Supporting Information: Overcoming nitrogen reduction to ammonia detection challenges: The case for leapfrogging to gas diffusion electrode platforms

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Miniaturized alkaline impurity trap

The removal of NH$_3$ and NO$_x$ contamination from the gas feed of the cell is crucial to avoid false positives while testing catalysts for NRR. Purifiers to achieve this typically consist of an inner and an outer tube. The inner tube is immersed into the outer tube which is filled with an oxidizing solution that traps the NH$_3$/NO$_x$. During operation, gas is bubbled into the oxidizing solution through the inner tube. The gas exits the outer tube through its headspace. Typically, both outer tube and inner tube are made of glass, because glass is very inert and easy to reshape. However, the smallest commercially available impurity traps of this design have several mL of headspace volume which would make them very expensive to flush during a $^{15}$N$_2$ experiment. Therefore, we propose to use an impurity trap made from inert polymers instead, as shown in Figure S1. The working principle of the design is identical to that of glass impurity traps but the inner and outer tube are made of inert polymer tubing. The headspace of the 1/32” outer diameter (OD) inner tubing and the tee is negligible so that the total headspace of the purifier can be estimated from the headspace of the ¼” outer diameter (OD) outer tube. In our experience approximately 1 cm of headspace in the outer tube is sufficient to prevent liquid from entering the gas channel. With an inner diameter (ID) of 5.6 mm the headspace of the outer tube is approximately 250 µL. This low headspace makes it ideal for cheap $^{15}$N$_2$ experiments in GDE cell. Additionally, it is comprised of standard connectors for easy, leak-tight, contamination-free connections. Unlike with glass impurity traps, it is possible to easily adjust the length of the outer tube depending on the required removal efficiency. The trap only consists of readily available, off-the-shelf parts which should improve standardization of this critical component.
Figure S1 Photograph of a miniaturized purifier to clean \( \text{NH}_3/\text{NO}_x \) contaminated gas streams with minimal additional headspace.

Table S1. Order list for an impurity trap with low headspace volume.

| Part #  | Name                                           | Quantity | Supplier | Price ($) |
|---------|------------------------------------------------|----------|----------|-----------|
| 1648    | Tefzel™ (ETFE) Tubing Natural 1/8" OD x .093" ID x 5ft | 1        | IDEX Health | 33.75     |
| U-665   | Adapter Assembly 1/2-20 Female x1/4-28 Female | 2        | IDEX Health | 37.50     |
| P-713   | PEEK Low PressureTee Assembly 1/8" PEEK .050 thru hole | 1        | IDEX Health | 38.63     |
| F-247   | NanoTight™ Sleeve Green 1/16" OD x .033" ID x 1.6" | 4        | IDEX Health | 2.84      |
| 1569    | PEEK Tubing Orange 1/32" OD x .020" ID x 5ft     | 1        | IDEX Health | 56.93     |
| P-703   | Union Assembly PEEK .050 thru hole, for 1/8" OD  | 2        | IDEX Health | 24.98     |
| P-249   | Super Flangeless™ One-Piece Fitting, 1/4-28 Flat-Bottom, for 1/16" OD | 6        | IDEX Health | 11.02     |
| P-311   | Plug Tefzel™ (ETFE) - 1/4-28                   | 1        | IDEX Health | 2.49      |
| 20533   | PTFE tubing tubing L × OD × ID 25 ft × 1/4 in. (6.35 mm) × 0.228 in. (5.8 mm) | 1        | Merck Sigma | 88.8      |
Calculation: nitrogen reduction reaction mass-transport limiting current in H-cell

We estimate the mass transport limiting current of the nitrogen reduction reaction $j_{\text{lim,NRR}}$ from the mass-transport limiting current of the CO$_2$ reduction reaction to CO $j_{\text{lim,CO2RR}}$ according to:

$$ j_{\text{lim,NRR}} \approx j_{\text{lim,CO2RR}} \frac{S_{N_2} D_{N_2} z_{NRR}}{S_{CO_2} D_{CO_2} z_{CO2RR}} $$

(1)

$$ = 10 \frac{mA}{cm^2} \frac{1.27 \times 10^{-5} x 1.77 \times 10^{-5} \frac{cm^2}{s} x 6}{7 \times 10^{-4} x 1.67 \times 10^{-5} \frac{cm^2}{s} x 2} $$

$$ = 0.6 \frac{mA}{cm^2} $$

where $S_i$, $D_i$, are the solubility and diffusion coefficient of nitrogen and carbon dioxide in water, respectively and $z_{NRR}$, $z_{CO2RR}$ are the number of electrons transferred in the electrochemical reduction of nitrogen to ammonia and of carbon dioxide to carbon monoxide per molecule of N$_2$/CO$_2$, respectively.$^{1-5}$

Calculation: accumulated NH$_3$ in the electrolyte

The concentration of NH$_3$ in the electrolyte was calculated according to:

$$ c_{NH_3} = \frac{i_{NH_3} t}{z F V} $$

(2)

where $c_{NH_3}$ is the concentration of NH$_3$ after electrolysis, $i_{NH_3}$ is the partial current density of NRR, $t$ is the duration of the experiment, $z$ is the number of electrons transferred per molecule of NH$_3$ produced, $F$ is the Faraday Constant and $V$ is the half-cell volume of the electrolyte, respectively.

Mathematical modelling of influence of ECSA on ammonia production and faradaic efficiency

The specific activity (defined as the ECSA normalized current density) $j_{ECSA}$ was calculated by assuming Butler-Volmer kinetics according to:
\[ j_{ECSA} = j_0(e^{-\alpha f\eta} - e^{(1-\alpha)f\eta}) \]  

where \( j_0 \) is the exchange current density, \( \alpha \) is the symmetry factor, \( f \) is the Faraday Constant \( F \) divided by the ideal gas constant \( R \) and the temperature \( T \) and \( \eta \) is the overpotential.\(^6\) The current density normalized by geometric surface area \( j_{\text{geometric}} \) was calculated by multiplying \( j_{ECSA} \) with the roughness factor of the electrode.

The faradaic efficiency was modelled by assuming that a potential window exists where NRR is favorable over HER and that the faradaic efficiency (FE) of NRR within this potential window can be described by a quadratic function:

\[ FE = a\eta^2 + b\eta + c \]  

where \( a, b, c \) are constant parameters.

The partial current density of NRR \( j_{NRR} \) was calculated by multiplying the faradaic efficiency with \( j_{\text{geometric}} \). The partial current density of NRR including mass transport effects \( j_{\text{mt,NRR}} \) was calculated by replacing \( j_{NRR} \) with the mass transport limiting current \( j_{\text{lim,NRR}} \) wherever \( j_{NRR} \) would otherwise have been lower than \( j_{\text{lim,NRR}} \):

\[ j_{\text{mt,NRR}} = \max(j_{NRR}, j_{\text{lim,NRR}}) \]  

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### Literature summary of reported levels of NH\(_3\)/NO\(_x\) contamination

*Table S2. Literature summary of ammonia and nitrate contaminations observed in nitrogen reduction studies.* *To make reports more comparable, contaminations reported as absolute amounts in nmol or as concentrations in a gas stream were converted into concentrations in the electrolyte by assuming the following parameters: electrolyte volume 10 mL, catalyst area: 1 cm\(^2\), catalyst amount: 1 mg, gas flow rate: 30 mL/min duration of gas flow: 2h.*

| Contamination source | NH\(_3\)/NO\(_x\) concentration | Reference |
|----------------------|---------------------------------|-----------|
| Human Breath         | 0.3-3 ppm NH\(_3\) in gas       | 7         |
| Human Breath         | 0.28-1.4 ppm NH\(_3\) in gas    | 8         |
| 0.05 M H\(_2\)SO\(_4\) open to air for 1h | 1.7 µM NH\(_3\) | 9         |
| 0.05 M H\(_2\)SO\(_4\) sealed for 1h | 0.6 µM NH\(_3\) | 9         |
| DI water open to air for 400 min | 8.8 µM NH\(_3\) | 10        |
| Nitrile gloves sonicated for 1h in DI water | 155.1 µM NH\(_3\) | 7         |
| Polypropylene sample storage container (initially) | 0.3 - 49.8 µM NO\(_x\) | 11        |
| Polypropylene sample storage container (after 10 days) | 3.4 - 65.3 µM NO\(_x\) | 11        |
| Cell, electrolyte, epoxy, electrodes | 18.9-21.5 µM NO\(_x\) | 11        |
| N impurities in CoMo film | 10 µM NH\(_3\) | 11        |
Rubber septa 630 µM NH₃, 270 µM NOₓ
Ar 1.3 ppb NOₓ in gas (0.02 µM NOₓ)*
N₂ 3.1 ppb NOₓ in gas (0.046 µM NOₓ)*
Ar, N₂, ¹⁵N₂ 200 ppb N₂O in gas (3 µM NOₓ)*
¹⁵N₂ 0.024 - 420 ppm ¹⁵NOₓ in gas (0.36-6290 µM ¹⁵NOₓ)*
0.014 - 1900 ppm ¹⁵NH₃ in gas (0.21 – 28454 µM ¹⁵NH₃)*

Bi₂O₃, Al₂O₃, Fe₂O₃ 10-120 µmol/g catalyst NOₓ (1-12 µM NOₓ)*
Commercial metallic iron 16343 – 406469 µM total N
¹⁵N₂ scrubbing solution 18.5 µM ¹⁵NH₃, 33 µM ¹⁵NH₃
Potential induced generation of NH₃ from Fe loaded on stainless steel 10 µM NH₃
Release of NH₃ from Nafion 117 membrane soaked in electrolyte containing 0.1 µg/mL of NH₃ 17.6 µM NH₃
Background 1.5 µM NH₃
Background 2 µM NOₓ
Background 0.5 µM NH₃

Literature summary of experimental parameters used during aqueous nitrogen electroreduction experiments

Table S3. Literature summary of experimental parameters used during aqueous NRR studies.

| Ref | Gas flow rate (mL/min) | Electrolyte volume (mL) | Electrode Area (cm²) | Electrolysis time (h) | ¹⁵N? [a] | QT? [b] | Flow rate₁⁵N (mL/min) | Electrolysis time₁⁵N (h) |
|-----|------------------------|-------------------------|----------------------|----------------------|--------|-------|----------------------|-------------------------|
| 18  | n.a.                   | n.a.                    | 1                    | 2                    | yes    | no    | n.a.                 | 10                      |
| 19  | 0.48                   | 100                     | n.a.                 | 2                    | yes    | no    | 0.48                 | 2                       |
| 20  | 250                    | n.a.                    | 6.25                 | 1                    | yes    | no    | 5                    | 1                       |
| 21  | n.a.                   | 30                      | 1                    | n.a.                 | yes    | no    | n.a.                 | 2                       |
| 22  | n.a.                   | 30                      | 1                    | 2                    | no     | no    | n.a.                 | n.a.                    |
| 23  | n.a.                   | 90                      | 2                    | 6                    | yes    | no    | 20 mL every 10 min  | 6                       |
| 24  | no flow?               | 30                      | 2                    | 2                    | yes    | no    | n.a.                 | 2                       |
| 25  | 0.07                   | n.a.                    | 2                    | 2                    | yes    | no    | n.a.                 | n.a.                    |
| 26  | n.a.                   | 50                      | 1                    | 2                    | yes    | no    | n.a.                 | 2                       |
| 27  | n.a.                   | 1                       | n.a.                 | no                   | no     | no    | n.a.                 | n.a.                    |
| 28  | n.a.                   | 1.5                     | n.a.                 | no                   | no     | no    | n.a.                 | n.a.                    |
| 29  | n.a.                   | 30                      | 1                    | 2                    | yes    | yes   | n.a.                 | 10                      |
| 30  | n.a.                   | 1                       | 2                    | no                   | no     | n.a. | n.a.                 | n.a.                    |
| 31  | n.a.                   | 35                      | 1                    | 2                    | no     | no    | n.a.                 | n.a.                    |
| 32  | n.a.                   | 25                      | 1                    | n.a.                 | yes    | no    | 20 mL every 10 min  | 6                       |
| 33  | 10                     | 30                      | 0.07                 | 3                    | yes    | no    | n.a.                 | n.a.                    |
| 3^4 | 60 | 10 | n.a. | n.a. | yes | yes | static | 0.5 |
|-----|----|----|------|------|-----|-----|--------|-----|
| 𝑥   | 40 | 30 | 1    | 2    |     |     |        |     |

[a] 15N?: Were control experiments with 15N performed?
[b] QT?: Was a quantitative agreement between 14NH3 and 15NH3 data demonstrated?

References

(1) Battino, R.; Rettich, T. R.; Tominaga, T. The Solubility of Nitrogen and Air in Liquids. *Journal of Physical and Chemical Reference Data* **1984**, *13* (2), 563–600. https://doi.org/10.1063/1.555713.

(2) Ferrell, R. T.; Himmelblau, D. M. Diffusion Coefficients of Nitrogen and Oxygen in Water. *1967, 12* (1), 5. https://doi.org/10.1021/je60032a036.

(3) Carroll, J. J.; Slupsky, J. D.; Mather, A. E. The Solubility of Carbon Dioxide in Water at Low Pressure. *Journal of Physical and Chemical Reference Data* **1991**, *20* (6), 1201–1209. https://doi.org/10.1063/1.555900.

(4) Jähne, B.; Heinz, G.; Dietrich, W. Measurement of the Diffusion Coefficients of Sparingly Soluble Gases in Water. *Journal of Geophysical Research* **1987**, *92* (C10), 10767. https://doi.org/10.1029/JC092iC10p10767.

(5) Clark, E. L.; Resasco, J.; Landers, A.; Lin, J.; Chung, L.-T.; Walton, A.; Hahn, C.; Jaramillo, T. F.; Bell, A. T. Standards and Protocols for Data Acquisition and Reporting for Studies of the Electrochemical Reduction of Carbon Dioxide. *ACS Catalysis* **2018**, *8* (7), 6560–6570. https://doi.org/10.1021/acscatal.8b01340.

(6) Bard, A. J.; Faulkner, L. R. In *Electrochemical methods: fundamentals and applications*; Wiley: New York, 2001; p 96.

(7) Andersen, S. Z.; Ćolić, V.; Yang, S.; Schwalbe, J. A.; Nielander, A. C.; McEnaney, J. M.; Enemark-Rasmussen, K.; Baker, J. G.; Singh, A. R.; Rohr, B. A.; Statt, M. J.; Blair, S. J.; Mezzavilla, S.; Kibsgaard, J.; Vesborg, P. C. K.; Cargnello, M.; Bent, S. F.; Jaramillo, T. F.; Stephens, I. E. L.; Nørskov, J. K.; Chorkendorff, I. A Rigorous Electrochemical Ammonia Synthesis Protocol with Quantitative Isotope Measurements. *Nature* **2019**, *570* (7762), 504–508. https://doi.org/10.1038/s41586-019-1260-x.

(8) Larson, T. V.; Covert, D. S.; Frank, R.; Charleston, R. J. Ammonia in the Human Airways: Neutralization of Inspired Acid Sulfate Aerosols. *Science* **1977**, *197* (4299), 161–163. https://doi.org/10.1126/science.877545.

(9) Duan, G. Y.; Ren, Y.; Tang, Y.; Sun, Y. Z.; Chen, Y. M.; Wan, P. Y.; Yang, X. J. Improving the Reliability and Accuracy of Ammonia Quantification in Electro- and Photochemical Synthesis. *ChemSusChem* **2020**, *13* (1), 88–96. https://doi.org/10.1002/cssc.201901623.

(10) Saigne, C.; Kirchner, S.; Legrand, M. ION-CHROMATOGRAPHIC MEASUREMENTS OF AMMONIUM, FLUORIDE, ACETATE, FORMATE AND METHANESULPHONATE IONS AT VERY LOW LEVELS IN ANTARCTIC ICE. *Analytica Chimica Acta*, **1987**, *203*, 11–21.

(11) Yu, W.; Buabthong, P.; Read, C. G.; Dalleska, N. F.; Lewis, N. S.; Lewerenz, H.-J.; Gray, H. B.; Brinkert, K. Cathodic NH₄⁺ Leaching of Nitrogen Impurities in CoMo Thin-Film Electrodes in Aqueous Acidic Solutions. *Sustainable Energy & Fuels* **2020**, *4* (10), 5080–5087. https://doi.org/10.1039/D0SE00674B.

(12) Boucher, D. L.; Davies, J. A.; Edwards, J. G.; Mennad, A. An Investigation of the Putative Photosynthesis of Ammonia on Iron-Doped Titania and Other Metal Oxides. *Journal of Photochemistry and Photobiology A: Chemistry* **1995**, *88* (1), 53–64. https://doi.org/10.1016/1010-6030(94)03994-6.

(13) Hodgets, R.; Du, H.-L.; MacFarlane, D. R.; Simonov, A. N. Electrochemically Induced Generation of Extraneous Nitrite and Ammonia in Organic Electrolyte Solutions during Nitrogen Reduction
Experiments. ChemElectroChem 2021, 8 (9), 1596–1604. https://doi.org/10.1002/celc.202100251.

(14) Dabundo, R.; Lehmann, M. F.; Treibergs, L.; Tobias, C. R.; Altabet, M. A.; Moisander, P. H.; Granger, J. The Contamination of Commercial 15N2 Gas Stocks with 15N–Labeled Nitrate and Ammonium and Consequences for Nitrogen Fixation Measurements. PLoS ONE 2014, 9 (10), e110335. https://doi.org/10.1371/journal.pone.0110335.

(15) Chen, Y.; Liu, H.; Na, N.; Licht, S.; Gu, S.; Li, W. Revealing Nitrogen-Containing Species in Commercial Catalysts Used for Ammonia Electrolysytis. Nat Catal 2020, 3 (12), 1055–1061. https://doi.org/10.1038/s41929-020-00527-4.

(16) Ren, Y.; Yu, C.; Tan, X.; Han, X.; Huang, H.; Huang, H.; Qiu, J. Is It Appropriate to Use the Nafion Membrane in Electrocataylatic N2 Reduction? Small Methods 2019, 3 (12), 1900474. https://doi.org/10.1002/smtd.201900474.

(17) Yu, W.; Lewis, N. S.; Gray, H. B.; Dalleska, N. F. Isotopically Selective Quantification by UPLC-MS of Aqueous Ammonia at Submicromolar Concentrations Using Dansyl Chloride Derivatization. ACS Energy Letters 2020, 5 (5), 1532–1536. https://doi.org/10.1021/acsenergylett.0c00496.

(18) Zhao, L.; Liu, X.; Zhang, S.; Zhao, J.; Xu, X.; Du, Y.; Sun, X.; Zhang, N.; Zhang, Y.; Ren, X.; Wei, Q. Rational Design of Bimetallic Ru0.6Ru0.4 Nanoalloys for Enhanced Nitrogen Reduction Electrocataylisis under Mild Conditions. Journal of Materials Chemistry A 2021, 9 (1), 259–263. https://doi.org/10.1039/D0TA09099A.

(19) Wei, X.; Vogel, D.; Keller, L.; Kriescher, S.; Wessling, M. Microtubular Gas Diffusion Electrode Based on Ruthenium-Carbon Nanotubes for Ambient Electrochemical Nitrogen Reduction to Ammonia. ChemElectroChem 2020, 7 (22), 4679–4684. https://doi.org/10.1002/celc.202001370.

(20) Kim, M.-C.; Nam, H.; Choi, J.; Kim, H. S.; Lee, H. W.; Kim, D.; Kong, J.; Han, S. S.; Lee, S. Y.; Park, H. S. Hydrogen Bonding-Mediated Enhanced of Bioinspired Electrochemical Nitrogen Reduction on Cu2−xS Catalysts. ACS Catalysis 2020, 10 (18), 10577–10584. https://doi.org/10.1021/acscatal.0c01750.

(21) Jin, Y.; Ding, X.; Zhang, L.; Cong, M.; Xu, F.; Wei, Y.; Hao, S.; Gao, Y. Boosting Electrocatalytic Reduction of Nitrogen to Ammonia under Ambient Conditions by Alloy Engineering. Chemical Communications 2020, 56 (77), 11477–11480. https://doi.org/10.1039/D0CC02489A.

(22) Jiang, X.; He, M.; Tang, M.; Zheng, Q.; Xu, C.; Lin, D. Nanostructured Bimetallic Ni–Fe Phosphide Nanoplates as an Electrocatalyst for Efficient N2 Fixation under Ambient Conditions. J Mater Sci 2020, 55 (31), 15252–15262. https://doi.org/10.1007/s10853-020-05085-5.

(23) Lin, Y.-X.; Zhang, S.-N.; Xue, Z.-H.; Zhang, J.-J.; Su, H.; Zhao, T.-J.; Zhai, G.-Y.; Li, X.-H.; Antonietti, M.; Chen, J.-S. Boosting Selective Nitrogen Reduction to Ammonia on Electron-Deficient Copper Nanoparticles. Nat Commun 2019, 10 (1), 4380. https://doi.org/10.1038/s41467-019-12312-4.

(24) Zhang, L.; Cong, M.; Ding, X.; Jin, Y.; Xu, F.; Wang, Y.; Chen, L.; Zhang, L. A Janus Fe-SnO2 Catalyst That Enables Bifunctional Electrochemical Nitrogen Fixation. Angew. Chem. Int. Ed. 2020, 59 (27), 10888–10893. https://doi.org/10.1002/anie.202003518.

(25) Li, Y.; Chen, J.; Cai, P.; Wen, Z. An Electrochemically Neutralized Energy-Assisted Low-Cost Acid-Alkaline Electrolyzer for Energy-Saving Electrolysis Hydrogen Generation. Journal of Materials Chemistry A 2018, 6 (12), 4948–4954. https://doi.org/10.1039/C7TA10374C.

(26) Zhao, S.; Liu, H.; Qiu, Y.; Liu, S.; Diao, J.; Chang, C.; Si, R.; Guo, X. An Oxygen Vacancy-Rich Two-Dimensional Au/TiO2 Hybrid for Synergistically Enhanced Electrochemical N2 Activation and Reduction. J. Mater. Chem. A 2020, 8 (14), 6586–6596. https://doi.org/10.1039/DOTA00658K.

(27) Wang, J.; Ren, Y.; Chen, M.; Cao, G.; Chen, Z.; Wang, P. Bismuth Hollow Nanospheres for Efficient Electrolysytis of Ammonia under Ambient Conditions. Journal of Alloys and Compounds 2020, 830, 154668. https://doi.org/10.1016/j.jallcom.2020.154668.

(28) Tong, Y.; Guo, H.; Liu, D.; Yan, X.; Su, P.; Liang, J.; Zhou, S.; Liu, J.; Lu, G. Q. (Max); Dou, S. X. Vacancy Engineering of Iron-Doped W18O49 Nanoreactors for Low-Barrier Electrochemical


Nitrogen Reduction. Angew. Chem. Int. Ed. 2020, 59 (19), 7356–7361. https://doi.org/10.1002/anie.202002029.

(29) Wang, J.; Huang, B.; Ji, Y.; Sun, M.; Wu, T.; Yin, R.; Zhu, X.; Li, Y.; Shao, Q.; Huang, X. A General Strategy to Glassy M-Te (M = Ru, Rh, Ir) Porous Nanorods for Efficient Electrochemical N₂ Fixation. Adv. Mater. 2020, 32 (11), 1907112. https://doi.org/10.1002/adma.201907112.

(30) Wang, F.; Lv, X.; Zhu, X.; Du, J.; Lu, S.; Alshehri, A. A.; Alzahrani, K. A.; Zheng, B.; Sun, X. Bi Nanodendrites for Efficient Electrocatalytic N₂ Fixation to NH₃ under Ambient Conditions. Chem. Commun. 2020, 56 (14), 2107–2110. https://doi.org/10.1039/C9CC09803H.

(31) Ohrelius, M.; Guo, H.; Xian, H.; Yu, G.; Alshehri, A. A.; Alzahrani, K. A.; Li, T.; Andersson, M. Electrochemical Synthesis of Ammonia Based on a Perovskite LaCrO₃ Catalyst. ChemCatChem 2020, 12 (3), 731–735. https://doi.org/10.1002/cctc.201901818.

(32) Xue, Z.-H.; Zhang, S.-N.; Lin, Y.-X.; Su, H.; Zhai, G.-Y.; Han, J.-T.; Yu, Q.-Y.; Li, X.-H.; Antonietti, M.; Chen, J.-S. Electrochemical Reduction of N₂ into NH₃ by Donor–Acceptor Couples of Ni and Au Nanoparticles with a 67.8% Faradaic Efficiency. J. Am. Chem. Soc. 2019, 141 (38), 14976–14980. https://doi.org/10.1021/jacs.9b07963.

(33) Song, P.; Wang, H.; Kang, L.; Ran, B.; Song, H.; Wang, R. Electrochemical Nitrogen Reduction to Ammonia at Ambient Conditions on Nitrogen and Phosphorus Co-Doped Porous Carbon. Chem. Commun. 2019, 55 (5), 687–690. https://doi.org/10.1039/C8CC09256G.

(34) Suryanto, B. H. R.; Wang, D.; Azofra, L. M.; Harb, M.; Cavallo, L.; Mitchell, D. R. G.; Chatti, M.; MacFarlane, D. R. MoS₂ Polymorphic Engineering Enhances Selectivity in the Electrochemical Reduction of Nitrogen to Ammonia. ACS Energy Letters 2019, 4 (2), 430–435. https://doi.org/10.1021/acsenergylett.8b02257.