

The potential economic feasibility of direct electrochemical nitrogen reduction as a route to ammonia

Gal Hochman,^{*a} Alan S. Goldman,^{*b} Frank A. Felder,^c James M. Mayer,^d Alexander J. M. Miller,^e Patrick L. Holland,^d Leo A. Goldman,^a Patricia Manocha,^a Ze Song,^a Saketh Aleti^a

^aDepartment of Agriculture, Food & Resource Economics, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08901, USA; Email: gal.hochman@rutgers.edu

^bDepartment of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, USA; Email: alan.goldman@rutgers.edu

^cCenter for Energy, Economic & Environmental Policy, Edward J. Bloustein School of Planning and Public Policy, Rutgers, The State University of New Jersey, 33 Livingston Avenue, New Brunswick, New Jersey 08901, USA Email: ffelder@rutgers.edu

^dDepartment of Chemistry, Yale University, New Haven, Connecticut 06511, USA. E-mail: patrick.holland@yale.edu, james.mayer@yale.edu

^eDepartment of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, USA. E-mail: ajmm@email.unc.edu

*Corresponding authors

Abstract

The Haber-Bosch synthesis produces ammonia from hydrogen and nitrogen gases in a globally important energy-intensive process that uses coal or natural gas as a fuel and as a hydrogen source. Direct electrochemical ammonia synthesis from nitrogen and water using renewable energy sources presents an alternative to the Haber-Bosch process that would be sustainable and environmentally benign. Additionally, the different production structure of direct electrochemical nitrogen reduction technology suggests a supply chain alternative to the ammonia industry, and a method for load-leveling of the electrical grid. This alternative route to ammonia from dinitrogen would not require the same large capital investments as does the Haber-Bosch process, nor would it require access to a fossil fuel supply. We show that under certain scenarios, at feasibly achievable levels of energy efficiency with a future electrocatalyst, direct nitrogen reduction would be economically competitive or advantageous compared with Haber-Bosch-based ammonia production.

1. Introduction

The world's crop production, which amounted to about 9.5×10^{15} calories in 2006, is projected to increase by 70% to 1.6×10^{16} calories by 2050.¹ To meet this growing demand, an increased input of nutrients, particularly nitrogen, is needed to support the intensification of agricultural production.² Specifically, ammonia (NH₃) is produced industrially either for direct use as fertilizer or as the feedstock from which other nitrogen-containing nutrients for plant growth are made.³⁻⁴ Ammonia is currently synthesized from nitrogen (N₂) and hydrogen (H₂) using the Haber-Bosch process (H-B) (eq 1).



Haber discovered the underlying catalytic process for H-B around 1908⁵ and it currently provides the nitrogen for virtually all synthetic fertilizer. Fertilizer synthesis from the H-B process led to huge increases in crop production in the 20th century⁵⁻⁶ and is projected to support half of the world's food production by 2025, with the share further increasing in subsequent decades.² Current ammonia production is ca. 180 million metric tons (mt) per year⁷ with a growth rate of ca. 4% projected through 2022.⁸

H-B is energy-intensive as currently applied. Natural gas or coal are typically used as fuel and as the source of hydrogen (via steam reforming). The chemical equilibrium of eq 1 lies far to the left side at temperatures required by the current catalytic system; thus, very high pressures (150-300 bar⁹) are used to drive the reaction to the right. Even at such pressures, however, at chemical equilibrium the conversion to NH₃ is only ca. 12-30%.⁹⁻¹¹ The process is also capital-intensive, requiring large centralized plants to be economical, and a significant input of energy above that of the actual product. It is estimated that about 2% of the world's fossil fuel is consumed by the process,¹² with the carbon released as CO₂. It is therefore critical to develop a sustainable route to ammonia that is not dependent on fossil fuel. An ideal alternative to H-B would also be a decentralized or distributed method, reducing transportation costs and enabling deployment in locations remote from current ammonia infrastructure.¹³

Ammonia has also received much attention as a medium for storage and transportation of energy.¹⁴⁻²² Energy sources in remote locations could be used for the production of ammonia which is relatively easy to ship or transport by pipeline. The ammonia could then be used in fuel cells or combusted for mechanical or electrical energy.

Electrolysis of water followed by H-B (hereinafter E/H-B), and direct electrochemical nitrogen reduction (hereinafter ENR)²³⁻²⁷, represent two methods that can use electricity, potentially from renewable energy sources, as the source of energy required for ammonia synthesis. Such processes could significantly reduce or even virtually eliminate the need for fossil fuel and the commensurate emissions of CO₂. E/H-B would still require centralized production, because the electrolysis-generated H₂ would be fed into a an H-B plant of the type currently in use. ENR, in contrast, could be more readily decentralized as it obviates the need for H-B. It would thus save the energy and capital costs of running H-B, and would permit the use of decentralized facilities and distributed

sources of electricity, thereby reducing the cost of transportation of ammonia to agricultural regions.

The discovery of active electrocatalysts for ENR has proceeded rapidly over the last few years although there are still no reported examples that approach a practical level of efficiency. Reported catalysts have a wide range of different chemical compositions, containing Bi, Au, Mo, Ag, Pd, Fe, and numerous other metals,²⁸⁻⁵¹ implying that there is promise for even more reactive and selective catalysts. Very low cathodic overpotentials (as low as 50 mV⁴⁸) have been reported. A representative leading catalyst uses molybdenum carbide nanorods to yield up to 95 micrograms NH₃ per hour per milligram of catalyst at a cathodic potential of -0.30 V.⁵² This catalyst system, like others recently reported, achieves a Faradaic efficiency of about 10% and at -0.30 V vs. RHE, a current density of ~25 mA/cm². It seems possible that higher current density and selectivity could be achieved at greater driving force using the flow cell strategy recently published by Robert and Berlinguette⁵³ for CO₂ reduction, enabling ENR to reach industrially relevant current densities above 150 mA/cm².

Technoeconomic aspects of ENR have been analyzed from several perspectives.^{10, 22, 41, 54-60} In this article we analyze the conditions that affect the potential economics of ENR, particularly relative to H-B-based ammonia production through either the conventional fossil-fuel based route or via H₂ derived from the electrolysis of water (E/H-B). In particular, we estimate costs using micro-level dynamic electricity pricing data⁶¹ to examine how current real-world price fluctuations could affect the costs of ammonia obtained by ENR and by E/H-B. Both ENR and E/H-B are complementary with renewable energy sources such as wind and solar which, due to their intermittency, lead to high variability in pricing due to mismatches between electrical output and demand. By selectively operating when pricing is favorable, such electrochemical processes can take advantage of these supply-demand mismatches. This not only favors their economic potential, but also allows them to act in a "load-leveling" capacity for an electric grid that is significantly based on renewables, thereby favoring the transition to a renewables-based energy system.⁶²⁻⁶³

2. Ammonia produced via the Haber-Bosch process based on fossil fuel: current practices

2a. Overview

The hydrogen feed for H-B can, in principle, be produced via various methods, including natural gas reforming or coal gasification (as well as electrolytic splitting of water in the case of E/H-B) (Fig. 1). Fossil fuel reforming or gasification is intrinsically linked to CO₂ production. Natural gas reformation is the most common source of H₂, currently used for 72% of world ammonia production. About 22% is based on coal gasification, and the remainder mostly based on fuel oil.¹⁶ Compared with the use of natural gas, other fossil fuels are associated with both significantly greater energy consumption per ton NH₃ produced via H-B and, additionally, higher emissions of CO₂ per unit energy consumed.^{16, 64}

The nitrogen feed for H-B may be produced as a co-product of coal gasification and natural gas reforming or extracted from air using an air separation unit (ASU). The ASU uses a combination

of compression, cooling, and expansion to separate the nitrogen from oxygen and other compounds in air, and therefore requires additional energy input.^{4, 65}

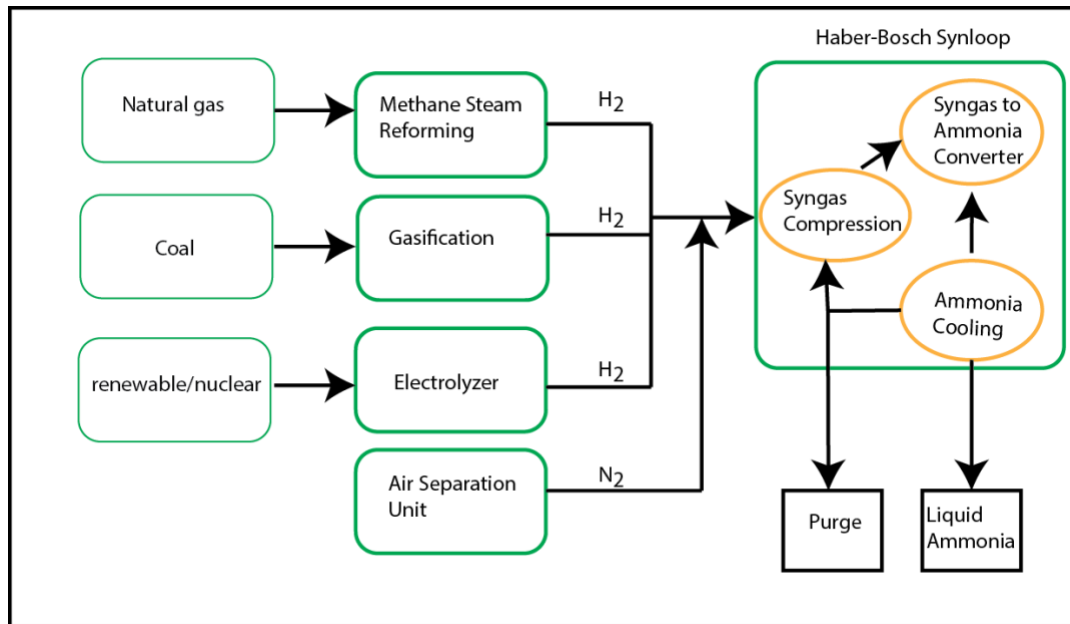


Figure 1: Ammonia synthesis based on Haber-Bosch synthesis using different energy sources

2.b. Energy requirements of H-B based on natural gas

As noted above, H-B is least energy intensive when based on natural gas among fossil fuels. The net energy input of a typical modern natural-gas-based H-B plant, expressed in MWh/mt-NH₃, is given in Table 1.¹¹ The value of 8.87 MWh/mt-NH₃ corresponds to 30.3 MBTU natural gas per mt-NH₃. This same value has been independently described as the Best Practice Technology benchmark value for ammonia production.⁶⁶

Table 1: Net energy consumption of a H-B ammonia plant based on natural gas reforming (from reference ¹¹)

| Unit Input/Output | Energy (MWh/mt-NH ₃) |
|---|----------------------------------|
| Feed and Fuel | 9.29 |
| Electricity | 0.05 |
| Steam Export (Output to external hosts) | -0.47 |
| Total | 8.87 |

2.c. Economics of the Haber-Bosch process

Following Bartels' (2008) comprehensive data analysis,⁶⁷ the construction cost for a natural-gas-based H-B production facility with a capacity of 2200 mt-NH₃ per day is \$740 million in 2007 dollars or \$889 million in 2017 dollars⁶⁸ (\$404,000 per mt-NH₃/day capacity). Of this, \$516 million is the cost of the H-B synloop and the ASU without the gas turbine (\$235,000 per mt-

NH₃/day capacity). The cost of the H-B synloop alone is \$294 million (\$134,000 per mt-NH₃/day capacity). Smaller H-B plants (100 to 600 mt-NH₃/day) have recently been constructed at costs corresponding to ca. \$700,000 per mt-NH₃/day.⁶⁹

Based on the value of 30.3 MBTU natural gas per mt-NH₃,^{11, 66} and using the average Henry Hub natural gas price of \$3.08/MBTU for January, 2017 through December, 2018, (with annual averages of \$2.99 and \$3.17 respectively)⁷⁰ the cost for the natural gas required by a plant of the type considered in Table 1 is \$93 per mt-NH₃ produced.

Using the above construction costs, we estimate the capital cost. We use the assumptions made in the U.S. Department of Energy H2A Distributed Hydrogen Production Model (Version 3),⁷¹ and considered a capital cost of 5.00% per year (corresponding to an interest rate of 4.00% per year repaid over 40 years). At this rate the construction cost of \$404,000 per mt-NH₃/day capacity corresponds to \$20,200/year per mt-NH₃/day capacity, corresponding to \$55/mt-NH₃. To approximate operation and maintenance (O&M) costs we use employment values reported for the recently built Yara/BASF ammonia plant (2018 start-up) in Freeport, TX, with a capacity of 2055 mt-NH₃/day with 35 full-time employees.⁷² We use DOE H2A⁷³ estimates of salary, administrative costs, and insurance costs, obtaining yearly expenses of \$16.6 million, or \$22/mt-NH₃.

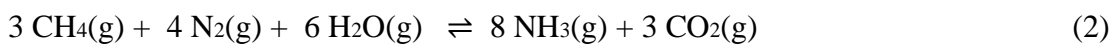
The estimated capital and O&M costs, \$55/mt-NH₃ and \$22/mt-NH₃ respectively, combine with the estimated cost of natural gas noted above (\$93/mt-NH₃) to contribute \$170/mt-NH₃ to the production cost of ammonia for large plants (Table 2). Smaller plants, ranging from 90 mt-NH₃/day to 550 mt-NH₃/day capacity, incur substantially greater per-ton capital and operating costs, with examples shown in Table 2.⁶⁹

Table 2. Estimated costs of ammonia production (\$/mt-NH₃) via H-B, by natural-gas-based H-B plants of varying capacity (based on a cost of \$3.08/MBTU natural gas)

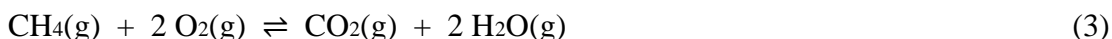
| | H-B plant size (mt-NH ₃ /day) | | |
|--------------------|--|--|--|
| | Large H-B (ca. 2000 mt/day) | Medium H-B (545 mt/day) ⁶⁹ | Small H-B (91 mt/day) ⁶⁹ |
| Natural gas | \$93 | \$93 | \$93 |
| Capital | \$55 | \$88 | \$113 |
| O&M | \$22 | \$62 | \$133 |
| Total | \$170 | \$243 | \$339 |

2.d. CO₂ emissions from a Haber-Bosch plant

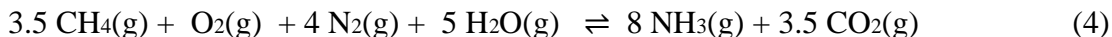
A minimum of 0.97 mt-CO₂ emissions per mt-NH₃ produced is required to provide the necessary hydrogen from the steam reforming of gas (or from direct reaction of gas with N₂), based only on consideration of the stoichiometry of eq 2 (3.0 mol CH₄ per mol NH₃). But as eq 2 and methane steam reforming are both endothermic, additional combustion of methane is required, thus increasing the minimum CO₂ emissions from a natural-gas-based H-B plant.



$$\Delta H^\circ_{450} = 7.10 \text{ kcal/mol}, \quad \Delta S^\circ_{450} = -106.9 \text{ cal/deg}\cdot\text{mol}, \quad \Delta G(450 \text{ }^\circ\text{C}) = 84.4 \text{ kcal/mol}$$



$$\Delta H^\circ_{450} = -191.2 \text{ kcal/mol}, \quad \Delta S^\circ_{450} = 0.2 \text{ cal/deg}\cdot\text{mol}, \quad \Delta G(450 \text{ }^\circ\text{C}) = -191.3 \text{ kcal/mol}$$



$$\Delta H^\circ_{450} = -65.4/\text{mol}, \quad \Delta S^\circ_{450} = -68.3 \text{ cal/deg}\cdot\text{mol}, \quad \Delta G(450 \text{ }^\circ\text{C}) = -11.3 \text{ kcal/mol}$$

Since eq 2 is only modestly endergonic, while methane combustion (eq 3) is highly exergonic, only a small amount of methane for combustion is thermodynamically required to drive the reaction of eq 2. (With 0.42 mol CH₄ combusted per 3.0 mol CH₄ required for hydrogen, as per eq 2, $\Delta G(450 \text{ }^\circ\text{C}) = 0$). Thus eq 4, in which 0.5 mol methane are combusted per 3 mol methane used as a hydrogen source, is highly exothermic and significantly exergonic. We will use this as the approximate theoretical lower limit of CO₂ production required for a methane-based H-B process, 3.5 mol CO₂ per 8 mol NH₃, or 1.13 kg-CO₂/kg-NH₃. In practice, various analyses of H-B plants conclude that CO₂ emissions range from 1.33 mt – 1.69 mt per mt-NH₃ produced.^{9, 11, 66, 74} (Note that these estimates do not include methane leakages, which may significantly increase Greenhouse Gas emissions from H-B.)

The values of energy input, monetary costs, and CO₂ emissions quoted and derived in this section are the benchmarks against which the E/H-B and ENR processes will be compared below.

3. Haber-Bosch using electrochemical H₂ production (E/H-B)

The economics and energy cost of E/H-B can be viewed in terms of the two major components that it comprises: (i) electrochemical H₂ production and (ii) the subsequent H-B to synthesize NH₃ according to eq 1. While the energy required for the H-B component of the overall process may be obtained from fossil fuel, in this section we examine the limiting case of a potentially carbon-free (in principle) E/H-B system, in which electric power serves as the source of energy to produce H₂ as well as the energy needed to drive the H-B synthesis.

The specific energy of H₂ is 143 MJ/kg or 39.7 kWh/kg. The energy efficiency of electrochemical H₂ production can be as high as ca. 80% corresponding to 49.6 kWh required per kg-H₂. For a reference point, at a price of \$0.05/kWh (\$50/MWh) this corresponds to a cost for electrical power of \$2480/mt-H₂. Assuming 100% efficiency for the H-B synthesis reaction (eq 1) (0.178 mt-H₂/mt-NH₃) this corresponds to \$441/mt-NH₃ for the H₂ feed (Table 3).

Table 3. Estimated costs of ammonia production (\$/mt-NH₃) via E/H-B, based on H2A model, PEM electrolyzer system with capacity 50 mt-H₂/day, with accompanying H-B plants of varying capacity, at a fixed benchmark electric power cost of \$50/MWh

| | H-B plant size (mt-NH ₃ /day) | | |
|--|--|----------------------------|--------------------------|
| | Large H-B (ca. 2000 mt/day) | Medium H-B (545 mt/day) | Small H-B (91 mt/day) |
| Electricity to produce H₂ feed (80% electrical efficiency) | \$441 | \$441 | \$441 |
| Capital cost (electrolyzer only) to produce H₂ feed | \$33 | \$33 | \$33 |
| O&M expenses (electrolyzer only) to produce H₂ feed | \$41 | \$41 | \$41 |
| Electricity to run accompanying H-B plant | \$67 | \$67 | \$67 |
| Capital cost for H-B plant and ASU unit (58% of full gas-based H-B plant) | \$32 | \$51 | \$66 |
| O&M expenses for H-B plant (58% of full gas-based H-B plant) | \$13 | \$36 | \$77 |
| Total | \$627 | \$669 | \$725 |

Considering the capital and O&M costs of the electrolysis plant to produce H₂, our starting point is the U.S. Department of Energy H2A Distributed Hydrogen Production Model (Version 3), specifically the modeling of a process for production of hydrogen from the electrolysis of water using grid-based electricity.⁷³ The system on which we focus is a standalone grid-powered PEM electrolyzer system with hydrogen capacity of 50,000 kg (50 mt) H₂/day (corresponding to 282 mt-NH₃/day). Our baseline model is the generic model, which uses process water and grid electricity. Costs are projected for 2040, in 2017 US dollars. The projected total of operating costs (including maintenance and repairs, labor, administrative costs, and insurance) is \$4.2 M per year, while the capital cost of \$67.4 M corresponds to \$3.4 M per year. Assuming that the plant is operating 24 h per day continuously throughout the year ("24/7"), these values correspond to capital costs of \$186/mt-H₂ and operating costs of \$230/mt-H₂, or \$33/mt-NH₃ and \$41/mt-NH₃ respectively, required to produce the necessary H₂ synthesis feed.

In addition to the energy required to produce the H₂ feed, the energy requirements to operate the associated H-B plant may be estimated, at least as a crude approximation, based on the total energy required of a highly integrated natural-gas-based H-B production facility. The most favorable estimate of such CO₂ emissions is 1.33 mt/mt-NH₃,⁷⁴ implying an efficiency of 85% compared with the theoretical value of 1.13 mt-CO₂/mt-NH₃. This implies that 15% of the full energy requirement of an integrated gas-based plant may be taken as a minimum for plant operation. Therefore, to a first approximation we use 4.55 MBTU (15% x 30.3 MBTU) or 1.33 MWh for plant operation per mt-NH₃. Assuming a fully fossil-fuel-free process (which is the goal of electrochemical systems for NH₃ production) and obtaining this energy as electrical power, using the benchmark electric power price of \$50/MWh this corresponds to \$67/mt-NH₃ for the energy required to power the H-B component of an E/H-B system.

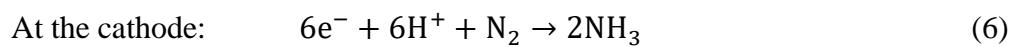
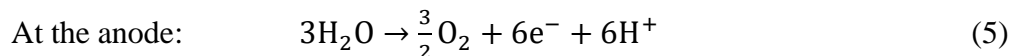
As noted in Section 2.c., the total capital for a 2200-mt/day ammonia plant, including H-B synloop and ASU, but without the gas turbine, is about \$516 million or 58% of the cost of a full H-B plant of the same capacity. This would contribute a capital cost of \$25.8 million/year, corresponding to \$32/mt-NH₃ assuming 24/7 operation. We will crudely approximate that O&M costs for this natural-gas-free (H₂-based) H-B plant will be of the same proportion to capital cost, i.e. 58% that of a full natural-gas-based H-B plant. Using the values estimated for the aforementioned Yara/BASF plant yields an O&M cost of \$13/mt-NH₃ for this H₂-based H-B plant. For smaller H₂-based H-B plants, which are of a size more commensurate with the 50-mt-H₂/day capacity of the electrolyzer for H₂ production under consideration, we will also estimate the capital cost and O&M costs to be of the same proportion (58%) to that of a natural-gas-based H-B plant of the same lower capacity. Specifically, we use the costs obtained for the same representative 545-mt-NH₃/day and 91-mt-NH₃/day plants considered in Section 2.c.

The total costs of ammonia production from E/H-B plants that use electrochemically produced H₂ for feed and fuel can now be estimated. The values obtained, based on the benchmark electric power price of \$50/MWh and other conditions assumed above, are summarized in Table 3. At the largest economy of scale, the total cost is estimated as \$627/mt-NH₃, with higher costs incurred with smaller-scale accompanying H-B plants.

4. Direct Electrochemical Nitrogen Reduction (ENR)

4.a. Overview

The ENR process comprises oxidation of water at the anode to yield O₂ and H⁺ (eq 5) and reduction of N₂ at the cathode and protonation to yield ammonia (eq 6) (Fig. 2).



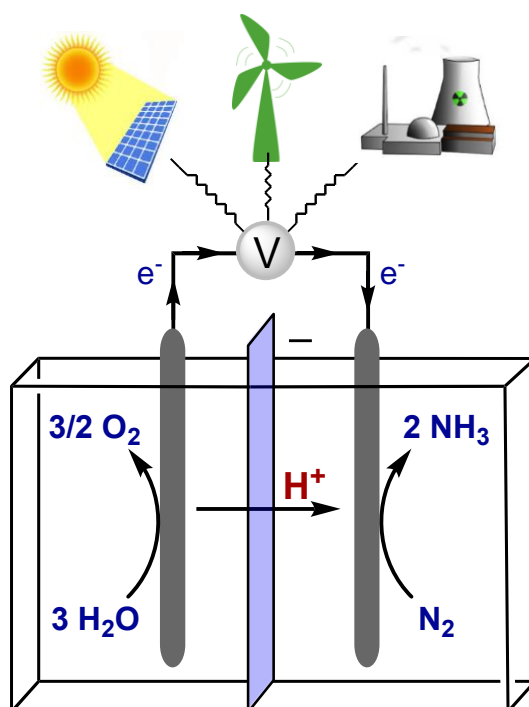
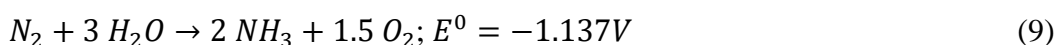
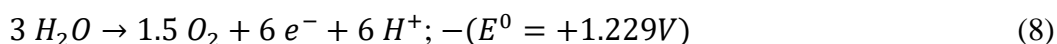
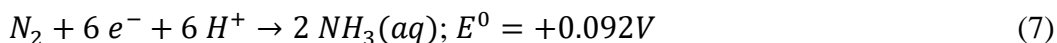


Figure 2. Schematic of sustainable electrochemical nitrogen reduction

The electrochemical potentials at standard state (1 M solutes, 1 atm gases, 298 K) for these half-reactions, and the potential for the overall reaction, are given in equations 7-9.⁷⁵⁻⁷⁶ All potentials are presented versus the standard hydrogen electrode, SHE.



From equation 9 and the Nernst equation we can obtain the baseline thermodynamic free-energy requirements for ENR, which corresponds to a minimum energy input of 5.37 MWh/mt-NH₃. (Note eqs 7–9 are at standard state conditions of 1 M H⁺, where NH₃ would be protonated as NH₄⁺, leading to an anodic shift in E^0 for eq 7 by +0.28 V vs SHE. The more general case of NH₃ production is considered here.)

The efficiency of an electrochemical synthesis such as ENR is determined by the overpotential required to generate product (i.e., the operating voltage that is beyond the thermodynamic potential) and the Faradaic efficiency (the fraction of the current that leads to the desired product). The electrochemical half-reactions of eq 7 and 8 will each have a distinct overpotential and Faradaic efficiency, which can be combined to estimate the overall overpotential and Faradaic efficiency of the full electrochemical cell. The overpotential derives from two factors, the need for higher voltage to drive the catalytic chemistry at each electrode and electrical resistive losses in the electrolyzer. On the basis of overpotential literature values for independent studies of the half-

reactions of eq 7 and eq 8, we consider 0.6 V to be a feasible aspirational full cell overpotential for eq 9,⁷⁷ and 1.2 V to be an approximate likely upper limit (considering that if greater cathodic overpotentials are used there is likely to be substantial undesired reduction of H⁺). We combine the full cell overpotential and Faradaic efficiency to define a total energy efficiency according to eq 10, where FE denotes Faradaic efficiency, TE denotes thermodynamic voltage requirement which equals 1.137 V, and TV denotes total voltage (TE plus full-cell overpotential). Table 4 gives EE as defined in eq 10 at several levels of FE and at 0.6 V and 1.2 V overpotential (as well as a limiting, purely theoretical, case of 0.0 V), and the resulting cost of electrical energy per mt-NH₃ produced, assuming a cost of \$50/MWh. For benchmarking purposes, we will focus on the aspirational values of 95% Faradaic efficiency and 0.60 V overpotential, at which EE is 62.2%. With a hypothetical electricity cost of \$50/MWh this yields an energy cost of \$432 per mt-NH₃ produced.

$$EE = FE \times \frac{TE}{TV} \quad (10)$$

Table 4. Energy input required for NH₃ production via ENR at overpotentials of 0.6 V and 1.2 V and various Faradaic efficiencies, and corresponding electrical energy costs per mt-NH₃ produced, at a fixed electricity price of \$50/MWh

| Overpotential (V) | FE | EE | Energy input (MWh/mt-NH ₃) | Electricity cost (\$/mt-NH ₃) |
|-------------------|------|--------|--|---|
| 0 | 100% | 100.0% | 5.37 | \$268.5 |
| 0.6 | 100% | 65.5% | 8.20 | \$410.2 |
| 1.2 | 100% | 48.7% | 11.04 | \$551.9 |
| 0.6 | 95% | 62.2% | 8.64 | \$431.8 |
| 1.2 | 95% | 46.2% | 11.62 | \$580.9 |
| 0.6 | 80% | 52.4% | 10.25 | \$512.7 |
| 1.2 | 80% | 38.9% | 13.80 | \$689.8 |
| 0.6 | 60% | 39.3% | 13.67 | \$683.6 |
| 1.2 | 60% | 29.2% | 18.40 | \$919.8 |

4.b. Economics of ENR at a fixed price of electrical power

We base our estimated projections of capital and operation costs for a ENR system on the same values as used for electrochemical H₂ production, using the same costs per unit of current, and assuming a fixed-proportion relation between cost structure and electric current. Thus, an ammonia plant would produce 5.63 g NH₃ (0.3333 mol x 17.03 g/mol) as compared with 1.0 g H₂ (0.5 mol x 2.016 g/mol) per unit current from a hydrogen plant. The H2A Project capacity of 50 mt-H₂/day thus implies 282 mt-NH₃/day produced with comparable investments and costs. Additionally, an air separation unit would be required for the ENR plant. Based on data from Andersson,⁵⁴ we estimate the cost of the ASU unit for such a plant to be \$4.6 M, which we add to the total capital

cost of \$67.4 M for the corresponding PEM electrolyzer system with hydrogen capacity of 50 mt-H₂/day, for a total of \$72.0 M. O&M expenses, as given above for the E/H-B system are \$4.2 M year. This baseline scenario suggests a cost of \$508/mt-NH₃, assuming electricity priced at \$50/MWh and the same parameters as applied to estimate costs of ammonia production via H-B and E/H-B (Table 5).

Table 5. Estimated costs of ammonia production (\$/mt-NH₃) via ENR, at 62.2% EE and a fixed benchmark electric power cost of \$50/MWh

| | Cost (\$/mt-NH ₃) |
|---|-------------------------------|
| Electricity to produce N₂ feed (62% EE) | \$432 |
| Capital | \$35 |
| O&M | \$41 |
| Total | \$508 |

4.c. Effects of fluctuations in electricity prices

We have identified above the parameters determining the cost of ENR at a given price for electric power. But electricity prices of course vary widely depending upon numerous factors, and can fluctuate significantly over time, within a day, over a week, and across seasons. We next investigate the economic viability of a simulated ENR ammonia plant while allowing production of NH₃ to vary depending on fluctuation in electricity prices, using pricing obtained from the Electric Reliability Council of Texas (ERCOT) in the U.S.⁷⁸ ERCOT manages the flow of electricity in most of Texas and performs financial settlement for the competitive wholesale bulk-power market and administers retail switching. Quarter-hourly wholesale ERCOT real-time market price data was used for the period January – December 2017. Variability in pricing is significant. For example, for the ERCOT West Hub, the average price was \$22.31/MWh while the price at the 99-percentile level was \$93.5/MWh and at the 1-percentile level was negative, at -\$2.62/MWh.

For purposes of this analysis we assume that the difference between industrial and wholesale ERCOT prices is fixed and therefore the difference between the industrial and wholesale prices equals the difference between the average annual industrial price and the average wholesale price. We use the U.S. EIA annual industrial electricity price data for Texas⁷⁹ together with ERCOT wholesale prices⁷⁸ (i.e., $p_{wholesale}^{ERCOT}$), to calculate this difference.

$$\Delta = \text{annual } p_{Industrial} - \text{annual } p_{wholesale} \quad (11)$$

We assume that the price obtained by the ENR ammonia plant would be less than or equal to the standard industrial price, $p_{Industrial}^{Calculated}$ (eq 12).

$$p_{Industrial}^{Calculated} = \Delta + p_{wholesale}^{ERCOT} \quad (12)$$

The average industrial electricity price paid in Texas in 2017 was \$53.5/MWh while the average wholesale electricity price the same year, for all hubs/loading zones in the ERCOT

system, was \$25.4/MWh. Thus, the average value of Δ is approximately \$30/MWh. We will consider this value, but we will also consider the likelihood that an ammonia plant, due to large scale, and especially by choosing a favorable location, might obtain a significantly more favorable price for delivery of electric power.

Based on quarter-hourly rates and Δ we calculate the annual cost of ammonia production by an ENR plant, assuming that production is discontinued when electricity costs rise above various values (“cut-offs”). These values correspond to various pricing percentiles; selected percentiles are shown in Table 6. The total cost per mt-NH₃, including electricity, capital, and O&M, is calculated according to eq 13.

$$\text{total cost/mt-NH}_3 = 5.37 \text{ MWh}(PE_{\text{cut}} + \Delta)/EE + FC/OT \quad (13)$$

- PE_{cut} : average price paid for electrical energy (per MWh) for operation times (i.e. when price per MWh is below the given cut-off)
- FC: Fixed annual costs (capital cost plus O&M) divided by 24/7 capacity in mt-NH₃/year
- OT: Operating time as a fraction of full time (equal to the percentile value corresponding to the cut-off price)

Lower price cut-offs will of course correspond to lower electricity costs per unit ammonia production, but fixed costs (capital and operating) will then be greater when calculated on a per-ton basis. Here we consider the lowest possible total cost per ton at which ammonia can be produced (including capital and O&M costs), at various assumed levels of EE, Δ , and fixed costs. This would allow a potential investor to determine if a plant could be profitable in the scenario of a given distribution of electrical pricing and a given ammonia price. Once the plant is operational, however, under this very simple model scenario, the plant would in principle produce ammonia whenever the cost of electricity (the marginal production cost) is less than the price for which the ammonia could be sold, allowing it to further maximize profit accordingly.

Assuming the various levels of energy efficiency given in Table 4, and various values of Δ , we calculate the annual per-ton cost of ammonia production at various electricity price cut-offs, each corresponding to a certain percentage (OT) of continuous operation. Values obtained using pricing from the ERCOT West Hub, which has the lowest average power cost of ERCOT hubs or loading zones, are shown in Table 6. The minimum per-mt-NH₃ production cost for each set of conditions is highlighted, and the minima for the aspirational 62.2% energy efficiency are shown in red.

Table 6. Total cost (USD, energy plus fixed costs) per mt-NH₃ produced via ENR as a function of EE, electricity cost, capital and operating expenses, with varying electricity pricing cut-offs for operation using 2017 ERCOT real-time market prices (ERCOT West Hub).

| | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|--|-------------------------------|---|--|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Energy Efficiency | | | 100% | 100% | 65% | 62% | 62% | 62% | 39% | 29% | 62% | 62% |
| Δ (\$/MWh) ^a | | | 20 | 30 | 25 | 10 | 20 | 30 | 25 | 25 | 25 | 25 |
| Fixed costs ^b (\$/MT) (24/7) | | | 75.7 | 75.7 | 75.7 | 75.7 | 75.7 | 75.7 | 75.7 | 75.7 | 151.4 | 37.85 |
| energy cost cut-off (\$/MWh) ^c | % time operating ^d | average energy cost (\$/MWh) ^e | Total cost (electricity plus fixed) (\$/MT-NH ₃) | | | | | | | | | |
| | 100 | 22.31 | 303 | 357 | 464 | 355 | 441 | 527 | 728 | 946 | 560 | 446 |
| 43.7 | 97 | 19.44 | 290 | 344 | 443 | 332 | 419 | 505 | 691 | 896 | 540 | 423 |
| 33.6 | 94 | 18.86 | 289 | 343 | 440 | 330 | 416 | 503 | 686 | 887 | 540 | 419 |
| 30.3 | 90 | 18.29 | 290 | 343 | 439 | 328 | 415 | 501 | 681 | 881 | 542 | 416 |
| 27.5 | 85 | 17.67 | 291 | 345 | 439 | 328 | 414 | 501 | 678 | 874 | 547 | 413 |
| 24.8 | 80 | 17.14 | 294 | 348 | 440 | 329 | 415 | 502 | 676 | 870 | 553 | 411 |
| 21.7 | 70 | 16.32 | 303 | 357 | 447 | 335 | 422 | 508 | 678 | 868 | 573 | 411 |
| 20.0 | 50 | 14.52 | 337 | 390 | 476 | 363 | 450 | 536 | 697 | 878 | 644 | 417 |
| 10.7 | 10 | 1.23 | 871 | 925 | 972 | 854 | 940 | 1027 | 1119 | 1240 | 1741 | 605 |
| -2.6 | 1 | -7.69 | 7636 | 7690 | 7712 | 7590 | 7676 | 7763 | 7809 | 7888 | 15289 | 3934 |
| per ton cost energy only (24/7) ^f | | | 120 | 120 | 183 | 193 | 193 | 226 | 308 | 410 | 193 | 193 |
| per ton cost energy + Δ (24/7) ^g | | | 227 | 281 | 388 | 279 | 365 | 530 | 653 | 870 | 409 | 409 |
| per ton fixed costs (24/7) ^h | | | 75.7 | 75.7 | 75.7 | 75.7 | 75.7 | 75.7 | 75.7 | 75.7 | 151.4 | 37.85 |
| per ton total costs (24/7) | | | 303 | 357 | 464 | 355 | 441 | 605 | 728 | 946 | 560 | 446 |

a) Δ : difference between wholesale electricity price and price paid

b) Fixed costs (capital and operating expenses) per mt assuming full-time operation at capacity

c) Greatest wholesale electricity price at percent operating time indicated (i.e. pricing at percentile indicated)

d) Percent time operating, assuming full operation at indicated pricing level or lower

e) Average cost of energy during time operating

f) Energy cost (not including Δ) per mt assuming full-time operation at capacity

g) Energy cost (including Δ) per mt assuming full-time operation at capacity

Considering first the purely theoretical case of a 100% energy-efficient process, and $\Delta = \$20/\text{MWh}$, the production cost of ammonia with this scenario is $\$303/\text{mt-NH}_3$ (Table 6, column 1) if the plant operates without interruption throughout the year ("24/7"). By discontinuing operation when prices are above $\$43.7/\text{MWh}$ (corresponding to 97% operation) a slightly lower production cost of $\$290/\text{mt-NH}_3$ can be achieved, with a very slightly lower minimum ($\$289/\text{mt-NH}_3$) achieved by operating about 94% of the time. If it is assumed that $\Delta = \$30/\text{MWh}$ (column 2) instead of $\$20/\text{MWh}$, the cost will be an additional $\$53.7/\text{mt-NH}_3$ at 100% efficiency (at which, production requires 5.37 MWh/mt-NH₃). Note that the value of Δ does not affect the percent of time operating at which minimum per-tonne cost is achieved.

Assuming a feasible energy efficiency of 62.2% (corresponding to the aspirational values of 0.6 V overpotential and 95% FE) the cost of 24/7 production is $\$355/\text{mt}$, $\$441/\text{mt}$ and $\$527/\text{mt}$ at Δ values of $\$10/\text{MWh}$, $\$20/\text{MWh}$ and $\$30/\text{MWh}$ respectively (columns 4-6). A greater savings is now achieved by taking advantage of dynamic electricity pricing since more energy is required to

produce a given quantity of ammonia [(5.37/0.62)MWh/mt-NH₃]. Operating only 85% of the time (corresponding to a cut-off of \$27.5/MWh), production costs that are 5-8% lower can be achieved.

Even in less favorable scenarios the cost of ammonia production via ENR is not exorbitantly high. With an energy efficiency of only 39% (corresponding, for example, to an overpotential of 1.2 V and FE = 80%) and assuming $\Delta = \$25/\text{MWh}$, ammonia production can be achieved at a cost of \$676/mt with an operating-time percentage of 80% (column 7). (Note that at these lower FEs, substantial quantity of H₂ is produced, which could have significant value, discussed below, partially offsetting the increased cost due to the "wasted" electrical current.) We also considered the possibility that the fixed cost (capital and operating costs) would be much higher than our estimates. Increasing this total by a factor of two, with an EE of 62% and $\Delta = \$25/\text{MWh}$, allows ammonia production at a total cost of \$540/mt, operating at 94% capacity (column 9). Conversely, lower fixed costs would allow the plant to take greater advantage of dynamic power pricing; decreasing fixed costs by a factor of two permits ammonia production at \$411/mt, operating at 70% capacity. It should be noted, however, that a greater quantity could be produced at an only slightly higher average cost (e.g. operating at 90% of capacity, the average cost of production from the additional 20% of capacity would be \$433/mt-NH₃, yielding a total average cost of \$416/mt-NH₃; Column 10); the actual optimum electricity price cut-off on any given day would presumably be dictated by ammonia prices.

The values in Table 6, as mentioned above, were obtained using electricity prices from the ERCOT West Hub which, offers the lowest average pricing of ERCOT Hubs/Loading-Zones. Variations between these Hubs/Zones, however, do not dramatically affect costs. The same analysis was conducted using pricing from the ERCOT Hub/Zone with *highest* average prices, the Houston Loading Zone, which offers an average price of \$29.1/MWh, 30.5% greater than that of the West Hub (\$22.3/MWh). However, due to the contributions from fixed costs and power delivery, at 62% EE and $\Delta = \$20/\text{MWh}$, for example, the cost of production when operating at 100% capacity is only 13% greater, \$500/mt-NH₃ vs. \$441/mt-NH₃ with West Hub pricing (see Appendix). Further, the higher average price is correlated with greater pricing variability; this would allow the plant to take greater advantage of dynamic pricing. Accordingly, the minimum total per-ton ammonia cost, using the pricing from the Houston Loading Zone, assuming 62% EE and $\Delta = \$20/\text{MWh}$, is \$440/mt-NH₃, achieved at ca. 80% capacity. This is only 6.3% higher than the minimum price (\$414/mt) obtained with West Hub pricing under these conditions.

Although the focus of this paper is on comparing the cost of ammonia production via H-B, E/H-B, and ENR, we note that the cost estimates projected in this study are well within the range of recent historical retail ammonia prices. For example, retail prices averaged \$480/mt-NH₃ in the US southern Plains in 2017, the period used for electrical pricing (and \$493/mt-NH₃ for 2018).⁸⁰ Wholesale prices, at the Gulf of Mexico, tend to be lower by about \$200/mt-NH₃,⁸⁰ but given the opportunities in decentralization offered by ENR, the local retail prices in agricultural areas may offer a better point of comparison.

4.d. Comparison of ENR and E/H-B economics.

A comparison of Tables 3 and 5 reveals the differences in ammonia production costs between ENR and E/H-B assuming a fixed electricity price of \$50/MWh.

We assume that reduction of H₂ to give H₂ in the E/H-B process will be more energy efficient than N₂ reduction to give ammonia in ENR. Nevertheless, because of the capital and energy expenses associated with the H-B component, even at the greatest economy of scale, ammonia production via E/H-B is projected to be more costly than ENR at the aspirational EE of 62%. This is illustrated, for a fixed energy cost of \$50/MWh, in Table 7 which summarizes the data in Tables 3 and 5. Note that the total electrical power required for E/H-B (electrolysis and H-B plant operation) is approximately equal to that required for nitrogen reduction via ENR; therefore any change in electricity prices will affect production costs of E/H-B and ENR equally in this scenario.

Table 7. Estimated costs of ammonia production (\$/mt-NH₃) via ENR compared with E/H-B with accompanying H-B plants of varying capacity, at a fixed benchmark electric power cost of \$50/MWh (from Tables 3 and 5)

| | ENR | E/H-B | | |
|---|--------------|--------------------------------------|---|--------------------------------|
| | | Large H-B plant (ca. 2000 mt/day) | Medium H-B plant (545 mt/day) | Small H-B plant (91 mt/day) |
| Electricity to produce H ₂ or NH ₃ | \$432 | \$441 | \$441 | \$441 |
| Capital cost (electrochemical stacks) | \$35 | \$33 | \$33 | \$33 |
| O&M expenses (electrolysis unit only) | \$41 | \$41 | \$41 | \$41 |
| Electricity to run accompanying H-B plant | 0 | \$67 | \$67 | \$67 |
| Capital cost for H-B plant and ASU unit | 0 | \$32 | \$51 | \$66 |
| O&M expenses for H-B plant | 0 | \$13 | \$36 | \$77 |
| Total | \$508 | \$627 | \$669 | \$725 |

Like ENR, E/H-B would allow exploitation of dynamic pricing of electrical energy, but to a lesser extent. Table 8 shows estimated costs of ammonia production via E/H-B, with operation of the electrolyzer discontinued at various electricity costs using the same the approach as taken above for ENR (Table 6). The cost is calculated according to eq 14.81 (PE_{avg} is the average price paid for electrical energy (per MWh) for 24/7 operation for the H-B plant.)

$$\text{total cost/mt-NH}_3 = (39.7 \text{ MWh})(\text{PE}_{\text{cut}} + \Delta)/(\text{EE} * 5.632) + \text{FC/OT} + 1.33 \text{ MWh} (\text{PE}_{\text{avg}} + \Delta) \quad (14)$$

Table 8. Total cost (USD, energy plus fixed costs) per mt-NH₃ produced as a function of EE, electricity cost, capital and operating expenses, with varying electricity pricing cut-offs for operation using 2017 ERCOT real-time market prices (ERCOT West Hub), shown for ENR (62% EE), and for E/H-B (80% EE) from systems that include accompanying large- or medium-scale H-B plants.

| | | | ENR | | | E/H-B (large H-B plant) ^h | | | E/H-B (medium H-B plant) ⁱ | | |
|--|-------------------------------|---|--|------------|------------|--------------------------------------|------------|------------|---------------------------------------|------------|------------|
| | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Energy Efficiency | | | 62% | 62% | 62% | 80% | 80% | 80% | 80% | 80% | 80% |
| Δ (\$/MWh) ^a | | | 10 | 20 | 30 | 10 | 20 | 30 | 10 | 20 | 30 |
| Fixed costs ^b (\$/mt) (24/7) | | | 76 | 76 | 76 | 119 | 119 | 119 | 161 | 161 | 161 |
| energy cost cut-off (\$/MWh) ^c | % time operating ^d | average energy cost (\$/MWh) ^e | Total cost (electricity plus fixed) (\$/MT-NH ₃) | | | | | | | | |
| | | | ENR | | | E/H-B | | | E/H-B | | |
| | 100 | 22.31 | 355 | 441 | 527 | 447 | 548 | 650 | 489 | 590 | 692 |
| 43.7 | 97 | 19.44 | 332 | 419 | 505 | 425 | 527 | 628 | 468 | 570 | 671 |
| 33.6 | 94 | 18.86 | 330 | 416 | 503 | 424 | 525 | 627 | 469 | 570 | 671 |
| 30.3 | 90 | 18.29 | 328 | 415 | 501 | 425 | 526 | 627 | 471 | 573 | 674 |
| 27.5 | 85 | 17.67 | 328 | 414 | 501 | 427 | 528 | 630 | 476 | 578 | 679 |
| 24.8 | 80 | 17.14 | 329 | 415 | 502 | 431 | 532 | 634 | 483 | 585 | 686 |
| 21.7 | 70 | 16.32 | 335 | 422 | 508 | 445 | 546 | 648 | 505 | 606 | 708 |
| 20.0 | 50 | 14.52 | 363 | 450 | 536 | 497 | 598 | 700 | 581 | 682 | 784 |
| 10.7 | 10 | 1.23 | 854 | 940 | 1027 | 1332 | 1433 | 1535 | 1752 | 1853 | 1955 |
| per ton cost energy only (24/7) ^f | | | 193 | 193 | 193 | 226 | 226 | 226 | 226 | 226 | 226 |
| per ton cost energy + Δ (24/7) ^g | | | 279 | 365 | 452 | 328 | 429 | 531 | 328 | 429 | 531 |
| per ton fixed costs (24/7) | | | 76 | 76 | 76 | 119 | 119 | 119 | 161 | 161 | 161 |
| per ton total costs (24/7) | | | 355 | 441 | 527 | 447 | 548 | 650 | 489 | 590 | 692 |

a) Δ = difference between wholesale electricity price and price paid

b) Fixed costs (capital and operating expenses) per ton assuming full-time operation at capacity

c) Greatest wholesale electricity price at percent operating time indicated (i.e. pricing at percentile indicated)

d) Percent time operating, assuming full operation at indicated pricing level or lower

e) Average cost of energy during time operating

f) Energy cost (not including Δ) per mt, full-time operation at capacity (including energy to run H-B plant for E/H-B)

g) Energy cost (including Δ) per mt, full-time operation at capacity (including energy to run H-B plant for E/H-B)

h) Associated H-B plant with capacity of ca. 2000 mt-NH₃/day (see Table 7)

i) Associated H-B plant with capacity of 545 mt-NH₃/day (see Table 7)

Selected results are shown in Table 8. (Results from Table 6 for ENR at 62% energy efficiency are shown in columns 1-3 of Table 8 for comparison.) Columns 4-6 show results assuming operation at a large scale (an accompanying H-B plant with ca. 2000 mt-NH₃/day capacity) and values in columns 7-9 are obtained assuming a "medium" scale H-B reactor (545 mt-NH₃ day), which is more commensurate with the size of the electrolysis unit used to calculate these value (50 mt-H₂/day corresponding to 282 mt-NH₃/day).

These calculations show that E/H-B is not only intrinsically more costly than an efficient ENR process, but also does not benefit as greatly as ENR from pricing fluctuations because of higher (fixed) capital costs and (to a much smaller extent) because the electrically powered H-B plant must run continuously (assuming no H₂ storage facility, the introduction of which would result in

higher capital/fixed costs), regardless of electricity prices.⁸² Moreover, we note that the conclusion that E/H-B is not as potentially economical as ENR is reached in spite of two simplifying assumptions we have made that favor the assessment of E/H-B: (i) a 100% yield of NH₃ from the synthesis process and (ii) the assumption that the smaller H-B plants operate with the same energy efficiency as the largest plants.

4.e. Alternative pathways for the reusing of H₂ and its implications

The energy efficiency estimated for the ENR process in the above analysis is a multiple of the Faradaic efficiency (FE) and a term accounting for overpotential (TE/TV). The plausible variability in FE is much greater than that of TE/TV. We consider that the latter term will likely range from 0.56 to 0.66 (corresponding to overpotentials of 0.6 V to 1.2 V), and thus a variation of only 17%. By contrast FE could in principle be any value up to 100% (values of FE ranging from 60% to 100% were used to obtain the per-mt costs shown in Table 6).

The term TE/TV represents (in an economic sense) "wasted energy" unless the resulting heat can be exploited. Any FE less than unity, however, does not necessarily represent "lost" energy because the primary competitive process is the reduction of H⁺ to H₂, which is a recoverable byproduct. Since the value of H₂ is very dependent on the circumstances and location where it is produced, it is beyond the scope of this study to estimate the economic value of the H₂. In the absence of a suitable market, perhaps the most obvious use of the H₂ in the context of ENR is to generate electricity that would be "recycled" to further increase the yield of NH₃ per unit electrical energy purchased externally. One could envision a separate hydrogen fuel cell generating electric power, or alternatively mixing the H₂ into the feed at the anode of the ENR cell, thereby lowering the oxidation potential.

An alternative use of H₂ byproduct of ENR would be for the air separation required to generate O₂-free N₂ for the electrocatalytic reaction. The N₂/O₂ molar ratio of air is 3.73, and the ratio of electrons required to reduce O₂ relative to N₂ is 4:6. From these values, one can calculate that 15% of the total electric current would afford enough H₂ to combust all the O₂ in an air feed, i.e. if FE ≤ 0.85 the system would produce enough H₂ to consume all the O₂ in the air feed. This could be an advantage over a typical air-separation module, with much lower capital and operations cost.

If the FE for ENR were above 85%, the smaller available quantities of H₂ could be used to reduce O₂ after an initial crude air-separation process. Likewise, even if H₂ sufficient to reduce all O₂ in the air feed were produced, it might be determined that an initial low-cost crude separation, followed by treatment with H₂, would permit more H₂ to be used for a more valuable application.

4.f. Comparison of economics of ENR with fossil-fuel-based H-B

The projected costs for ammonia production by ENR shown in Table 6 (as well as those for E/H-B in Table 8) are based on prices for electrical power that is obtained in part from renewable

sources, but primarily from fossil fuels. The primary energy mix for ERCOT in 2017 consisted of natural gas (39%), coal (32%), wind (17%), and nuclear (11%).⁸³⁻⁸⁴

The high capital cost of a H-B plant notwithstanding, if the source of electrical power for ENR (or any other electrochemical process) is primarily natural gas, the cost of such ammonia production will presumably always be greater than that of large-scale natural-gas-based H-B production. The energy loss involved in the overall ENR process in generating electricity from natural gas, and then in using that electrical power to reduce N₂, will presumably outweigh both capital costs and energy loss of a modern H-B plant. This is reflected in the estimated production costs for ENR and H-B for the same time period (and thus at the same price of natural gas); ENR production costs, using ERCOT pricing and taking advantage of fluctuating prices (Table 6), are estimated to be at least \$150 per mt-NH₃ above H-B costs in the case of a large-scale H-B plant (Table 2).

The low cost, to the producer, of ammonia via natural-gas-based H-B notwithstanding, this process has major implications for global greenhouse gas (GHG) emissions (section 2).⁸⁵ As noted above, production based on natural gas feedstock results in at least 1.33 mt-CO₂ produced per mt-NH₃. Including the cost of this negative externality yields a significant increase in the *total* (social and private) cost of ammonia produced via a natural-gas-based H-B process relative to production via ENR based on carbon-free electricity. The magnitude of this effect of course depends on the social cost of carbon, estimates of which vary greatly. A detailed survey by Pindyck yields a mean value of \$174/mt-CO₂ based on responses from economists, and \$316/mt-CO₂ based on responses from climate scientists (corresponding to \$231/mt-NH₃ and \$421/mt-NH₃, respectively) with an overall value of \$291/mt-CO₂ (\$387/mt-NH₃) based on responses from all experts surveyed.⁸⁶ Ricke *et al.* in a recent extensive study determined the median estimated social cost to be \$417/mt-CO₂ (\$555/mt-NH₃), with \$177-\$805 (\$235-\$1070/mt-NH₃) representing 66% confidence intervals.⁸⁷ Additionally, natural gas use is associated with methane emissions (primarily from natural gas extraction). Emissions of methane associated with H-B ammonia production equal 0.35% of CO₂ emissions, and the 100-year Global Warming Potential of methane is 28 times that of CO₂;⁸⁸ thus associated methane emissions may be considered to have an additional social cost equal to 10% that of the CO₂ emissions.

ENR would therefore become increasingly cost competitive with H-B as the externalities of CO₂ emissions are incorporated (directly or indirectly) into the cost of ammonia produced from natural gas. This may occur most directly in the form of a carbon tax or a cap-and-trade system. Alternatively, renewably produced ammonia could be favored by subsidies or other measures commensurate with the value of avoided CO₂ emissions. More extreme measures are also possible such as legislation requiring a carbon-free or low-carbon economy; the state of New York, for example, has recently passed a legal resolution to achieve the former goal by 2050.⁸⁹

Decreases in the cost of renewable energy, which are widely projected,⁹⁰⁻⁹² will of course also favor an ENR approach to ammonia. Levelized costs of electricity from both onshore wind and solar photovoltaic are projected to be ca. \$50/MWh for sources scheduled to go online in 2023,⁹³ with large scale solar photovoltaic power selling for as little as \$20/MWh by that year.⁹⁴ Conversely, it is far from certain that natural gas prices will remain at current, historically low,

level of ca. \$3/MBTU. In the AEO2019 reference case of the U.S. EIA, natural gas is projected to rise to \$5 per MBTU by 2050 with scenarios at two extremes giving respective prices of slightly over \$3 and slightly over \$8 per MBTU (all prices in 2018 dollars).⁹⁰

In sum, even if only the low end of the estimated ranges of social costs of CO₂ emissions is incorporated into the cost of fossil-fuel-based H-B, then renewable-power-based ENR at ca. 60% energy efficiency would already be competitive. Alternatively or in parallel, limitations on GHG-emissions could favor ENR over H-B. Additionally, the economic advantage of ENR will only increase as renewable energy costs will presumably decrease,⁹⁰⁻⁹² and natural gas prices may significantly increase.⁹⁰ Moreover, as the market penetration of renewables continues to grow,^{92-93, 95-97} its value to the electric grid decreases⁹⁸ due to issues of intermittency; therefore, consumers of electricity with flexible demand will have increasing opportunity to purchase power at a price below the 24/7 average. Finally, the cost of any energy loss due to Faradaic inefficiency in a ENR process will be offset in some part by the value of the hydrogen by-product.

Although there is far too much uncertainty (particularly, but not only, in the social cost of carbon) to allow a comparison of the economics of H-B with ENR or E/H-B with any significant degree of precision, a crude estimate of the potential relative economics may be useful. For this purpose we employ values projected for 2040 (in present dollars) for the total-system levelized cost of electricity (including transmission) from onshore wind (\$40.2/MWh),⁹⁹ the mid-range 2040 projected price of natural gas (\$4.1/MBTU),⁹⁰ and Pindyck's mean value for the social cost of carbon (\$291/mt-CO₂ corresponding to \$387/mt-NH₃). For the purposes of this crude comparison we neglect the ability to exploit dynamic pricing in the case of ENR or E/H-B. The results (Table 9) highlight that the economic competitiveness of ammonia production via ENR relative to H-B is very strongly dependent on whether (and to what extent) the social cost of carbon emissions is incorporated into the cost of production via H-B.

Table 9. Estimated costs, projected for 2040, of ammonia production (\$/mt-NH₃) via gas-based H-B (full-scale plant), ENR, and E/H-B with accompanying H-B plants of varying capacity. Projected prices

for electricity and natural gas are \$40.2/MWh⁹⁹ (fixed) and \$4.1/MBTU⁹⁰ respectively. Social cost of carbon emissions is the mean value reported in reference 86.

| | H-B Large H-B plant (2000 mt/day) | | ENR | E/H-B | |
|---|--------------------------------------|---------------|--------------------------|--|--|
| | not including SCC | including SCC | | Large H-B plant (2000 mt/day) ^a | Small H-B plant (91 mt/day) ^a |
| Electricity to produce H ₂ or NH ₃ ^b | 0 | 0 | \$347 | \$354 | \$354 |
| Capital cost (electrochemical stacks) | 0 | 0 | \$35 | \$33 | \$33 |
| O&M expenses (electrolysis unit only) | 0 | 0 | \$41 | \$41 | \$41 |
| Electricity to run accompanying H-B plant | 0 | 0 | 0 | \$42 | \$42 |
| Capital cost for H-B plant | \$55 | \$55 | 0 | \$32 | \$66 |
| O&M expenses for H-B plant | \$22 | \$22 | 0 | \$13 | \$77 |
| Natural gas | \$124 | \$124 | 0 | 0 | 0 |
| Social cost of carbon emissions | - | \$387 | 0 | 0 | 0 |
| Total | \$201 | \$588 | \$423^c | \$515^c | \$613^c |

a) Cost for H-B plant for E/H-B assumed to equal 58% of costs of full gas-based H-B plant (large or small).

b) 62% EE and 80% EE assumed for ENR and E/H-B respectively.

c) Costs would presumably be lowered somewhat by taking advantage of dynamic electricity pricing.

5. Concluding remarks

The goal of this paper is to break down the ENR cost structure and allow comparison with conventional H-B and with E/H-B alternatives. The analysis drew from work on hydrogen production (the H2A project) to predict the capital costs expected to be associated with ENR.

Unsurprisingly, the cost of electricity is predicted to be the major determinant of the cost of ammonia production via ENR. We quantify the potential decrease of the levelized cost of ammonia production that is obtained by conducting plant operation only below various prices of electric power, and at various levels of electrical efficiency and fixed (capital and operating) costs.

An ENR process operating at our aspirational levels of FE and overpotential is shown here to be intrinsically more economical than the primary carbon-free alternative, the electrolysis of water followed by the Haber-Bosch process (E-H/B). The reduction potential of N₂ is slightly more favorable than that of H₊,⁷⁶ corresponding to a theoretical energy requirement ca. 7.5% less for the formation of NH₃ relative to the formation of the H₂ required for hydrogenation of N₂. Even more importantly, ENR does not require the energy consumption and high capital costs of an accompanying H-B plant required by E/H-B. Thus, even at our benchmarked 62% level of energy efficiency, the ENR process would be significantly more economical than E/H-B with electrolysis of water at 80% energy efficiency. Moreover, the less capital-intensive cost structure of ENR is particularly favored by volatility in electrical pricing. Likewise, in addition to the greater ability to respond to the pricing of electrical power, ENR would also provide more opportunity to discontinue and resume production according to fluctuations in ammonia pricing or demand.

Lastly, removing the need for a H-B plant also allows a much greater degree of decentralization which potentially has benefits for farming even in areas that are well connected to infrastructure, and much more so for those that are not.

Nitrogen fixation is critical to the agricultural production necessary to feed humanity and is potentially of tremendous value for the storage, transportation, and consumption of renewable energy. But while the cost to the producer of conventional natural-gas-based H-B production is generally quite low, its combined social and private cost is very high if typical estimates of social costs of GHG emission are taken into account. These costs are expected to be increasingly reflected in taxes and/or regulations on emissions. In addition to the social cost of GHG emissions, the reliance on fossil fuels also results in vulnerability to volatility in global market prices and a complex intersection with the geo-political landscape.¹⁰⁰ Conversely, as the cost of renewable (carbon-free) energy continues to decline, methods based on it for ammonia production become economically more attractive.

At this time, E/H-B is the only technology that is efficient enough to feasibly replace H-B on the scale necessary for fertilizer production. The results of this study, however, indicates that the development of a feasibly efficient ENR process is the more desirable solution to this long-term need. The potentially lower production cost via ENR may suggest that it is also the only process that could take practical advantage of the opportunities that nitrogen reduction offers for the storage and transportation of energy. It must be emphasized that the current state of ENR technology is still far from economically feasible for fertilizer production, and even less so for economically viable energy storage. Based on fundamental considerations illuminated in this work, however, we conclude that development of an efficient ENR technology is a goal with enormous potential reward.

References

- (1) Searchinger, T.; Hanson, C.; Ranganathan, J.; Lipinski, B.; Waite, R.; Winterbottom, R.; Dinshaw, A.; Heimlich, R., The great balancing act: installment 1 of creating a sustainable food future. *World Resources Institute* **2013**.
- (2) "The future of food and agriculture – Trends and challenges." Food and Agriculture Organization of the United Nations (FAO). Rome, 2017 <http://www.fao.org/3/a-i6583e.pdf>
- (3) Smil, V., Nitrogen cycle and world food production. *World Agriculture* **2011**, *2*, 9-13.
- (4) *Catalytic Ammonia Synthesis, Fundamentals and Practice*; Jennings, J. R., Ed. Springer US: 1991.
- (5) Smil, V., *Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food Production*. MIT Press: Cambridge, MA, 2004.
- (6) Erisman, J. W.; Sutton, M. A.; Galloway, J.; Klimont, Z.; Winiwarter, W., How a century of ammonia synthesis changed the world *Nat. Geosci.* **2008**, *1*, 636-639.
- (7) Pattabathula, V.; Richardson, J., Introduction to Ammonia Production. *CEP Magazine* September, 2016, 2016.
- (8) "Ammonia Market 2018 Outlook to 2022" Reuters VCNewsNetwork, 5 September 2018 <https://www.reuters.com/brandfeatures/venture-capital/article?id=49951> (retrieved June 30, 2019)
- (9) Morgan, E. R. Techno-Economic Feasibility Study of Ammonia Plants Powered by Offshore Wind. PhD, University of Massachusetts Amherst, Open Access Dissertations. 697, 2013.
- (10) Frattini, D.; Cinti, G.; Bidini, G.; Desideri, U.; Cioffi, R.; Jannelli, E., A system approach in energy evaluation of different renewable energies sources integration in ammonia production plants *Renewable Energy* **2016**, *99*, 472-482.
- (11) Noelker, K.; Ruether, J., Low Energy Consumption Ammonia Production: Baseline Energy Consumption, Options for Energy Optimization. In *Nitrogen + Syngas Conference*, Duesseldorf, 2011.
- (12) Rafiqul, I.; Weber, C.; Lehmann, B.; Voss, A., Energy efficiency improvements in ammonia production—perspectives and uncertainties *Energy* **2005**, *30*, 2487-2504.

- (13) Tallaksen, J.; Bauer, F.; Hulteberg, C.; Reese, M.; Ahlgren, S., Nitrogen fertilizers manufactured using wind power: greenhouse gas and energy balance of community-scale ammonia production *J. Clean. Prod.* **2015**, *107*, 626-635.
- (14) Churchard, A. J.; Banach, E.; Borgschulte, A.; Caputo, R.; Chen, J.-C.; Clary, D.; Fijalkowski, K. J.; Geerlings, H.; Genova, R. V.; Grochala, W.; Jaroń, T.; Juanes-Marcos, J. C.; Kasemo, B.; Kroes, G.-J.; Ljubić, I.; Naujoks, N.; Nørskov, J. K.; Olsen, R. A.; Pendolino, F.; Remhof, A.; Románszki, L.; Tekin, A.; Vegge, T.; Zäch, M.; Züttel, A., A multifaceted approach to hydrogen storage *Phys. Chem. Chem. Phys.* **2011**, *13*, 16955-16972.
- (15) Aziz, M.; Oda, T.; Morihara, A.; Kashiwagi, T., Combined nitrogen production, ammonia synthesis, and power generation for efficient hydrogen storage *Energy Procedia* **2017**, *143*, 674-679.
- (16) Giddey, S.; Badwal, S. P. S.; Munnings, C.; Dolan, M., Ammonia as a Renewable Energy Transportation Media *ACS Sustain. Chem. Eng.* **2017**, *5*, 10231-10239.
- (17) Valera-Medina, A.; Xiao, H.; Owen-Jones, M.; David, W. I. F.; Bowen, P. J., Ammonia for power *Progress in Energy and Combustion Science* **2018**, *69*, 63-102.
- (18) Service, R. F., Liquid sunshine *Science (Washington, DC, U. S.)* **2018**, *361*, 120-123.
- (19) Yapicioglu, A.; Dincer, I., A review on clean ammonia as a potential fuel for power generators *Renew. Sustain. Energy Rev.* **2019**, 96-108.
- (20) Juangsa, F. B.; Aziz, M., Integrated system of thermochemical cycle of ammonia, nitrogen production, and power generation *Int. J. Hydrog. Energy* **2019**, *44*, 17525-17534.
- (21) Bicer, Y.; Dincer, I., Exergoeconomic analysis and optimization of a concentrated sunlight-driven integrated photoelectrochemical hydrogen and ammonia production system *Int. J. Hydrog. Energy* **2019**, *44*, 18875-18890.
- (22) Bargiacchi, E.; Antonelli, M.; Desideri, U., A comparative assessment of Power-to-Fuel production pathways *Energy* **2019**, *183*, 1253-1265.
- (23) Suryanto, B. H. R.; Du, H.-L.; Wang, D.; Chen, J.; Simonov, A. N.; MacFarlane, D. R., Challenges and prospects in the catalysis of electroreduction of nitrogen to ammonia *Nat. Catal.* **2019**, *2*, 290-296.
- (24) Foster, S. L.; Bakovic, S. I. P.; Duda, R. D.; Maheshwari, S.; Milton, R. D.; Minter, S. D.; Janik, M. J.; Renner, J. N.; Greenlee, L. F., Catalysts for nitrogen reduction to ammonia *Nat. Catal.* **2018**, *1*, 490-500.
- (25) Chen, J. G.; Crooks, R. M.; Seefeldt, L. C.; Bren, K. L.; Bullock, R. M.; Darensbourg, M. Y.; Holland, P. L.; Hoffman, B.; Janik, M. J.; Jones, A. K.; Kanatzidis, M. G.; King, P.; Lancaster, K. M.; Lyman, S. V.; Pfromm, P.; Schneider, W. F.; Schrock, R. R., Beyond fossil fuel-driven nitrogen transformations *Science* **2018**, *360*, eaar6611.
- (26) Singh, A. R.; Rohr, B. A.; Schwalbe, J. A.; Cargnello, M.; Chan, K.; Jaramillo, T. F.; Chorkendorff, I.; Nørskov, J. K., Electrochemical Ammonia Synthesis—The Selectivity Challenge *ACS Catal.* **2017**, *7*, 706-709.
- (27) Montoya, J. H.; Tsai, C.; Vojvodic, A.; Nørskov, J. K., The Challenge of Electrochemical Ammonia Synthesis: A New Perspective on the Role of Nitrogen Scaling Relations *ChemSusChem* **2015**, *8*, 2180-2186.
- (28) Yang, D.; Chen, T.; Wang, Z., Electrochemical reduction of aqueous nitrogen (N₂) at a low overpotential on (110)-oriented Mo nanofilm *J. Mater. Chem. A* **2017**, *5*, 18967-18971.
- (29) Zhang, L.; Ji, X.; Ren, X.; Ma, Y.; Shi, X.; Tian, Z.; Asiri, A. M.; Chen, L.; Tang, B.; Sun, X., Electrochemical Ammonia Synthesis via Nitrogen Reduction Reaction on a MoS₂ Catalyst: Theoretical and Experimental Studies *Adv. Mater.* **2018**, *30*, 1800191.
- (30) Han, J.; Ji, X.; Ren, X.; Cui, G.; Li, L.; Xie, F.; Wang, H.; Li, B.; Sun, X., MoO₃ nanosheets for efficient electrocatalytic N₂ fixation to NH₃ *J. Mater. Chem. A* **2018**, *6*, 12974-12977.
- (31) Ren, X.; Cui, G.; Chen, L.; Xie, F.; Wei, Q.; Tian, Z.; Sun, X., Electrochemical N₂ fixation to NH₃ under ambient conditions: Mo₂N nanorod as a highly efficient and selective catalyst *Chem. Commun.* **2018**, *54*, 8474-8477.
- (32) Zhang, L.; Ji, X.; Ren, X.; Luo, Y.; Shi, X.; Asiri, A. M.; Zheng, B.; Sun, X., Efficient Electrochemical N₂ Reduction to NH₃ on MoN Nanosheets Array under Ambient Conditions *ACS Sustain. Chem. Eng.* **2018**, *6*, 9550-9554.
- (33) Suryanto, B. H. R.; Kang, C. S. M.; Wang, D.; Xiao, C.; Zhou, F.; Azofra, L. M.; Cavallo, L.; Zhang, X.; MacFarlane, D. R., Rational Electrode-Electrolyte Design for Efficient Ammonia Electrosynthesis under Ambient Conditions *ACS Energy Lett.* **2018**, *3*, 1219-1224.
- (34) Li, X.; Li, T.; Ma, Y.; Wei, Q.; Qiu, W.; Guo, H.; Shi, X.; Zhang, P.; Asiri, A. M.; Chen, L.; Tang, B.; Sun, X., Boosted Electrocatalytic N₂ Reduction to NH₃ by Defect-Rich MoS₂ Nanoflower *Adv. Energy Mater.* **2018**, *8*, 1801357.
- (35) Lv, C.; Yan, C.; Chen, G.; Ding, Y.; Sun, J.; Zhou, Y.; Yu, G., An Amorphous Noble-Metal-Free Electrocatalyst that Enables Nitrogen Fixation under Ambient Conditions *Angew. Chem., Intl. Ed.* **2018**, 6073-6076.
- (36) Shi, M.-M.; Bao, D.; Wulan, B.-R.; Li, Y.-H.; Zhang, Y.-F.; Yan, J.-M.; Jiang, Q., Au Sub-Nanoclusters on TiO₂ toward Highly Efficient and Selective Electrocatalyst for N₂ Conversion to NH₃ at Ambient Conditions *Adv. Mater.* **2017**, *29*, 1606550.

- (37) Li, S.-J.; Bao, D.; Shi, M.-M.; Wulan, B.-R.; Yan, J.-M.; Jiang, Q., Amorphizing of Au Nanoparticles by CeO_x-RGO Hybrid Support towards Highly Efficient Electrocatalyst for N₂ Reduction under Ambient Conditions *Adv. Mater.* **2017**, *29*, 1700001.
- (38) Bao, D.; Zhang, Q.; Meng, F.-L.; Zhong, H.-X.; Shi, M.-M.; Zhang, Y.; Yan, J.-M.; Jiang, Q.; Zhang, X.-B., Electrochemical Reduction of N₂ under Ambient Conditions for Artificial N₂ Fixation and Renewable Energy Storage Using N₂/NH₃ Cycle *Adv. Mater.* **2017**, *29*, 1604799.
- (39) Kong, J.; Lim, A.; Yoon, C.; Jang, J. H.; Ham, H. C.; Han, J.; Nam, S.; Kim, D.; Sung, Y.-E.; Choi, J.; Park, H. S., Electrochemical Synthesis of NH₃ at Low Temperature and Atmospheric Pressure Using a γ -Fe₂O₃ Catalyst *ACS Sustain. Chem. Eng.* **2017**, *5*, 10986-10995.
- (40) Chen, S.; Perathoner, S.; Ampelli, C.; Mebrahtu, C.; Su, D.; Centi, G., Electrocatalytic Synthesis of Ammonia at Room Temperature and Atmospheric Pressure from Water and Nitrogen on a Carbon-Nanotube-Based Electrocatalyst *Angew. Chem., Intl. Ed.* **2017**, *56*, 2699-2703.
- (41) Kyriakou, V.; Garagounis, I.; Vasileiou, E.; Vourros, A.; Stoukides, M., Progress in the Electrochemical Synthesis of Ammonia *Catal. Today* **2017**, *286*, 2-13.
- (42) Liu, Q.; Zhang, X.; Zhang, B.; Luo, Y.; Cui, G.; Xie, F.; Sun, X., Ambient N₂ fixation to NH₃ electrocatalyzed by a spinel Fe₃O₄ nanorod *Nanoscale* **2018**, *10*, 14386-14389.
- (43) Han, J.; Liu, Z.; Ma, Y.; Cui, G.; Xie, F.; Wang, F.; Wu, Y.; Gao, S.; Xu, Y.; Sun, X., Ambient N₂ fixation to NH₃ at ambient conditions: Using Nb₂O₅ nanofiber as a high-performance electrocatalyst *Nano Energy* **2018**, *52*, 264-270.
- (44) Liu, Y.; Su, Y.; Quan, X.; Fan, X.; Chen, S.; Yu, H.; Zhao, H.; Zhang, Y.; Zhao, J., Facile Ammonia Synthesis from Electrocatalytic N₂ Reduction under Ambient Conditions on N-Doped Porous Carbon *ACS Catal.* **2018**, *8*, 1186-1191.
- (45) Lee, H. K.; Koh, C. S. L.; Lee, Y. H.; Liu, C.; Phang, I. Y.; Han, X.; Tsung, C.-K.; Ling, X. Y., Favoring the unfavored: Selective electrochemical nitrogen fixation using a reticular chemistry approach *Science Advances* **2018**, *4*, eaar3208.
- (46) Kugler, K.; Luhn, M.; Schramm, J. A.; Rahimi, K.; Wessling, M., Galvanic deposition of Rh and Ru on randomly structured Ti felts for the electrochemical NH₃ synthesis *Phys. Chem. Chem. Phys.* **2015**, *17*, 3768-3782.
- (47) Kordali, V.; Kyriacou, G.; Lambrou, C., Electrochemical synthesis of ammonia at atmospheric pressure and low temperature in a solid polymer electrolyte cell *Chem. Commun.* **2000**, 1673-1674.
- (48) Wang, J.; Yu, L.; Hu, L.; Chen, G.; Xin, H.; Feng, X., Ambient ammonia synthesis via palladium-catalyzed electrohydrogenation of dinitrogen at low overpotential *Nat. Commun.* **2018**, *9*, 1795.
- (49) Song, Y.; Johnson, D.; Peng, R.; Hensley, D. K.; Bonnesen, P. V.; Liang, L.; Huang, J.; Yang, F.; Zhang, F.; Qiao, R.; Baddorf, A. P.; Tschaplinski, T. J.; Engle, N. L.; Hatzell, M. C.; Wu, Z.; Cullen, D. A.; Meyer, H. M.; Sumpter, B. G.; Rondinone, A. J., A physical catalyst for the electrolysis of nitrogen to ammonia *Science Advances* **2018**, *4*, e1700336.
- (50) Qiu, W.; Xie, X.-Y.; Qiu, J.; Fang, W.-H.; Liang, R.; Ren, X.; Ji, X.; Cui, G.; Asiri, A. M.; Cui, G.; Tang, B.; Sun, X., High-performance artificial nitrogen fixation at ambient conditions using a metal-free electrocatalyst *Nat. Commun.* **2018**, *9*, 3485.
- (51) Abghoui, Y.; Garden, A. L.; Hlynsson, V. F.; Bjoergvinsdottir, S.; Olafsdottir, H.; Skulason, E., Enabling electrochemical reduction of nitrogen to ammonia at ambient conditions through rational catalyst design *Phys. Chem. Chem. Phys.* **2015**, *17*, 4909-4918.
- (52) Ren, X.; Zhao, J.; Wei, Q.; Ma, Y.; Guo, H.; Liu, Q.; Wang, Y.; Cui, G.; Asiri, A. M.; Li, B.; Tang, B.; Sun, X., High-Performance N₂-to-NH₃ Conversion Electrocatalyzed by Mo₂C Nanorod *ACS Cent. Sci.* **2019**, *5*, 116-121.
- (53) Ren, S.; Joulié, D.; Salvatore, D.; Torbensen, K.; Wang, M.; Robert, M.; Berlinguette, C. P., Molecular electrocatalysts can mediate fast, selective CO₂ reduction in a flow cell *Science* **2019**, *365*, 367.
- (54) Andersson, J.; Lundgren, J., Techno-economic analysis of ammonia production via integrated biomass gasification *Applied Energy* **2014**, *130*, 484-490.
- (55) Bañares-Alcántara, R.; III, G. D.; Fiaschetti, M.; Grünewald, P.; Lopez, J. n. M.; Tsang, E.; Yang, A.; Ye, L.; Zhao, S. *Analysis of Islanded Ammonia-based Energy Storage Systems*; University of Oxford: 2015.
- (56) Dana, A. G.; Elishav, O.; Bardow, A.; Shter, G. E.; Grader, G. S., Nitrogen-Based Fuels: A Power-to-Fuel-to-Power Analysis *Angew. Chem., Intl. Ed.* **2016**, *55*, 8798-8805.
- (57) Elishav, O.; Lewin, D. R.; Shter, G. E.; Grader, G. S., The nitrogen economy: Economic feasibility analysis of nitrogen-based fuels as energy carriers *Applied Energy* **2017**, *185*, Part 1, 183-188.
- (58) Wang, L.; Xia, M.; Wang, H.; Huang, K.; Qian, C.; Maravelias, C. T.; Ozin, G. A., Greening Ammonia toward the Solar Ammonia Refinery *Joule* **2018**, *2*, 1055-1074.
- (59) Ikäheimo, J.; Kiviluoma, J.; Weiss, R.; Holttinen, H., Power-to-ammonia in future North European 100 % renewable power and heat system *Int. J. Hydrog. Energy* **2018**, *43*, 17295-17308.
- (60) Andersson, J.; Grönkvist, S., Large-scale storage of hydrogen *Int. J. Hydrog. Energy* **2019**, *44*, 11901-11919.

- (61) Dutta, G.; Mitra, K., A literature review on dynamic pricing of electricity *J. Oper. Res. Soc.* **2017**, *68*, 1131-1145.
- (62) Denholm, P.; Hand, M., Grid flexibility and storage required to achieve very high penetration of variable renewable electricity *Energy Policy* **2011**, *39*, 1817-1830.
- (63) Lund, P. D.; Lindgren, J.; Mikkola, J.; Salpakari, J., Review of energy system flexibility measures to enable high levels of variable renewable electricity *Renew. Sust. Energy Rev.* **2015**, *45*, 785-807.
- (64) "Feeding the Earth, Energy Efficiency and CO₂ emissions in ammonia production. Dec 2009" International Fertilizer Industry Association.
https://www.fertilizer.org/images/Library_Downloads/2009_IFA_energy_efficiency.pdf
- (65) Smith, A. R.; Klosek, J., A review of air separation technologies and their integration with energy conversion processes *Fuel Process. Technol.* **2001**, *70*, 115-134.
- (66) Industrial Efficiency Technology Database, Ammonia Benchmarks, <http://ietd.iipnetwork.org/content/ammonia-benchmarks> (downloaded 2 June, 2019)
- (67) Bartels, J. R. "A feasibility study of implementing an Ammonia Economy" Iowa State University – Digital Repository, 2008. <http://lib.dr.iastate.edu/etd/11132/>
- (68) Producer Price Index, Construction machinery mfg - PCU333120333120, Bureau of Labor Statistics, annual average prices 2007-2017) <https://data.bls.gov/cgi-bin/surveymost?pc> (retrieved June 30, 2019)
- (69) For examples of smaller plants: (a) A 600 short-ton-per-day plant was reported to be built in Rock Springs, WY for a cost of \$350 M, or \$643,000 per MT-NH₃/day capacity. Brown, T. Ammonia Industry "Rock Springs, WY - Simplot" 13 January, 2014: <https://ammoniaindustry.com/rock-springs-wy-simplot/> (b) A 331-short-ton-per-day plant is planned for completion in Iowa in 2020 at a cost of \$220 M or \$730,000 per MT-NH₃/day capacity. Brown, T. Ammonia Industry "Garner, IA — Greenfield Nitrogen" 14 May, 2018: <https://ammoniaindustry.com/garner-ia-greenfield-nitrogen/> (c) A 100 short-ton-per-day plant was completed in Nebraska in 2018 at a cost of \$75 M or \$826,000 per MT-NH₃/day capacity. Brown, T. Ammonia Industry "Geneva, NE – Fortigen" <https://ammoniaindustry.com/geneva-ne-fortigen/>
- (70) U.S. Energy Information Administration, Henry Hub Natural Gas Spot Price <https://www.eia.gov/dnav/ng/hist/rngwhhdm.htm>
- (71) Project documentations available at http://www.hydrogen.energy.gov/h2a_production.html
- (72) A 750,000 MT-NH₃/year (2055 MT-NH₃/day) plant (Yara/BASF) built in Freeport, TX, at a cost of \$600M, is reported to employ 35 permanent workers. Brown, T. Ammonia Industry "Freeport, TX — Yara/BASF" 31 July, 2018: <https://ammoniaindustry.com/freeport-tx-yara-basf/>
- (73) Saur, G.; Ramsden, T.; James, B.; Colella, W. Future Distributed Hydrogen Production from Grid PEM Electrolysis NREL, 2018 <https://www.nrel.gov/hydrogen/h2a-production-case-studies.html>
- (74) Makhlof, A.; Serradj, T.; Cheniti, H., Life cycle impact assessment of ammonia production in Algeria: A comparison with previous studies *Environmental Impact Assessment Review* **2015**, *50*, 35-41.
- (75) Kugler, K.; Ohs, B.; Scholz, M.; Wessling, M., Towards a carbon independent and CO₂-free electrochemical membrane process for NH₃ synthesis *Phys. Chem. Chem. Phys.* **2014**, *16*, 6129-6138.
- (76) Lindley, B. M.; Appel, A. M.; Krogh-Jespersen, K.; Mayer, J. M.; Miller, A. J. M., Evaluating the Thermodynamics of Electrocatalytic N₂ Reduction in Acetonitrile *ACS Energy Lett.* **2016**, 698-704.
- (77) Xue, X.; Chen, R.; Yan, C.; Zhao, P.; Hu, Y.; Zhang, W.; Yang, S.; Jin, Z., Review on photocatalytic and electrocatalytic artificial nitrogen fixation for ammonia synthesis at mild conditions: Advances, challenges and perspectives *Nano Research* **2019**, *12*, 1229-1249.
- (78) ERCOT Market Prices, Historical Real-Time Market Load Zone and Hub Prices <http://www.ercot.com/mktinfo/prices> . For more detailed information about ERCOT see <http://www.ercot.com/about>
- (79) U.S. Energy Information Administration, "Electricity. Average Price by State by Provider" (1990-2017) <https://www.eia.gov/electricity/data/state/> Electricity Price and Expenditure Estimates, 2017 https://www.eia.gov/state/seds/data.php?incfile=/state/seds/sep_fuel/html/fuel_pr_es.html&sid=US (downloaded June 30, 2019)
- (80) Farm Futures <https://www.farmprogress.com/story-weekly-fertilizer-review-0-30765>
- (81) Coefficients in eq 14: 39.7 MWh is the theoretical energy required to produce 1 mt-H₂; 5.632 is the ratio of mass of NH₃ produced per unit mass of H₂ assuming 100% efficiency of the H-B synthesis; 1.33 MWh is the energy required to run the H-B plant per mt-NH₃ produced.
- (82) This consideration also implies (although not added to the total costs shown in Table 8) the need for additional H₂ storage capacity for times when H₂ is not being produced by the electrolyzer.
- (83) St. John, Jeff "Texas Grid Operator Reports Fuel Mix Is Now 30% Carbon-Free" , Greentechmedia, January 23, 2019, <https://www.greentechmedia.com/articles/read/a-snapshot-of-texas-growing-appetite-for-wind-and-solar-power-gs.lkrpiy>
- (84) Popovich, N., How Does Your State Make Electricity? *New York Times* December 24, 2018.
- (85) Pfromm, P. H., Towards sustainable agriculture: Fossil-free ammonia *J. Renew. Sustain. Energy* **2017**, *9*, 034702.

- (86) Pindyck, R. S., The social cost of carbon revisited *J. Environ. Econ. Manage.* **2019**, *94*, 140-160.
- (87) Ricke, K.; Drouet, L.; Caldeira, K.; Tavoni, M., Country-level social cost of carbon *Nature Clim. Change* **2018**, *8*, 895-900.
- (88) IPCC, 2014: Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)]. IPCC, Geneva, Switzerland, p 87.
- (89) McKinley, J.; Plumer, B., New York to Approve One of the World's Most Ambitious Climate Plans. *New York Times* June 18, 2019, 2019.
- (90) Annual Energy Outlook 2019 With Projections to 2050, U. S. Energy Information Administration, <https://www.eia.gov/outlooks/aeo/pdf/aeo2019.pdf>
- (91) Creutzig, F.; Agoston, P.; Goldschmidt, J. C.; Luderer, G.; Nemet, G.; Pietzcker, R. C., The underestimated potential of solar energy to mitigate climate change *Nat. Energy* **2017**, *2*, 17140.
- (92) Gilbert, A. Q.; Sovacool, B. K., Looking the wrong way: Bias, renewable electricity, and energy modelling in the United States *Energy* **2016**, *94*, 533-541.
- (93) Levelized Cost and Levelized Avoided Cost of New Generation Resources in the Annual Energy Outlook 2019, U. S. Energy Information Administration, February 2019
https://www.eia.gov/outlooks/aeo/pdf/electricity_generation.pdf
- (94) Service, R. F., Solar plus batteries is now cheaper than fossil power *Science* **2019**, *365*, 108.
- (95) Audoly, R.; Vogt-Schilb, A.; Guivarch, C.; Pfeiffer, A., Pathways toward zero-carbon electricity required for climate stabilization *Applied Energy* **2018**, *225*, 884-901.
- (96) Sachs, J. D.; Schmidt-Traub, G.; Williams, J., Pathways to zero emissions *Nat. Geosci.* **2016**, *9*, 799.
- (97) Meckling, J.; Sterner, T.; Wagner, G., Policy sequencing toward decarbonization *Nat. Energy* **2017**, *2*, 918-922.
- (98) Sivaram, V.; Kann, S., Solar power needs a more ambitious cost target *Nat. Energy* **2016**, *1*, 16036.
- (99) Levelized Cost and Levelized Avoided Cost of New Generation Resources in the Annual Energy Outlook 2019, U.S. Energy Information Administration, Appendix B, Table B3
https://www.eia.gov/outlooks/aeo/pdf/electricity_generation.pdf
- (100) Grigas, A., *The New Geopolitics of Natural Gas*. Harvard University Press: Cambridge, MA, 2017.

Acknowledgements

We thank the NSF Chemical Catalysis Program of the Chemistry Division for funding this collaborative project through Grants CHE-1665146 (GH and ASG), CHE-1665137 (JMM and PLH), and CHE-1665135 (AJMM).

Competing interests

The authors declare no competing interests.

Appendix

Table S1. Total cost (USD, energy plus fixed costs) per mt ammonia produced as a function of energy efficiency, energy costs, capital and operating expenses, with varying energy pricing cut-offs for operation using 2017 ERCOT real-time market prices (ERCOT Houston Loading Zone).

| LZ_HOUSTON_LZEW | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|--|-------------------------------|---|---|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Energy Efficiency | | | 100% | 100% | 65% | 62% | 62% | 62% | 39% | 29% | 62% | 62% |
| Δ (\$/MWh) ^a | | | 20 | 30 | 25 | 10 | 20 | 30 | 25 | 25 | 25 | 25 |
| Fixed costs ^b (\$/MT) (24/7) | | | 75.7 | 75.7 | 75.7 | 75.7 | 75.7 | 75.7 | 75.7 | 75.7 | 151.4 | 37.9 |
| energy cost cut-off (\$/MWh) ^c | % time operating ^d | average energy cost (\$/MWh) ^e | Total cost (electricity plus fixed) (\$/MT-NH3) | | | | | | | | | |
| | 100 | 29.10 | 339 | 393 | 520 | 413 | 500 | 586 | 822 | 1071 | 619 | 505 |
| 53.6 | 97 | 22.59 | 307 | 360 | 468 | 359 | 446 | 532 | 735 | 953 | 567 | 450 |
| 39.0 | 94 | 21.88 | 305 | 359 | 465 | 356 | 442 | 529 | 727 | 943 | 566 | 445 |
| 33.1 | 90 | 21.28 | 306 | 359 | 464 | 354 | 441 | 527 | 723 | 936 | 568 | 442 |
| 30.5 | 85 | 20.67 | 307 | 361 | 464 | 354 | 440 | 527 | 719 | 929 | 573 | 439 |
| 28.6 | 80 | 20.11 | 310 | 364 | 465 | 355 | 441 | 527 | 717 | 924 | 579 | 437 |
| 24.5 | 70 | 19.19 | 319 | 372 | 471 | 360 | 447 | 533 | 718 | 921 | 598 | 436 |
| 20.9 | 50 | 17.95 | 355 | 409 | 504 | 393 | 479 | 565 | 744 | 941 | 674 | 447 |
| 17.1 | 10 | 12.94 | 934 | 988 | 1068 | 955 | 1041 | 1128 | 1280 | 1455 | 1842 | 706 |
| 2.6 | 1 | -0.36 | 7675 | 7729 | 7772 | 7653 | 7740 | 7826 | 7910 | 8023 | 15353 | 3998 |
| per ton cost energy only (24/7) ^f | | | 156 | 156 | 280 | 295 | 295 | 295 | 402 | 535 | 295 | 295 |
| per ton cost energy + Δ (24/7) ^g | | | 264 | 317 | 521 | 396 | 497 | 598 | 746 | 995 | 548 | 548 |
| per ton fixed costs (24/7) ^h | | | 73.5 | 73.5 | 73.5 | 73.5 | 73.5 | 73.5 | 73.5 | 73.5 | 147.0 | 36.75 |
| per ton total costs (24/7) | | | 337 | 391 | 594 | 469 | 571 | 672 | 820 | 1068 | 695 | 585 |

a) Δ : difference between wholesale electricity price and price paid

b) Fixed costs (capital and operating expenses) per mt assuming full-time operation at capacity

c) Greatest wholesale electricity price at percent operating time indicated (i.e. pricing at percentile indicated)

d) Percent time operating, assuming full operation at indicated pricing level or lower

e) Average cost of energy during time operating

f) Energy cost (not including Δ) per mt assuming full-time operation at capacity

g) Energy cost (including Δ) per mt assuming full-time operation at capacity