

Oxidation Catalysis in Plasma for N₂ fixation: A New Route Around the Haber-Bosch-Ostwald Mountains

Joint research proposal, submitted to the Resnick Sustainability Center for Catalysis

Assoc. Prof. David Eisenberg, Schulich Faculty of Chemistry

Assoc. Prof. Joseph K. Lefkowitz, Aerospace Engineering

Technion – Israel Institute of Technology

ז' ניסן תשפ"ד, 2024-04-15

Abstract

We propose developing and investigating a low-emission catalytic process towards nitrogen fixation, based on the oxidation of N₂ in a plasma reactor, using nothing more than air, water and electricity. Our proposed catalytic reactor will employ gliding arc plasma and interface to an FTIR spectrometer for monitoring product distribution in real time. By combining the expertise of the Eisenberg lab in the design of catalytic oxide materials, with the specialty of the Combustion and Diagnostics Lab (of PI Lefkowitz) in *operando* monitoring and modelling of high energy reactions in the nitrogen cycle, we hope to achieve breakthroughs in catalysis science, and practical advances in sustainable production of fuels and chemical feedstocks.

Background and Significance

Nitrogen is vital for life, being a crucial component of proteins and DNA. Despite the abundance of atmospheric N₂, its inert nature precludes direct biological uptake. This underscores the importance of nitrogen fixation: transforming atmospheric N₂ into useful forms like nitrate (NO₃⁻) and ammonia (NH₃), which are readily absorbed by living organisms. Until a century ago, ammonia was mostly produced by bacteria, but thanks to the invention of the Haber-Bosch process in 1909, we can now produce it industrially (Figure 1).^[1,2] About 131 million ton ammonia is generated every year, consuming about 1-2% of the global energy production, and producing 1.673 ton of CO₂ per ton NH₃.^[3]

The challenge is breaking the triple N≡N bond ($\Delta H_f = 946$ kJ/mol). Most research into Haber-Bosch alternatives are in electrocatalysis, attempting the direct *reduction* of N₂ into NH₃. The ultra-low yields (1-70 $\mu\text{g h}^{-1} \text{cm}^{-2}$) reflect the competition with H₂ production, inherent to the reductive environment.

But what about *oxidation* of N₂, rather than reduction? We propose a two-step process: First, we break the strong N≡N bond by oxidation, producing a mix of nitrogen oxides (NO_x). Then, we reduce the NO_x electrocatalytically.^[4-6] It might seem counter-intuitive to first oxidize and then reduce, but this allows breaking the strong N≡N bond in an

oxidizing environment, removing the competition with H_2 formation. Nitrogen can react directly with oxygen through reactions such as^[7]:

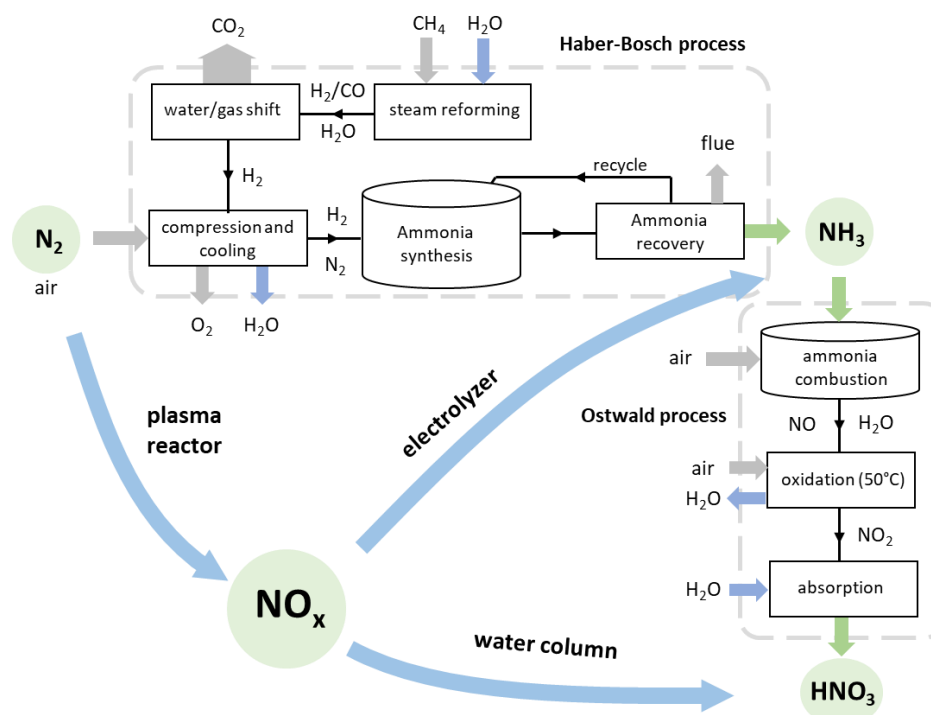
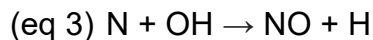
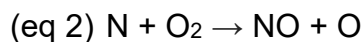


Figure 1. Overview of the existing Haber-Bosch (top) and Ostwald (right) processes towards NH_3 and HNO_3 – and the alternative pathway proposed here (left-bottom), enabled by catalytic plasma-assisted N_2 oxidation to NO_x .

We propose generating the oxidizing species by ‘cold’ plasma, which is typically dominated by the desired O and O_3 species – but introducing catalysis to the reactor, hopefully changing the entire field. Non-catalytic plasma-based oxidation of N_2 has been researched for over a century, since the Birkeland-Eyde process in Norway in 1903.^[8] Table 1 summarizes the best processes reported so far.^[9] The highest NO_x yields have been reported with microwave plasma together with a magnetic field in the 1980s, but has never been reproduced (also, the cost for operating at reduced pressure was not included in the calculation of the plasma energy cost). More realistically, gliding arc plasmas yield up to 2% NO_x at a 2.8 MJ/mol energy cost.^[9]

Catalysis has been direly lacking from this century of studies. The first experimental explorations of catalytic plasma-assisted N_2 oxidation only appeared in the late 2010s. These works have shown promise, operating with a handful of simple catalysts, based on MoO_3 , Al_2O_3 and TiO_2 .^[10–13] Not only is there still a universe of catalysts to explore, but mechanistic understanding is totally lacking in the field. This calls for designing plasma-assisted catalytic reactors, directly coupled to spectrometers, enabling *operando* studies of catalysis – and hopefully leading to new breakthroughs in this emerging, highly important field of study.

Plasma type	Concentration*	Energy cost	Ref.
Electric arc (Birkeland-Eyde)	2% NO	2.0 – 3.28 MJ mol ⁻¹ HNO ₃	4–6
RF crossed discharge	-	24 - 108 MJ mol ⁻¹ HNO ₃	7
Laser-produced plasma	-	8.9 MJ mol ⁻¹ NO _x	8
Pulsed corona discharge	-	186 MJ mol ⁻¹ HNO ₃	9,10
(+/-) DC corona discharge	-	43 MJ mol ⁻¹ NO _x	11
(Pulsed)/Spark discharge	-	1057/1673 MJ mol ⁻¹ NO _x	11–13
Packed DBD	0.5% NO _x	10 – 60 MJ mol ⁻¹ NO _x	14
DBD	0.6% NO _x	18 MJ mol ⁻¹ NO _x	15
Pin-to-plane ns-pulsed spark discharge	-	56 – 140 MJ mol ⁻¹ NO _x	15
Pin-to-plane DC glow discharge	-	5.0 – 7.7 MJ mol ⁻¹ NO _x	15
Pin-to-pin DC glow discharge	-	7 MJ mol ⁻¹ NO _x	15
Pin-to-pin DC glow discharge	0.7% NO _x	2.8 MJ mol ⁻¹ NO _x	16
DC plasma arc jet	6.5% NO	3.6 MJ mol ⁻¹ NO	17
Propeller arc	0.4% NO _x	3.6 MJ mol ⁻¹ NO	15
Pulsed milli-scale gliding arc	0.4% NO _x	4.2 MJ mol ⁻¹ NO _x	15
Gliding arc plasmatron	1–2% NO _x	2.8 - 4.8 MJ mol ⁻¹ NO _x	18,19
Microwave plasma	1.5% NO _x	3.6 MJ mol ⁻¹ NO _x	20
Microwave plasma with catalyst	0.6% NO _x	3.76 MJ mol ⁻¹ NO _x	21
Microwave plasma with magnetic field	6% NO	0.84 MJ mol ⁻¹ NO	22
	14% NO	0.28 MJ mol ⁻¹ NO	23

* For certain plasma types, the NO_x concentration is not reported.

Table 1. NO_x concentration and energy cost produced in different plasma types (ref ^[9]).

Research Goals

Within the Resnick-funded collaboration, we expect to complete Goals 1 and 2, which will allow us to apply for external funding for investigating Goals 3 and 4 in depth.

1. Reactor Design and Integration with Product Monitoring

- 1.1. Design and construct a plasma catalysis reactor for N₂ oxidation with both gliding-arc and barrier-discharge plasma capabilities [**Eisenberg lab**]
- 1.2. Integrate the reactor with an FTIR spectrometer for monitoring of NO_x (NO, NO₂, N₂O) production [**Lefkowitz lab**]

2. Catalytic Plasma-Based N₂ Oxidation

- 2.1. Investigate plasma processes for N₂ → NO_x conversion, establishing a baseline protocol by variation of feedstock ratios and oxygen donors [**Eisenberg + Lefkowitz labs**]
- 2.2. Synthesize a broad library of metal oxide powder catalysts, based on metals with known activity in the nitrogen cycle [**Eisenberg lab**]
- 2.3. Investigate the effect of catalysis on the reaction, employing oxide-based catalysts, combined with *operando* spectroscopic analysis of the NO_x product yield and selectivity [**Eisenberg + Lefkowitz labs**]

3. Mechanistic Studies

Formulate kinetic mechanisms for plasma-assisted catalytic N₂ oxidation, based on insights from product species composition and optical emission spectroscopic temperature and excited/ionized species measurements [**Lefkowitz lab**]

4. Catalyst Development

Synthesize variants of the best-performing oxide families, in terms of composition and microstructure, to investigate structure—activity links in N₂ oxidation during plasma-assisted catalysis [**Eisenberg lab**].

Research Plan

In this collaboration, we propose combining the specialty of the Eisenberg lab in developing catalytic materials and reactors, including based on oxides,^[14–16] with the specialty of the Lefkowitz lab in *operando* spectroscopic monitoring, and microkinetic modeling, of plasma chemistry in the nitrogen cycle.

First, we will design a reactor where different oxide catalysts can be screened for NO_x production. Preliminary results include the CAD design of such a unique reactor (Figure 2), by Dr. Thierry Slot, a post-doctoral fellow in the Eisenberg lab, and a specialist in instrument design. The NO_x can be detected using gas-phase FTIR,^[10] chemiluminescence,^[17] and mass spectrometry.^[18] The first milestone will be building a working plasma reactor that produces >6.6 L of NO_x (>2 mol%) per hour.

We will design catalysts for the reactor, varying composition and structure. The metal oxides of choice will start from simple Group 1, 2, and 3 oxides, and continue with doping with transition metals relevant to nitrogen cycle catalysis (V, Fe, Mo). Since catalytic activity improves with smaller particles,^[10] we will develop aerosolized catalysts (50–200 nm) to intensify the contact with the short-lived activated nitrogen species. In some cases, the NO_x output was also doubled by simple additives such as water,^[19] suppressing O₃ formation in favor of O. Moreover, by changing the reactant stream (N₂ / O₂ ratio), we will vary the reaction selectivity (towards N₂O / NO₂).

To elucidate which mechanisms govern NO_x formation, we will simulate the plasma using a well-validated air plasma model in 0D, using the measured temperature and product species of the plasma operating in the absence of catalysts. This model will then be extended to include surface reactions, and “calibrated” using various catalyst loadings in the reactor, similar to the method of Hong *et al.*^[20] The model can then be used to determine, via path flux analysis, the pathways leading to NO_x formation and lend insight into how to optimize the process.

The Novelty and Impact of the Collaboration

The Electrochemistry and Energy Lab of PI Eisenberg specializes in electrocatalysis, in the design of catalytic oxides,^[14,15] in broad-scope material characterization, and the formulation of structure-activity links. Dr. Thierry Slot, a postdoctoral fellow in the lab, is highly skilled in instrument design and heterogeneous catalysis,^[21,22] so he will build the reactor, synthesize the materials, and test catalytic activity.

The Combustion and Diagnostics Lab of PI Lefkowitz specializes in plasma chemical processes,^[23,24] plasma-assisted combustion,^[25] and spectroscopic analysis of gases.^[26] Mr. Max Bernard is an MSc student in the lab, and is currently under training in spectroscopic measurements for NH₃ plasma analysis. He will assist Dr. Thierry Slot in testing the reactor and measuring species and temperatures *operando*.

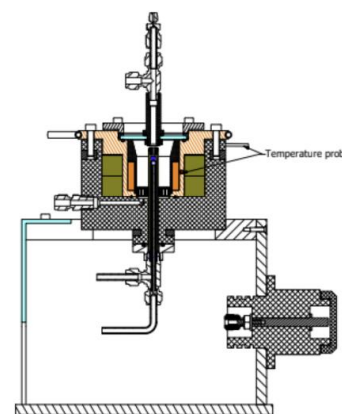


Figure 2. Preliminary results: computer-assisted design of a plasma-catalysis reactor (Eisenberg lab).

By joining forces, we propose taking plasma catalysis – a crucial yet under-researched approach towards N₂ fixation – to new heights. By combining a broad variety of fields, from synthesis, material characterization, and catalytic testing, to powerful *operando* spectroscopy and microkinetic modelling, we hope to reveal the mechanisms of N₂ oxidation, and to discover the next generation of active and selective catalysts. Such breakthroughs in catalysis science will enable practical advances in the sustainable production of fuels and chemical feedstock, only from air and electricity.

Budget Estimate

Item	Estimate (\$)
Post-doc salary (partial, Eisenberg lab)	17,000
Chemicals and consumables (Eisenberg lab)	8,000
MSc salary (partial, Lefkowitz lab)	15,000
Electronics and consumables (Lefkowitz lab)	10,000
Total	50,000

References

- [1] F. Haber, R. L. Rossignol, *Z. Für Elektrochem. Angew. Phys. Chem.* **1913**, 19, 53–72.
- [2] A. Mittasch, W. Frankenburg, in *Adv. Catal.* (Eds.: W.G. Frankenburg, V.I. Komarewsky, E.K. Rideal), Academic Press, **1950**, pp. 81–104.
- [3] C. Smith, A. K. Hill, L. Torrente-Murciano, *Energy Environ. Sci.* **2020**, 13, 331–344.
- [4] G.-F. Chen, Y. Yuan, H. Jiang, S.-Y. Ren, L.-X. Ding, L. Ma, T. Wu, J. Lu, H. Wang, *Nat. Energy* **2020**, 5, 605–613.
- [5] J. Long, S. Chen, Y. Zhang, C. Guo, X. Fu, D. Deng, J. Xiao, *Angew. Chem. Int. Ed.* **2020**, 59, 9711–9718.
- [6] S.-M. Chen, Y. O. Su, *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, 280, 189–194.
- [7] A. Schmidt-Bleker, R. Bansemer, S. Reuter, K.-D. Weltmann, *Plasma Process. Polym.* **2016**, 13, 1120–1127.
- [8] T. Hager, *The Alchemy of Air: A Jewish Genius, a Doomed Tycoon, and the Scientific Discovery That Fed the World but Fueled the Rise of Hitler*, Crown, **2008**.
- [9] F. Jardali, S. Van Alphen, J. Creel, H. Ahmadi Eshtehardi, M. Axelsson, R. Ingels, R. Snyders, A. Bogaerts, *Green Chem.* **2021**, 23, 1748–1757.
- [10] B. S. Patil, N. Cherkasov, J. Lang, A. O. Ibhaddon, V. Hessel, Q. Wang, *Appl. Catal. B Environ.* **2016**, 194, 123–133.
- [11] E. Vervloessem, M. Aghaei, F. Jardali, N. Hafezkhiaabani, A. Bogaerts, *ACS Sustain. Chem. Eng.* **2020**, 8, 9711–9720.
- [12] I. Jögi, K. Erme, J. Raud, S. Raud, *Catal. Lett.* **2020**, 150, 992–997.
- [13] N. Cherkasov, A. O. Ibhaddon, P. Fitzpatrick, *Chem. Eng. Process. Process Intensif.* **2015**, 90, 24–33.
- [14] D. Eisenberg, T. K. Slot, G. Rothenberg, *ACS Catal.* **2018**, 8, 8618–8629.
- [15] T. K. Slot, D. Eisenberg, G. Rothenberg, *ChemCatChem* **2018**, 10, 2119–2124.
- [16] S. Chakrabarty, I. Offen-Polak, T. Y. Burshtein, E. M. Farber, L. Kornblum, D. Eisenberg, *J. Solid State Electrochem.* **2021**, 25, 159–171.
- [17] E. J. Dunlea, S. C. Herndon, D. D. Nelson, R. M. Volkamer, F. San Martini, P. M. Sheehy, M. S. Zahniser, J. H. Shorter, J. C. Wormhoudt, B. K. Lamb, E. J. Allwine, J. S. Gaffney, N. A. Marley, M. Grutter, C. Marquez, S. Blanco, B. Cardenas, A. Retama, C. R. Ramos Villegas, C. E. Kolb, L. T. Molina, M. J. Molina, *Atmospheric Chem. Phys. Discuss.* **2007**, 7, 569–604.
- [18] J. Hong, S. Prawer, A. B. Murphy, *ACS Sustain. Chem. Eng.* **2018**, 6, 15–31.
- [19] W. S. Partridge, R. B. Parlin, B. J. Zwolinski, *Ind. Eng. Chem.* **1954**, 46, 1468–1471.
- [20] J. Hong, S. Pancheshnyi, E. Tam, J. J. Lowke, S. Prawer, A. B. Murphy, *J. Phys. Appl. Phys.* **2017**, 50, 154005.
- [21] T. K. Slot, D. Eisenberg, D. van Noordenne, P. Jungbacker, G. Rothenberg, *Chem. - Eur. J.* **2016**, 22, 12307–12311.
- [22] T. K. Slot, N. R. Shiju, G. Rothenberg, *Angew. Chem. Int. Ed.* **2019**, 58, 17273–17276.
- [23] G. Faingold, J. K. Lefkowitz, *Proc. Combust. Inst.* **2021**, 38, 6661–6669.
- [24] G. Faingold, O. Kalitzky, J. K. Lefkowitz, *Fuel Commun.* **2022**, 12, 100070.
- [25] S. Shen, I. Laso, N. Rozin, J. K. Lefkowitz, *Proc. Combust. Inst.* **2023**, 39, 5487–5498.
- [26] J. K. Lefkowitz, S. D. Hammack, C. D. Carter, T. M. Ombrello, *Proc. Combust. Inst.* **2021**, 38, 6671–6678.