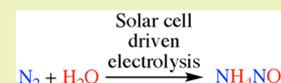
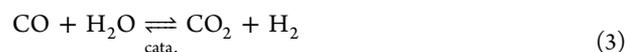
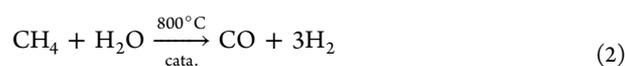


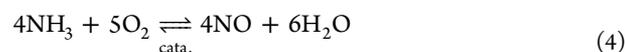
Electrocatalytic Nitrogen Fixation for Distributed Fertilizer Production?

Michael Jewess[†] and Robert H. Crabtree^{*,‡}[†]The Long Barn, Townsend, Harwell, Oxfordshire OX11 0DX, United Kingdom[‡]Chemistry Department, Yale University, 225 Prospect Street, New Haven, Connecticut 06520, United States**ABSTRACT:** Recent advances in the title topic are discussed in relation to sustainable distributed production of nitrogen fertilizer by electrolysis of air.**KEYWORDS:** Nitrogen fixation, Solar energy, Ammonia oxidation, Hydrogen storage, Chatt cycle

Our rising population implies a growing need for food production and for the appropriate fertilizers, but nitrogen fertilizers from the Haber process (eq 1) have a considerable carbon footprint resulting from the high energy inputs required. In addition, the H_2 required in eq 1 typically comes from natural gas by high temperature steam reforming (eq 2) followed by the water gas shift process (eq 3), thus ultimately deriving from fossil fuel with liberation of CO_2 . The needed N_2 comes from air but requires cryogenic separation from the O_2 , another energy-intensive process. The total energy input has been estimated¹ at a substantial 9500 kWh/ton NH_3 and said² to account for ~3% of world CO_2 emissions.



Forming NH_4NO_3 requires a subsequent ammonia oxidation via the high temperature, two-step Ostwald process, which goes via NO in the intermediate step (eq 4). This step is not completely selective, however, and can lead^{3,4} to release of some N_2O , a global warming and ozone-depleting gas. The second step involves low temperature oxidation of NO (eq 5), followed by hydrolytic disproportionation (eq 6) to give aq. HNO_3 and NO , which is recycled.



Sustainable alternatives are thus gaining attention. Natural nitrogen fixation⁵ typically takes place symbiotically: specific green plants store chemical energy derived from photosynthesis and pass some of it along to nitrogen fixing bacteria lodged in the plant's root nodules. Can something similar be envisaged for sustainable nitrogen fertilizer production?

Distributed aqueous NH_4NO_3 production on farms from air and water with solar energy input could meet the case.² At a

stroke, this could eliminate most transport costs and permit winter sunshine to be put to work in a season where plants are generally dead or dormant. The decreasing costs of conventional silicon solar arrays make these an attractive stand-in for the green plant. Now we just need an efficient electrocatalytic reduction of atmospheric nitrogen to ammonia. With judicious cell design, a part of this ammonia might be oxidized at the anode to form nitrate, thus producing dilute NH_4NO_3 that could be directly applied to the fields. Not only would this sidestep both the Haber and Ostwald processes, but the resulting NH_4NO_3 solution would be stored or applied to the fields. NH_4NO_3 would also never need to be produced as a pure material—another advantage of the scheme because it would minimize explosion hazard risks, either accidental or malicious.

The best known synthetic bioinorganic work in nitrogen fixation models the metal-based binding site of N_2 in the enzyme, nitrogenase,⁵ that brings about natural nitrogen fixation. This has mostly involved stable metal complexes and their reduction products, valuable for the mechanistic insights they provide, as embodied, for example, in the Chatt⁶ (Figure 1) or Schrock⁷ cycles, but this approach was never intended to

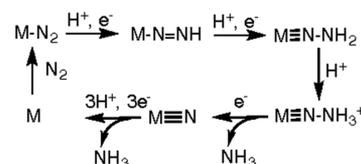


Figure 1. A simplified version of the Chatt cycle based on isolable intermediates seen in early work on the problem. Other possible pathways are certainly not excluded. The six electrons involved come from oxidation of the original zerovalent Mo or W to the hexavalent state.

Special Issue: Building on 25 Years of Green Chemistry and Engineering for a Sustainable Future

Received: June 28, 2016

Revised: September 24, 2016

Published: September 28, 2016

provide commercially viable, robust, high-turnover catalysts. With a catalytic goal in mind, stable complexes are not specially sought. Instead, unstable complexes and intermediates are generally thought more likely to produce active catalysts. Because the hardest step in the sequence $\text{N}_2 \rightarrow \text{NH}_3 \rightarrow \text{NO}_3^-$ is the first, we emphasize it here.

As the Chatt cycle suggests, alternating electron transfer (ET) and proton transfer (PT) is one likely path to ammonia. In recent work, proton coupled electron transfer (PCET) which combines PT and ET in one concerted step,⁸ has been shown to lower reaction barriers in a number of cases and is plausible here. Whether we envisage ET/PT or PCET, electrocatalysis is well suited: the cathode provides the electrons and the electrolyte provides the protons. Protons are automatically formed at the anode during the $\text{NH}_3 \rightarrow \text{NO}_3^-$ oxidation step and these can diffuse to the cathode to take part in the $\text{N}_2 \rightarrow \text{NH}_3$ step, thus closing the cycle. A plausible net equation for the complete reaction (eq 7) together with the appropriate half reactions (eqs 8 and 9) is shown nearby.



Early work often tends to get forgotten, and in this case we can go back more than 200 years to a report that is little known by present-day workers in the field. As early as 1807, Humphry Davy⁹ reported the production of ammonia and nitric acid when “pure water” containing dissolved air was electrolyzed between gold electrodes, but this did not happen in the absence of air or under H_2 . Of course characterization methods were crude and the early nomenclature used can be obscure, but similar results were later obtained by Fichter and Suter in 1922.¹⁰ After reviewing this and other reports of nitrogen fixation by electrolysis, they indeed obtained small amounts of ammonia by electrolysis of dilute sulfuric acid between a platinum black cathode and a platinum wire anode under 200 atm. of nitrogen. Their reaction was very inefficient—only 3 mg of NH_3 were seen for every Faraday of current passed—but any nonzero result can be the starting point for optimization, particularly if electrocatalysts are included in the mix. Indeed, recent work on electrolytic N_2 reduction not only makes the reality of the effect unambiguous but has also greatly improved the efficiency.¹ For example, restricting the discussion to NH_3 electrosyntheses that are successful at moderate temperature and pressure and in aqueous solvents, Lan, Irvine and Tao¹¹ have reported significant results at 1.2–1.6 V applied potential (vs NHE, Pt electrodes) with air and water as the only reactants and NH_4^+ -loaded Nafion as membrane. The Faradaic efficiency of NH_3 production rose from 0.15%–0.5% as the applied voltage was varied between 1.2 and 1.6 V. Xu et al.¹² have employed $\text{SmFe}_{0.7}\text{Cu}_{0.1}\text{Ni}_{0.2}\text{O}_3$ cathodes at 25°–100° and up to 2 V applied potential to form ammonia from H_2 and moist N_2 with a current efficiency said to be as high as 90%. Licht et al.¹³ have reported the electrolysis of air and steam at 1.2 V with Ni electrodes in molten NaOH/KOH , containing iron oxide nanoparticles as catalyst, achieving a current efficiency of 35% for ammonia production. As might be expected, going to much more extreme conditions can permit higher performance. Marnellos and Stoukides¹⁴ found 78% current efficiency for NH_3 production from 1 atm. H_2 and N_2 in a solid state proton-

conducting cell at 570° in which the required protons came from H_2 oxidation at the anode.

Selective electrocatalysts are clearly needed. Skúlason¹⁵ and coauthors have provided a theoretical evaluation of possible transition metal electrocatalysts: precious metals such as Ru and Rh were identified, but cheap metals such as Fe and Mo were also considered viable. Howalt¹⁶ and coauthors also looked at this problem, discussing the types of intermediates reminiscent of the Chatt cycle; they also find that H atoms show a higher heat of adsorption over N atoms, a result that may help explain why proton reduction to H_2 is often found to be dominant over N_2 reduction to NH_3 .

Electrocatalysis has recently gained attention in connection with the related problem of proton reduction to H_2 , a topic also of interest for alternative energy applications. Artificial photosynthesis schemes involve anodic water oxidation to O_2 combined with cathodic proton reduction to H_2 as a fuel-forming step. Molecular catalysts, with their ready tunability and high selectivity have taken a leading role in this area. Among electrocatalysts, water reduction catalysts that convert H^+ to H_2 seem best adapted to our needs. The Dubois catalyst of Figure 2, for example, has a metal site that accepts electrons

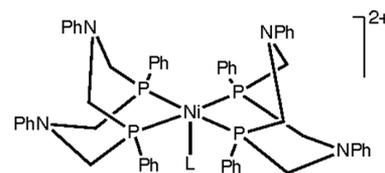


Figure 2. Exceedingly active water reduction catalyst that features a Ni active site and a basic pendant nitrogen that greatly enhances catalysis, presumably by acting as a reversible proton transfer unit ($L = \text{MeCN}$).

and protons and an adjacent proton donor site that efficiently transfers protons from the protonated nitrogen to the Ni–H intermediate postulated in the cycle.¹⁷ For the N_2 case, it may help to replace M–H by M–N_2 and place the proton donor site one bond further removed from the metal so as to allow protonation of the distal N. N_2 is not a particularly good ligand, and so one challenge in such a plan would be to suppress competitive proton reduction. Thus, poor proton reduction catalysts might be appropriate here.

Interestingly, N_2 ase is also a hydrogenase⁵ in the sense that if no N_2 is available, proton reduction takes over, and even at the highest pressures of N_2 , N_2 ase still produces a minimum of one mole of H_2 per mole of N_2 reduced. Thus, it is plausible to think that N_2 ase has successfully evolved from an H_2 ase by partial suppression of H_2 formation. This leads to the suggestion that if electrolytic N_2 reduction were carried out with more or less sophisticated electrocatalysts attached to the electrode, efficiencies might be greatly enhanced.

If the selectivity for N_2 reduction is low, as expected, a large amount of H_2 will form from water reduction. This raises a problem in that explosive H_2 /air mixtures must not be allowed to form. Fortunately, there is a simple solution: it should be possible¹⁸ to deplete greatly the O_2 content of air by reaction with some of the excess of H_2 in a fuel cell, thus providing an air-derived gas stream that cannot form an explosive mixture with H_2 . The near-absence of O_2 is also advantageous in that O_2 reduction will not then occur to any great extent at the cathode, a process that would otherwise waste some of the applied electric power. An additional advantage of an appended

fuel cell is that much of the energy lost in the undesired formation of H_2 can be recouped by using the power produced by the fuel cell from the excess H_2 to supplement the power input into the reactor cell. The excess of the H_2 byproduct, if stored, could also partially counter the solar intermittency problem, so that when solar energy was unavailable, the H_2 fuel cell could still provide power to the reactor cell. Table 1 collects the data on the chief electrocatalytic methods discussed.

Table 1. Examples of Electrolytic Nitrogen Reduction Discussed Here

reference	date	electrode	product	Faradaic efficiency %
9	1807	Au	$NH_4NO_3(?)$	low
10	1922	Pt	NH_3	low
11	2013	Pt	NH_3	0.15–0.5
13	2014	Ni	NH_3	35
14	1998	Pd	NH_3	78

Moving to the $NH_3 \rightarrow NO_3^-$ step, we need to avoid the production of N_2 , which would just reverse the $N_2 \rightarrow NH_3$ reduction step. Thus, the type of catalyst to be preferred here is one that transfers successive O atoms to the substrate. Such catalysts are well-known in artificial photosynthesis, being involved in the water oxidation half reaction.^{19,20} Many such catalysts are known, including some of our own. We have seen how our own water oxidation catalysts²⁰ can be almost entirely redirected to $C-H \rightarrow C-OH$ oxidation in the presence of a suitable hydrocarbon substrate.²¹ In one case, for example, the preference for $C-H$ over water oxidation was found to be 10^4 . This gives hope that such catalysts may be good candidates for the $NH_3 \rightarrow NO_3^-$ step. Electrocatalytic oxidation of NH_3 has previously always been directed toward N_2 production as the desirable product because the goal of these studies has been cleanup of ammonia contaminants. Occasionally, however, selectivity “failures” have occurred and nitrate has been formed as a significant product.²²

Beyond fertilizer production, ammonia has also been proposed as a hydrogen carrier in a future energy economy, because it contains a substantial 17.6% H by weight.^{23,24} Liquid NH_3 is easily storable at room temperature under a modest 10 atm. pressure—in contrast to free H_2 , another common candidate energy carrier—and it can either be cracked to H_2 or even be used directly as a fuel in an internal combustion engine.¹

In summary, we hope that a combination of the molecular, electrochemical and catalytic approaches will in future permit development of a low-carbon-footprint process for distributed fertilizer production on farms, driven by conventional silicon solar arrays. This underappreciated challenge deserves a higher profile in the sustainable chemistry area.

AUTHOR INFORMATION

Corresponding Author

*R. H. Crabtree. Email: robert.crabtree@yale.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the U.S. DOE, BES, (DE-FG02-07ER15909) for suggesting the problem, and Professors Gary Brudvig and Victor Batista for discussions.

REFERENCES

- Giddey, S.; Badwal, S. P. S.; Kulkarni, A. Review of electrochemical ammonia production technologies and materials, *Int. J. Hydrogen Energy* **2013**, *38*, 14576–14594.
- Renner, J. N.; Greenlee, L. F.; Herring, A. M.; Ayres, K. E. Electrochemical Synthesis of Ammonia: A Low Pressure, Low Temperature Approach. *Electrochem. Soc. Interface* **2015**, *24*, 51–57.
- Koch, T. A. Production of Nitric Oxide. U.S. Patent US5478549-A, December 26, 1995.
- Heck, R. M.; Bonacci, J. C.; Hatfield, W. R.; Hsiung, T. H. A new research pilot-plant unit for ammonia oxidation processes and some gauze data comparisons for nitric-acid process. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 73–79.
- Hoffman, B. M.; Lukoyanov, D.; Yang, Z. Y.; Dean, D. R.; Seefeldt, L. C. Mechanism of Nitrogen Fixation by Nitrogenase: The Next Stage. *Chem. Rev.* **2014**, *114*, 4041–4062.
- Pickett, C. J. The Chatt cycle and the mechanism of enzymic reduction of molecular nitrogen. *JBIC, J. Biol. Inorg. Chem.* **1996**, *1*, 601–606.
- Schrock, R. R. Catalytic Reduction of Dinitrogen to Ammonia at a Single Molybdenum Center. *Acc. Chem. Res.* **2005**, *38*, 955–962.
- Weinberg, D. R.; Gagliardi, C. J.; Hull, J. F.; Murphy, C. F.; Kent, C. A.; Westlake, B. C.; Paul, A.; Ess, D. H.; McCafferty, D. G.; Meyer, T. J. Proton-Coupled Electron Transfer. *Chem. Rev.* **2012**, *112*, 4016–4093.
- Davy, H. On some Chemical Agencies of Electricity. *Phil Trans.* **1807**, *97*, 1–56.
- Fichter, F.; Suter, R. Zur Frage der kathodischen Reduktion des elementaren Stickstoffs. *Helv. Chim. Acta* **1922**, *5*, 246–255.
- Lan, R.; Irvine, J. T. S.; Tao, S. Synthesis of ammonia directly from air and water at ambient temperature and pressure. *Sci. Rep.* **2013**, *3*, 1145–1145.
- Xu, G.; Liu, R.; Wang, J. Electrochemical synthesis of ammonia using a cell with a Nafion membrane and $SmFe_{0.7}Cu_{0.3-x}Ni_xO_3$ ($x = 0-0.3$) cathode at atmospheric pressure and lower temperature. *Sci. China, Ser. B: Chem.* **2009**, *52*, 1171–1175.
- Licht, S.; Cui, B.; Wang, B.; Li, F.-F.; Lau, J.; Liu, S. Ammonia synthesis by N_2 and steam electrolysis in molten hydroxide suspensions of nanoscale Fe_2O_3 . *Science* **2014**, *345*, 637–640.
- Marnellos, G.; Stoukides, M. Ammonia synthesis at atmospheric pressure. *Science* **1998**, *282*, 98–100.
- Skúlason, E.; Bligaard, T.; Gudmundsdóttir, S.; Studt, F.; Rossmeisl, J.; Abild-Pedersen, F.; Vegge, T.; Jónsson, H.; Nørskov, J. K. A theoretical evaluation of possible transition metal electro-catalysts for N_2 reduction. *Phys. Chem. Chem. Phys.* **2012**, *14*, 1235–1235.
- Howalt, J. G.; Bligaard, T.; Rossmeisl, J.; Vegge, T. DFT based study of transition metal nano-clusters for electrochemical NH_3 production. *Phys. Chem. Chem. Phys.* **2013**, *15*, 7785–7795.
- Wilson, A. D.; Newell, R. H.; McNevin, M. J.; Muckerman, J. T.; Rakowski DuBois, M.; DuBois, D. L. Hydrogen Oxidation and Production Using Nickel-Based Molecular Catalysts with Positioned Proton Relays. *J. Am. Chem. Soc.* **2006**, *128*, 358–366.
- Zhang, J. L.; Xie, Z.; Zhang, J. J.; Tang, Y. H.; Song, C. J.; Navessin, T.; Shi, Z. Q.; Song, D. T.; Wang, H. J.; Wilkinson, D. P.; Liu, Z. S.; Holdcroft, S. High temperature PEM fuel cells. *J. Power Sources* **2006**, *160*, 872–891 and refs cited.
- Karkas, M. D.; Verho, O.; Johnston, E. V.; Akermark, B. Artificial Photosynthesis: Molecular Systems for Catalytic Water Oxidation. *Chem. Rev.* **2014**, *114*, 11863–12001.
- Blakemore, J. D.; Crabtree, R. H.; Brudvig, G. W. Molecular Catalysts for Water Oxidation. *Chem. Rev.* **2015**, *115*, 12974–13005.
- Zhou, M.; Schley, N. D.; Crabtree, R. H. Cp*Ir Complexes Give Catalytic Alkane Hydroxylation with Retention of Stereochemistry. *J. Am. Chem. Soc.* **2010**, *132*, 12550–12551.
- Pérez, G.; Saiz, J.; Ibañez, R.; Urriaga, A. M.; Ortiz, I. Assessment of the formation of inorganic oxidation by-products during the electrocatalytic treatment of ammonium from landfill leachates. *Water Res.* **2012**, *46*, 2579–2590.

(23) Lan, R.; Irvine, J. T. S.; Tao, S. Ammonia and related chemicals as potential indirect hydrogen storage materials. *Int. J. Hydrogen Energy* **2012**, *37*, 1482–1494.

(24) Christensen, C. H.; Johannessen, T.; Sørensen, R. Z.; Nørskov, J. K. Towards an ammonia-mediated hydrogen economy? *Catal. Today* **2006**, *111*, 140–144.