Effect of Electrolyte and Electrode Configuration on Cu-Catalyzed Nitric Oxide Reduction to Ammonia

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Reduction of nitric oxide was investigated using Cu electrodes in acid and neutral pH conditions. Analysis of Cu discs in stagnant electrolyte by Electrochemical Mass Spectrometry (EC-MS), revealed the favorable formation of ammonia (and hydrogen) in acidic electrolyte, while $N_2O$ and $N_2$ are formed in significant quantities at neutral conditions. Additional performance evaluation of Cu electrodes in hollow fiber geometry, was performed using 10 vol % NO in Ar supplied through the porous electrode structure and off-line determination of ammonia by $^1H$ NMR spectroscopy. The pH dependent performance of the Cu hollow fiber is in agreement with EC-MS data at low gas flow rates, showing the highest ammonia selectivity in acidic conditions. However, at relatively high gas flow rates, almost 90% faradaic efficiency and a $NH_3$ production rate of 400 $\mu$mol h$^{-1}$ cm$^{-2}$ were obtained in neutral electrolyte at $-0.6$ V vs RHE, likely due to enhanced availability of NO at the electrode surface, suppressing the hydrogen evolution reaction. This approach shows conversion of waste NO gas to valuable green fertilizer components is possible.

Introduction

Ammonia is an essential chemical for the production of fertilizers, and thus crucial for the global food supply. Currently, ammonia is predominantly produced by the energy intensive Haber-Bosch process,[1] leading to significant carbon dioxide emissions. Thus, non-conventional, potentially green ammonia synthesis routes are presently explored.[2,3] Compared to the traditional centralized production, emerging routes are of particular interest for small-scale, localized fertilizer production[2] and might additionally provide potential as energy storage technology.[3] Among other technologies, electrochemical synthesis appears to be of interest allowing for ammonia synthesis from abundant sources, i.e. nitrogen and water, at ambient conditions.[4] Yet, electrochemical ammonia synthesis from nitrogen is hampered by the stability of molecular $N_2$ and thus a low selectivity towards the desired product. In fact it appears to be difficult to produce ammonia at concentrations above adventitious $NH_3$ levels and false positive results can easily be obtained.[5–8]

Alternative feedstocks for ammonia synthesis are nitrogen oxides ($NO_x$), which are usually considered as pollutants.[9] Most studies concerning electrochemical conversion of $NO_x$ focus on selective reduction to $N_2$.[10] Only recently NO, utilization for ammonia production was reported.[11–15] Nitric oxide, one of the major air pollutants, is formed in various combustion processes.[16] Reduction of NO is thermodynamically favored over $N_2$ reduction, see for example eq. 1 to eq. 4.[8]

\[ \begin{align*}
2NO + 2H^+ + 2e^- &\rightleftharpoons N_2O + H_2O, E^0 = 1.59 \text{ V vs RHE} & (1) \\
2NO + 4H^+ + 4e^- &\rightleftharpoons N_2 + 2H_2O, E^0 = 1.68 \text{ V vs RHE} & (2) \\
2NO + 6H^+ + 6e^- &\rightleftharpoons 2NH_2OH, E^0 = 0.38 \text{ V vs RHE} & (3) \\
2NO + 10H^+ + 10e^- &\rightleftharpoons 2NH_3 + 2H_2O, E^0 = 0.71 \text{ V vs RHE} & (4)
\end{align*} \]

So far only a few materials have been proposed for electrochemical formation of ammonia from NO. Besides Bi, Au/\(C,[11]\) Ag,[17] and Fe[18] electrodes, copper was demonstrated to be a promising material for $NH_3$ formation by both theoretical and experimental investigations in neutral and alkaline conditions.[12,19–21] Using Cu foam electrodes, ammonia production rates of 517 $\mu$mol h$^{-1}$ cm$^{-2}$ (faradaic efficiencies of 93.5 %) were achieved in neutral pH electrolyte at $-0.9$ V vs RHE using a pure NO (100%) stream provided by sparging into the solution close to the electrode surface.[12] It is worth noting that NO feeds are usually not purified and thus higher nitrogen oxides[22] might be present in the feed, complicating a precise performance evaluation.

One of the big challenges associated with electrochemical conversion of NO to $NH_3$ is the low solubility of NO in aqueous electrolytes resulting in mass transport limitations and unfavor-
able conversion. Moreover, when considering NO utilization from combustion processes, any feasible process should be able to operate at relatively low NO concentration.\textsuperscript{[23]} Electrolyte engineering was proposed to overcome those limitations by using a Fe-based complex able to capture NO, thus increasing its concentration in the electrochemical cell.\textsuperscript{[17]} However, the presence of metal complexes in the electrolyte can be detrimental for direct application of the produced ammonia as green fertilizer.

Herein, we further explore the influence of the electrolyte composition on the performance of Cu electrodes using acid and neutral electrolytes and propose a non-conventional type of electrode geometry in the form of hollow fiber electrodes\textsuperscript{[24]} to minimize mass transport limitations in NO electroreduction to ammonia. While acidic conditions appear favorable to prevent formation of partially reduced products in mass transfer limited conditions, Cu-decorated Ti hollow fibers are shown to enable ammonia production at production rates of 400 μmol h\(^{-1}\) cm\(^{-2}\) (at −0.6 V vs RHE with almost 90% faradaic efficiency) using diluted nitric oxide streams (10% NO) in a flow-through configuration, and sodium sulphate as pH neutral electrolyte.

**Results and Discussion**

**EC-MS analysis of NO electroreduction on Cu**

As outlined, copper is one of the most promising electrode materials for ammonia synthesis from nitric oxide.\textsuperscript{[12]} To investigate the potential-dependent product formation during NO reduction in acidic and neutral electrolyte, EC-MS analysis was performed. CVs in the absence and presence of NO along with the corresponding MS analysis are shown in Figure 1 (reference measurements are provided in Figure S5).

In acid electrolyte (blue trace), hydrogen evolution was observed at −0.38 V, while in neutral conditions −0.55 V was required. This is in agreement with the sluggish kinetics of the HER in neutral electrolyte, caused by the required water dissociation step.\textsuperscript{[25,26]} In the presence of NO two reductive current maxima are clearly present, of which the first, depending on the electrolyte, has an onset potential of −0.1 V vs RHE in acidic, and at −0 V vs RHE in neutral conditions, respectively, maximizing at −0.1 V vs RHE independent of the electrolyte used. We assume this current response can be assigned to reduction of NO\(_2\), which is present in the feed due to insufficient purification of the NO used for the EC-MS experiments. A smaller, second minimum can be observed at −0.4 and −0.55 V, respectively in acid and neutral conditions. In addition, a limiting current plateau, likely associated with the transport limited reduction of NO, is revealed before hydrogen evolution occurs. The transport limitation of NO was additionally confirmed by rotating disc electrode measurements (Figure S6). Here, with increasing rotation rate an increase in current in the potential range of interest is observed, confirming that NO diffusion limitations must be minimized to achieve efficient ammonia formation by bulk electrolysis.

When scanning in the negative potential direction (light green domain in Figure 1b), mass spectrometry does not show any product formation in acidic conditions up to −0.4 V. This suggests that the current measured at −0.1 V should be assigned to the formation of surface adsorbed or liquid-dissolved products, such as NH\(_4\)\(^+\) (see also control experiments performed without NO in solution, Figure S5, where no products are detected besides H\(_2\) at the most negative potentials). Scanning in the negative potential direction in neutral conditions (Figure 1c) results in MS N\(_2\)O formation initiating at −0 V vs RHE, (m/z: 30 alongside with its m/z: 28 fragment of much lower intensity, referred to as the N\(_2\) signal in Figure 1c). This is in agreement with literature, showing FeNC catalysts to be more active for N\(_2\)O formation from NO at higher pH.\textsuperscript{[18]} Despite this agreement with literature, it should be mentioned that the reduction of NO\(_2\), usually a contaminant in NO,\textsuperscript{[27]} might also contribute to the formation of N\(_2\)O. At more negative potentials a decrease in N\(_2\)O signal is associated with an increase in N\(_2\) (m/z: 28), maximizing at −0.6 V vs RHE. Formation of N\(_2\) is initially in majority associated with the secondary reduction of N\(_2\)O, rather than primary reduction of NO.\textsuperscript{[28]} In fact, the sharp decrease in N\(_2\)O signal initiating at −0.4 V vs RHE in neutral electrolyte matches the onset of N\(_2\) formation. Moreover, we observe a drop in N\(_2\)O signal below the baseline level (see also Figure S7) at potentials where peak formation of N\(_2\) is observed, which suggests NO is likely contaminated with N\(_2\)O. Finally, in the last stages of the negative scan, close to the lower limit of the applied potential,

![Figure 1](https://doi.org/10.1002/celc.202101273)  
Figure 1. EC-MS measurements of NO electroreduction on a Cu disc. (a) Cyclic voltammetry curves (10 mV/s) and desorbed products in (b) 0.05 M H\(_2\)SO\(_4\) and (c) 0.05 M Na\(_2\)SO\(_4\). The green domains represent reductive scans, while the violet domains represent oxidative scans in the CV.
a secondary increase in \( N_2 \) signal suggests a minor contribution of direct NO reduction to \( N_2 \).

Interestingly, in the positive scan direction (see gray domains in Figures 1b and 1c), significantly more gaseous products are detected. In acid conditions a decrease of the signal associated with m/z 30 is observed, which corresponds to consumption of NO, agreeing with positive MS responses in \( N_2 \) (m/z: 28) and possibly \( NH_3 \) (m/z: 17). To the best of our knowledge \( NH_3 \) formation in acidic electrolyte in bulk electrolysis experiments has not yet been previously reported. The \( NH_3 \) MS signal shows a similar response in shape to the response of \( H_2 \), which is of much higher intensity. Due to the small EC-MS cell volume and relatively high reduction currents for \( H_2 \) evolution, a pH change induced by proton reduction might allow for partial transformation of \( NH_3 \) to \( NH_4^+ \) and thus allows for detection of ammonia. Note that m/z: 17 is only detected at highly negative potentials while \( NH_4^+ \) formation at more positive potentials should not be excluded, as shown by theory as well as experimental work. Further work is required to rule out any contribution of water to m/z 17, potentially changing in concentration during NO reduction (see eq. 1–4).

Although shifted by \(-0.2\) V, the product evolution in neutral conditions is quite similar to that observed in acid conditions. However, due to the higher current densities observed, acidic conditions seem to be more favorable for NO electroreduction to ammonia, in particular in conditions when NO supply is limited.

The results obtained by cyclic voltammetry are in good agreement with chronoamperometric data (Figure S8), where the onset of gaseous product formation is clearly observed, confirming that \( H_2 \) is being produced at \(-0.3\) V and \(-0.5\) V vs RHE in acidic and neutral electrolyte, respectively.

**NO electroreduction on Cu-Ti hollow fiber:**

**Cu-Ti electrode characterization**

As shown above by EC-MS and RDE experiments ammonia formation occurs on Cu electrodes, likely with the highest FE in acid conditions. Still mass transport limitations in NO (and local pH changes) influence the selectivity in conversion of NO. Hollow fiber electrodes allow for efficient supply of gaseous NO to the electrode surface, similar to widely-applied gas diffusion electrodes. Transport of liquid-dissolved species toward hollow fiber electrodes is, however, based on convection rather than diffusion. Cu-based hollow fiber electrodes were prepared to evaluate the effect of enhanced transport of NO on the faradic efficiency towards ammonia production.

In the hollow fiber electrode geometry gas is supplied from the inside of the tube. Due to the porous structure (Figure 2) and pore-filling with electrolyte, a pressure buildup in the electrode is observed. It is expected that only the outer part of the electrode is forming an electroactive three-phase boundary and thus only the outer surface of a Ti hollow fiber was modified with Cu. XRD patterns as well as SEM images of the prepared electrodes confirm successful decoration of Ti hollow fibers with metallic Cu (Figure 2). Moreover, SEM images of Cu–Ti electrodes reveal a uniform distribution of Cu on the Ti surface (Figure 2c and Figure S9). After modification with Cu, a narrowing of the pores of the electrode is noticeable (compare SEM of Ti electrode in Figure S10) due to the presence of smaller Cu particles. Additional confirmation of smaller pores is obtained by pore size distribution measurements (Figure 2d).

**The effect of NO supply methodology on current density**

Linear scan voltammetry was performed (Figure 3) in acidic and neutral pH electrolyte to investigate the influence of flow configurations and flow rates on the potential-current behavior of as-prepared Cu–Ti hollow fiber electrodes. In both electrolytes only a minor increase in current was observed when NO was supplied in flow-by configuration (dotted lines – for magnification in the active region see Figures S11 and S12), when compared to reference measurements performed in pure Ar flow. In agreement with the EC-MS data, the presence of NO results in a larger current enhancement in acidic environment, than in neutral conditions. When NO was supplied through the

![Figure 3. LSVs of Cu–Ti electrodes in flow-by and flow-through operation, at different NO flow rates in (a) 0.05 M HSO\(_4\) and (b) 0.05 M NaSO\(_4\). Note that the reductive current in pure Ar flow in 0.05 M HSO\(_4\), (Figure 3a) is assigned to SO\(_4^{2-}\) adsorption on the Cu electrode (see also Figure S14). Also note the difference in scale of current density in Figures 3(a) and 3(b).](image-url)
hollow fiber electrode (solid lines in Figure 3) at 5 mL min⁻¹ in acidic conditions (Figure 3a), a significant current enhancement associated with the presence of NO is observed, prior to the onset of hydrogen evolution, indicating that the NO concentration at the electrode-electrolyte interface is significantly increased and a limiting current density of ~8 mA cm⁻² is obtained. For feed gas compositions with higher NO concentration (Figure S13), even higher current densities were observed. Therefore, efficient transport of NO to the electrode surface in hollow fiber electrode configuration is demonstrated.

It is interesting to note that also unmodified Ti hollow fibers appear to be active for NO reduction (Figures S11 and S13). Still, compared to Cu–Ti electrodes, the significant cathodic shift in onset potential renders the use of bare Ti electrodes less useful for NO electroreduction. Moreover, based on previous reports, the selectivity for ammonia formation is expected to be higher for Cu-based electrodes.¹²

In neutral conditions the effect of applying 5 mL min⁻¹ of gas flow through the fiber is more dramatic (note the difference in scales of Figures 5a and b), leading to high current densities in NO reduction.

Since supplying NO through the electrode increases the current densities measured, the influence of gas flow rate was evaluated in both electrolyte compositions (Figure 3). A diffusion limited current of ~20 mA cm⁻² at highest flow rates is obtained at ~0.35 V for measurements in acidic electrolyte whereas the current plateau is only apparent for low flow rates of max. 5 mL min⁻¹ in neutral conditions and already exceeds ~50 mA cm⁻² at ~0.55 V.

In agreement with the measurements obtained by EC-MS two distinct potential regimes are identified in both electrolytes. The first regime in the potential window from 0 to ~−0.2 V vs RHE appears to be almost flow rate independent (see Figure S12 and S15 for magnification in acidic and neutral electrolyte respectively). Considering the similarities with the EC-MS measurements, the current is assigned to NO₂ reduction still being present in low quantities despite of careful NO purification²⁷ (see SI specifically S6 and S16 for additional information, also discussing the possible role of contamination of NO with NO₃⁻).²⁸

A second flow rate and electrolyte dependent current regime is observed in the potential range between ~0.2 V and ~5.0 V vs RHE, i.e. before hydrogen evolution occurs (~0.3 V vs RHE, compare also to EC-MS data) for measurements performed in acidic electrolyte. With increasing NO flow rate, as expected the limiting current increases. Considering that at flow rates above 30 mL/min the influence of flow rate becomes less relevant as shown in Figure S17, measurements at higher flow rates were not performed.

In neutral electrolyte, the onset of the potential window associated with flow induced NO reduction occurs at a significantly lower potential (below ~0.4 V vs RHE). Also the hydrogen evolution is again showing a shift in onset potential, in agreement with CVs measured using Cu discs (Figure 1a). Moreover, the observed current increase is predominantly related to enhanced NO availability at the electrode interface as also revealed by RDE experiments and measurements performed at high NO concentration. Particularly due to an inhomogeneous pore size distribution (Figure 2d), pore-opening depends on the actual flow rate, as a higher pressure (thus higher flow rate) is required to remove liquid from smaller pores. Thus, only at high flow rates an efficient formation of a three-phase boundary layer occurs (for a schematic representation of this phenomena see Figure S18). This is supported by capacitance measurements revealing a decrease in electrochemical surface area at higher flow rates (Figure S19) as well as decreasing intensity of the SO₄²⁻ adsorption peak in Ar saturated electrolyte (Figure S20).

The significant difference in current density between the electrolytes could be related to a change of the hydrogen surface coverage of the Cu surface, the general suppression of the hydrogen evolution in electrolytes of higher pH or possibly a change in reaction mechanism caused by a surface pH increase in neutral electrolyte, which can cause interaction of NO with OH⁻ forming NO₃⁻/NO₂⁻.²⁹ However, additional studies into the NO electroreduction mechanism on Cu surfaces are needed to fully resolve this behavior.

**Selectivity of NO electroreduction on the Cu-Ti hollow fiber**

Based on the obtained results the applicability of Cu–Ti hollow fiber electrodes for ammonia electrosynthesis from nitric oxide was studied using chronoamperometry in the relevant potential range of NO reduction, i.e. ~−0.1 to −0.6 V vs RHE in acidic and ~−0.1 to ~−0.6 V vs RHE in neutral electrolyte at varying gas flow rate. Faradaic efficiency and NH₃ production rate were determined over 60 min and 30 min of constant potential electrolysis for acidic and neutral electrolyte, respectively (Figure 4).

First, the data of Figure 4 can be compared to the EC-MS data. If one compares the FE in the absence of flow at the potentials applied in the EC-MS measurements, and for the hollow fiber electrode, the effect of the electrolyte appears consistent. In Figure 4e only 25%–40% FE is achieved in neutral conditions in flow-by mode (Figure 4e) or at low NO velocity (Figure 4c), while in acid conditions the FE is 60–80% in the potential range also investigated in the EC-MS (the remainder being formation of H₂). Despite the general decrease in FE at lower potentials, higher flow rates resulted in an overall increase in FE to ammonia as well as its production rate. This is assigned to opening of pores and the resulting favorable interaction of NO with the Cu surface. It is worth noting that a similar behavior was observed on Ti electrodes (Figure S21 and S22) but due to generally larger pores the effect is less pronounced. Considering the relatively low current densities in flow-through mode in acid conditions, the obtained production rates are relatively low and maximize at ~80 μmol h⁻¹ cm⁻². Note that significantly lower production rates are obtained in neutral conditions in flow by mode (Figure 4f), or at low gas velocities (Figure 4d) (see also Figure S23).

The low FE in neutral conditions is assigned to formation of either N₂O and N₂ (at more positive potentials) and H₂ (at more negative potentials) in agreement with EC-MS data. The general trend observed here for the product-potential dependency
matches well with literature[31] where N₂O is expected to be produced at more positive potentials and NH₃ at potentials < −0.1 V vs RHE. It is worth noting that minor quantities of hydroxylamine were detected (Figure S24 and S25).

Overall, an averaged faradaic efficiency of 85% was obtained inacid conditions, nevertheless the measurements suffered from stability of the electrode and a stable current was not maintained for extended periods of time (Figure S26a). In fact roughening of the electrode surface was observed by SEM (Figure S26b and c) and pressure changes in the hollow fiber throughout the measurement indicated copper corrosion/detachment (Figure S27).

The most striking result of Figure 4 is the significant effect of flow rate on the performance of the Cu–Ti electrodes inneutral conditions. The faradaic efficiency for NO reduction to ammonia reached almost 90% at −0.6 V vs RHE in flow-through mode (40 ml/min flow rate), with very little competing hydrogen evolution (compare to Figure S25b and c where combined faradaic efficiency of NH₃ and NH₂OH is shown). This translates in an ammonia production rate of ~400 μmol h⁻¹ cm⁻² (see Figure 4f). As previously stated, applying the increased flow rate, suppresses the formation of hydrogen due to enhanced availability of NO which is the main reason for increased FE to NH₃ compared to fiber operation in flow-by conditions. In addition, formation of N₂O and N₂ is also suppressed which could be related to a secondary effect of the increasing gas velocity, i.e. minimizing changes in pH due to convective mixing induced by the exiting gas bubbles. Moreover, for the Cu–Ti hollow fiber electrode stability was verified over the period tested, i.e. 30 min electrolysis (Figure S27, S28, S29 and associated description in the supplementary information).

The results obtained here are in fact comparable to recent reports using Cu foam electrodes.[12] Importantly, significantly lower concentrations of NO have been utilized in this study, i.e. 10% NO, being of relevance when considering NO utilization from combustion processes.

A detailed comparison of faradaic efficiency and production rate of NH₃ obtained by electrochemical reduction of NO and N₂ obtained in recent studies is shown in Figure 5. Although N₂ seems to be the most relevant feed for ammonia synthesis due to its abundancy, electrochemical NO reduction appears to be promising considering that the amount of produced ammonia significantly overcomes adventitious contamination. Using NO as a feed for electrochemical green ammonia synthesis is more facile than N₂ as long as decentralized production of ammonia at sites with NO waste streams is targeted. Despite the high faradaic efficiencies for ammonia formation from NO, the overall energy demand is still high. The well-established Haber-Bosch process requires approx. 10 kWh/kg of NH₃[33,34] which compared to results in this study is ~2 times lower (see Figure S30). However, it is worth noting that further improvements can be achieved. The benefit of ammonia formation in our system compared to present literature is due to the beneficial properties of our flow-through hollow fiber electrode compared to widely used flow-by systems. Moreover, lower NO concentrations were utilized while maintaining a high conversion rate. For practical application the electrochemical conversion of nitrogen oxides holds promise, as ammonia separation is not needed since the electrolyte has the potential to be used as green fertilizer directly after electrolysis.

Conclusion

The effect of electrolyte and electrode geometry for the reduction of nitric oxide to ammonia at low NO concentrations

![Figure 4. Selectivity in NO electroreduction to NH₃ using the Cu–Ti hollow fiber electrode. Faradaic efficiency and NH₃ production rate are shown in (a, b) for 0.05 M H₂SO₄ and in (c, d) for 0.05 M Na₂SO₄ electrolyte in flow-through electrode configuration. (e, f) Comparison of Faradaic efficiency and NH₃ production rate in flow-through (at 40 ml/min) and flow-by configuration in 0.05 M Na₂SO₄ electrolyte.

![Figure 5. NH₃ production rate vs faradaic efficiency on different catalysts in N₂ electroreduction compared to NO electroreduction in neutral electrolyte in this study. NO reduction data reproduced with modification from[33,34].](doi.org/10.1002/celc.202101273)
has been investigated using Cu electrodes. In mass transfer limited conditions, acid conditions favor the formation of ammonia, minimizing partial reduction of NO to N₂O and/or N₂. It is shown however that hollow fiber electrodes are very efficient to achieve a high reactant concentration at the electrode surface which significantly increases current density for conversion of NO to NH₃, in particular at neutral pH. Faradaic efficiencies of almost 90% with NH₃ production rates of 400 μmol h⁻¹ cm⁻² were obtained in neutral electrolyte at −0.6 V vs RHE in a flow-through system configuration. Importantly feed gases containing only 10% NO were used. It is expected that further improvements in NO conversion will be obtained by adjusting the surface distribution and morphology of Cu as well as the general pore size distribution.

**Experimental Section**

Ti hollow fibres (Figure S1a) were prepared by dry-wet spinning according to the previously reported method.[29] In brief, Ti powder was mixed with PES and NMP to form a homogeneous suspension. The spinning mixture was pressed through a spinneret with water as bore liquid. Fibers where thermally treated in order to remove the polymer and to form the metallic hollow fiber.

Cu–Ti fibers were prepared by air spraying of Cu-particle suspensions on as-prepared Ti hollow fibers. 40 mg of 1 μm Cu particles was dispersed in 2 ml of isopropanol and sprayed in three sequential steps using an air gun. During spraying a 5 cm long Ti fiber was rotated horizontally. Modified fibers were dried at 80 °C in-between every spraying step. A final layer using 25 nm Cu particles was included in the procedure to achieve a homogeneous surface coating. Finally, Cu–Ti fibers were thermally treated at 600 °C for 2 h in Ar atmosphere with 10 °C/min heating rate (see Figure S1b). Prepared electrodes were characterized using X-ray diffraction (XRD, Bruker Phaser D2) and Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive Xray Spectroscopy (EDS) (using a JSM-6010LA, JEOL system). The pore size distribution was measured by capillary flow porometry based on the liquid extrusion technique, using a Porolux 500 Porometer.

Hollow fiber electrode assemblies were prepared using silver epoxy glue to ensure electrical contacts to Swagelok stainless steel tube (Figure S1c). The assembly was covered with two-compartment adhesive glue to prevent either silver or the stainless steel tube to get in contact with the electrolyte. To ensure homogeneous distribution of NO through the fibers, the open-end of the fiber was also covered with adhesive.

All electrochemical measurements were carried out at room temperature using a BioLogic VSP potentiostat. A gas tight, H-type cell (Nafion 117 membrane for used for compartment separation) was used for linear scan voltammetry and chronoamperometry experiments. In addition to experiments with hollow fibers, rotating disc electrode measurements using Cu disc (Pine research, polished) were performed in 0.05 M H₂SO₄ (pH 1). A graphite rod and a Ag/AgCl (3 M NaCl, BASI) were used as counter and reference electrode, respectively. Measured potentials were converted to potentials vs RHE using:

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \, \text{pH} + E_{\text{Ag/AgCl}}^0 \]

The measured potentials were corrected for solution resistance (IR drop).

The cell was purged with Ar for 30 min to remove oxygen while cleaning the electrode (cyclic voltammetry, 50 cycles in the potential range of 0.35 to −0.75 V vs RHE). Afterwards the cell was purged with 10% NO in Ar for 30 min to achieve saturation of the electrolyte with NO. Electrochemical measurements were performed using gas flow rates as specified using either flow-through (gas flow through the hollow fiber electrode) or flow-by (gas was introduced through an external sparging line next to the hollow fiber electrode) conditions. A schematic representation of the reactant feed gas supply is shown in Figure S2c. Chronoamperometry experiments were performed for 1 h in acidic electrolyte and 30 min in neutral electrolyte to allow for sufficient accumulation of ammonia in the electrolyte and a reliable product detection. The electrochemical surface area of the hollow fiber electrodes for both gas feed configurations was estimated from capacitance measurements. To determine the capacitance, cyclic voltammetry in the capacitive potential region was performed at variable scan rates from 20 to 100 mV/s in Ar saturated 0.1 M HClO₄.

The concentration of ammonia was determined by ¹H NMR spectroscopy based on methods described elsewhere.[35,36] Calibration was performed using standard NH₃Cl solutions with known concentration. Generally 0.5 ml of the (standard) solution was mixed with 50 μl of 0.5 M H₂SO₄ containing 10 mM maleic acid (internal standard) and 25 μl of DMSO-d₆ as locking solvent. ¹H NMR spectra were recorded on a Bruker 400 MHz spectrometer with 1000 scans (Figure S3). The area ratio of the NH₃ peak at 6.79 ppm and the maleic acid peak at 6.22 ppm were plotted versus NH₃ concentration (see Figure S3c).

The hydroxylamine content was determined by gas chromatography according to a method published elsewhere.[37] In short, samples obtained after electrolysis were neutralized by addition of NaOH or H₂SO₄ solution. To allow for quantification, hydroxylamine was reacted with acetone to form acetone oxime by addition of 2 μl of methanol/acetonitrile (1:1 v/v) to 4 ml of neutralized sample solution. Acetone oxime was quantitatively detected by gas chromatography (GC-FID, see Figure S4a). Following the procedures described above, the calibration curve was prepared using standard solutions of hydroxylamine hydrochloride (Figure S4b). An quantification error of 5% was estimated based on the analytical techniques used.

Additionally, EC-MS measurements (SpectroInlets, Copenhagen, Denmark, Figure S2a) were employed to further elucidate the reduction of NO at Cu surfaces. He or NO (pure, unpurified) were used as carrier gas (1 ml/min). Ag/AgCl (sat. KCl, CH Instrument) and a Pt mesh were used as reference and counter electrode, respectively.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Copper · Electrochemistry · Green fertilizer · Hollow fiber electrodes · Nitric oxide

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