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Electrochemical nitration for organic C–N bond formation: a current view on possible N-sources, mechanisms, and technological feasibility

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Growing awareness of the environmental impact caused by the chemical industry drives considerations towards a circular economy and the use of renewable electricity. A key role will be played by ammonia (NH_3) currently produced in the Haber Bosch process at elevated temperature and pressure from fossil hydrogen leaving an enormous CO_2 footprint. A more sustainable production is to be realized by electrochemically generated hydrogen or all-electrochemical synthesis. Aside from the crucial role in fertilizer production, NH_3 is necessary for the synthesis of organic intermediates and monomers *via* C–N bond formation reactions. This perspective highlights different strategies for electrochemical C–N functionalisation focusing on electrophilic nitration. Based on literature from one century, syntheses involving different inorganic nitrogen sources are discussed and their potential is evaluated. Finally, a perspective for more sustainable electrochemical nitration using NH_3 and atmospheric nitrogen (N_2) is presented. This way, a possibility to bypass the Haber Bosch process shall be demonstrated especially for decentralized small-scale productions.

Introduction

Rising global average temperature and scarcity of fossil resources show that a transition towards circular energy economy is imperative. A key player in this regard is the electri-

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fication of industrial processes utilizing ecologically friendly harvested energy from wind, water, or solar power.

That is why sustainability nowadays extends to the largest chemical productions such as Haber–Bosch.[1] Conventional ammonia (NH_3) synthesis *via* the Haber–Bosch process for its application in fertilizer production is worth 1–2% of global energy consumption and a similar share of CO_2 emissions.[2–4] This is because, fossil hydrogen (H_2)[4] is pressurised to 150–250 bar at 400–450 °C to react with nitrogen (N_2).[5] Although, H_2 may in the future be taken from water electrolysis[6] to reduce the carbon footprint, the energy demand for the process itself remains. Therefore, a direct N_2 reduction is highly desired. However, in the renaissance of electrochemistry as a green tool for the chemical industry,[7–11] N_2 activation remains a great challenge.[12–15] A detailed overview of the scientific approaches and crucial experimental considerations was provided by Stephens, Chorkendorff, Shao-Horn, and co-workers in 2021.[16] Even if an atom-, redox-, and energy-economic synthesis of NH_3 or also nitrate (NO_3^-) is realised, bulk chemical production is currently limited by the economies of scale.[17,18]

Meanwhile, a second branch of electrochemical research focuses on products providing a higher margin[19–21] or downstream processing of biogenic materials.[22–24] These approaches of organic electrosynthesis usually name inherent advantages of electrochemistry for a decentralized production matching the upcoming energy infrastructure.[25] For example, the elimination of harsh reaction temperatures and high pressures provides easier access to larger-scale production equipment. Also, high flexibility towards fluctuating substrate streams and energy supply can be achieved.[8,18]

Since multiple classes of target molecules such as monomers, pesticides, and pharmaceuticals possess C–N bonds,[26] the formation of these bonds by electrochemical methods is receiving increasing attention.[27–33] In 2018, Kärkäs presented a comprehensive review article describing electrochemical C–H activation for, among other things, C–N functionalization.[34] Most of the included studies consider organic nitrogen sources (N-sources), *i.e.* the reaction of two organic molecules.

On the other hand, the inorganic electrochemistry of nitrogen compounds has been intensively studied, for example, by Koper's group in 2009.[35] Here, the authors described the nitrogen cycle across eight oxidation states comparing natural and synthetic conversions. This article was later supplemented with an important review article on NH_3 oxidation by Bunce and Bejan.[36] They focused on electrocatalytic conversion using different electrocatalysts. The number of review articles on electrochemical N_2 reduction is vast[14,37–40] and the respective conversions are not in the scope of this perspective.

Currently, the literature lacks a linkage between the organic and inorganic scientific approaches. The activation of N_2 has hitherto encountered difficulties on technical scales due to energy or cost efficiency. However, for organic target compounds, the margin is much higher.[41,42] Activation of inorganic nitrogen compounds for introduction into organic structures would therefore have the potential to exploit the higher value increase of organic products. An envisioned way to realise this is the electrochemical nitration reaction, which is the subject of this review article.

Accordingly, the first section comprises existing approaches to electrochemical nitration. Starting from early studies to understand the selectivity of electrophilic aromatic substitution (S_EAr) reactions,[43–45] over different N-sources employed.[46–48] A connection will be made to the state of the art findings in sustainable electrochemical nitration recently presented by the Waldvogel group.[49] Then, further strategies of electrochemical C–N bond formation will be discussed in both organic and inorganic reactions.[50,51] Alongside, the available insights in activation mechanisms of nitrogen species are reviewed including spectroscopic and computational studies.[52–55] At the end, a perspective that evaluates the opportunities of electrochemical N_2 activation for organic C–N bond formation and scientific starting points for further research is provided.

Electrochemical nitration

In organic synthesis, ammonia represents one way to introduce nitrogen into large molecules like pharmaceuticals, pesticides, or generally advanced intermediates. Due to the higher margin of these fine chemicals,[41,42] the hourly production rate is of less importance than for the bulk synthesis of ammonia. Therefore, electrochemical nitrogen activation should be reassessed in this context targeting organic nitro compounds instead of ammonia or nitric acid. Direct incorporation of N_2 into organic molecules would additionally reduce the number of reaction steps leading to an overall more elegant and thus more sustainable synthesis. To realize this, first, active nitrogen species must be identified.

For functionalizing organic molecules, especially oxidative pathways yielding electrophilic nitrating agents are of interest. Typically, this is realised by the activation of nitric acid using and acidic catalyst like sulfuric acid.[56,57] Industrial processes are conducted on a scale of several million tons per year[58] and recently, effort is made to explore more sustainable alternatives.[57] Despite that, the organic nitration reaction is not a particularly active research field, which provides room for innovation for groups wishing to enter the field. Furthermore, already in 1971, the electrochemical nitration of aromatic compounds in the presence of nitrate was reported.[43] Recently, an environmentally benign and hazard reduced pathway involving a soluble nitrite salt was developed.[49] The field of electrochemical nitration hence comprises a period of 50 years in which conceptual knowledge was collected. This provides the basis for a fresh discussion of electrochemical nitration in the context of new issues such as the efficient use of electricity

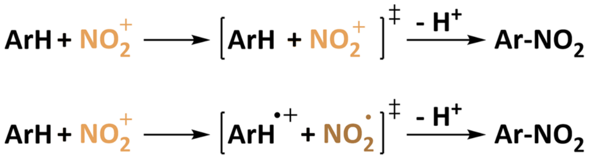

Fig. 1 Proposed mechanism for the nitration of aromatics according to Olah (top) and Perrin (bottom).

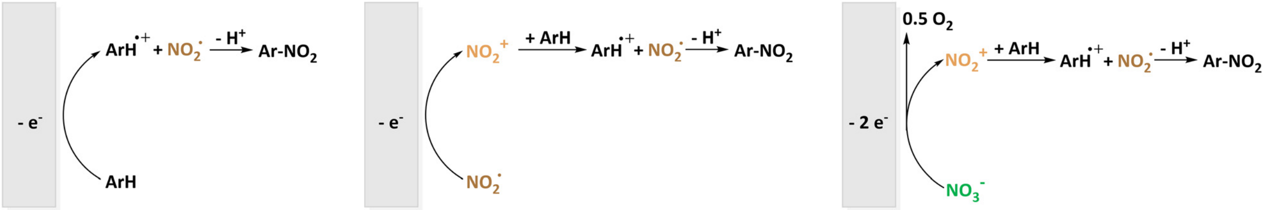

Fig. 2 Electrochemical nitration using $NO_2^{\bullet}$ as nitrating agent below (left) and above (middle) its potential of oxidation to NO_2^+ and similarity to the reaction pathway using NO_3^- as source of $NO_2^{\bullet}$ (right).

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and decentralised production. The revision of literature is started with the question about the active species in electrophilic nitration using the mixture of sulfuric acid and nitric acid, sometimes called nitrating acid. Here, it is suggested that the textbook mechanism involving the nitronium ion (NO_2^+)[59] gives no conclusive explanation of the observed intramolecular selectivity without intermolecular selectivity. While from a mixture of aromatics all react at a similar rate,[60] the position of the nitro group in the target compounds represents the selectivity of an electrophilic attack.[61] Olah explained this by a complex formed from aromatic and NO_2^+.[45]

Perrin later states that a single electron transfer from the π-system to NO_2^+ leaves a radical pair $ArH^{\bullet+}/NO_2^{\bullet}$ that collapses to form the organic nitro compound (Fig. 1). Evidence is given by electrochemical formation of the aryl cation and subsequent reaction with $NO_2^{\bullet}$ yielding the same selectivity.[44] This is later on affirmed in studies on naphthalene which is repeatedly used in electrochemical nitration.[62,63] The most common electrode material in these studies is platinum.[63–65] In fact, yields of up to 75% of nitronaphthalene were reported for the electrochemical nitration using N_2O_4 which is oxidized to NO_2^+ in anhydrous sulfolane.[65] Generally, reactions at potentials suitable for the oxidation of the aromatic compound[63,64] are discriminated from reactions at potentials above 1.75 *vs.* Ag/Ag$^+$ at which both aryl and nitrogen dioxide can be oxidized.[66] This already indicates the possibility of using nitrite and nitrate as nitrating agent precursors by the recombination of ArH^+ and the negatively charged nitrogen species. Exploring the opportunities of electrochemical nitration to avoid toxic nitrating agents such as $NO_2^{\bullet}/N_2O_4$, this approach highlights two potentially attractive active species to be generated *in situ*. As mentioned above, the abundant and highly soluble nitrate (NO_3^-) was investigated alongside this discussion. Fig. 2 shows the reaction mechanisms using $NO_2^{\bullet}$ or NO_3^- as nitrating agents. Nyberg reported the nitration of mesitylene with tetrabutylammonium nitrate in nitromethane. The highest selectivity of 39% was obtained using a carbon anode at 1.5 V (presumably *vs.* SHE) and a mesitylene : nitrate ratio of 5 : 1. Accordingly, mesitol was the main product with 56% selectivity.[43]

The more common electrochemical nitrating agent compared to nitrate is nitrite (NO_2^-). Very recently, the Waldvogel group published an environmentally benign method for the nitration of 20 aromatic compounds using NBu_4NO_2 as soluble nitrite source in MeCN. The employed graphite electrodes represent a metal-free, low-cost material underlining the demonstrated scalability of the reaction to gram-scale maintaining satisfactory yields of 85%.[49] Previously, electrochemical nitration with NO_2^- was shown for the prominent model substance naphthalene in MeCN by the Sereno group as well.[48] In the discussion of the reaction mechanism, $NO_2^{\bullet}/N_2O_4$ is referred to as the active species. The different pathways are depicted in Fig. 3.

Interestingly, $NO_2^{\bullet}/N_2O_4$ formation is suggested to be not only due to NO_2^- oxidation but also *via* recombination of NO_2^- and NO_2^+ to N_2O_4 if there is an excess of NO_2^-.[48] In follow-up investigations, the effect of the non-ionic surfactant polyoxyethylen(23)-laurylether on the same nitration system was examined. The pre-concentration of both compartmentalized substrate and nitrating agent reactants enhances the desired reaction pathway.[46,47] Laurent *et al.* also studied nitration starting from a nitrite source reacting with $ArH^{\bullet+}$.[67] Additionally, they described the interconversion of NO_x species under oxidative conditions including NO_2^-, $N_2O_4^-$, NO_3^-, N_2O_3, N_2O_5, and NO_2^+ underlining the versatility of these reaction systems.

Aside from electrochemical nitration, NO_2^- and NO_3^- can be used to electrochemically form N–N bonds in an *N*-nitrosation or *N*-nitration of secondary amines.[68,69] In this process, a carbon anode facilitates the oxidation of organic substrates, whereas the active NO_x species are generated thermally from $Fe(NO_3)_3$. This mechanism was verified by radical capture tests. Here, $NO^{\bullet}$ recombined with 2,2,6,6-tetramethyl-1-piperidi-nyloxy (TEMPO) and 2,4-di-*tert*-butyl-4-methylphenol (BHT) with the pyrazole radical indicating a biradical mechanism. Follow-up DFT calculations confirmed opposite selectivity of pyrazole and morpholine towards $NO^{\bullet}$ and $NO_2^{\bullet}$ leading to either the nitrosamine or the nitramine.[69] This emphasises the versatility of the NO_x radical chemistry and possible reaction pathways for the targeted C–N functionalization.

Further strategies for C–N bond formation and nitrogen activation

In 2018, Kärkäs revised organic C–N bond formation reactions.[34] Examples are the C–N coupling of pyrrolidones to anilines in a Shono oxidation,[70] intramolecular amine formation

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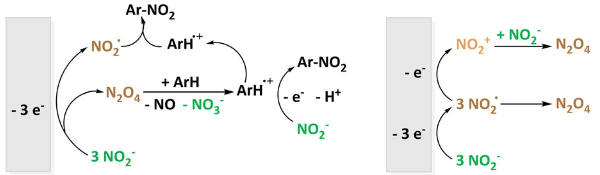

Fig. 3 Electrochemical nitration using soluble NO_2^- as source of the nitrating agent according to the groups of Waldvogel (left) and Sereno (right).

from olefines,[71,72] synthesis of primary amines of aromatics,[73,74] and α-amination of ketones.[75] Additionally, recent publications describe reductive amination of biogenic substrates for C–N bond formation in the context of amino acids[31,33] or pyrrolidone synthesis.[27] Most of these conversions are realized by coupling two organic molecules whereas there is a limited number of examples of inorganic N-sources such as NH_3 or N_3^-.[34]

Further strategies for C–N bond formation from small, inorganic N-sources are recently discussed in the field of CO_2 utilization.[51,76–79] For the strategies discussed here, a comparison of reaction pathways from urea synthesis displayed in Fig. 4 is of particular interest.

On one hand, the C–N coupling is achieved by reduction of NO_3^-,[80–82] NO_2^-,[50,83,84] or NO[85] to a $*NH_2$ surface species which attacks surface bound *CO. Not only the number of electrons transferred in the process but also the activation energy indicate that excess CO is formed. In this regard, bifunctional catalysts are applied as adsorption and activation of different molecules has to be facilitated.[86] On the other hand, activation of N_2 for an attack of CO originating from CO_2RR is discussed. According to DFT calculations, this leads to a *NCON* species described as tower-like which is selectively hydrogenated to form *NCONH*. A combined process of hydrogenation and CO release to build intermediates of NH_3 formation is unfavoured according to DFT calculation because $*N_2H$ is energetically disadvantageous. Once again, bifunctional materials are necessary. The PdCu alloy provides comparably negatively charged Cu and facilitates the addition of H atoms to Cu-bound nitrogen.[51] In both reaction systems, urea formation competes with CO_2RR and NRR and outlines the variety of active carbon and nitrogen species accessible with electrochemical methods. For a detailed discussion of reactions pathways of electrocatalytic urea synthesis from CO_2 and NO_x species, we refer the interested reader to a recent review by the Jin group.[87]

In this perspective, different nitrogen species have been elaborated, which can potentially be used for electrochemical nitration. One opportunity to access them is the ammonia oxidation reaction (AOR). Research in this field is mostly driven by the hydrogen-fuel properties of ammonia[88] and its removal from wastewater.[89] In 2011, Bunce and Bejan described the electrocatalytic AOR mechanisms in a review article.[36] These reactions target dinitrogen as product and consider nitrogen oxides unwanted side products. Therefore, faradaic efficiencies are often not discussed for the latter. Below the potential range of the oxygen evolution reaction (OER) in aqueous medium, ammonia is electrolyzed at platinum in alkaline solution to form N_2 and NO_3^-.[90] Under these conditions, NO_2^- was only formed in traces, unless the solution additionally contained $Cu(OH)_2$.[91] The key intermediate in the reaction sequence leading to NO_2^- and NO_3^- is NH_2OH,[52] whereas adsorbed NH_y species are attributed to N_2 formation.[53] To enhance the NH_2OH and thus NO_2^- and NO_3^- production, potentials in the range of both AOR and OER must be applied to couple N–O. Therefore, the pathways were divided into above and below OER potential as displayed in Fig. 5.

The possibility of oxidizing NH_2OH to NO_2^- and NO_3^- at potentials around 0.6 V *vs.* Ag/AgCl was confirmed on a rotating ring disk electrode (RRDE) providing a Ni ring.[92] These elevated potentials yielded traces of the same products also

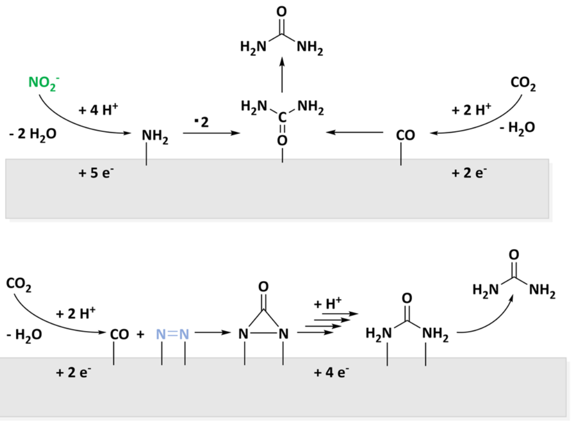

Fig. 4 Reaction pathways of electrochemical urea synthesis *via* NO_2^- (top) or N_2 (bottom) activation and parallel CO_2 reduction to CO.

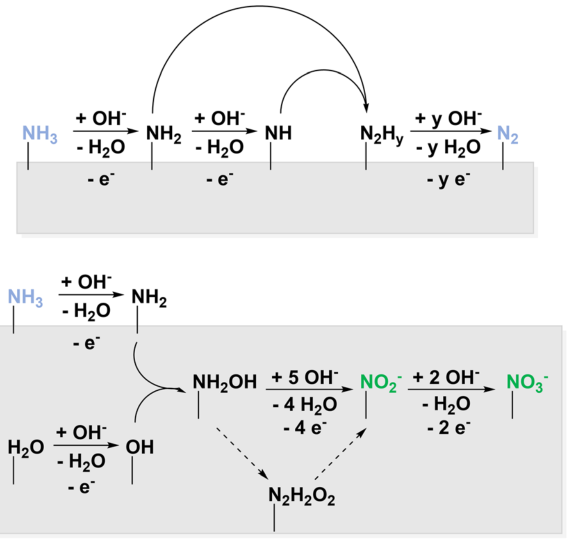

Fig. 5 Electrochemical NH_3 oxidation below (top) and above (bottom) the potential of OER.

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when Pt-based materials were used.[93,94] This verifies that in a potential range of both AOR and OER, mixed oxidized products N_zO_x can be observed.[94] In acidic solution, also $NO^•$ is detected at elevated oxidation potentials on Pt.[95] Following the RRDE investigation described above, $Ni/Ni(OH)_2$ was employed yielding NO_3^- and a non-specified mixture of N_2 and NO_x. Additionally, a strong pH dependence of the reaction occurred indicating the effective oxidation of NH_3 and not soluble NH_4^+ species at elevated pH.[96] Furthermore, NH_3 oxidation on boron-doped diamond (BDD) was studied with the unexpected result that, unlike most organics, the oxidation does not proceed *via* hydroxyl radicals giving access to NO_3^- and $NO_2^•$ in different concentrations with respect to the reaction conditions.[97] Recently, the Klinkova group reported $Ni(OH)_2$ to catalyse the AOR with current efficiencies of either 72% to NO_3^- or 60% to NO_2^- through slight changes in reaction conditions.[98] Adaptive catalytic systems of this kind are particularly interesting for decentralised, flexible production. To summarize, AOR yields NO_x, NO_2^-, and NO_3^- at potentials where parallel OER is observed. Here, NH_2OH is involved instead of NH_y species which are intermediates in N_2 formation.[36] AOR is therefore a possible starting point for electrochemical nitration of organic compounds. For full electrification of the process, ammonia might be used that was produced electrochemically.

As the electrochemical ammonia production remains challenging,[13–15,99] this step might be circumvented, by using N_2 gas directly as the source of nitrating agents. Also, oxidative pathways to activate molecular nitrogen have been reported. Like in AOR, the competition to OER is the main restriction. The direct electrochemical oxidation of N_2 to NO_3^- bypasses not only energy-intensive Haber–Bosch but also the subsequent Ostwald process and can therefore be considered a dream reaction.[89] In an experimental study from 2019 by Wang *et al.*, the electrochemical synthesis of NO_3^- from N_2 on Pt was achieved with a faradaic efficiency of around 1% and a maximum productivity of 0.06 μmol h^{-1} cm^{-2}.[55] The proposed mechanism proceeds *via* surface bound *NO which desorbs from the surface to form HNO_3 and HNO_2 in aqueous, oxygen containing environment (Fig. 6).

Also, consecutive oxidation to $*NO_2$ before desorption and formation of HNO_3 as depicted in Fig. 7 is discussed.[55]

The role of *NO is supported by a computational study identifying the reaction of N_2 to $*N_2O$ as the rate-determining step before further oxidation and dissociation.[54] This is most likely to occur by the activation with *O and therefore preferably on metal oxides with weak *O adsorption. Additionally, strong N_2 binding is necessary which is in line with experimental results for Ru-doped TiO_2 showing a maximum faradaic efficiency of 26%.[100] Other experimental studies using mixed metal oxides supplement this trend.[101,102]

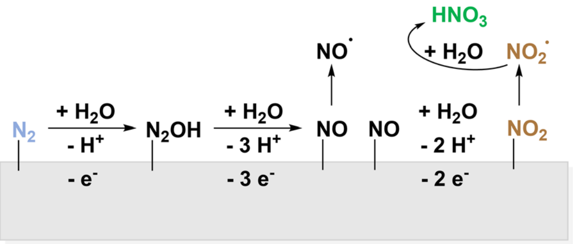

Fig. 6 Electrochemical activation of N_2 *via* surface bound $*N_2OH$ and *NO to yield $NO_2^•$.

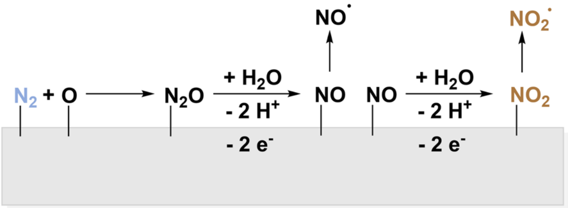

Fig. 7 Electrochemical activation of N_2 *via* surface bound $*N_2O$ and *NO to yield $NO_2^•$.

The second reaction pathway in the computational study involves $*N_2OH$ as intermediate species while adsorption of OH on metal oxides impedes the activation of N_2.[54] However, under the addition of sulphate, this pathway is promoted on Rh nanoparticles. The study also confirmed the general presence of *NO and $*NO_2$ in the NOR by *in situ* IR spectroscopy as well as $NO^•$ formation *via* gas analysis.[103] The third possibility of direct N_2 activation and bond cleavage proved to be unlikely for the investigated metal oxides.[54] Another computational study compared pathways for OER and NOR for both a good (IrO_2) and a poor (TiO_2) OER catalyst in detail. In either case, OH is most likely to adsorb to the surface and N_2 is not directly activated. Consecutively, *O is formed and reacts to N_2O over TiO_2 because of its decreased stability. Still, the reaction is energetically difficult, and the article cannot account for a complete description of possible oxidation pathways.[104]

Evaluation of electrochemical nitration

Different examples of electrochemical nitration of organic molecules were presented. The first study was published in 1971[43] when organic electrochemistry was a niche technique driven by scientific curiosity.[19,20,105] In contrast, the most recent investigation from 2021 follows the principles of green chemistry and directly aims at technical applicability.[49] Aside few similarities like aromatic substrates and using standard anode materials like Pt and graphite, the overall reaction conditions differ a lot as does the focus of the collected publications. Because of this very heterogenous literature base, we decided to select chemical yield as a common performance indicator to compare existing technologies as shown in Table 1. Depending on the reaction conditions employed (N-source, solvent, electrode material and electrolyte), maximum yields between 26–96% were obtained in the electrochemical nitration reaction. The performance of NH_3 or N_2 oxidation is evaluated for selected examples of the demonstrated literature.

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Table 1 Reaction conditions of electrochemical nitration for different N-sources. A classification of solvents may be done according to Snyder.[106] Y_m = maximum yield reported

N-Source	Y_m (%)	Product	Solvent	pH	Electrode	Electrolyte	ref.
$NO_2^{\bullet}/N_2O_4$	26 ± 5	Nitronaphthalene	MeCN	—	Pt	$LiBF_4$	63
	59	Nitronaphthalene	DCM	—	Pt	Bu_4NPF_6	64
	75	Nitronaphthalene	Sulfolane	—	Pt	—	65
NO_2^-	92	Aromatics/olefins	MeCN	—	Pt	$AgNO_2$	67
	85	Nitronaphthalene	MeCN	—	Pt	$NaNO_2$	48
	32	Nitronaphthalene[a]	Water + surfactant	Neutral	Pt	$NaNO_2$ + $NaClO_4$	47
	32			Low	Pt		46
	96	Aromatics	MeCN + HFIP	Low	C	Bu_4NNO_2	49
NO_3^-	39	Nitromesitylene	$MeNO_2$	—	C	Bu_4NNO_3	43
NH_3	>99	N_2	Water	High	Pt	KOH	53
	63[b]	N_2	Water	High	Pt	NaOH	90
	37[b]	NO_3^-					
	11	NO_3^-	Water	High	$Ni/Ni(OH)_2$	NaOH	96
	72[b]	NO_3^-	Water	High	$Ni(OH)_2$	K_2SO_4	98
	60[b]	NO_2^-				NaOH	
N_2	0.06 $\mu mol\ cm^{-2}\ h^{-1}$	NO_3^- [c]	Water	Neutral	Pt-foil	K_2SO_4	55
	77.7 $\mu mol\ g_{cat}^{-1}\ h^{-1}$			High	$Pd_{0.9}Ru_{0.1}O_2$	KOH	101
	161.9 $\mu mol\ g_{cat}^{-1}\ h^{-1}$			Neutral	$Ru_rTi_tO_2$ [d]	Na_2SO_4	100
	130 $\mu mol\ g_{cat}^{-1}\ h^{-1}$			High	$ZnFe_{0.4}Co_{1.6}O_4$	KOH	102

[a] Very similar conditions and results were obtained from ref. 47 and 46. [b] Maximum current efficiency from two separate experiments under different conditions. [c] NO_3^- yield is given as production per catalyst and time. [d] The stoichiometric composition was not defined in 100 but rather Ru-doping of TiO_2 in wt%.

With this comparison at hand, we evaluate the potential of the presented technologies based on particular advantages and disadvantages of the N-sources. As the two soluble sources, NO_2^- and NO_3^-, require very similar process design, they will be considered together in the following. The same applies to the novel nitrating agents NH_3 and N_2. To provide an easy approach to evaluating the different N-sources, a simple list of advantages and disadvantages is provided in Table 2.

Overall, we think that already existing pathways using $NO_2^{\bullet}/N_2O_4$ or soluble N-sources are promising and their rejuvenation should be pushed as demonstrated by the Waldvogel group. This will lead to a broader library of electrocatalysts and methods as well as mechanistically improved understanding of the electrochemical nitration using different N-sources. Thereby, more challenging activation mechanisms as for NH_3 and N_2 can be addressed by research to potentially find even more elegant and benign synthesis of organic nitro compounds.

Table 2 Advantages and disadvantages of different N-sources for the electrochemical nitration. So far, utilisation of NH_3 or N_2 was not reported for this reaction

	$NO_2^{\bullet}/N_2O_4$	NO_2^-, NO_3^-	NH_3, N_2
+	Active species reported	Soluble N-source	Abundant (if NH_3 is decentralised)
	Reactions proceed *via* $NO_2^{\bullet}$ for every N-source	Active species reported	Design of sustainable production route
−	Toxic, pressurized gas	Previous production of N-precursor	Active species not described yet
	Solubility and multiphase system		Solubility and multiphase system

Perspective

In recent years, the electrochemical oxidation of N_2 was achieved to a certain extent and efforts were made to understand the reaction mechanism using *in situ* spectroscopy, online analytics, and DFT calculations. Nonetheless, the active species and rate-determining steps have not conclusively been identified and are, as is often the case, material dependent. The efficient conversion of N_2 to (inorganic) bulk chemicals therefore remains challenging. An alternative is the activation of N_2 to produce (surface) intermediates that can potentially react with organic molecules exposed to them in a nitration reaction to fine chemicals. A key step is the simultaneous production of reactive N- and C-species for C–N-bond formation. This was already demonstrated in numerous studies of electrochemical nitration during the last century and very recently in the context of sustainable electrocatalysis, *i.e.* urea synthesis. To activate NH_3 or N_2 for electrochemical nitration, three main challenges must be overcome: first, suitable electrode materials and geometries are essential to catalyse the reaction. Furthermore, to work at the gas–liquid interface, the design of an appropriate reactor is required. Finally, the reaction conditions should be optimized regarding yield and faradaic efficiency as well as a sufficiently broad substrate scope.

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Catalyst design

The most atom-efficient and environmentally benign C–N bond formation strategy is to use atmospheric nitrogen in an electrochemical nitration reaction although the mechanisms to activate nitrogen are challenging. Currently, an overview that summarizes the different N-sources and oxidation mechanisms, *e.g.* nitrogen and ammonia, is absent. For the AOR, platinum was discussed and provides access to NH_2OH, NO_2^- and NO_3^- as well as different N_2O_x species. Other electrodes of major interest are Ni/Ni(OH)$_2$ and BDD.[96,97] The investigation of BDD also presented the opportunity to deliver ammonia in the form of NH_4ClO_4 matching the supporting electrolyte.[97]

A comparable situation can be expected for N_2 activation. Here, also noble metal catalysts or alloys were employed to access different N_xO_x intermediates.[55,100,101] Additionally, a noble metal free spinel oxide was reported to be active.[102] Based on this, mechanisms are proposed to capture the active nitrogen oxide species with organic aryls displayed in Fig. 8. The active nitrating agents are $NO_2^\bullet$, NO_2^-, and NO_2^+. The species detected in experimental studies and predicted with computational methods suggest that basically all conceivable radical or ionic nitrogen oxides are accessible from NH_3 or N_2. However, it should be investigated whether a species active for nitration must desorb from the catalyst surface before reacting with the organic molecules. Considering the reaction of $NO_2^\bullet$ and NO_2^-, parallel oxidation of the organic compound is necessary. To deepen the mechanistic understanding and rationalising the catalyst design, *in situ* spectroscopic insights can be very useful. Therefore, the already introduced ATR-SEIRAS[103] should be considered alongside advanced electrochemical techniques like RRDE measurements[92] for the development of new materials.

Regarding the gaseous substrates NH_3 and N_2, the mass transport will be of major importance like in CO_2 electrolysis.[107,108] Also, suitable reaction conditions are sought to access nitrogen species active for nitration of aromatic substrates. An expected challenge is that AOR and NOR take place in aqueous media, while electrochemical nitration is usually performed in organic solvents. Here, surface modification of the electrode to tailor hydrophobicity[109,110] may be an important tool in combination with the choice of solvent and electrolyte. As an interplay of hydroxide and nitrogen oxidation is mentioned in AOR and NOR literature, an aqueous reaction system may be inevitable.[36,54,104] To deliver the organic substrate, also a surfactant could be utilized as demonstrated for nitration using $NO_2^\bullet$.[47]

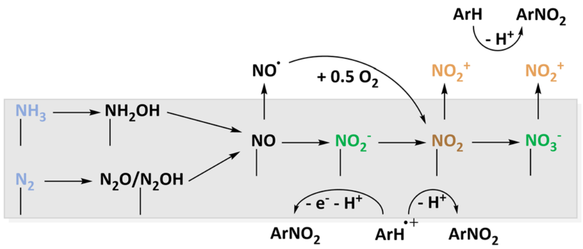

Fig. 8 Proposed reaction sequence leading to different surface intermediates suitable for electrochemical nitration which are caught by organic molecules.

Based on this, the research with a bulk Pt catalyst and the perspective of dispersed noble metal oxides with a final goal of (noble) metal free materials can be considered as potential direction to develop efficient electrode materials. Besides, after a proof of enhanced catalytic activity, the development of a gas diffusion electrode (GDE) geometry and surface modification to tailor the solid–gas–liquid three-phase interface will be necessary to improve the overall performance.

Reactor design

While development and testing of electrocatalysts is mostly performed in H-cells or even undivided 3-electrode cells, plant-scale setups demand for a different level of sophistication. As the interest in modular electrolysers for decentralised application is increasing, the development of cells gains importance. The envisioned process of electrochemical nitration using NH_3 or N_2 N-sources works at a gas–liquid interphase. While ammonia dissolves relatively easily in many aqueous electrolytes,[111] the solubility of nitrogen in them is very low.[112] Thus, mass transport is of utmost importance and is currently discussed for the NRR.[113] Further inspiration may once again be found looking at developments for CO2RR. Generally, (micro)flow electrolysers and membrane electrode assemblies (MEA) are used in CO2RR.[114,115] Flow electrolysers enhance the mass transport using gas-diffusion electrodes trough which a gaseous substrate is brought in contact with the liquid electrolyte. Material properties like pore dimension and wetting behaviour allow for a tailored mass transport and high current densities. MEAs are derived from fuel cell technology in which the electrocatalyst is in direct contact with the membrane. Also here, GDEs are employed but the electrolyte may be humidified CO_2 gas in case of the CO2RR.[115] For the rapid-prototyping of electrochemical reactors, additive manufacturing techniques recently gain importance.[116–120] Such 3D-printed reactors are also tested in CO2RR, although different challenges like chemical tolerance of the materials or tightness occur.[118,121]

Therefore, to start, reliable catalytic activity should be demonstrated in an analytical H-cell reactor configuration. The electrosynthesis can then directly be transferred to a flow electrolyser allowing the use of GDEs.

Optimisation

As for any electrochemical system, a rigorous screening study of reaction conditions such as solvent, electrolyte, pH, current density, and potential is necessary. In the vision of a sustainable process, the solvent of choice is water which is common to electrochemistry and already discussed for the oxidation of NH_3 or N_2. Nonetheless, literature on electrochemical nitration is built around organic solvents because of the solubility of the organic substrates. In electrochemistry, often also mixed solvents improve the reaction. A suitable electrolyte enables elec-

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tric conductivity without interfering with the actual reaction, which is why strong acids or bases are often desired and N-containing molecules should be circumvented in this process to control the actual N-source. Furthermore, it can mediate the solubility of aromatic substrates. The pH must be adapted to the electrode material and allows certain control over OER as major side reaction. While noble metals are stable over a broad range of pH, the use of other materials may require rigorous pH control. Finally, current density and potential are crucial to control selectivity, mass transport, and productivity.

Hence, we expect that an aqueous system and emulsifying electrolyte at elevated pH can enable electrochemical nitration using NH_3 or N_2. Still, both gases show descent solubility in organic solvents[122–124] *so that conditions closer to the original literature on electrochemical nitration can be chosen. Based on industrially established electrochemical processes for organic fine chemicals,*[125] *a current density of 10–40 mA cm^{-2} is desirable to be productive and should be targeted when tailoring the catalyst, cell, and conditions.*

Additionally, to understand the selectivity of the envisioned electrochemical nitration process, a broad substrate scope should be considered. This includes typical examples of nitration substrates such as naphthalene or mesitylene as well as functionalized aromatics to understand electronic effects. The tolerance of halogens, methoxy groups, and already multi-substituted aromatics forms a typical scope. Finally, for certain medicinal molecules it would be interesting to evaluate which impurities may result from an electrochemical process. For example, the antibiotic nitrofurantoin can be synthesised from 5-nitrofurfural[126] which is an example for nitrofuranes[127] accessible from the biogenic platform molecule furfural[128,129] *via* electrophilic nitration.

Author contributions

Nils Kurig: conceptualisation, formal analysis, visualisation, writing – original draft. Regina Palkovits: conceptualisation, resources, funding acquisition, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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