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Beyond acceptable limits: intrinsic contamination in commercial $^{15}N_2$ impedes reliable N_2 reduction experiments†

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The validity of N_2 reduction experiments relies on control experiments with isotopically labeled $^{15}N_2$. Here we discovered significant $^{15}NH_3$ contamination (73 ppm) in commercial $^{15}N_2$ and also observed the prescence of oxidized ^{15}N in amounts comparable to the typical reported ammonia yields.

Introduction

The Haber–Bosch (HB) process, with its high carbon intensity (4.21 tCO_2/tNH_3), accounts for about 1.3% of the world's CO_2 emissions through the production of ammonia.[1,2] Over the past few years, various alternative synthesis routes for ammonia have been proposed. Amongst them is the direct nitrogen reduction reaction (NRR) in aqueous conditions (eqn (3)). This approach omits the use of a carbon-based hydrogen source and can operate at pressures and temperatures close to ambient. However, irrefutable experimental evidence for actual (photo)electrochemical ammonia formation at the cathode is typically elusive, this is mainly due to the extremely low reported ammonia production rates (10^{-12}–10^{-9} mol s^{-1}). Moreover, the omnipresence of reactive nitrogen species, which are more easily converted to ammonia than the extremely stable dinitrogen, has led to concerns about false positives in many studies. In response, validation strategies as well as rigorous experimental protocols have been implemented. While most studies stress the use of high-purity reagents, blank tests, controls, *etc.*, the cornerstone of NRR validation lies in the use of isotopically labelled nitrogen gas ($^{15}N_2$). Detection of $^{15}NH_3$ post reaction is typically taken as an indicator of NRR occurrence. However, until now, there has been a lack of comprehensive information regarding the purity of commercial $^{15}N_2$ gas, and the impact of activated, ^{15}N labelled impurities on the measured ammonia yield. Furthermore, there is a notable absence of precise, quantitative comparison between NRR experiments conducted under $^{14}N_2$ and $^{15}N_2$.

False positives and contaminants in the $^{14}N_2$ feed gas

In a typical electrochemical NRR experiment, nitrogen gas is bubbled through the cathode compartments' aqueous electrolyte solution, where it serves as nitrogen source to generate ammonia. Depending on the pH, either gaseous NH_3 or dissolved NH_4^+ is formed (eqn (1.1) and (1.2)). The required protons originate from the oxidation of water, conducted in a separate anode compartment (eqn (2.1) and (2.2)). The cathode's production rate and selectivity are typically determined by quantifying the ammonia yield over the course of a few hours.

Cathode:
pH = 0

$$N_2\ (g) + 6e^- + 8H^+\ (aq) \rightarrow 2NH_4^+\ (aq) \quad E^\circ = +0.275\ V \tag{1.1}$$

pH = 14

$$N_2\ (g) + 6e^- + 6H_2O\ (l) \rightarrow 2NH_3\ (g) + 6OH^-(aq) \quad E^\circ = -0.772\ V \tag{1.2}$$

Anode:
pH = 0

$$2H_2O\ (l) \rightarrow O_2\ (g) + 4e^- + 4H^+(aq) \quad E^\circ = -1.229\ V \tag{2.1}$$

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† Electronic supplementary information (ESI) available: Materials and methods, technical drawing of the custom setup and obtained SIFT-MS data. See DOI: **https://doi.org/10.1039/d3gc04272c**

pH = 14

$$4OH^-(aq) \rightarrow O_2\ (g) + 4e^- + 2H_2O\ (l) \quad E^\circ = -0.401\ V \quad (2.2)$$

Overall:

$$2N_2\ (g) + 6\ H_2O\ (l) \rightarrow 4\ NH_3 + 3\ O_2 \quad E^\circ_{cell} = -1.17\ V \quad (3)$$

Considering that the reported ammonia production rates are typically small (10^{-12}–10^{-9} mol s^{-1} cm^{-2} of cathode), the challenge lies in verifying that the measured ammonia indeed originates from N_2 reduction and not from more easily reducible, activated nitrogen species such as NO_3^-, NO_2^-, NO, NO_2, NH_2OH, *etc*. These latter species are often found as contaminants in the reaction system, for instance, being inherently present in the electrolytes, catalyst materials and/or the feed gasses.[3,4] While the concentration of these activated nitrogen species in the reaction system can be reduced, they cannot be entirely eliminated. Notably, even under optimal conditions, their amounts match typical ammonia yields.

A key distinction exists between oxidized nitrogen species like NO_3^- or NO_x and NH_3/NH_4^+. While background levels of NH_3 (g) and NH_4^+ (aq.) in the experimental setup can be factored in *via* blank tests and careful analysis of the reagents and electrodes, identifying contributions from oxidized nitrogen species poses a more significant challenge. Moreover, the ubiquitous and heavily fluctuating presence of ammonia in the atmosphere and on labware, complicate the accurate quantification of a background level.[5–7]

One contamination source of oxidized nitrogen species is the feed gas. Our mass spectrometry results (ESI Fig. 2a†) reveal that a commercial, high-purity (N6) $^{14}N_2$ gas cylinder contains approximately 52 ppb of $^{14}NH_3$, 254 ppb of ^{14}NO, and 22 ppb of $^{14}NO_2$ (Table 1). The $^{14}NO_x$ and $^{14}NH_3$ contamination levels found in a lower purity (N3) $^{14}N_2$ gas was found to be comparable and in the same order of magnitude as the 220 ppb of $^{14}N_2O$ reported previously by Choi *et al.* in N5 purity $^{14}N_2$.[5] In these feed gasses, the background level of ammonia is approximately 5–6 times lower than the total amount of oxidized nitrogen species. For typical NRR experiments with $^{14}N_2$ feed gas flowing through the cell at 100 ml min^{-1}, the total amount of oxidized nitrogen species introduced from high purity $^{14}N_2$ gas (N6) can be expected in the order of 10^{-11}mol cm^{-2} s^{-1} (for a cathode of 1 cm^2). As this molar flux of contaminants matches the ammonia production rate of many reported electrocatalysts, it is important to consider that reduction of contaminants in the feed gas alone could potentially account for the entire ammonia output, overshadowing the reduction of N_2.

The credibility of a given NRR study is primarily based on the ammonia production rate of the cathode. Consequently, thresholds to determine the plausibility of electrochemical NRR have been suggested by Choi *et al.*[5] Given typical contamination levels, electrodes exhibiting production rates lower than 10^{-10} mol cm^{-2} s^{-1} are not considered promising, while promising NRR experiments should present ammonia production rate exceeding 10^{-8} mol cm^{-2} s^{-1}. Taking this threshold and the above mentioned feed-gas contaminant quantification into account; at modest flow rates, the risk of measuring false positives due to contaminated feed gas is rather limited if high purity (N6) $^{14}N_2$ gas is used. Obviously, this needs to be assessed for each individual case and researchers should always establish background contamination levels prior to performing NRR experiments.

Contamination levels of commercial $^{15}N_2$ gas

While the contamination level in high-purity (N6) $^{14}N_2$ gas is relatively minor compared to the literature-reported ammonia production thresholds, contamination in the form of NH_3/NH_4^+ and oxidized nitrogen (^{14}N) species such as NO_3^-, NO_2^-, NH_2OH, *etc*., present in the used electrolytes, chemicals, and labware is significantly higher – orders of magnitude above the threshold for plausible NRR. As an example, Li *et al.* measured a NO_3^- concentration of 11 ppm in an aqueous 0.5 M Li_2SO_4 electrolyte solution.[7] Distinctly separating the reduction of these contaminants to ammonia from the NRR proves even more challenging than eliminating the contribution of background NH_3/NH_4^+ in the system. As a consequence, adopting isotopically labelled N_2 gas ($^{15}N_2$) and subsequent quantification of the produced $^{15}NH_3$ has been proposed as a valid strategy to confirm ammonia production truly originates from N_2.[5,8] By switching to $^{15}N_2$ feed gas, the interference of previously mentioned contaminants decreases sub-

Table 1 Absolute concentrations of NH_3, NO and NO_2 in commercially obtained high purity (N6) and low purity (N3) $^{14}N_2$ gas as well as $^{15}N_2$ (≥98 at%), determined by SIFT-MS

	Background NH_3	Oxidized nitrogen species		
	$^{14}NH_3$ (ppb)	^{14}NO (ppb)	$^{14}NO_2$ (ppb)	$^{14}N_2O$ (ppb)
$^{14}N_2$ (N6 purity)	52	254	22	220[a]
$^{14}N_2$ (N3 purity)	76	220	34	NA
	$^{15}NH_3$ (ppb)	^{15}NO (ppb)	$^{15}NO_2$ (ppb)	$^{15}N_2O$ (ppb)
$^{15}N_2$ (98 at%)	73 293	659	20	230[a]

[a] N_2O concentration reported by Choi *et al.* for commercially obtained $^{14}N_2$ (N5) and $^{15}N_2$ (N3).

stantially, as the natural abundance of the ^{15}N isotope is only 0.33–0.42%.[9]

Previous research by Choi and Dabundo pointed out the existence of contaminants such as $^{15}NO_x$ in commercial $^{15}N_2$ gas. However, these studies were limited in their capability to provide precise quantifications of ^{15}N labelled contaminants.[10] Dabundo's approach relied on indirect means of measurement, identifying the presence but not the exact amounts of reactive ^{15}N species in the gas.[10] In contrast, our study employs mass spectrometry to explicitly quantify both oxidized ^{15}N species (^{15}NO and $^{15}NO_2$) and $^{15}NH_3$ in the gas phase. Alarmingly, our findings show that commercial $^{15}N_2$ is considerably contaminated with $^{15}NH_3$ (Table 1, ESI Fig. 3†) (approx. 73 ppm), consistent with dissolved $^{15}NH_4^+$ concentrations reported by Dabundo (34–1900 ppm). Herein lies a profound risk of measuring false positives: using as-obtained $^{15}N_2$ gas bubbled at a 100 ml min^{-1} flow rate either during the pre-experimental electrolyte saturation step or consistently throughout the entire experiment introduces sufficient $^{15}NH_3$ to account for an apparent ammonia yield of approximately 1×10^{-8} mol s^{-1}. This exceeds most reported ammonia production rates by factors of 100–1000. It is important to note that despite the evident risks, many recent NRR studies continue to use unpurified $^{15}N_2$, even though pre-experimental gas purification has been suggested.[5,8,11–13]

NRR experiments using $^{15}N_2$ and $^{14}N_2$

To effectively demonstrate the impact of ^{15}N labelled impurities on the reported ammonia yield, we conducted NRR experiments at a constant potential (−0.91 V *vs.* RHE), using bismuth, reportedly a highly active element for N_2 reduction, as cathode.[14] We performed two sets of experiments under $^{14}N_2$ and $^{15}N_2$ saturated conditions (Fig. 1). Regularly sampling the catholyte revealed a measurable increase in ammonium content in the $^{15}N_2$ experiment. Specifically, after four hours, the $^{15}N_2$ experiment showed 8.6 μmol of NH_4^+, compared to only 0.68 μmol NH_4^+ in the $^{14}N_2$ experiment (Fig. 2). This result clearly demonstrates that when using unpurified $^{15}N_2$ even at low flow rates (20 mL min^{-1}), a considerable amount of ammonia will be detected, primarily originating from the ^{15}N labelled impurities rather than from the direct reduction of $^{15}N_2$. If the $^{15}N_2$ contamination were overlooked, an apparent ammonia yield of 6×10^{-10} mol s^{-1} would be calculated for the $^{15}N_2$ experiment. This figure is over ten times higher than the ammonia yield (5×10^{-11} mol s^{-1}) of the same experiment under $^{14}N_2$.

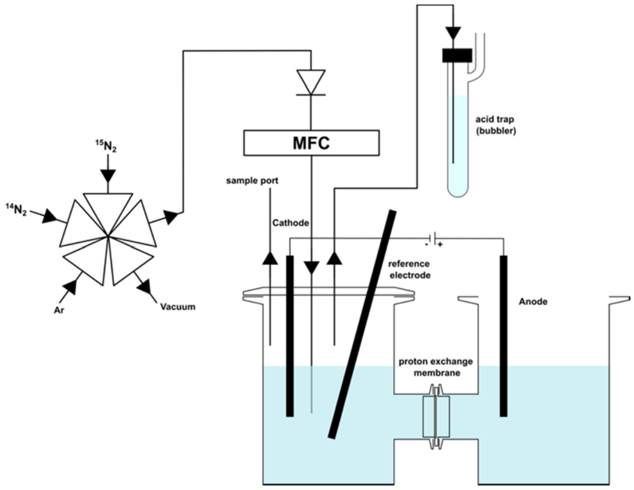

Fig. 1 Schematic representation of the setup used for studying the NRR under $^{14}N_2$ or $^{15}N_2$ atmospheres. NRR experiments were conducted in an H-cell configuration. Feed gases ($^{14}N_2$ and $^{15}N_2$) were continuously bubbled into the cathode compartment at a predefined flow rate of 20 mL min^{-1}. An acid trap was employed at the exit to completely isolate the cathode compartment from the surrounding atmosphere and to trap any gaseous ammonia.

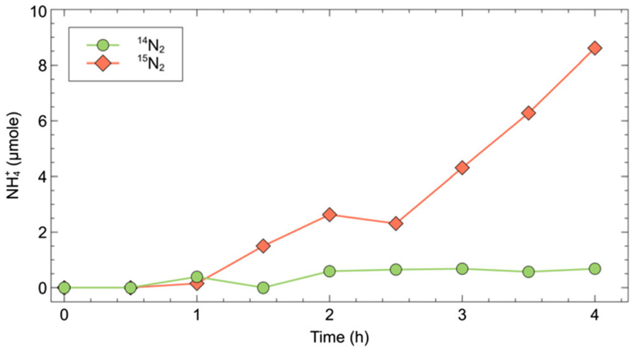

Fig. 2 Cumulative ammonium production ($^{15}NH_4^+$ or $^{14}NH_4^+$) in a four hour NRR experiment with a Bismuth cathode.

Mitigation strategies for the ^{15}N contaminants

Our precise quantification reveals that the level of oxidized ^{15}N species in this gas is nearly three times higher than in both high (N6) and low purity (N3) $^{14}N_2$ gases, exacerbating the risk of false positives in control experiments. Purifying commercial $^{15}N_2$ gas, which comes in extremely limited volumes of 500–1000 cc at 1 to 5 atm, presents significant technical and economic challenges for NRR research. Traditional methods for purification, such as bulky, home-made scrubbers or acid traps, are neither practical nor effective in removing all ^{15}N contaminants, and even more advanced solutions like small, commercial gas filters require complex, leak-tight setups for recirculating the limited $^{15}N_2$ supply. Moreover, to ensure data reliability, continuous monitoring of activated $^{15}N_x$ species using sensitive techniques like mass spectrometry is necessary, as is the tracking of $^{15}NH_4^+$ levels in solution over time, rather than relying on a single post-reaction measurement, as is often performed nowadays.

Given these constraints, the risk of false positives in isotopic control experiments for NRR studies is significantly larger when using $^{15}N_2$ gas than $^{14}N_2$, regardless of purity level. This casts serious doubt on the reliability and cost-effectiveness of using $^{15}N_2$ gas as it currently stands and highlights the urgent need for alternative validation methods in NRR research that can reliably account for these challenges.

Conclusion

In recent years, the predominant strategy to exclude false positives in NRR experiments has centered on using isotopically labelled $^{15}N_2$ gas as a feed. While Choi *et al.* warned researchers about potential interferences from isotopically labelled reactive nitrogen species in these gasses, a comprehensive understanding of the precise contamination levels of these gaseous, ^{15}N labelled contaminants remained elusive. In this work, we quantify the exact levels of $^{15}N_x$ contaminants in commercially obtained $^{15}N_2$, typically used for performing NRR control experiments. Alarmingly, the contamination levels in these gasses make them unsuitable, increasing the chances of obtaining false positives. Thus, given the current gas purity, validation experiments with $^{15}N_2$ do not enhance the credibility of the NRR study when the production rate is low (*e.g.* $<10^{-8}$ mol cm^{-2} s^{-1}), neither do they confirm NRR is occurring. Moreover, the ^{15}N labelling experiments might even mislead researchers into wrongly attributing the measured $^{15}NH_3$ to $^{15}N_2$ reduction at the cathode; as we clearly demonstrated in our comparative NRR experiments. Indeed, the ammonia production rates originating from ^{15}N labelled impurities in the feed gas is in the order 10^{-9}–10^{-10} mol s^{-1}, which is comparable to most reported NRR studies in aqueous conditions. Therefore, the most convincing proof for successful NRR is consistently measuring high ammonia yields (*e.g.* $>10^{-8}$ mol s^{-1}), particularly when using purer $^{14}N_2$, which is more realistic to purify, over the scarce $^{15}N_2$.

Author contributions

M. D. R wrote the paper and assisted in performing the SIFT-MS measurements. M. B. J. R. participated in the writing and editing of the manuscript. L. H., J. A. M. and J. H. participated in the revision of the manuscript. T. L., B. M. N. and M. L. A. T. M. H contributed to scientific discussions and setting up the methodology.

Conflicts of interest

There are no conflicts to declare.

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