Future Energy

Electrocatalytic Nitrate Reduction for Sustainable Ammonia Production

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There is a recent upsurge in scientific papers on electrocatalytic reduction of nitrate to ammonia.[1–6] In this process, nitrate-containing wastewater streams are used as a nitrogen source for the production of ammonia, a versatile compound that can be used as fertilizer, chemical, or fuel (Figure 1). This route would enable the utilization of nitrate to produce this valuable molecule, while the conventional removal of nitrate from wastewater, known as "denitrification", aims at the conversion of nitrate to dinitrogen.[7]

In general, the conversion or removal of nitrate is an important challenge that is necessary to restore the globally perturbed nitrogen cycle. Over many decades, various human activities have contributed to an imbalance in the global nitrogen cycle by the release of reactive nitrogen into the environment. Nitrate release is one of the most harmful consequences because it can leach out of the soil and pollute ground and surface waters, thereby contributing to eutrophication and the disturbance of ecosystems.[7]

The major part of nitrate ending up in the environment originates from the excessive use of fertilizer for production of crops or livestock. The discovery of the Haber-Bosch process made the large-scale production of ammonia for fertilizer possible and therefore caused the biggest disturbance of the nitrogen cycle. In the Haber-Bosch process, ammonia is produced in a reaction between H_2 and N_2 at high pressure and temperature. As a consequence, the Haber-Bosch process depends on the use of fossil fuels for the production of H_2 and is an energy-intensive process leading to high operational costs. By contrast, the electrochemical conversion of nitrate to ammonia does not involve the use of H_2 and can be coupled to electricity that is ideally locally produced from sustainable sources, like wind and solar energy. Additionally, it would facilitate decentralized ammonia production at room temperature. Therefore, the electrocatalytic conversion of nitrate to ammonia would provide a solution for restoring the imbalance in the global nitrogen cycle and simultaneously provide a sustainable alternative for the Haber-Bosch process.

In this Future Energy, we address the potential of this process by summarizing the current developments on electrocatalysts for the reduction of nitrate to ammonia in relation to the available

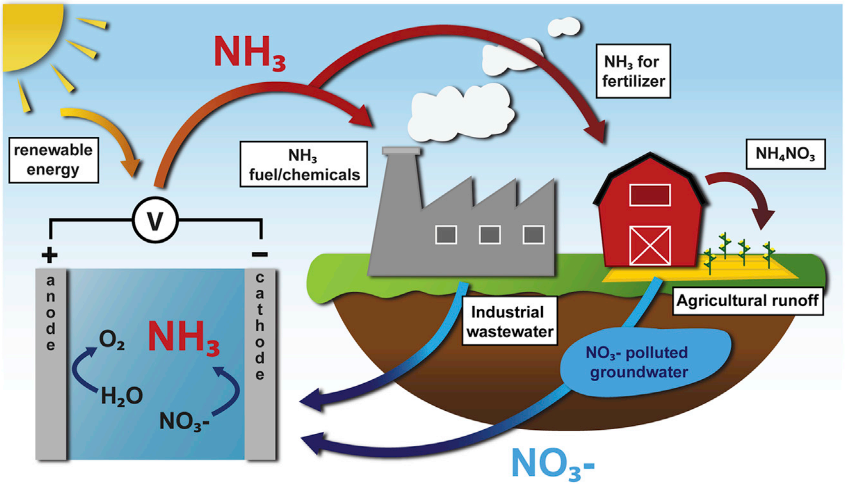

Figure 1. Concept Cycle for Ammonia Synthesis from Waste Nitrates

nitrate-rich wastewater streams and by comparing these to alternative processes for ammonia production. These considerations raise a number of future challenges for the large-scale application of nitrate reduction for sustainable ammonia production, which will be outlined at the end of the article.

Nitrate Reduction to Ammonia

Large-scale application of electrocatalytic denitrification has been limited by the lack of catalysts with a high selectivity of nitrate reduction to N_2 and low energy consumption and by the lack of research on long-term operational stability of electrode materials in electrochemical reactors, both under practical conditions.[7] In the case of N_2 production from nitrate, the second-order formation of the N-N bond is in competition with the first-order reaction to make other reduction products such as NH_3 or H_2NOH, hampering the selectivity. For example, on noble-metal electrodes, the stepwise formation of N_2 will only take place if adsorbed N_2O is present, which originates from the reduction of NO_2^-. However, N_2O can desorb from the surface before further reduction to N_2 can occur. Additionally, several other nitrogen species can evolve from adsorbed NO_2^-, hampering the formation of adsorbed N_2O and thus eventually N_2.[7] Thus, even though 3 more electrons are required to reduce nitrate to ammonia compared to N_2, nitrate reduction to ammonia is much easier from a catalytic point of view as no N-N bond needs to be formed. That a high selectivity to ammonia (compared to $N_{2)}$ should be easier to achieve is confirmed by looking at catalysts previously developed for the purpose of denitrification. While these catalysts aim at the production of N_2, often good selectivity to ammonia was reported.[8] In some cases, the evolution of N_2 was subsequently enhanced by electrochlorination of ammonia.

Only recently, the development of catalysts that actually aim at the selective electrocatalytic reduction of nitrate to ammonia gained interest, and Table 1 collects results from these recent papers. Zhang et al. demonstrated that high ammonia selectivity can be achieved by making use of novel electrode materials. They found that oxygen vacancies in TiO_2 electrodes improve the overall faradaic efficiency (FE), catalytic stability, nitrate conversion, and selectivity by weakening the N-O bond.[1] In another study, they showed that CuO nanowire arrays, electrochemically reduced to Cu/Cu_2O, result in excellent FE and selectivity to ammonia and the suppression of the competing hydrogen evolution reaction (HER).[2]

A comparable strategy to enhance the catalytic activity and selectivity was used by Sargent et al.[3] They developed copper-nickel alloys, resulting in a change in the electronic structure of the catalyst, thereby leading to a 6-fold increase in nitrate reduction activity compared to regular Cu electrodes. They attributed this improvement to modified adsorption energies of the catalytic intermediates and highlighted the importance of rational design of catalysts in order to improve the selective conversion of nitrate to ammonia.

Using a Ti cathode, Jaramillo et al.[4] comprehensively studied the effect of the pH, nitrate concentration, and applied potential on attaining high ammonia selectivity. Interestingly, a large variation of the FE to NH_3, ranging from ~1% to ~82%, could be observed depending on the applied conditions. The best FE to ammonia was obtained under strongly acidic conditions and moderate to high ammonia concentrations, which was attributed to the higher availability of nitrate ions to react with protons, which suppresses the HER and thus favors the formation of ammonia.

The suppression of the HER was also attributed in the production of NH_3 of the catalyst reported by Wang et al.[5] The structure of their copper-incorporated crystalline 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) catalyst would boost the formation of N-H bonds. Additionally, improved yield and selectivity were attributed to incorporation of the PTCDA, which delivers protons and electrons to the active Cu site.

The highest FE of nitrate to ammonia, reaching almost 100%, has recently been reported by Yu et al.[6] In their study, the use of strained Ru nanoclusters is claimed to promote the generation of hydrogen radicals, which accelerates the hydrogenation of nitrate reduction products to the formation of ammonia.

Table 1. Reported Catalysts for the Selective Electrocatalytic Reduction of Nitrate to Ammonia

Cathode Material	Maximum FE to NH_3	Partial Current Density to NH_3	Maximum NH_3 Production Reported	Conditions	Reference
TiO_{2-X}	85%	-	0.045 mmol mg_{cat}^{-1} h^{-1}	3.6 mM NO_3^-, 0.5 M $NaSO_4$, −1.6 V versus SCE	[1]
TiO_2	66.3%	-	0.024 mmol mg_{cat}^{-1} h^{-1}	3.6 mM NO_3^-, 0.5 M $NaSO_4$, −1.6 V versus SCE	[1]
Cu/Cu_2O NWAs	95.8%	-	0.2449 mmol h^{-1} cm^{-2}	14.3 mM NO_3^-, 0.5 M $NaSO_4$, −0.85 V versus RHE	[2]
Copper-nickel alloys	99%	−90 mA/cm^2	-	100 mM NO_3^-, 1 M KOH, pH 14, −0.1 V versus RHE	[3]
Ti	82%	−22 mA/cm^2	-	0.3 M KNO_3, 0.1 M HNO_3, acidic pH, −1 V versus RHE	[4]
Cu-incorporated PTCDA	85.9%	-	0.0256 mmol h^{-1} cm^{-2} (77% FE)	36 mM NO_3^-, 0.1 mM PBS, pH 7, −0.4 V versus RHE	[5]
Strained Ru nanoclusters	~100%	−120 mA/cm^2	5.56 mol g_{cat}^{-1} h^{-1} (1.17 mmol h^{-1} cm^{-2})	1 M NO_3^-, 1 M KOH, −0.2 V versus RHE	[6]

Nitrate-Rich Waste Streams

Various types of wastewater have previously been used, or modeled, in studies on electrocatalytic denitrification and form a convenient starting point for considering nitrate sources for the production of ammonia (Table 2). A high concentration of nitrate would make the production of ammonia easier and more cost efficient but limits the type of wastewater that can be utilized. The highest level of nitrate is found in low-level nuclear waste, a wastewater stream that has extensively been studied in electrocatalytic denitrification as biological treatment is not possible.[9] Lower concentrations of nitrate are found in industrial runoff,[10] for example from the textile industry.[11] A more widely available wastewater stream is polluted groundwater, for example from agricultural runoff, where increased levels of nitrate can be also detected.[12] Nevertheless, these concentrations are still low for an electrolysis process considering that electricity will be likely utilized for side reactions, such as the HER. A possible solution for this problem is to concentrate the nitrate prior to reduction. Though this adds an extra step to the production process, the usage of agricultural runoff encourages decentralized ammonia production and provides clean water for aggregation of farmland at the same time.

Apart from the concentration of nitrate, the overall composition of the aforementioned wastes can be very important for the efficiency of the nitrate reduction process. For example, in nuclear waste, the presence of waste hexavalent chromium (from Na_2CrO_4) forms a potential hindrance under reductive conditions,[9] whereas in textile wastewater a high level of chemical oxygen demand (COD) can inhibit the reduction of nitrate.[11] The low conductivity of ground water due to the nearly neutral pH conditions and the relatively low concentration of ions creates a major challenge for the direct utilization of nitrate from ground water. In general, future systematic works are needed to understand the effect of electrolyte composition on nitrate reduction to enable the efficient generation of ammonia using wastewater streams as those described above.

NO_3^- versus N_2 Reduction

An alternative strategy for electrocatalytic ammonia production is the electrochemical reduction of N_2 from air. To carry out this process, various heterogeneous electrocatalysts are currently being developed, though in general, the N_2 conversion is low due to the highly stable and apolar N_2 bond and the competing HER. At elevated temperatures (400–500°C), the FE of the reaction improves, but the rate of the reverse reaction increases, leading to ammonia decomposition. Upscaling of the process requires high FEs, which at the moment limits the industrial application of electrochemical ammonia production from N_2.[13]

While many studies focus on improving the N_2-to-NH_3 efficiency, a persistent problem with low-temperature electrochemical ammonia synthesis from N_2 is that the amount of ammonia produced is in general still very low, to the extent that the produced NH_3 cannot always clearly be attributed to nitrogen fixation but could also have evolved from nitrogen impurities present in the nitrogen gas stream or from ambient ammonia.[14] Therefore, extra caution is required in studies on electrochemical ammonia synthesis from dinitrogen, a problem that is less evident in ammonia production from nitrate, as the high rates exclude that impurities can make a significant contribution.

NO_3^- Reduction versus the Haber-Bosch Process

Nowadays, the Haber-Bosch process consumes approximately 500 kJ for the production of 1 mol ammonia.[15] This corresponds to the consumption of almost 4 kWh per kg of ammonia produced. It is interesting to compare this energy consumption to the catalysts from Table 1, especially the strained Ru nanoclusters catalyst, as Yu et al. report an electrocatalytic rate for ammonia production of 5.56 mol g_{cat}^{-1} h^{-1} for 100 h, which even outperforms the Haber-Bosch process.[6] For the production of 1 kg ammonia, the strained Ru nanoclusters catalyst requires approximately 22 kWh based on the cell voltage, partial current density, and production rate.

Table 2. Available Nitrate-Rich Wastewater Streams

Type of Wastewater	pH	Ions Present	Nitrate Concentration	Reference
Low-level nuclear wastewater	Alkaline	$NaNO_3$, $NaNO_2$, NaOH, $NaAl(OH)_4$, Na_2SO_4, Na_2CO_3, NaCl, NaF, Na_2SiO_3, Na_3PO_4, Na_2CrO_4, $NaB(C_6Hs)_4$, $Na_2\{Ru(NO(NO_2)_4(OH)\}$, $HgCl_2$	1.95 M	[9]
Industrial wastewater	pH 7.9	NO_3^-, NH_4^+, Cl^-	41.6 mM	[10]
Textile wastewater	pH 7	NO_3^-, Cl^-, COD	7.4 mM	[11]
Polluted ground water	Unknown	NO_3^-, NO_2^-, NH_4^+	0.88 - 1.26 mM	[12]

(Calculations based on a cell potential of 2 V and 100% FE, current density of 223.3 mA cm^{-2}, and ammonia production rate of 1.17 mmol h^{-1} cm^{-2}, see Li et al., 2020.[6])

For a rough estimation, it can be assumed that the price of electricity for electrocatalytic ammonia synthesis will constitute a large part of the overall expenses if nitrate-rich wastewater is (locally) available and the reaction takes place at room temperature. Based purely on electricity costs, the price of ammonium nitrate fertilizer produced by electrocatalytic nitrate conversion can easily be estimated in this way. Considering again the strained Ru nanoclusters catalyst with an energy consumption of 22 kWh per kilo ammonia, approximately 4.8 kWh are required for the production of 1 kg of NH_4NO_3. Based on the price of electricity in the Netherlands (€0.137/kWh), this results in production costs of approximately US $776/metric ton ammonium nitrate, investment and maintenance costs not included. This is close to the price of ammonium nitrate from the Haber-Bosch process sold in the US ($560/metric ton). Additionally, the production costs can easily be reduced by making use of locally produced electricity from renewable sources, like wind or solar energy, and local waste streams. In this way, the electrocatalytic ammonia synthesis might become an attractive alternative for the Haber-Bosch process.

In order to complete this analysis, other costs like supply, maintenance, material costs, separation, etc., play a big part in the final costs of both processes. It is likely that, even if nitrate-rich wastewater is locally available, the low concentration of nitrate in wastewater complicates the process, as well as the final separation of produced ammonia, and this increases the overall production costs. Unfortunately, it is difficult to include this in the comparison, as such costs for electrochemical ammonia synthesis have never been analyzed. Additionally, it is important to note that many reaction conditions used in Table 1 are still far from those required at an industrial level, and as always, one should be careful extrapolating promising lab results to large-scale applications.

Key Challenges

Recent studies on the conversion of nitrate to ammonia have opened up the field for an alternative, sustainable route for ammonia synthesis. Besides that this process does not depend on the use of fossil fuels and can be powered by renewable electricity, another advantage is that the reaction conditions of the conversion of nitrate allow the local production of ammonia. When decentralized, smaller-scale production can be realized, contributing to a more even distribution of ammonia over the world by providing better access to fertilizers in developing countries. Additionally, recent events have shown that storage of large quantities of ammonium nitrate comes with a serious risk, which can result in devastating explosions. The electrocatalytic process will contribute to significantly safer situations because it facilitates the production of fertilizer on demand, resulting in storage of smaller quantities of ammonium nitrate.

Though the field is still developing, promising results indicate that the electrocatalytic conversion of nitrate to ammonia will not be the bottleneck for the future implementation of this process. However, it is hard to predict the full potential of this process, as the concept of selectively producing ammonia electrochemically from nitrate is still very recent, while the Haber-Bosch process is a mature technology that has been studied extensively over more than a century, and nitrate reduction aiming at N_2 has been a matter of study for the last few decades. No data on the durability and performance of the catalysts in long-term electrolysis are available at the moment. It will be important that the reporting of performance parameters of newly developed catalysts including their characterization follow a consistent well-established protocol.

Another challenge that might arise at a large scale is the hydrogen that is produced as a side product during electrolysis. Large quantities form a safety issue, a problem that becomes prominent when the concentration of nitrate is low. It is likely that this hydrogen can be vented off in the atmosphere, but more research on the transition to practical operation is required.

Even if the catalytic performance is good, large volumes of wastewater need to be dealt with, resulting in the need of a large reactor and long reaction times. It is therefore hard to foresee if sufficient amounts of wastewater can be supplied. It is expected that concentration of nitrate prior to the reduction process will be necessary to avoid dealing with large volumes of wastewater, requiring further research. No studies on the large-scale treatment of real wastewater from different sources have been carried out yet, hampering predictions on what will be the most useful source of nitrate.

From the above discussion, it is clear that the renewed interest in nitrate reduction can contribute to the development of an alternative, sustainable production process for ammonia. From a first analysis, we find that the catalysts developed for the reduction of nitrate can compete with current technologies for electrochemical ammonia production, and a rough estimation suggests that the fertilizer price can compete with fertilizer produced in the Haber-Bosch process. Taken together, it should be emphasized that current literature lacks clear benchmarks and data on the practical application of the process. Additionally, for future research an analysis that considers the capital investment, the upkeep, wastewater supply, and product separation is required to fully address the feasibility of this process.

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