Electronic Supplementary Material (ESI) for Green Chemistry.


# Beyond Acceptable Limits: Intrinsic Contamination in Commercial $^{15}N_2$ Impede Reliable $N_2$ Reduction Experiments

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## Materials and Methods

High purity $^{14}N_2$ (≥99.999%) was obtained from Air Liquide (Alphagaz 2). Isotopically labelled $^{15}N_2$ was obtained from Merck (99.3 atom % $^{15}N$). Both gasses were used without any further purification. Low purity $^{14}N_2$ originated from the boil-off of an Air Liquide liquid $N_2$ tank.

Sulfuric acid (Sulfuric acid 96% Ultrapur, Supelco), Bismuth (powder, −100 mesh, 99% trace metals basis), Nafion perfluorinated resin solution (1100W, 5 wt.% in lower aliphatic alcohols), Ethanol (Uvasol®), potassium phosphate monobasic ($KH_2PO_4$, ACS reagent, ≥99.0%) and potassium phosphate dibasic ($K_2HPO_4$, reagent grade, ≥98.0%) were obtained from Merck (Sigma Aldrich) and used without any further purification. All solutions were prepared using ultrapure water.

Carbon paper (Toray Carbon Paper 060, Wet Proofed) was obtained from Fuel cell store (www.fuelcellstore.com). Nafion proton exchange membranes (Nafion 117) were obtained from Ion Power and soaked in ultrapure water for at least 24 hours prior to use.

## Gas sampling

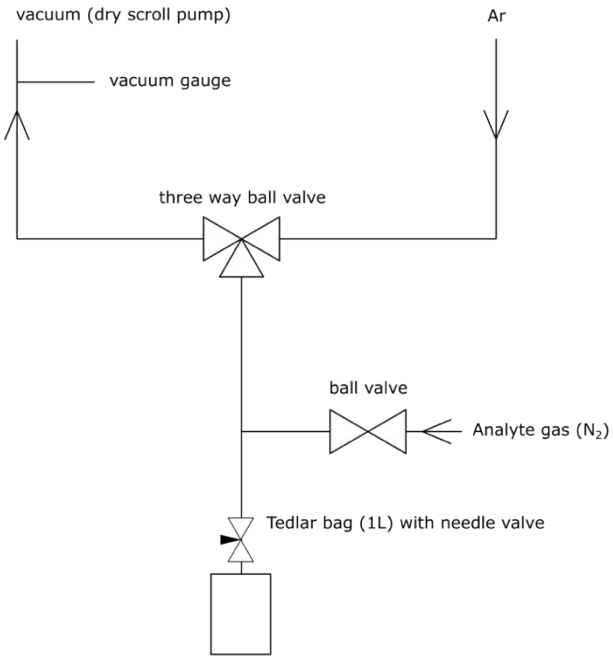
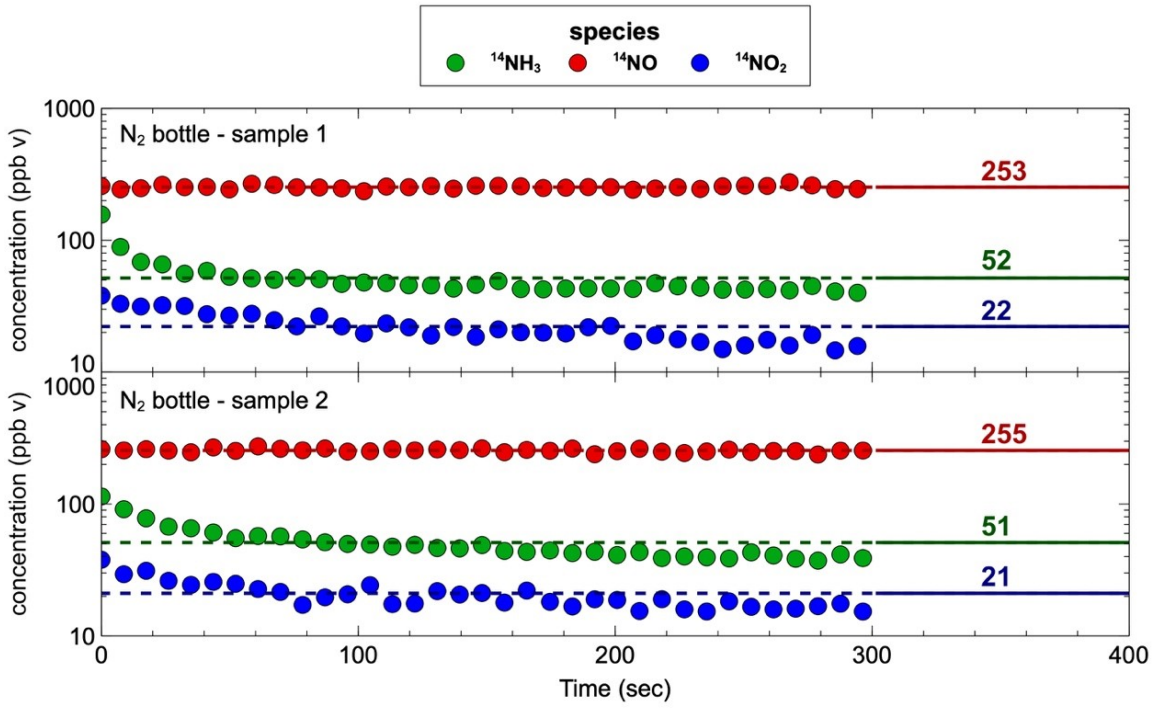



*Figure S1: custom setup used for evacuating, purging, and filling the sample bags. The analyte gas was fed to the Tedlar bag using 1/8" (OD) 316 stainless steel tubing (Swagelok). The dry scroll pump from Leybold was connected to the three way valve with ¼" (OD) 316 stainless steel tubing (Swagelok). All fittings and valves were also obtained from Swagelok and the system was leak tested before use. A Thyracont VSR53DL vacuum gauge was used to monitor the pressure during pump down and purge.*

Gaseous samples were collected in 1L Tedlar sample bags with single polypropylene fitting (MediSense, Netherlands). The sample bags were evacuated, purged with Ar and filled using a custom setup (fig 1.)

## SIFT-MS

SIFT-MS quantitative measurements were performed on a Syft Voice200ultra® (Syft Technologies Ltd., Christchurch, New Zealand). The gaseous samples were injected directly from the sample bags at a flowrate of 21.5mL/min. A Selected Ion Mode (SIM) scan method was constructed using LabSyft 1.6.2 software (SyftTM technologies). The m/z ratios of product ions, generated from the reaction of the analyte with reagent ions $H_3O^+$, $NO^+$ and $O_2^+$ were monitored. The scan time was fixed at 300ms, scan limit at 1000ms and a count limit of 10000 for each m/z was used. The analyte's concentration is calculated based on the obtained product concentrations.



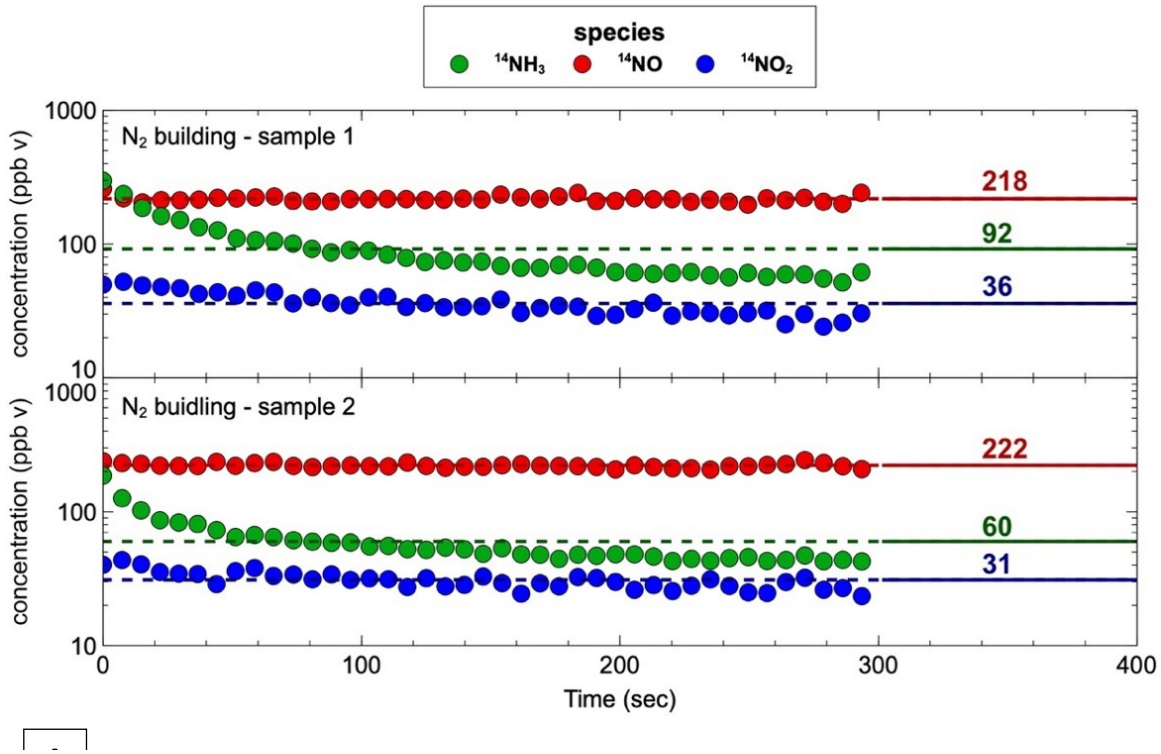




*Figure S2: mass spectrometry data for a) high purity $^{14}N_2$ samples (6N) and b) low purity $^{14}N_2$ samples (3N) , represented as an absolute concentration over a 300sec measurement. The solid lines and corresponding values indicate the average concentration (ppb, volumetric) over the entire measurement.*

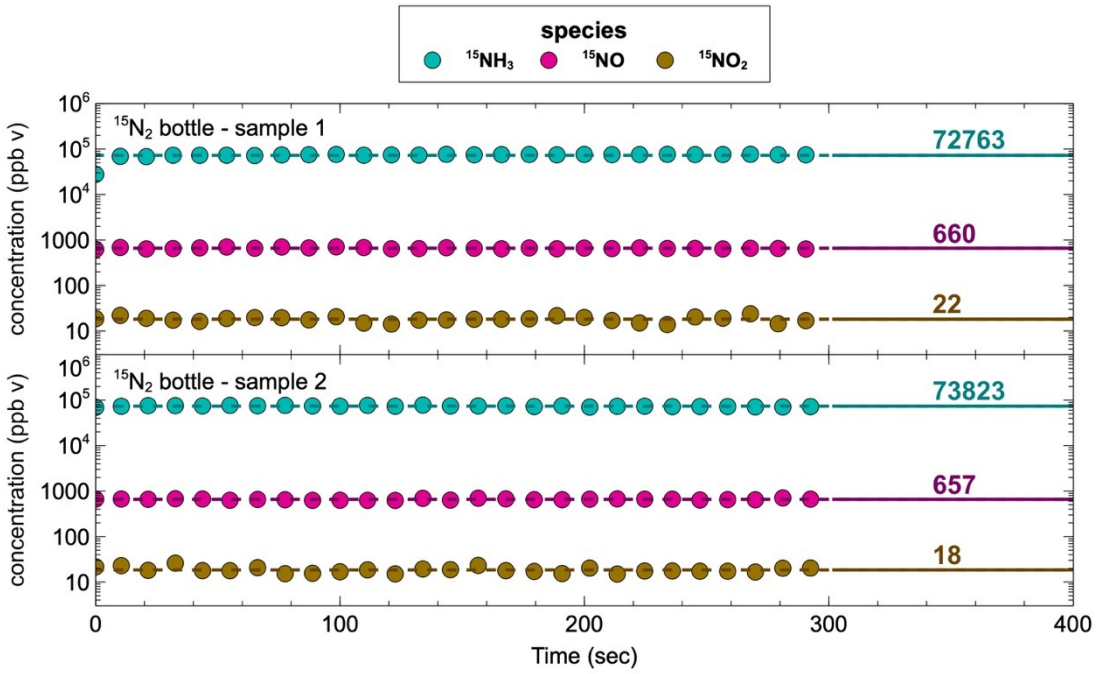



*Figure S3: mass spectrometry data for $^{15}N_2$ samples, represented as an absolute concentration over a 300sec measurement. The solid lines and corresponding values indicate the average concentration (ppb, volumetric) over the entire measurement.*

**Electrode preparation**

The working electrode was prepared by cutting a 2x2cm$^2$ piece of carbon cloth, connecting a 0,5mm$^2$ copper conductor (Lapp 4510141) to the back using conductive silver paste (RS PRO Silver Conductive Lacquer) and covering it with epoxy (Griffon, two component quick set epoxy) to prevent any contact

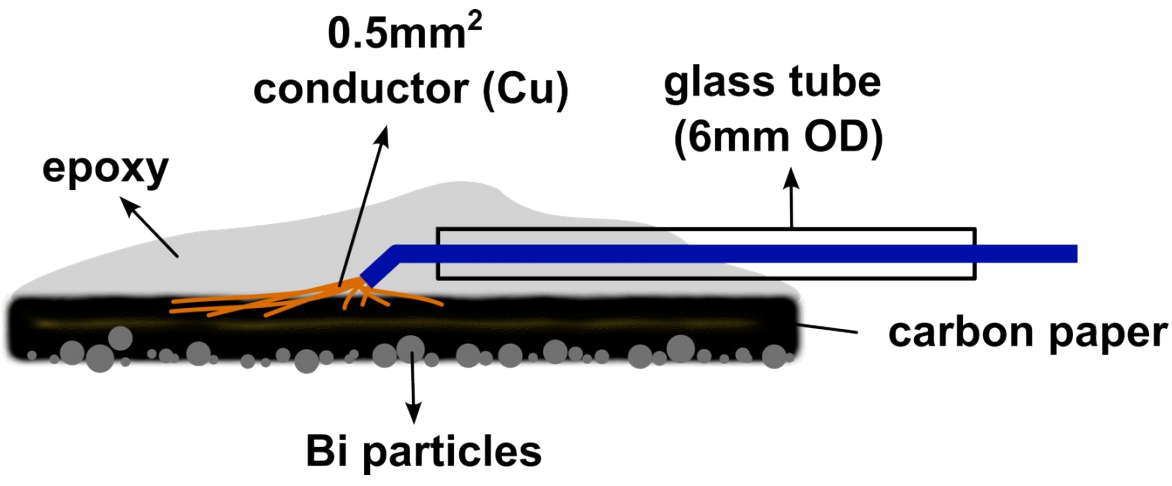



*Figure S4 illustration of a typical working electrode used for NRR experiments.*

between the silver paste and the electrolyte. The assembly was secured to a 6mm OD glass tube with epoxy to ensure a gas-tight seal.

Subsequently, an ink was made by weighing 40mg of bismuth particles and suspending them in a mixture of 1.8mL ethanol and 200 µl of a 5 wt.% Nafion solution. After sonification, the ink was carefully drop casted on the 4cm$^2$ carbon paper electrode and left to dry (Figure S4). Subsequently, the electrode was rinsed three times with ultrapure water and dried under a $N_2$ flow prior to use.

**Electrochemical experiments**

All electrochemical experiments were carried out on a BioLogic VMP-300 potentiostat. A custom electrochemical cell was made from borosilicate glass; the cathode compartment housing the working electrode and a Ag/Ag$^+$ (3M KCl sat. with AgCl) reference electrode with double junction (Prosene QM713X-8x100). The anode compartment housed a 50x50mm$^2$ mixed metal oxide mesh (Ti-shop) for water oxidation. A custom PEEK holder was made which houses a Nafion 117 proton exchange membrane (Ion Power) to separate the anode from cathode compartment.

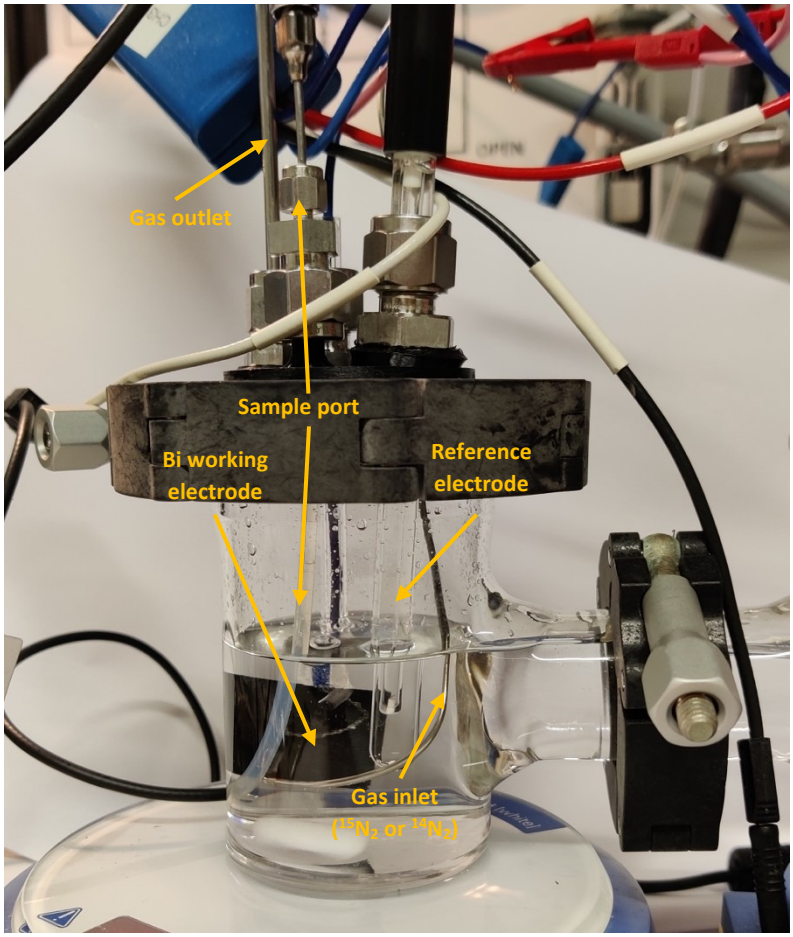



*Figure S5a Side view from the custom electrochemical H-cell showing the working and reference electrodes, the gas inlet (1/16 stainless tubing) close to the working electrode, sample port and gas outlet, inside the cathode compartment filled with 100mL electrolyte.*

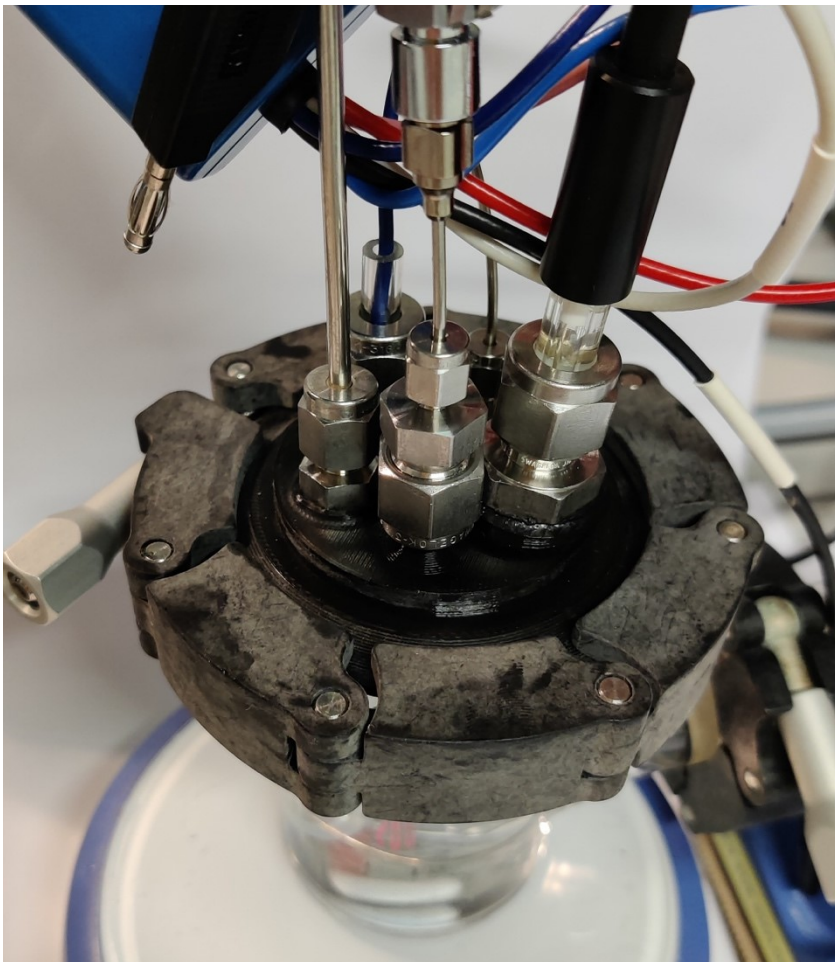


*Figure S5b Top view showing the lid of the custom electrochemical cell for NRR experiments. All feedthroughs and inserts were made with stainless steel Swagelok compression fittings to ensure a fully gastight setup.*

The gasses ($^{15}N_2$, $^{14}N_2$) were fed to the cathode compartment of the cell by 316 SS tubing (1/16" OD). The flow was set by an Agilent mass flow controller (controlled via FlowVision). All feedthroughs were made gastight using 316 SS compression fittings (Swagelok). A bubbler containing 15mL 0.1M $H_2SO_4$ solution was attached to the gas outlet to trap any ammonia leaving the cell as well as prevent diffusion of contaminants into the cell.

The cathode and anode compartment contained 50mL of phosphate buffer (1M at pH=6,5) which was purged for one hour with the reagent gas at 100mL/min for $^{14}N_2$ and at 10mL/min for $^{15}N_2$. During the reaction, the flow was set at 20mL/min for both $^{14}N_2$ and $^{15}N_2$ experiments.

The applied potentials were corrected for Ohmic drop using the current interrupt method (J=2,5mA/cm$^2$). The uncompensated resistance was compensated at 80% for every experiment. The measured uncompensated resistance (Ru) and applied compensation (Rc) are given below:

*Table S1 Measured uncompensated resistances (Ru) and the applied compensations (Rc) in different conditions. This table presents Ru and Rc values obtained in Ar, $^{14}N_2$ and $^{15}N_2$ saturated electrolytes, as determined using the current interrupt method.*

| | Ru (Ohm) | Rc (Ohm) |
|---|---|---|
| Ar | 3,052 | 2,441 |
| $^{14}N_2$ | 2,686 | 2,148 |
| $^{15}N_2$ | 2,658 | 2,126 |

The applied potentials were subsequently converted from the Ag/Ag$^+$ standard to the reversible hydrogen electrode (RHE) by using following equation:

$$E(V \text{ vs RHE}) = E(V \text{ vs Ag/Ag+ 3M KCl}) + 0{,}210V + 0{,}059*pH$$

The chronoamperometric experiments were performed at -0.91V vs RHE (-1.5V vs Ag/Ag+) for four hours while taking 1mL samples of the cathode electrolyte every 30 minutes. The acid trap was sampled before and after each experiment.

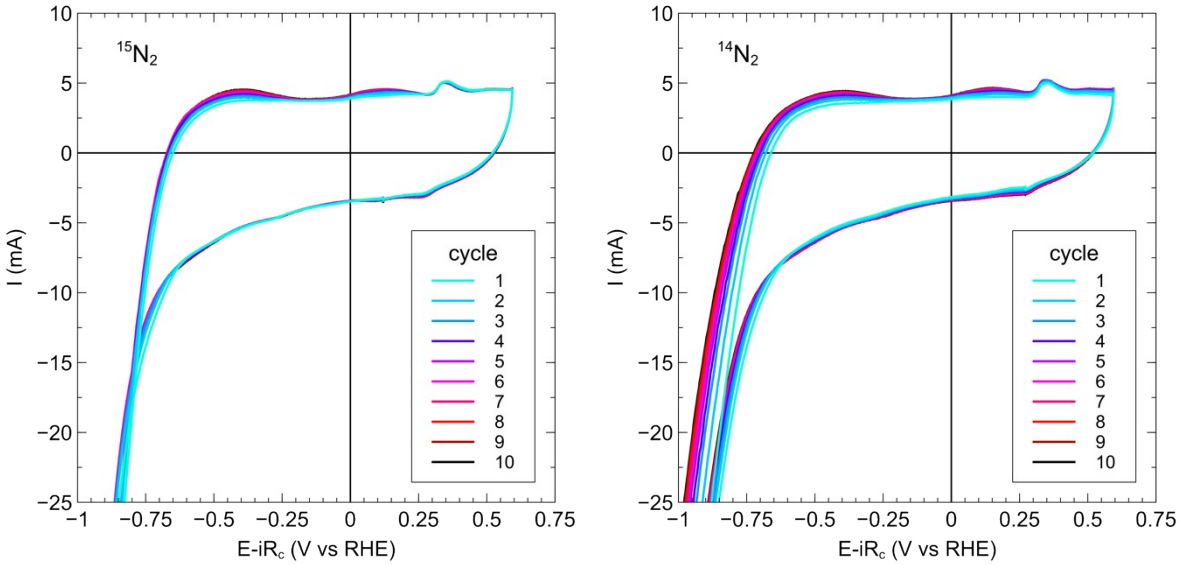



*Figure S6: Cyclic voltammograms of as-prepared bismuth cathodes. The reductive and oxidative peaks at 0.27 and 0.34V vs RHE are likely due to the Bi(0)/Bi(III) redox couple. A clear onset of the hydrogen evolution is observed at potentials below -0.75V vs RHE.*

**Ammonium quantification**

The quantification of ammonium was performed on a Metrohm Eco IC equipped with a Metrosep C Supp 2 250/4 column. Samples were diluted 10x prior to injection and injected automatically via a 863 compact autosampler; a 20µl loop was used. The peak areas were integrated, and corresponding concentrations were calculated based on the calibration curve using the MagIC software by Metrohm. For the calibration curve, a total of six standards were prepared from a 1000mg/l standard solution of $NH_4Cl$ (TraceCERT®, 1000 mg/L $NH_4^+$ in water). The ammonium peak is expected around 10min elution time. The calibration curve was fitted with a linear regression line.

*Table S2 Ammonium concentrations and corresponding integrated peak areas for calibration curve construction. This table lists the aqueous concentrations of various ammonium standards alongside their integrated peak areas, which were utilized to establish the calibration curve.*

| Standard | cNH4+ (µg/l) | Integrated peak area (µS/cm*min) |
|---|---|---|
| 1 | 10 | 0,004226 |
| 2 | 20 | 0,007837 |

| | | |
|---|---|---|
| 3 | 50 | 0,010747 |
| 4 | 100 | 0,022024 |
| 5 | 200 | 0,044619 |
| 6 | 500 | 0,116090 |

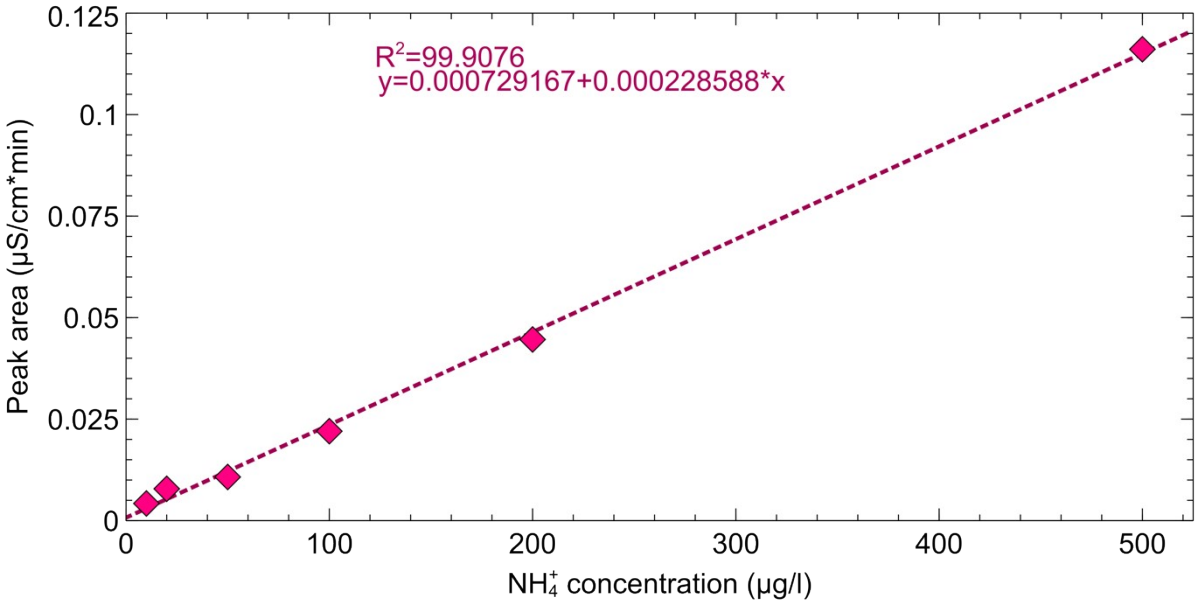



*Figure S7 Calibration curve for ammonia quantification in NRR experiments*

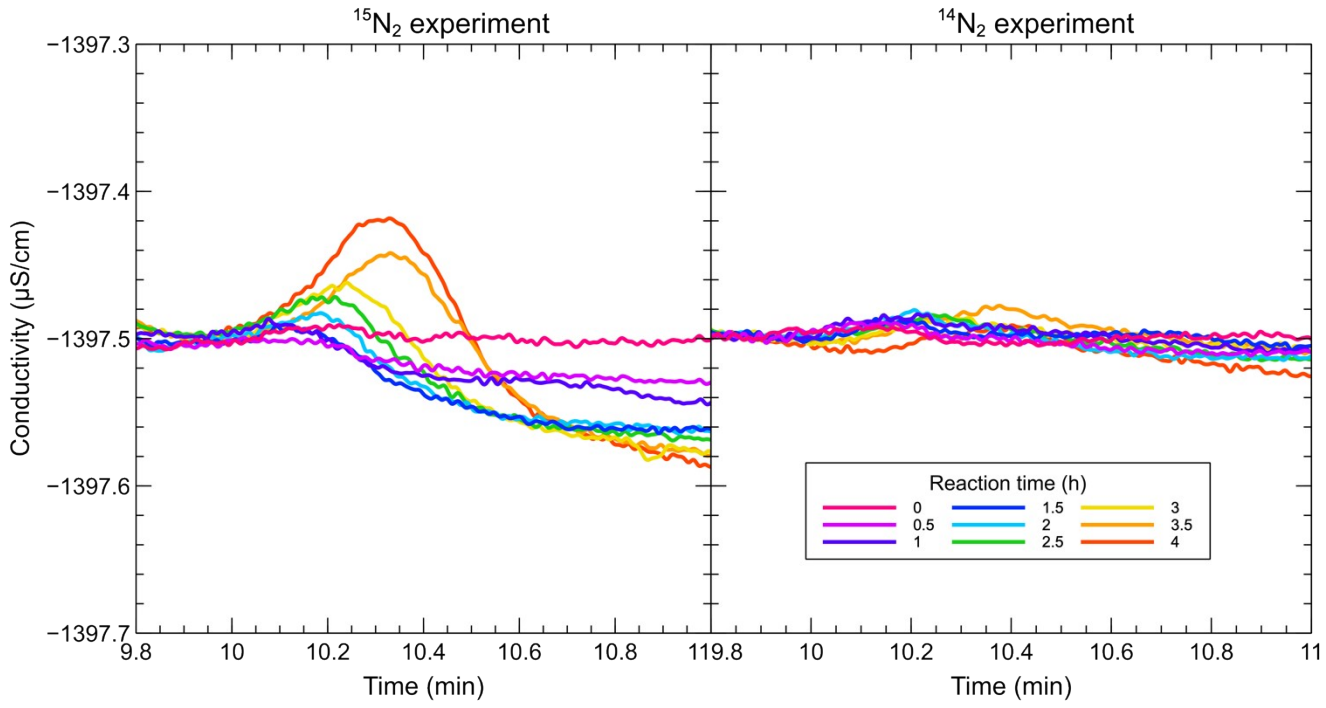



*Figure S8: Chromatograms from $^{15}N_2$ and $^{14}N_2$ NRR experiments.*

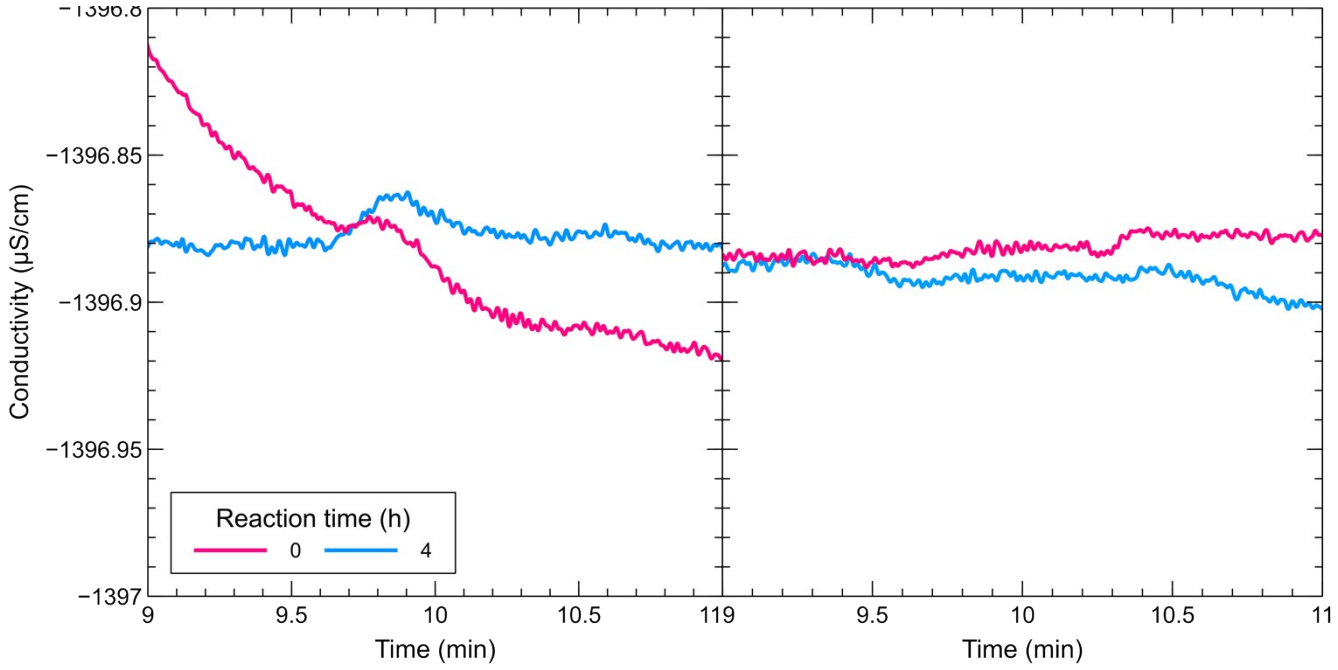



*Figure S9: Chromatograms obtained from the sampling the acid trap before and after each NRR experiment. It highlights the slight increase in ammonium content observed in the $^{15}N_2$ experiment, in contrast to the ammonium content in the $^{14}N_2$ samples which remained below the detection limit of the method.*

| 15N2 cathode | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sample | Time (h) | sample volume (ml) | measured NH4+ concentraion (µg/l) | NH4+ concentraion after dilution (µg/l) | NH4+ in sample (µmole) | Cathode volume (ml) | total #NH4+ in cell (µmole) |
| 1 | 0 | 1 | *0* | *0* | 0,00000 | 100 | 0,00 |
| 2 | 0,5 | 1 | *0* | *0* | 0,00000 | 99 | 0,00 |
| 3 | 1 | 1 | *27,693* | *2,7693* | 0,00154 | 98 | 0,15 |
| 4 | 1,5 | 1 | *278,585* | *27,8585* | 0,01548 | 97 | 1,50 |
| 5 | 2 | 1 | *489,234* | *48,9234* | 0,02718 | 96 | 2,63 |
| 6 | 2,5 | 1 | *428,825* | *42,8825* | 0,02382 | 95 | 2,31 |
| 7 | 3 | 1 | *812,174* | *81,2174* | 0,04512 | 94 | 4,31 |
| 8 | 3,5 | 1 | *1193,216* | *119,3216* | 0,06629 | 93 | 6,28 |
| 9 | 4 | 1 | *1648,702* | *164,8702* | 0,09159 | 92 | 8,61 |
| **14N2 cathode** | | | | | | | |
| Sample | Time (h) | sample volume (ml) | measured NH4+ concentraion (µg/l) | NH4+ concentraion after dilution (µg/l) | NH4+ in sample (µmole) | Cathode volume (ml) | total #NH4+ in cell (µmole) |
| 1 | 0 | 1 | *0* | *0* | 0 | 100 | 0,00 |
| 2 | 0,5 | 1 | *0* | *0* | 0,00000 | 99 | 0,00 |
| 3 | 1 | 1 | *72,314* | *7,2314* | 0,00402 | 98 | 0,39 |
| 4 | 1,5 | 1 | *0* | *0* | 0,00000 | 97 | 0,00 |
| 5 | 2 | 1 | *109,431* | *10,9431* | 0,00608 | 96 | 0,59 |
| 6 | 2,5 | 1 | *120,527* | *12,0527* | 0,00670 | 95 | 0,65 |
| 7 | 3 | 1 | *127,466* | *12,7466* | 0,00708 | 94 | 0,68 |
| 8 | 3,5 | 1 | *104,963* | *10,4963* | 0,00583 | 93 | 0,57 |
| 9 | 4 | 1 | *126,822* | *12,6822* | 0,00705 | 92 | 0,68 |

*Table S3: Summary of the measured ammonium concentrations and calculated ammonia yields. A recorded concentration of zero indicates that the ammonium level in the sample was below the detection limit of our method.*

| 15N2 acid trap | | | | | | | calculated production rate (mole/s) |
|---|---|---|---|---|---|---|---|
| Sample | Time (h) | sample volume (ml) | measured NH4+ concentraion (µg/l) | NH4+ in sample (µmole) | Volume (ml) | total #NH4+ in cell (µmole) | 6,05E-10 |
| 1 | 0 | 1 | *6,96* | 0 | 15 | 0,005800 | |
| 2 | 4 | 1 | *152,247* | 0 | 14 | 0,118801 | |
| **14N2 acid trap** | | | | | | | **calculated production rate (mole/s)** |
| Sample | Time (h) | sample volume (ml) | measured NH4+ concentraion (µg/l) | NH4+ in sample (µmole) | Volume (ml) | total #NH4+ in cell (µmole) | 4,70769E-11 |
| 1 | 0 | 1 | *0* | 0 | 15 | 0,00 | |
| 2 | 4 | 1 | *0* | 0 | 14 | 0,00 | |

*Table S4 Overview of the measured ammonium levels in the acid traps for the $^{14}N_2$ and $^{15}N_2$ experiments and the calculated overall production rate.*