couple. Furthermore, a second oxidation emerged at a more positive potential, which was attributed to the oxidation of ammonia.<sup>34</sup> Based on these observations, they concluded that ammonia oxidation occurs only when the Ni electrode mainly consists of Ni(III) species. Following these results, they investigated the influence of pH on ammonia oxidation. They observed that the ammonia oxidation peaks shift towards more positive potentials with increasing pH until the peak completely overlapped with the oxygen evolution and was no longer visible. Finally, they performed a 12 h control experiment in 1 M NaClO<sub>4</sub> at pH 11 under a current of 20 mA cm<sup>-2</sup>. In this experiment, they saw the amount of total ammonia and nitrogen continuously decrease, whereas the amount of nitrate increased over time.<sup>34</sup> At the end of the experiment, ~55% of the ammonia was converted and 11% was recovered as nitrate, leaving 34% for the production of gaseous N-species, such as N<sub>2</sub> and maybe even N<sub>2</sub>O and NO. Noticeable is the lack of nitrite produced by the reaction. While they measured this

species as well, none was observed since the amounts were below the detection limit. From all of these results, they concluded that N<sub>2</sub> is formed *via* a direct electron transfer reaction, where the ammonia adsorbs on the surface and is oxidized by external electrons, without changing the oxidation state of the electrode. Meanwhile, nitrate can be formed during the oxygen transfer reaction in which water is activated, resulting in the transfer of an oxygen atom to the ammonia molecule.

In a similar manner, Medvedev *et al.* also proposed a general mechanism that considers pathways to N<sub>2</sub> and  $\text{NO}_x^-$  products based on their experimental results.<sup>1</sup> For their mechanism, they proposed that NiOOH is the active material and that the oxidation of Ni(OH)<sub>2</sub> is the first step of the reaction, as shown in Fig. 2. On the oxidized NiOOH surface, NH<sub>3</sub> coordinates to a Ni atom, breaking one Ni–O bond (Fig. 2b). After adsorbing on the surface, NH<sub>3</sub> undergoes the first oxidation and deprotonation step. This \*NH<sub>2</sub> intermediate then replaces an \*OH to form a bridge structure.<sup>40</sup> Thereafter, \*NH<sub>2</sub> undergoes two spontaneous deprotonation steps, forming \*NH and \*N species.<sup>40</sup> The intermediate \*NH species can couple with an identical species to form \*N<sub>2</sub>H<sub>2</sub>, which can further deprotonate to form N<sub>2</sub>. Furthermore, the \*N species can also dimerize, which also results in the formation of N<sub>2</sub> as the oxidation product. Alternatively, adsorbed \*N can undergo hydroxylation to obtain NO<sub>2</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup> (Fig. 2c). Out of these two products, NO<sub>2</sub><sup>-</sup> can be formed on the NiOOH surface without applied potential due to the high oxidative activity of Ni(III). The origin of the OH<sup>-</sup> for the hydroxylation reactions can be either the electrolyte or the NiOOH lattice itself. Finally, \*NO<sub>2</sub>H species can undergo a two-electron electro-oxidation to \*NO<sub>3</sub>H, which can be deprotonated and desorbed to obtain NO<sub>3</sub><sup>-</sup>.<sup>43</sup> Despite the experimental evidence and DFT calculations supporting the validity of this mechanism, it still

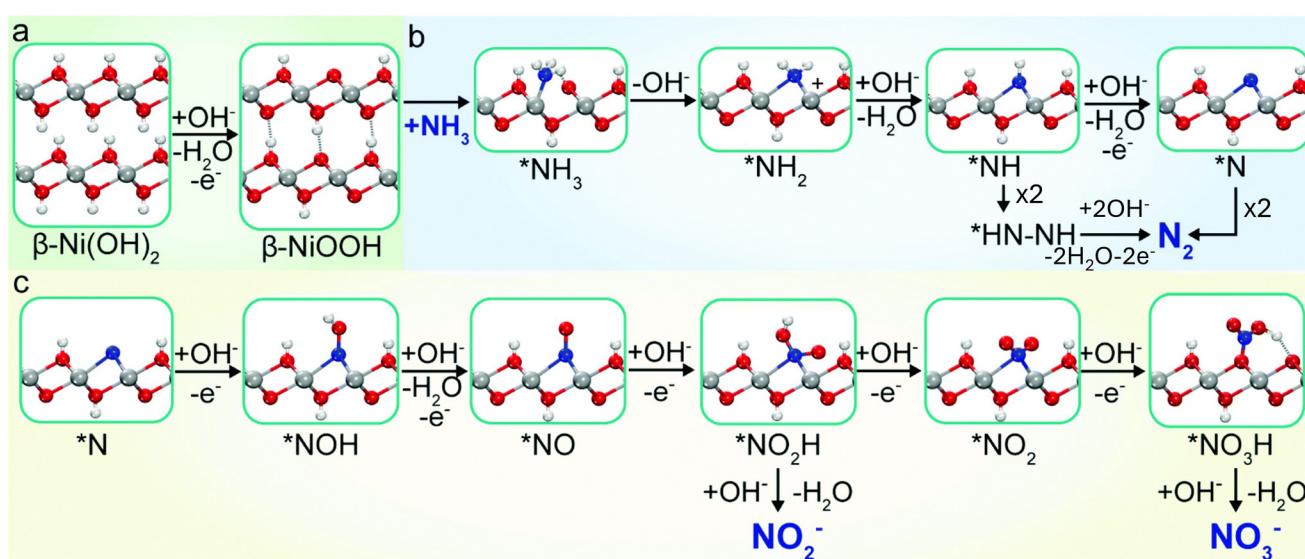


Fig. 2 Proposed mechanism of the AOR under Ni-based catalysts: electrochemical dehydrogenation of the Ni(OH)<sub>2</sub> catalyst with the formation of the active NiOOH surface, (a) followed by ammonia adsorption and oxidation to N<sub>2</sub> (b) and nitrite and nitrate (c). Adapted from ref. 1 with permission from RSC Green Chemistry, copyright 2022.

remains unclear why ammonia-to-nitrite can proceed spontaneously on NiOOH, while the oxidation to nitrate can only happen electrochemically.<sup>1</sup> Some of the possible explanations given by Medvedev *et al.* are: (1) the high energy barrier for configurational changes in  $^*\text{NO}_2$  and (2) stabilization of  $^*\text{NO}_3\text{H}$  by deprotonated  $^*\text{OH}$  groups. However, further mechanistic elucidation of these phenomena is required and will be a subject of future studies.

### Nitrogen oxidation reaction (NOR)

Historically, the plasma-based Birkeland–Eyde process performed nitrogen oxidation to NO using air in a high energy plasma. As previously mentioned, the direct oxidation of nitrogen using electrochemistry is a relatively new reaction of interest. Therefore, only few papers have been published on this electrochemistry-based reaction.<sup>11,45–56</sup> These papers explore a wide range of different catalysts for the NOR, from noble metals to mixed metal oxides. However, these papers have a couple of factors in common. When comparing their obtained results with the rest of the field, they compare the highest value of faradaic efficiency and yield, rather than the values measured under the same conditions. This means that to compare the activity of their catalysts, one needs to read through the entire results section and find corresponding values for efficiency and yield that belong together. In Table 2, the results of various nitrogen oxidation catalysts are shown. Here, we note that the reported values are all obtained at the indicated potential. This means that the highest obtained values are not compared with each other, but instead the as-obtained values can be compared.

Overall, the results seem promising, showing a faradaic efficiency up to 35% and yield rates up to  $22 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$ .<sup>44,53</sup> However, often only nitrate is reported as the singular product. This implies that most of the electrons are going to

unspecified reactions. If these by-products were identified as well, we might be able to observe similarities between the nitrogen oxidation reaction and the ammonia oxidation reaction. This could, for instance, teach us whether the selectivity of the reaction is pH dependent and if changing pH could steer selectivity towards either nitrate or nitrite, similar to the AOR.<sup>1</sup>

Furthermore, in view of the difficult  $\text{N}_2$  activation in the related nitrogen reduction field, these papers lack important control experiments that are expected to be necessary when operating with low product concentrations. Therefore, similar to the nitrogen reduction reaction (NRR), the NOR is prone to false positives due to contamination sources providing activated N sources like  $\text{NH}_3$  and  $\text{NO}_x$ . These sources vary from the  $\text{N}_2$  feed gas itself to the electrolyte and membrane used in the electrochemical setup. Wang *et al.* proposed a rigorous test protocol for the NOR to avoid false positives from contaminations.<sup>46</sup> The test protocol proposed by Wang *et al.* provides a clear and complete experiment to both identify and eliminate extraneous nitrogen sources. Additionally, we have also investigated extraneous nitrogen sources found during nitrogen reduction reaction experiments.<sup>26</sup> With these tools in hand, researchers should be able to minimize influences from external nitrogen sources and avoid the publication of false positives. More recent papers on nitrogen reduction have already implemented rigorous testing procedures to exclude any false positives. These control experiments include flowing Ar instead of  $\text{N}_2$  and using  $^{15}\text{N}_2$  to determine the source of N in the  $\text{NH}_3$ ; such controls are equally relevant for nitrogen oxidation research.

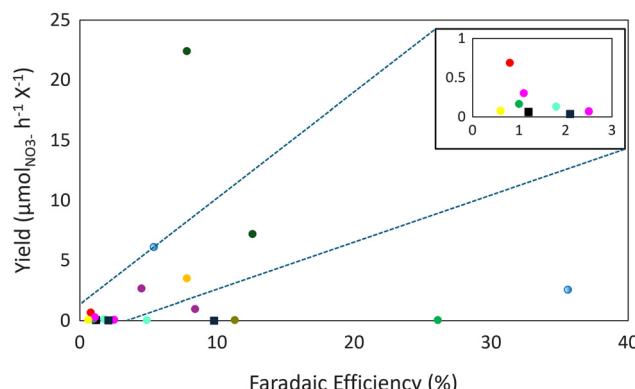
Table 2 data are also included in Fig. 3 to illustrate the scatter of available values of the combination of yield *versus* faradaic efficiency. In the future, it would be advantageous to perform the experiment at set current densities and known  $\text{N}_2$  flow rates. Plotting faradaic efficiency and the potential against

**Table 2** Overview of the results published for the dinitrogen oxidation reaction

| Catalyst   | <i>E</i>       | Electrolyte                     | Faradaic efficiency              | Yield  | Ref. |
|--|----------------|---------------------------------|----------------------------------|--|------|
| Pt foil  | 2.19 V vs. RHE | 0.3 M $\text{K}_2\text{SO}_4$   | 1.2% $\text{FE}(\text{NO}_3^-)$  | $0.06 \mu\text{mol h}^{-1} \text{cm}^{-2} \text{NO}_3^-$               | 11   |
| Fe– $\text{SnO}_2$                               | 1.96 V vs. RHE | 0.05 M $\text{H}_2\text{SO}_4$  | 0.8% $\text{FE}(\text{NO}_3^-)$  | $0.69 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$  | 45   |
| 2.79 wt% Ru/TiO <sub>2</sub>                     | 1.8 V vs. RHE  | 0.1 M $\text{Na}_2\text{SO}_4$  | 26.1% $\text{FE}(\text{NO}_3^-)$ | $0.05 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$  | 46   |
| 2.79 wt% Ru/TiO <sub>2</sub>                     | 2.2 V vs. RHE  | 0.1 M $\text{Na}_2\text{SO}_4$  | 1% $\text{FE}(\text{NO}_3^-)$    | $0.161 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$ | 46   |
| AD-Fe NS <sup>a</sup>                            | 2.4 V vs. RHE  | 0.05 M $\text{K}_2\text{SO}_4$  | 5.4% $\text{FE}(\text{NO}_3^-)$  | $6.12 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$  | 47   |
| AD-Fe NS <sup>a</sup>                            | 2.1 V vs. RHE  | 0.05 M $\text{K}_2\text{SO}_4$  | 35.6% $\text{FE}(\text{NO}_3^-)$ | $2.56 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$  | 47   |
| $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$     | 1.5 V vs. RHE  | 1 M KOH                         | 4.9% $\text{FE}(\text{NO}_3^-)$  | $0.049 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$ | 48   |
| $\text{ZnFe}_{0.4}\text{Co}_{1.6}\text{O}_4$     | 1.6 V vs. RHE  | 1 M KOH                         | 1.8% $\text{FE}(\text{NO}_3^-)$  | $0.13 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$  | 48   |
| Pd-s PNSS <sup>b</sup>                           | 1.55 V vs. RHE | 1 M KOH                         | 2.5% $\text{FE}(\text{NO}_3^-)$  | $0.071 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$ | 50   |
| Pd-s PNSS <sup>b</sup>                           | 1.75 V vs. RHE | 1 M KOH                         | 1.1% $\text{FE}(\text{NO}_3^-)$  | $0.3 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$   | 50   |
| Pd <sub>0.9</sub> Ru <sub>0.1</sub>              | 1.7 V vs. RHE  | 0.1 M KOH                       | ~0.6% $\text{FE}(\text{NO}_3^-)$ | $0.077 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$ | 51   |
| Pd/Mxene   | 2.03 V vs. RHE | 0.01 M $\text{Na}_2\text{SO}_4$ | 11.3% $\text{FE}(\text{NO}_3^-)$ | $0.045 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$ | 52   |
| $\text{Nb}_2\text{O}_{5-x}$                      | 2.2 V vs. RHE  | 0.1 M $\text{Na}_2\text{SO}_4$  | 9.8% $\text{FE}(\text{NO}_3^-)$  | $0.015 \mu\text{mol h}^{-1} \text{cm}^{-2} \text{NO}_3^-$              | 53   |
| $\text{Nb}_2\text{O}_{5-x}$                      | 2.4 V vs. RHE  | 0.1 M $\text{Na}_2\text{SO}_4$  | 2.1% $\text{FE}(\text{NO}_3^-)$  | $0.037 \mu\text{mol h}^{-1} \text{cm}^{-2} \text{NO}_3^-$              | 53   |
| np-B <sub>13</sub> C <sub>2</sub>                | 2.2 V vs. RHE  | 0.1 M $\text{Na}_2\text{SO}_4$  | 8.4% $\text{FE}(\text{NO}_3^-)$  | $0.968 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$ | 54   |
| np-B <sub>13</sub> C <sub>2</sub>                | 2.4 V vs. RHE  | 0.1 M $\text{Na}_2\text{SO}_4$  | 4.5% $\text{FE}(\text{NO}_3^-)$  | $2.674 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$ | 54   |
| $\text{Mo}(\text{O}-\text{C}_2)_4$               | 2.35 V vs. RHE | 0.1 M $\text{Na}_2\text{SO}_4$  | 7.8% $\text{FE}(\text{NO}_3^-)$  | $3.5 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$   | 55   |
| L-V <sub>2</sub> O <sub>5</sub> NDS <sup>c</sup> | 1.8 V vs. RHE  | 0.1 M $\text{Na}_2\text{SO}_4$  | 12.6% $\text{FE}(\text{NO}_3^-)$ | $7.2 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$   | 56   |
| L-V <sub>2</sub> O <sub>5</sub> NDS <sup>c</sup> | 2.4 V vs. RHE  | 0.1 M $\text{Na}_2\text{SO}_4$  | 7.8% $\text{FE}(\text{NO}_3^-)$  | $22.4 \mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$  | 56   |

<sup>a</sup> Atomically dispersed Fe-based catalyst on N-doped carbon nanosheets. <sup>b</sup> Tensile-strained Pd porous nanosheets. <sup>c</sup> Colloidal  $\text{V}_2\text{O}_5$  nanodots.





**Fig. 3** The data of Table 2, with round symbols referring to  $\mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1} \text{NO}_3^-$  and squares to  $\mu\text{mol h}^{-1} \text{cm}^{-2} \text{NO}_3^-$ . The typical background levels may be expected to lie in the range of  $0.15\text{--}2 \mu\text{mol h}^{-1} \text{X}^{-1} \text{NO}_3^-$ ,<sup>26</sup> as those depend on the impurities from the cell, catalyst, and also  $\text{N}_2$  flow (not reported) with its potential impurity content.

current density in one graph and the yield against current density in a second graph would provide further insight on catalyst activity. Such information is currently missing.

Recently, a hydrogen peroxide-mediated nitrogen reduction on a Pd catalyst has been reported.<sup>57</sup> The occurrence of an 'OH radical adsorbed on Pd (111) in a water-based electrolyte was indicated to provide a reactive oxidative species equivalent to applying a potential of +2.73 V vs. NHE, and such would then be able to form  $\text{NO}_3^-$ . Experiments were conducted in  $\text{N}_2$ -saturated 0.1 M  $\text{K}_2\text{SO}_4$  at a neutral pH and with or without (*in situ*) generated ~100 ppm  $\text{H}_2\text{O}_2$ . However, the  $\text{N}_2$  feed was indicated to contain  $\text{NH}_3$  traces that will still be present at measurable amounts also after advanced purification steps, as was recently reported in ref. 26. The characterisation of the removal of those  $\text{NH}_3$  impurities reported in the study<sup>57</sup> using electrochemical oxidation at 1.2 V vs. RHE unfortunately did not consider that – as described above in eqn (2) and (3) – the electrochemical oxidation of  $\text{NH}_3$  can produce dissolved nitrite and nitrates in amounts depending on the electrocatalyst, next to the intended removal of  $\text{NH}_3$  by conversion to  $\text{N}_2$ . For the  $\text{H}_2\text{O}_2$ -mediated pathway, it means that the presence of NO as a marker for  $\text{N}_2$  oxidation is unfortunately not excluding NO resulting from the electrooxidation of  $\text{NH}_3$  impurities in the  $\text{N}_2$  gas source. Furthermore, the presence of  $\text{H}_2\text{O}_2$  can also alter the yield of nitrate from the potential  $\text{NH}_3$  impurities, which can explain the presence of  $^{18}\text{O}$ -labelled nitrate when using  $^{18}\text{O}$ -labelled  $\text{H}_2\text{O}_2$ . So the challenge becomes to determine the origin of the  $\text{NO}_x$ , being unwanted traces of  $\text{NH}_3$  in the  $\text{N}_2$  or the  $\text{N}_2$  itself. The approach in the  $\text{N}_2$  reduction field has been to use labelled  $^{15}\text{N}_2$ <sup>58</sup> and detect  $^{15}\text{NO}_x$  as coming from the labelled  $^{15}\text{N}_2$  source, which is an approach to be applied here as well. This still has the risk that it may also contain traces of  $^{15}\text{NH}_3$ , but at least that would have different concentrations and numerical results. Another test could be to purify  $^{14}\text{N}_2$  (or  $^{15}\text{N}_2$ ) and remix the flow in known ratios with the  $\text{N}_2$  source and to observe how the currents and  $\text{NO}_x$  yields vary with the impurity concen-

tration. No variation would indicate  $\text{N}_2$  oxidation, while a linear dependence would indicate a direct dependence on the  $\text{NH}_3$  impurity concentration. To come to reliable results, one would need to wait for an equilibrium result and one would need to use  $\text{NH}_3$  repelling (hydrophobic)  $\text{N}_2$  feed tubings to prevent  $\text{NH}_3$  impurities from adsorbing on the walls and from interfering with the results.<sup>29</sup> These are extensive experimental efforts but they use mostly the existing equipment.

Apart from these considerations, the use of nitrate Pd salts for the catalyst preparation also poses challenges for proving that there are no nitrogen active traces present, as has been the case in false positives in  $\text{N}_2$  reduction reports.<sup>24,55</sup> The challenge therefore becomes to use non-nitrate salts to synthesize the same catalysts. With regard to modelling of metallic catalyst surfaces, one should realise that one is now modelling an oxidation reaction at relatively positive potentials, *i.e.* assuming a metal atom surface will depend on the exact potentials and electrolyte applied. In the example in ref. 57, the assumption that Pd [111] is active is therefore difficult to justify, as at the applied potentials and pH, the Pd surface should already be oxidised to  $\text{Pd}^{2+}$  as in  $\text{Pd}(\text{OH})_2$ , while increasing the potential further would result in conversion to  $\text{Pd}^{4+}$  in  $\text{PdO}_2$ , according to the Pourbaix diagram. The yield of the catalyst is given as  $\sim 8.5 \text{ nmol s}^{-1} \text{cm}^{-2}$ , or  $30 \mu\text{mol h}^{-1} \text{cm}^{-2}$  with a FE of 25.6% at 1.9 V vs. RHE (SI Table S4), which is very high compared to the other reports. The above questions raise the point that there is still uncertainty if  $\text{N}_2$  oxidation mediated by  $\text{H}_2\text{O}_2$  occurs as  $\text{NH}_3$  or catalyst impurities could be responsible for the nitrate yield. Therefore, further confirmation of the results is required along the lines indicated above.

Since this field is still in its infancy, we want to stress the importance of proper scientific protocols and conduct. This means that all necessary control experiments should be performed and reported. Furthermore, results should be reported properly. This requires reporting of the yield and FE as measured at the same voltage and not the best obtained values for either value where both results were obtained under different conditions. Alternatively, when reporting the best results for both yield and FE, the voltage at which both were obtained should be mentioned.

## Conclusions

We have reviewed the electrochemical synthesis of nitrate, specifically focusing on two different pathways. The first pathway is the electrochemical oxidation of ammonia. This reaction is the more readily studied reaction since it has been applied for wastewater treatment. Furthermore, this  $\text{NH}_3$  oxidation reaction is easier to achieve at somewhat lower potentials than the second pathway, which involves the activation of  $\text{N}_2$ , *i.e.* breaking of the triple nitrogen bond. For this second reaction pathway of  $\text{N}_2$  oxidation, a few different catalysts have been reported, mainly based on the transition metals nickel and copper in an alkaline environment. This means the reaction is achievable without the use of expensive

noble metals. Furthermore, it was shown that reaction conditions could greatly influence the selectivity. This will mean that the materials and catalysts investigated for wastewater treatment should be investigated again under different reaction conditions to change the selectivity from molecular nitrogen gas to value added products such as nitrite and nitrate. The  $\text{NH}_3$  concentration at industrially relevant concentrations would enable higher current densities, and also the pH and  $T$  of the reaction are important to investigate, as well as the competing  $\text{N}_2$  and  $\text{O}_2$  formation in relation to the applied overpotentials.

The electrochemical oxidation of molecular dinitrogen is a relatively novel field of research, starting to emerge from 2019. Similar to the nitrogen reduction reaction, this field faces low yields and faradaic efficiencies, owing to the high activation energy of dinitrogen. Furthermore, some of the reported results could come from contaminations rather than dinitrogen oxidation, leading to false positive results. Since this is the case, rigorous testing procedures are required to exclude any product formation from external contamination sources. These procedures include rigorous cleaning of the setup and the materials used, as well as adequate control experiments. Finally, the reporting needs to be done properly. At the moment, some of the publications are reporting the best values for two different parameters, while these parameters are not obtained under the same experimental conditions. Also the typical unpreventable impurity level and its potential impact on  $\text{NO}_x$  yields should be considered in relation to the observed yields.

Overall, the electrochemical synthesis of nitric acid seems a promising, flexible and small- to large-scale alternative to the current industrial large-scale continuous processes. From  $\text{NH}_3$  gas in an alkaline electrolysis environment and also starting from ammonia from wastewater, it would lead to an alternative source of activated nitrogen oxides. This means that locally produced  $\text{NH}_3$  or wastewater could be used to produce nitrogen-based fertilizers, creating small-scale nitrogen cycling. Overall, this would lead to an electrochemical process as an alternative for the oxidation of ammonia to nitrate in the Ostwald process. When using wastewater, it can simultaneously reduce environmental ammonia impact and allow for the production of nitric acid without relying on both the Haber–Bosch process and the Ostwald process. When starting from dinitrogen, this reaction is still very much unexplored and significant effort needs to be put into the field to come to conclusive results.

## Author contributions

Conceptualization: PJ and FM. Data curation: PJ and FM. Writing – original draft: PJ and FM. Review and editing: PJ, RK and FM. Funding acquisition: FM and RK.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results, software or codes have been included and no new data were generated or analysed as part of this perspective.

## Acknowledgements

This research is funded by the Nitrogen Activation and Ammonia Oxidation project within the Electron to Chemical Bonds consortium with project number P17-08, which is financed by The Netherlands Organization for Scientific Research (NWO) and affiliated industrial partners.

## References

- 1 J. J. Medvedev, Y. Tobolovskaya, X. V. Medvedeva, S. W. Tatarchuk, F. Li and A. Klinkova, Pathways of ammonia electrooxidation on nickel hydroxide anodes and an alternative route towards recycled fertilizers, *Green Chem.*, 2022, **24**(4), 1578–1589, DOI: [10.1039/D1GC04140A](https://doi.org/10.1039/D1GC04140A).
- 2 J. Lim, C. A. Fernández, S. W. Lee and M. C. Hatzell, Ammonia and Nitric Acid Demands for Fertilizer Use in 2050, *ACS Energy Lett.*, 2021, **6**(10), 3676–3685, DOI: [10.1021/acsenergylett.1c01614](https://doi.org/10.1021/acsenergylett.1c01614).
- 3 M. Thiemann, E. Scheibler and K. W. Wiegand, Nitric Acid, Nitrous Acid, and Nitrogen Oxides, in *Ullmann's Encyclopedia of Industrial Chemistry*, ed. Wiley, Wiley-VCH, 1st edn, 2000. DOI: [10.1002/14356007.a17\\_293](https://doi.org/10.1002/14356007.a17_293).
- 4 C. Smith, A. K. Hill and L. Torrente-Murciano, Current and future role of Haber–Bosch ammonia in a carbon-free energy landscape, *Energy Environ. Sci.*, 2020, **13**(2), 331–344, DOI: [10.1039/C9EE02873K](https://doi.org/10.1039/C9EE02873K).
- 5 M. Wang, *et al.*, Can sustainable ammonia synthesis pathways compete with fossil-fuel based Haber–Bosch processes?, *Energy Environ. Sci.*, 2021, **14**(5), 2535–2548, DOI: [10.1039/D0EE03808C](https://doi.org/10.1039/D0EE03808C).
- 6 D. Saygin, *et al.*, Ammonia Production from Clean Hydrogen and the Implications for Global Natural Gas Demand, *Sustainability*, 2023, **15**(2), 2, DOI: [10.3390/su15021623](https://doi.org/10.3390/su15021623).
- 7 Z. Zhao, *et al.*, Nitrogenase-inspired mixed-valence MIL-53 (FeII/FeIII) for photocatalytic nitrogen fixation, *Chem. Eng. J.*, 2020, **400**, 125929, DOI: [10.1016/j.cej.2020.125929](https://doi.org/10.1016/j.cej.2020.125929).
- 8 K. Tanifuji, *et al.*, Structure and Reactivity of an Asymmetric Synthetic Mimic of Nitrogenase Cofactor, *Angew. Chem., Int. Ed.*, 2016, **55**(50), 15633–15636, DOI: [10.1002/anie.201608806](https://doi.org/10.1002/anie.201608806).
- 9 J. Chapman, A. Ismail and C. Dinu, Industrial Applications of Enzymes: Recent Advances, Techniques, and Outlooks, *Catalysts*, 2018, **8**(6), 238, DOI: [10.3390/catal8060238](https://doi.org/10.3390/catal8060238).
- 10 J. Arnau, D. Yaver and C. M. Hjort, Strategies and Challenges for the Development of Industrial Enzymes Using Fungal Cell Factories, *Grand Challenges Fungal Biol.*



*Biotechnol.*, 2019, 179–210, DOI: [10.1007/978-3-030-29541-7\\_7](https://doi.org/10.1007/978-3-030-29541-7_7).

11 Y. Wang, Y. Yu, R. Jia, C. Zhang and B. Zhang, Electrochemical synthesis of nitric acid from air and ammonia through waste utilization, *Natl. Sci. Rev.*, 2019, 6(4), 4, DOI: [10.1093/nsr/nzw019](https://doi.org/10.1093/nsr/nzw019).

12 Y. Wang, W. Zhou, R. Jia, Y. Yu and B. Zhang, Unveiling the Activity Origin of a Copper-based Electrocatalyst for Selective Nitrate Reduction to Ammonia, *Angew. Chem., Int. Ed.*, 2020, 59(13), 5350–5354, DOI: [10.1002/anie.201915992](https://doi.org/10.1002/anie.201915992).

13 V. Kyriakou, I. Garagounis, A. Vourros, E. Vasileiou and M. Stoukides, An Electrochemical Haber-Bosch Process, *Joule*, 2020, 4(1), 1, DOI: [10.1016/j.joule.2019.10.006](https://doi.org/10.1016/j.joule.2019.10.006).

14 A. J. Martín, T. Shinagawa and J. Pérez-Ramírez, Electrocatalytic Reduction of Nitrogen: From Haber-Bosch to Ammonia Artificial Leaf, *Chem.*, 2019, 5(2), 2, DOI: [10.1016/j.chempr.2018.10.010](https://doi.org/10.1016/j.chempr.2018.10.010).

15 X. Zhang, R.-M. Kong, H. Du, L. Xia and F. Qu, Highly efficient electrochemical ammonia synthesis via nitrogen reduction reactions on a VN nanowire array under ambient conditions, *Chem. Commun.*, 2018, 54(42), 42, DOI: [10.1039/C8CC00459E](https://doi.org/10.1039/C8CC00459E).

16 G. Jeerh, P. Zou, M. Zhang, S. Chen, J. Humphreys and S. Tao, Electrooxidation of ammonia on A-site deficient perovskite oxide  $\text{La}_0.9\text{Ni}_0.6\text{Cu}_0.35\text{Fe}_0.05\text{O}_3-\delta$  for wastewater treatment, *Sep. Purif. Technol.*, 2022, 297, 121451, DOI: [10.1016/j.seppur.2022.121451](https://doi.org/10.1016/j.seppur.2022.121451).

17 F. Habibzadeh, S. L. Miller, T. W. Hamann and M. R. Smith, Homogeneous electrocatalytic oxidation of ammonia to  $\text{N}_2$  under mild conditions, *Proc. Natl. Acad. Sci. U. S. A.*, 2019, 116(8), 8, DOI: [10.1073/pnas.1813368116](https://doi.org/10.1073/pnas.1813368116).

18 A. C. A. de Vooys, M. T. M. Koper, R. A. van Santen and J. A. R. van Veen, The role of adsorbates in the electrochemical oxidation of ammonia on noble and transition metal electrodes, *J. Electroanal. Chem.*, 2001, 506(2), 127–137, DOI: [10.1016/S0022-0728\(01\)00491-0](https://doi.org/10.1016/S0022-0728(01)00491-0).

19 L. Huang, L. Li, W. Dong, Y. Liu and H. Hou, Removal of Ammonia by OH Radical in Aqueous Phase, *Environ. Sci. Technol.*, 2008, 42(21), 8070–8075, DOI: [10.1021/es8008216](https://doi.org/10.1021/es8008216).

20 Q. Xue, *et al.*, PtRu nanocubes as bifunctional electrocatalysts for ammonia electrolysis, *J. Mater. Chem. A*, 2021, 9(13), 8444–8451, DOI: [10.1039/D1TA00426C](https://doi.org/10.1039/D1TA00426C).

21 S. L. Vot, D. Reyter, L. Roué and D. Bélanger, Electrochemical Oxidation of  $\text{NH}_3$  on Platinum Electrodeposited onto Graphite Electrode, *J. Electrochem. Soc.*, 2012, 159(4), F91, DOI: [10.1149/2.105204jes](https://doi.org/10.1149/2.105204jes).

22 A. Jain, *et al.*, Commentary: The Materials Project: A materials genome approach to accelerating materials innovation, *APL Mater.*, 2013, 1(1), 011002, DOI: [10.1063/1.4812323](https://doi.org/10.1063/1.4812323).

23 M. Anand, C. S. Abraham and J. K. Nørskov, Electrochemical oxidation of molecular nitrogen to nitric acid – towards a molecular level understanding of the challenges, *Chem. Sci.*, 2021, 12, 6442–6448, DOI: [10.1039/D1SC00752A](https://doi.org/10.1039/D1SC00752A).

24 S. Licht, B. Cui, B. Wang, F.-F. Li, J. Lau and S. Liu, Ammonia synthesis by  $\text{N}_2$  and steam electrolysis in molten hydroxide suspensions of nanoscale  $\text{Fe}_2\text{O}_3$ , *Science*, 2014, 345(6197), 637–640, DOI: [10.1126/science.1254234](https://doi.org/10.1126/science.1254234).

25 B. Izelaar, *et al.*, Revisiting the Electrochemical Nitrogen Reduction on Molybdenum and Iron Carbides: Promising Catalysts or False Positives?, *ACS Catal.*, 2023, 13(3), 1649–1661, DOI: [10.1021/acscatal.2c04491](https://doi.org/10.1021/acscatal.2c04491).

26 B. Izelaar, D. Ripepi, D. D. van Noordenne, P. Jungbacker, R. Kortlever and F. M. Mulder, Identification, Quantification, and Elimination of  $\text{NO}_x$  and  $\text{NH}_3$  Impurities for Aqueous and Li-Mediated Nitrogen Reduction Experiments, *ACS Energy Lett.*, 2023, 3614–3620, DOI: [10.1021/acsenergylett.3c01130](https://doi.org/10.1021/acsenergylett.3c01130).

27 M. Schalenbach, A. R. Zeradjanin, O. Kasian, S. Cherevko and K. J. J. Mayrhofer, A Perspective on Low-Temperature Water Electrolysis – Challenges in Alkaline and Acidic Technology, *Int. J. Electrochem. Sci.*, 2018, 13(2), 1173–1226, DOI: [10.20964/2018.02.26](https://doi.org/10.20964/2018.02.26).

28 H. Wu, *et al.*, Recent developments of iridium-based catalysts for the oxygen evolution reaction in acidic water electrolysis, *J. Mater. Chem. A*, 2022, 10(25), 13170–13189, DOI: [10.1039/D1TA10324E](https://doi.org/10.1039/D1TA10324E).

29 R. Zaffaroni, D. Ripepi, J. Middelkoop and F. M. Mulder, Gas Chromatographic Method for In Situ Ammonia Quantification at Parts per Billion Levels, *ACS Energy Lett.*, 2020, 5(12), 3773–3777, DOI: [10.1021/acsenergylett.0c02219](https://doi.org/10.1021/acsenergylett.0c02219).

30 A. Iranzo and F. M. Mulder, Nickel-iron layered double hydroxides for an improved Ni/Fe hybrid battery-electrolyser, *Mater. Adv.*, 2021, 2(15), 5076–5088, DOI: [10.1039/D1MA00024A](https://doi.org/10.1039/D1MA00024A).

31 T. Katan and A. B. Campa, Vapor Pressure of Ammonia in Aqueous Potassium Hydroxide Solutions, *J. Chem. Eng. Data*, 1963, 8(4), 574–575, DOI: [10.1021/je60019a031](https://doi.org/10.1021/je60019a031).

32 S. Johnston, L. Kemp, B. Turay, A. N. Simonov, B. H. R. Suryanto and D. R. MacFarlane, Copper-Catalyzed Electrosynthesis of Nitrite and Nitrate from Ammonia: Tuning the Selectivity via an Interplay Between Homogeneous and Heterogeneous Catalysis, *ChemSusChem*, 2021, 14(21), 4793–4801, DOI: [10.1002/cssc.202101557](https://doi.org/10.1002/cssc.202101557).

33 A. Allagui, S. Sarfraz, S. Ntais, F. Al momani and E. A. Baranova, Electrochemical behavior of ammonia on  $\text{Ni}_{98}\text{Pd}_2$  nano-structured catalyst, *Int. J. Hydrogen Energy*, 2014, 39(1), 41–48, DOI: [10.1016/j.ijhydene.2013.10.024](https://doi.org/10.1016/j.ijhydene.2013.10.024).

34 Y.-J. Shih, Y.-H. Huang and C. P. Huang, *In situ* electrochemical formation of nickel oxyhydroxide ( $\text{NiOOH}$ ) on metallic nickel foam electrode for the direct oxidation of ammonia in aqueous solution, *Electrochim. Acta*, 2018, 281, 410–419, DOI: [10.1016/j.electacta.2018.05.169](https://doi.org/10.1016/j.electacta.2018.05.169).

35 A. Kapałka, A. Cally, S. Neodo, C. Comninellis, M. Wächter and K. M. Udert, Electrochemical behavior of ammonia at  $\text{Ni}/\text{Ni}(\text{OH})_2$  electrode, *Electrochim. Commun.*, 2010, 12(1), 1, DOI: [10.1016/j.elecom.2009.10.026](https://doi.org/10.1016/j.elecom.2009.10.026).

36 R. Wang, H. Liu, K. Zhang, G. Zhang, H. Lan and J. Qu, Ni (II)/Ni(III) redox couple endows Ni foam-supported  $\text{Ni}_2\text{P}$



with excellent capability for direct ammonia oxidation, *Chem. Eng. J.*, 2021, **404**, 126795, DOI: [10.1016/j.cej.2020.126795](https://doi.org/10.1016/j.cej.2020.126795).

37 X. Jiang, *et al.*, Identification of the role of Cu site in Ni-Cu hydroxide for robust and high selective electrochemical ammonia oxidation to nitrite, *Electrochim. Acta*, 2020, **345**, 136157, DOI: [10.1016/j.electacta.2020.136157](https://doi.org/10.1016/j.electacta.2020.136157).

38 M. Gonzalez-Reyna, M. S. Luna-Martínez and J. F. Perez-Robles, Nickel supported on carbon nanotubes and carbon nanospheres for ammonia oxidation reaction, *Nanotechnology*, 2020, **31**(23), 235706, DOI: [10.1088/1361-6528/ab73b6](https://doi.org/10.1088/1361-6528/ab73b6).

39 F. Almomani, R. Bhosale, M. Khraisheh, A. Kumar and M. Tawalbeh, Electrochemical oxidation of ammonia on nickel oxide nanoparticles, *Int. J. Hydrogen Energy*, 2020, **45**(17), 10398–10408, DOI: [10.1016/j.ijhydene.2019.11.071](https://doi.org/10.1016/j.ijhydene.2019.11.071).

40 Y.-J. Shih and C.-H. Hsu, Kinetics and highly selective N<sub>2</sub> conversion of direct electrochemical ammonia oxidation in an undivided cell using NiCo oxide nanoparticle as the anode and metallic Cu/Ni foam as the cathode, *Chem. Eng. J.*, 2021, **409**, 128024, DOI: [10.1016/j.cej.2020.128024](https://doi.org/10.1016/j.cej.2020.128024).

41 J. Huang, Z. Chen, J. Cai, Y. Jin, T. Wang and J. Wang, Activating copper oxide for stable electrocatalytic ammonia oxidation reaction via *in situ* introducing oxygen vacancies, *Nano Res.*, 2022, **15**, 5987–5994, DOI: [10.1007/s12274-022-4279-5](https://doi.org/10.1007/s12274-022-4279-5).

42 D. Reyter, D. Bélanger and L. Roué, Study of the electroreduction of nitrate on copper in alkaline solution, *Electrochim. Acta*, 2008, **53**, 5977.

43 R. M. Choueiri, S. W. Tatarchuk, A. Klinkova and L. D. Chen, Mechanism of ammonia oxidation to dinitrogen, nitrite, and nitrate on  $\beta$ -Ni(OH)<sub>2</sub> from first-principles simulations, *Electrochem. Sci. Adv.*, 2022, **2**(6), e2100142, DOI: [10.1002/elsa.202100142](https://doi.org/10.1002/elsa.202100142).

44 M. Zhu, *et al.*, Deciphering NH<sub>3</sub> Adsorption Kinetics in Ternary Ni-Cu-Fe Oxyhydroxide toward Efficient Ammonia Oxidation Reaction, *Small*, 2021, **17**(7), e2005616, DOI: [10.1002/smll.202005616](https://doi.org/10.1002/smll.202005616).

45 L. Zhang, *et al.*, A Janus Fe-SnO<sub>2</sub> Catalyst that Enables Bifunctional Electrochemical Nitrogen Fixation, *Angew. Chem., Int. Ed.*, 2020, **59**(27), 10888–10893, DOI: [10.1002/anie.202003518](https://doi.org/10.1002/anie.202003518).

46 M. Kuang, *et al.*, Efficient Nitrate Synthesis via Ambient Nitrogen Oxidation with Ru-Doped TiO<sub>2</sub>/RuO<sub>2</sub> Electrocatalysts, *Adv. Mater.*, 2020, **32**(26), 2002189, DOI: [10.1002/adma.202002189](https://doi.org/10.1002/adma.202002189).

47 Y. Guo, *et al.*, Electrochemical Nitrate Production via Nitrogen Oxidation with Atomically Dispersed Fe on N-Doped Carbon Nanosheets, *ACS Nano*, 2022, **16**(1), 655–663, DOI: [10.1021/acsnano.1c08109](https://doi.org/10.1021/acsnano.1c08109).

48 C. Dai, Y. Sun, G. Chen, A. C. Fisher and Z. Xu, Electrochemical Oxidation of Nitrogen towards Direct Nitrate Production on Spinel Oxides, *Angew. Chem., Int. Ed.*, 2020, **59**(25), 9418–9422, DOI: [10.1002/anie.202002923](https://doi.org/10.1002/anie.202002923).

49 Y. Wang, T. Li, Y. Yu and B. Zhang, Electrochemical Synthesis of Nitric Acid from Nitrogen Oxidation, *Angew. Chem.*, 2022, **134**(12), e202115409, DOI: [10.1002/ange.202115409](https://doi.org/10.1002/ange.202115409).

50 S. Han, C. Wang, Y. Wang, Y. Yu and B. Zhang, Electrosynthesis of Nitrate via the Oxidation of Nitrogen on Tensile Strained Palladium Porous Nanosheets, *Angew. Chem.*, 2021, **60**(9), 4474–4478, DOI: [10.1002/ange.202014017](https://doi.org/10.1002/ange.202014017).

51 T. Li, *et al.*, Ru-Doped Pd Nanoparticles for Nitrogen Electrooxidation to Nitrate, *ACS Catal.*, 2021, **11**(22), 14032–14037, DOI: [10.1021/acscatal.1c04360](https://doi.org/10.1021/acscatal.1c04360).

52 W. Fang, *et al.*, Boosting efficient ambient nitrogen oxidation by a well-dispersed Pd on MXene electrocatalyst, *Chem. Commun.*, 2020, **56**(43), 5779–5782, DOI: [10.1039/D0CC01759K](https://doi.org/10.1039/D0CC01759K).

53 Y. Zhang, *et al.*, Electrocatalytic fixation of N 2 into NO 3 – : electron transfer between oxygen vacancies and loaded Au in Nb<sub>2</sub>O<sub>5</sub>-x nanobelts to promote ambient nitrogen oxidation, *J. Mater. Chem. A*, 2021, **9**(32), 17442–17450, DOI: [10.1039/D1TA03128G](https://doi.org/10.1039/D1TA03128G).

54 J. Lan, M. Luo, J. Han, M. Peng, H. Duan and Y. Tan, Nanoporous B13C2 towards Highly Efficient Electrochemical Nitrogen Fixation, *Small*, 2021, **17**(39), 2102814, DOI: [10.1002/smll.202102814](https://doi.org/10.1002/smll.202102814).

55 S. Zhang, *et al.*, Ambient Electrochemical Nitrogen Fixation over a Bifunctional Mo-(O-C<sub>2</sub>)<sub>4</sub> Site Catalyst, *J. Phys. Chem. C*, 2022, **126**(2), 965–973, DOI: [10.1021/acs.jpcc.1c10039](https://doi.org/10.1021/acs.jpcc.1c10039).

56 W. Li, *et al.*, Ambient electrochemical nitrogen fixation with aqueous V<sub>2</sub>O<sub>5</sub> nanodots in a fluidized electrocatalysis system, *Chem. Eng. J.*, 2023, **452**, 139494, DOI: [10.1016/j.cej.2022.139494](https://doi.org/10.1016/j.cej.2022.139494).

57 K. Dong, *et al.*, H<sub>2</sub>O<sub>2</sub>-mediated electrosynthesis of nitrate from air, *Nat. Synth.*, 2024, **3**(6), 763–773, DOI: [10.1038/s44160-024-00522-8](https://doi.org/10.1038/s44160-024-00522-8).

58 S. Z. Andersen, *et al.*, A rigorous electrochemical ammonia synthesis protocol with quantitative isotope measurements, *Nature*, 2019, **570**(7762), 504–508, DOI: [10.1038/s41586-019-1260-x](https://doi.org/10.1038/s41586-019-1260-x).