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1. Here the electrochemical production of $NO_x$ 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 fertiliser and chemical feedstock. They may also provide an alternative pathway to enable electrochemical synthesis of ammonia from $NO_x$ as future large scale carbon free energy storage. 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 to 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.

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# Electrochemical nitrogen oxide formation from ammonia and dinitrogen

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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 compounds 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.

## Introduction

The human population is ever increasing. To enable sufficient global food production, artificial fertilizers are necessary.[1] 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 most applied, and over the past 50 years their use has significantly increased.[2] 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 what is the problem? The problem lies in the feedstock used to make these fertilizers. These nitrogen containing fertilizers are produced from ammonia, of which the production is expected to become fossil fuel and $CO_2$ emission-free in the coming decades.

Conventionally, ammonia is produced via the Haber-Bosch process. In this process, $N_2$ and $H_2$ gas are passed over Fe or Ru-based catalysts under high pressures and high temperatures. These reaction conditions are around 450-500 °C and 150-200 atm.[2] Additionally, part of the 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.[3] Combined, 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 produced by steam methane reforming. In this process, methane is used as hydrogen source and $CO_2$ 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 fitting in a new renewables 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 $NH_3$, and subsequently convert that to nitrates in the Ostwald process.[4], [5], [6] 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.[7], [8] 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.[9], [10] 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

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performed under ambient temperature and pressure.[11], [12] Furthermore, the process could potentially operate 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 $NH_3$ and $N_2$. We will focus on this process specifically, since the nitrogen reduction reaction to $NH_3$ has already been studied extensively at this point.[13], [14], [15] Specifically, we address the current state of the electrochemical nitric acid synthesis starting from $NH_3$ or $N_2$ and discuss published literature studies in comparison to 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 have 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.[16], [17], [18], [19] Therefore, the desired product of this reaction has been environmental benign nitrogen gas. When noble metals, such as Pt, are used for the ammonia oxidation, dinitrogen is the main product.[20], [21] However, when nitrates are intended products, converting ammonia to dinitrogen is a loss, since a molecule with 'active' nitrogen is converted into the almost inert nitrogen molecule.
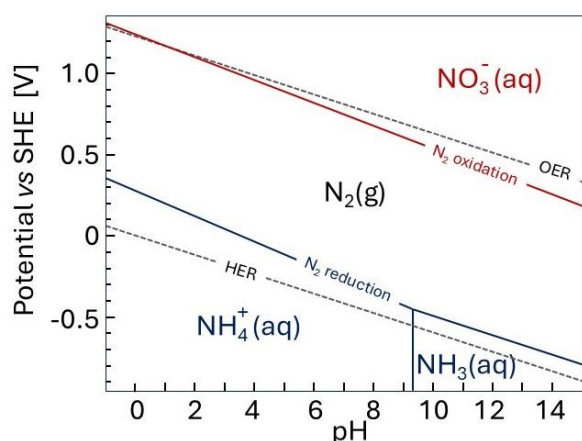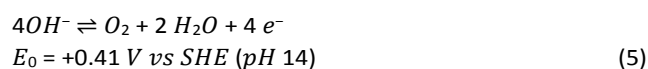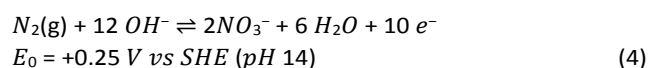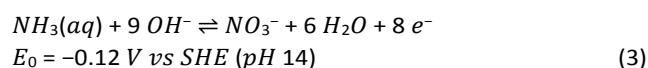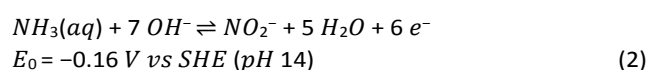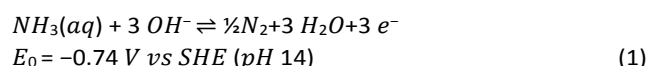


*Figure 1. Pourbaix diagram of nitrogen, showing the stable species of nitrogen at different pH and potentials calculated from* [22].

When looking at the Pourbaix diagram of nitrogen in Figure 1 we can see that the reaction thermodynamically can take place inside the stable potential regime of water, given between the dotted lines for OER and HER. This means that the electrochemical oxidation of ammonia to nitrate in aqueous electrolytes 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 $N_2$ reduction and oxidation lines. The equations below give possible half reactions of ammonia and the relevant potentials deduced from ΔG, the Gibbs free energy of the products at the nitrogen oxidation working electrode and the hydrogen evolution counter electrode at RHE, minus that of the respective input species. The obtained working electrode potential vs RHE is then calculated *vs* SHE using the pH. The potential indicate that nitrite and nitrate can be formed below the $N_2$ oxidation line in Figure 1 and the potential in Eq. (4). These potentials are also all below the (competing) oxygen evolution reaction (OER) in Eq. (5).

$$NH_3(aq) + 3\ OH^- \rightleftharpoons \tfrac{1}{2}N_2 + 3\ H_2O + 3\ e^-$$
$$E_0 = -0.74\ V\ vs\ SHE\ (pH\ 14) \tag{1}$$

$$NH_3(aq) + 7\ OH^- \rightleftharpoons NO_2^- + 5\ H_2O + 6\ e^-$$
$$E_0 = -0.16\ V\ vs\ SHE\ (pH\ 14) \tag{2}$$

$$NH_3(aq) + 9\ OH^- \rightleftharpoons NO_3^- + 6\ H_2O + 8\ e^-$$
$$E_0 = -0.12\ V\ vs\ SHE\ (pH\ 14) \tag{3}$$

$$N_2(g) + 12\ OH^- \rightleftharpoons 2NO_3^- + 6\ H_2O + 10\ e^-$$
$$E_0 = +0.25\ V\ vs\ SHE\ (pH\ 14) \tag{4}$$

$$4OH^- \rightleftharpoons O_2 + 2\ H_2O + 4\ e^-$$
$$E_0 = +0.41\ V\ vs\ SHE\ (pH\ 14) \tag{5}$$

Unlike the ammonia oxidation reaction, the dinitrogen oxidation reactions (NOR) such as in Eq. (4) have barely been explored. Only recently has this possible route to nitrate received attention from researchers. To the extent of our knowledge, the first paper on this subject was published no earlier than 2019.[11] Since then, there have been some additional publications investigating this reaction, however this reaction still has significantly less 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 the ammonia oxidation. To convert dinitrogen to nitrate, the triple bond in dinitrogen needs to be activated,[23] which requires a significant amount of energy. It's potential in Eq. (4) is also higher than the AOR Eq. (1-3) and therefore closer but still below the competing OER potential. In addition there will be overpotentials for 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 from OER yield (if present) than for NOR when one would have a good NOR catalyst and sufficient sensitivity to measure the product $NO_x$. Furthermore, the challenging dinitrogen activation may cause that the nitrogen oxidation research development resembles 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 amount of papers published on this specific reaction. However, more recently highly cited papers have been retracted due to

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faulty results.[24] Unfortunately, this seems to be a common occurrence within the field of $N_2$ activation research.[25], [26] The published results either suffer from very low reaction rates or the results are irreproducible and faulty. These faulty results mainly come from low ammonia yields which makes that 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 $N_2$ 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 electrolytes the only relatively active and stable options available for the oxygen evolution reaction (OER) are $IrO_2$ based catalysts with possibly $RuO_2$ additives and $TiO_2$ substrates.[27], [28] In alkaline media non-noble metals such as Ni, Fe, Co provide stable oxyhydroxide surfaces such as NiOOH and (Ni,T)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 $NH_3(aq)$ side in Eq. (5).[29]

$$NH_{3(g)} \rightleftharpoons NH_{3(aq)} \underset{pH > 11}{\overset{H_2O}{\rightleftharpoons}} NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$(5)$$
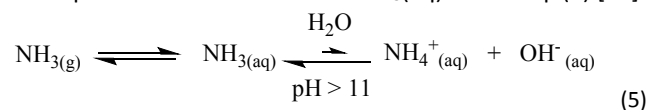
Here it is indicated that the gas phase ammonia ($NH_{3(g)}$), dissolved ammonia ($NH_{3(aq)}$) and ammonium ion ($NH_4^+$) equilibria depend on the pH. For a pH higher than 11 the equilibrium is completely shifted to the left side of the equation. The relevant equilibrium to be considered is then between ammonia in the gas phase ($NH_{3(g)}$) and dissolved ammonia ($NH_{3(aq)}$).

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

Research on the electrochemical ammonia oxidation reaction (AOR) to nitrite and nitrate can be split in two groups based on the investigated electrode materials. The first materials we will discuss, are nickel based catalysts for the AOR. An overview of 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.*.[1] Therein, they demonstrate an efficient route towards $NH_4NO_3$-based fertilizers via $Ni(OH)_2$-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 $NH_4NO_3$ 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.[1] During these experiments they found that the oxidation of ammonia to nitrite might occur spontaneously on their charged $Ni(OH)_2$ electrode. To prove this hypothesis, they charge the $Ni(OH)_2$ electrode by passing a constant current of 50 mA cm$^{-2}$ through the anode for 20 min. During this charging the $Ni(OH)_2$ is oxidized to NiOOH in the reaction given in Equation 6.[30]

$$Ni(OH)_2 + OH^- \longrightarrow NiOOH + H_2O + e^- \quad (6)$$

The oxidation reaction of $Ni(OH)_2$ takes place with a standard equilibrium potential of +0.49 V vs. SHE during charging.

The charged electrode is consequently removed from the cell and submersed in a 0.1 M NaOH solution containing 0.2 M $NH_3$. 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 as a kinetic effect of faster catalysis at higher T, but also a faster $H^+$ and $e^-$ charge transport from within the charged $NiOOH/Ni(OH)_2$ electrode towards its surface. Following these results, they tried the same procedure but replaced the ammonia with nitrite. However, no 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 $Ni(OH)_2/NiOOH$ electrode, while the oxidation to nitrate occurs purely electrochemically. The relatively high concentration of 0.2M $NH_3$ also introduces a non-negligible $NH_3(g)$ vapour pressure [31]; this also means that application of $NH_3$ pressure above the liquid increases the $NH_3$ concentration near the catalyst surface, which will enable higher limiting currents for the oxidation reaction. However, at higher currents the $OH^-$consumption will decrease the local pH and with it raise the required potentials in equations (2,3) accordingly. Applying higher pH by using higher NaOH or (KOH) concentration can counteract that, however, then increased $NH_3$ pressure needs to be applied to keep the $NH_3(aq)$ concentration high [31].

Special care needs to be taken when working at low, ppm scale $NH_3$ 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 $NH_3$ reactant. Nor is there any mention of the accumulation of $NO_x$ 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, $NO_x$ 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.

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Copper-based materials are another promising option for ammonia oxidation electrocatalyst as the work of Johnston *et al.* illustrates.[32] 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.[32] Furthermore, they claim that changing these parameters could even lead to highly selective AOR to either nitrite or nitrate.

Moreover, they find that the AOR follows two main pathways on copper electrodes. The first is a heterogeneous pathway of which $NO_3^-$ is the main product. The second is a homogeneous mediated reaction pathway, where the primary product is $NO_2^-$. The mediator of the second pathway is $[Cu(OH)_4]^-$ where the copper cycles between the 2+ and 3+ oxidation states. The best overall yield was obtained at 2.0 $V_{RHE}$ in 0.11 M KOH, giving an selectivity of 25% FE for $NO_3^-$ and 42% FE for $NO_2^-$.[32] These results indicate that the homogeneous pathway is the more prevalent of the two.

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

| Anode | E or J | pH | Electrolyte | Results | Ref. |
|---|---|---|---|---|---|
| Ni(OH)$_2$/NF[a] | 1.6 $V_{RHE}$ (~6 mA cm$^{-2}$)[b] | 11.3[c] | 0.2 M NH$_3$ + 0.1 M Na$_2$SO$_4$ | FE$_{(N2)}$ 51% | [1] |
| Ni(OH)$_2$/NF[a] | 1.9 $V_{RHE}$ (~30.5 mA cm$^{-2}$)[b] | 11.5[c] | 0.3 M NH$_3$ + 0.1 M K$_2$SO$_4$ | FE$_{(NO3-)}$ 72%[d] | [1] |
| Ni(OH)$_2$/NF[a] | 1.6 $V_{RHE}$ (~10 mA cm$^{-2}$)[b] | 13[c] | 0.2 M NH$_3$ + 0.1 M NaOH | FE$_{(NO2-)}$ 58% | [1] |
| Ni$_{98}$Pd$_2$ | 20 mA cm$^{-2}$ | 10.5 | 0.2 M NH$_4$NO$_3$ + 1 M NaNO$_3$ | FE$_{(N2)}$ 38.7% | [33] |
| NF[a] | 0.7 $V_{Hg/HgO}$ | 11 | 20 ppm NH$_3$ + 0.1 M Na$_2$SO$_4$ | FE$_{(N2)}$ 50% | [34] |
| NF[a] | 0.85 $V_{Hg/HgO}$ | 11 | 20 ppm NH$_3$ + 0.1 M Na$_2$SO$_4$ | FE$_{(NO3-)}$ 10% | [34] |
| Activated Ni | 20 mA cm$^{-2}$ | 11 | 50 mM NH$_4$ClO$_4$ + 1 M NaClO$_4$ | No FE are given. **3:1 N$_2$:NO$_3^-$ ratio** | [35] |
| Ni$_2$P/NF[a] | 15 mA[e] | 13 | 1000 ppm NH$_3$ + 0.1 M KOH | Up to 50% CE without specification **(N$_2$ major; NO$_2^-$, NO$_3^-$ ~1:1)** | [36] |
| Ni$_x$Cu$_{1-x}$(OH)$_2$ | 1.53 $V_{RHE}$ | 13 | 1 mM NH$_3$ + 0.1 M KOH | >80% FE of NO$_2^-$ Minor oxidation of NH$_3$ was observed without applied voltage | [37] |
| CNT-Ni[f] | 1.5 $V_{RHE}$ | 11 | 130 ppm NH$_3$ + 10 mM Na$_2$SO$_4$ | No FE are given. ~14:1 N$_2$:NO$_3^-$ ratio | [38] |
| CNS-Ni[g] | 1.5 $V_{RHE}$ | 11 | 130 ppm NH$_3$ + 10 mM Na$_2$SO$_4$ | No FE are given. ~16:1 N$_2$:NO$_3^-$ ratio | [38] |
| NiO NPs[h] | 30 mA cm$^{-2}$ | 9 | 200 mM NH$_4$OH + 100 mM NaNO$_3$ | No FE are given. **(N$_2$ major; NO$_2^-$, NO$_3^-$ ~1:2)** | [39] |
| NiO NPs[h]/NF[a] | 2 mA cm$^{-2}$ | 9 | 100 ppm NH$_3$ + 0.1 M Na$_2$SO$_4$ | 80% removal; 90% N$_2$ selectivity | [40] |
| NiCoO$_x$ NPs[h]/Ni | 2 mA cm$^{-2}$ | 9 | 130 ppm NH$_3$ + 0.1 M Na$_2$SO$_4$ | 98% removal; 80% NO$_3^-$ selectivity | [40] |

**[a] NF is nickel foam [b] Average current density in the first two hours of electrolysis [c] Initial pH of the electrolyte [d] Total FE in the end of 52h electrolysis [e] current is reported instead of current density [f] CNT is carbon nanotubes [g] CNS is carbon nanospheres [h] NPs is nanoparticles.**

The second study highlighting the potential of copper as electrocatalyst is by Huang *et al.*.[41] 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 with online MS analysis of gas products. Out of the three tested catalysts, V$_o$-poor CuO seems the most promising catalyst for the purpose. This material has the highest selectivity towards nitrite as a product, which is a known intermediate in the current industrial

synthesis of nitric acid. They report a FE of 72.2% toward nitrite for their catalyst.[41]

It may be noted that catalysts for the reverse reaction of $NO_x$ to $NH_3$ are based on copper and its alloys.[12], [29], [42] Therefore further leads to copper-based catalysts may be deduced from $NO_x$ 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 $NO_x$ products, but can also be seen in the field of waste water treatment.[34] In this field, Kapalka et al. investigated the electrochemical behavior of ammonia at a Ni/Ni(OH)$_2$ 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.[34] 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 shifts 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 1M $NaClO_4$ at pH 11 under a current of 20 mAcm$^{-2}$. In this experiment they saw the amount of total ammonia and nitrogen continuously decrease whereas the amount of nitrate increased over time.[34] 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 $N_2$ and maybe even $N_2O$ 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 $N_2$ 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 the 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.
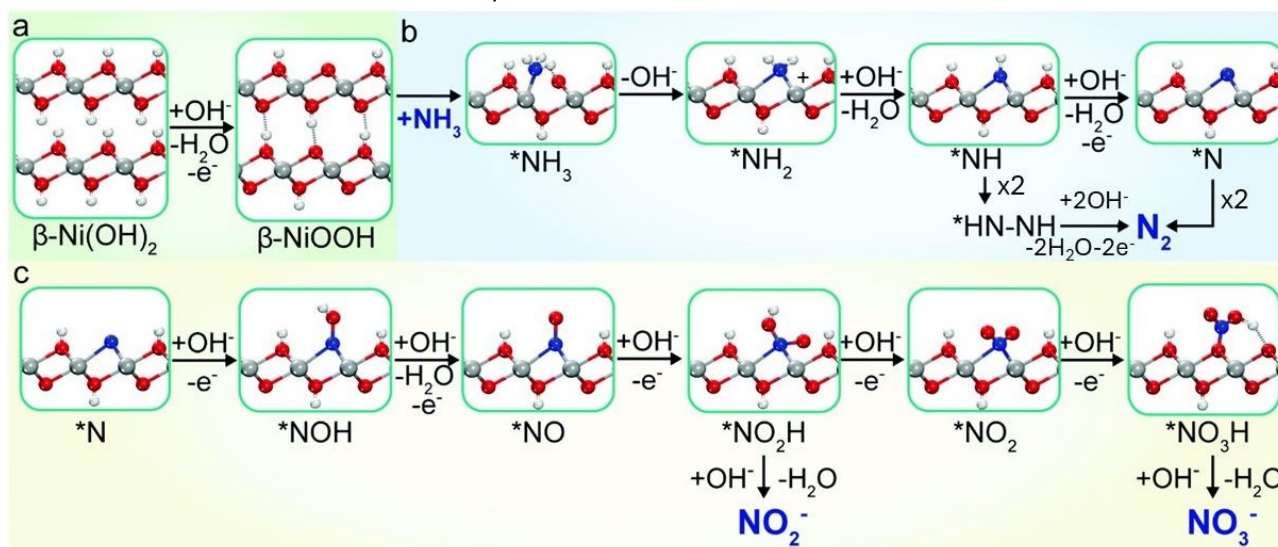


*Figure 2. Proposed mechanism of AOR at Ni-based catalysts: electrochemical dehydrogenation of Ni(OH)$_2$ catalyst with the formation of the active NiOOH surface (a) followed by ammonia adsorption and oxidation to $N_2$ (b) and nitrite and nitrate (c). Adapted from ref [1] with permission from RSC Green Chemistry, copyright 2022.*

In a similar fashion, Medvedev et al. also proposed a general mechanism that considers pathways to $N_2$ and $NO_x^-$ products based on their experimental results.[1] For their mechanism they propose that NiOOH is the active material and that the oxidation of Ni(OH)$_2$ is the first step of the reaction as shown in Figure 2. On the oxidated NiOOH surface the $NH_3$ coordinates to a Ni atom, breaking one Ni-O bond (Figure 2b). After adsorbing on the surface the $NH_3$ undergoes the first oxidation and deprotonation step. This *$NH_2$ intermediate then replaces an *OH to form a bridge structure.[40] Thereafter, *$NH_2$ undergoes two spontaneous deprotonation steps, forming *NH

and *N species.[40] The intermediate *NH species can couple with an identical species to form *$N_2H_2$, which can further deprotonate to form $N_2$. Furthermore, the *N species can also dimerize, which also results in the formation of $N_2$ as the oxidation product. Alternatively, adsorbed *N can undergo hydroxylation to obtain $NO_2^-$ or $NO_3^-$ (Figure 2c). Out of these two products, $NO_2^-$ can be formed on the NiOOH surface without applied potential, due to the high oxidative activity of Ni(III). The origin of the OH$^-$ for the hydroxylation reactions can be either the electrolyte or the NiOOH lattice itself. Finally, *$NO_2H$ species can undergo a two-electron electro-oxidation to

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*NO$_3$H, which can be deprotonated and desorbed to obtain NO$_3^-$.[41] Despite the experimental evidence and DFT calculations supporting the validity of this mechanism, it still remains unclear why ammonia-to-nitrite can proceed spontaneously on NiOOH, while the oxidation to nitrate can only happen electrochemically.[1] Some of possible explanations given by Medvedev *et al.* are: 1) the high energy barrier for configurational changes in *NO$_2$, 2) stabilization of *NO$_3$H by deprotonated *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.[11], [45], [46], [47], [48], [49], [50], [51], [52], [53], [54], [55], [56] 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 at 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 is 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 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$.[44], [53] However, often only nitrate is reported as the singular product. This implies that most of the electrons are going to unspecified reactions. If these byproducts 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.[1]

Furthermore, in view of the difficult 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 NH$_3$, NO$_x$. These sources vary from the N$_2$ feed gas itself to the electrolyte and membrane used in the electrochemical setup. Wang *et al.* proposed a rigorous test protocol for NOR to avoid false positives from contaminations.[46] 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.[26] 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 N$_2$, and using $^{15}$N$_2$ to determine the source of N in the NH$_3$; such controls are equally relevant for nitrogen oxidation research.

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

| Catalyst | E | Electrolyte | Faradaic Efficiency | Yield | Ref. |
|---|---|---|---|---|---|
| Pt-foil | 2.19 V *vs.* RHE | 0.3 M K$_2$SO$_4$ | 1.2% FE$_{(NO3-)}$ | 0.06 μmol h$^{-1}$ cm$^{-2}$ NO$_3^-$ | [11] |
| Fe-SnO$_2$ | 1.96 V *vs.* RHE | 0.05 M H$_2$SO$_4$ | 0.8% FE$_{(NO3-)}$ | 0.69 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [45] |
| 2.79$^{wt}$% Ru/TiO$_2$ | 1.8 V *vs.* RHE | 0.1 M Na$_2$SO$_4$ | 26.1% FE$_{(NO3-)}$ | 0.05 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [46] |
| 2.79$^{wt}$% Ru/TiO$_2$ | 2.2 V *vs.* RHE | 0.1 M Na$_2$SO$_4$ | 1% FE$_{(NO3-)}$ | 0.161 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [46] |
| AD-Fe NS$^a$ | 2.4 V *vs.* RHE | 0.05 M K$_2$SO$_4$ | 5.4% FE$_{(NO3-)}$ | 6.12 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [47] |
| AD-Fe NS$^a$ | 2.1 V *vs.* RHE | 0.05 M K$_2$SO$_4$ | 35.6% FE$_{(NO3-)}$ | 2.56 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [47] |
| ZnFe$_{0.4}$Co$_{1.6}$O$_4$ | 1.5 V *vs.* RHE | 1 M KOH | 4.9% FE$_{(NO3-)}$ | 0.049 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [48] |
| ZnFe$_{0.4}$Co$_{1.6}$O$_4$ | 1.6 V *vs.* RHE | 1 M KOH | 1.8% FE$_{(NO3-)}$ | 0.13 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [48] |
| Pd-s PNSs$^b$ | 1.55 V *vs.* RHE | 1 M KOH | 2.5% FE$_{(NO3-)}$ | 0.071 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [50] |
| Pd-s PNSs$^b$ | 1.75 V *vs.* RHE | 1 M KOH | 1.1% FE$_{(NO3-)}$ | 0.3 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [50] |
| Pd$_{0.9}$Ru$_{0.1}$ | 1.7 V *vs.* RHE | 0.1 M KOH | ~0.6% FE$_{(NO3-)}$ | 0.077 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [51] |
| Pd/MXene | 2.03 V *vs.* RHE | 0.01 M Na$_2$SO$_4$ | 11.3% FE$_{(NO3-)}$ | 0.045 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [52] |
| Nb$_2$O$_{5-x}$ | 2.2 V *vs.* RHE | 0.1 M Na$_2$SO$_4$ | 9.8% FE$_{(NO3-)}$ | 0.015 μmol h$^{-1}$ cm$^{-2}$ NO$_3^-$ | [53] |
| Nb$_2$O$_{5-x}$ | 2.4 V *vs.* RHE | 0.1 M Na$_2$SO$_4$ | 2.1% FE$_{(NO3-)}$ | 0.037 μmol h$^{-1}$ cm$^{-2}$ NO$_3^-$ | [53] |
| np-B$_{13}$C$_2$ | 2.2 V *vs.* RHE | 0.1 M Na$_2$SO$_4$ | 8.4% FE$_{(NO3-)}$ | 0.968 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [54] |
| np-B$_{13}$C$_2$ | 2.4 V *vs.* RHE | 0.1 M Na$_2$SO$_4$ | 4.5% FE$_{(NO3-)}$ | 2.674 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [54] |
| Mo(O-C$_2$)$_4$ | 2.35 V *vs.* RHE | 0.1 M Na$_2$SO$_4$ | 7.8% FE$_{(NO3-)}$ | 3.5 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [55] |
| L-V$_2$O$_5$NDs$^c$ | 1.8 V *vs.* RHE | 0.1 M Na$_2$SO$_4$ | 12.6% FE$_{(NO3-)}$ | 7.2 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [56] |
| L-V$_2$O$_5$NDs$^c$ | 2.4 V *vs.* RHE | 0.1 M Na$_2$SO$_4$ | 7.8% FE$_{(NO3-)}$ | 22.4 μmol h$^{-1}$ mg$_{cat}^{-1}$ NO$_3^-$ | [56] |

**a** atomically dispersed Fe-based catalyst on N-doped carbon nanosheets **b** tensile-strained Pd porous nanosheets **c** colloidal $V_2O_5$ nanodots

The Table 2 data are also included in Figure 3 to illustrate the scatter of available values of the combination of yield versus faradaic efficiency. In future it would be advantageous to perform the experiment at set current densities and known $N_2$ flow rates. Plotting faradaic efficiency and the potential against current density in one graph, and yield against current density in a second graph would provide further insight on catalyst activity. Such information is currently missing.
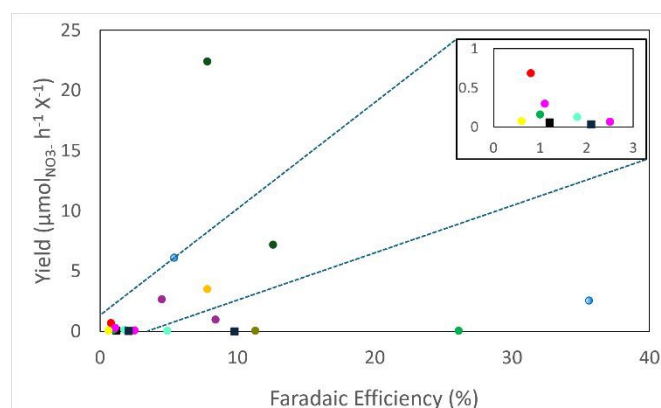


*Figure 3. The data of Table 2, with round symbols referring to $\mu mol\ h^{-1}\ mg_{cat}^{-1}\ NO_3^-$, and squares to $\mu mol\ h^{-1}\ cm^{-2}\ NO_3^-$. The typical background levels may be expected to lie in the range $0.15 - 2\ \mu mol\ h^{-1}\ X^{-1}\ NO_3^-$,[26] as those depend on the impurities from the cell, catalyst, and also $N_2$ flow (not reported) with its potential impurity content.*

Recently a hydrogen peroxide mediated nitrogen reduction on a Pd catalyst was reported [57]. The occurrence of a ᐧOH radical, adsorbed on Pd (111) in a water based electrolyte was indicated to provide a reactive oxidative species equivalent to applying a potential of +2.73V vs NHE, and such would then be able to form $NO_3^-$. Experiments were conducted in $N_2$-saturated 0.1 M $K_2SO_4$ at a neutral pH and with or without (in-situ) generated ~100 ppm $H_2O_2$. However, the $N_2$ feed was indicated to contain $NH_3$ traces that will still be present at measurable amounts also after advanced purification steps, as was recently reported in [26]. The characterisation of the removal of those $NH_3$ impurities reported in the study[57], using electrochemical oxidation at 1.2 V vs RHE unfortunately did not consider that - as described above in Eq. (2) and (3)- the electrochemical oxidation of $NH_3$ can produce dissolved nitrite and nitrates in amounts depending on the electrocatalyst, next to the intended removal of $NH_3$ by conversion to $N_2$. For the $H_2O_2$ mediated pathway that means that the presence of NO as a marker for $N_2$ oxidation is unfortunately not excluding NO resulting from electrooxidation of $NH_3$ impurities in the $N_2$ gas source. Furthermore, the presence of $H_2O_2$ can also alter the yield of nitrate from the potential $NH_3$ impurities, which can explain the presence of $^{18}O$ labelled nitrate when using $^{18}O$ labelled $H_2O_2$.

So the challenge becomes to determine the origin of the $NO_x$, being unwanted traces of $NH_3$ in the $N_2$ or the $N_2$ itself. The approach in the $N_2$ reduction field has been to use labelled $^{15}N_2$ [58], and the detect $^{15}NO_x$ as coming from the labelled $^{15}N_2$ source, which is an approach to be applied here as well therefore. This still has the risk that it may also contain traces of $^{15}NH_3$, but at least that would have different concentration and numerical results. Another test could be to purify the $^{14}N_2$ (or $^{15}N_2$), and remix the flow in known ratio's with the $N_2$ source and to observe how the currents and $NO_x$ yields vary with the impurity concentration. No variation would indicate $N_2$ oxidation, while a linear dependence would indicate a direct dependence on the $NH_3$ impurity concentration. To come to reliable results one would need to wait for an equilibrium result and one would need to use $NH_3$ repelling (hydrophobic) $N_2$ feed tubings to prevent $NH_3$ impurities to adsorb on the walls and to interfere with the results.[29] These are extensive experimental efforts but they use mostly the existing equipment.

Apart from these considerations, also the use of nitrate Pd salts for the catalyst preparation poses challenges for proving that there are no nitrogen active traces present, as has been the case in false positives in $N_2$ reduction reports [24], [55]. The challenge therefore becomes to use non-nitrate salts to synthesize the same catalysts. With regards 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 [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 $Pd^{2+}$ as in $Pd(OH)_2$, while raising the potential further would result in conversion to $Pd^{4+}$ in $PdO_2$, according to the Pourbaix diagram. The yield of the catalyst is given as ~8.5 nmol $s^{-1}cm^{-2}$, or 30 $\mu mol\ h^{-1}cm^{-2}$ with a FE 25.6%, at 1.9V vs RHE (their SI Table 4), which is very high compared to the other reports. The above questions raise the point that there is still uncertainty if $N_2$ oxidation mediated by $H_2O_2$ occurs as $NH_3$ 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

**ARTICLE**

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 waste water treatment. Furthermore, this $NH_3$ oxidation reaction is easier to achieve at somewhat lower potentials than the second pathway which involves the activation of $N_2$ i.e. breaking of the triple nitrogen bond. For this second reaction pathway of $N_2$ oxidation a few different catalysts have been reported, mainly based on the transition metals nickel and copper in 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 waste water 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 $NH_3$ concentration at industrial 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 $N_2$ and $O_2$ 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 $NO_x$ yields should be considered in relation to the observed yields.

Overall, the electrochemical synthesis of nitric acid seems a promising flexible and small up to large scale alternative to the current industrial large scale continuous processes. From $NH_3$ gas in alkaline electrolysis environment and also starting from ammonia from waste water, it would lead to an alternative source of activated nitrogen oxides. This means that locally produced $NH_3$ or waste water could be used to produce nitrogen based fertilizers, creating a 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 waste water it can simultaneously reduce environmental ammonia impact and allow for the production of nitric acid, without relying on both the Haber-Bosch process and 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, FM. Data curation: PJ, FM. Writing original draft: PJ, FM, Review and Editing: PJ,RK,FM, Funding acquisition: FM, RK.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

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

## Acknowledgements

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**Data availability statement**

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