ACS Energy LETTERS
http://pubs.acs.org/journal/aelccp

Cost and Performance Targets for Fully Electrochemical Ammonia Production under Flexible Operation

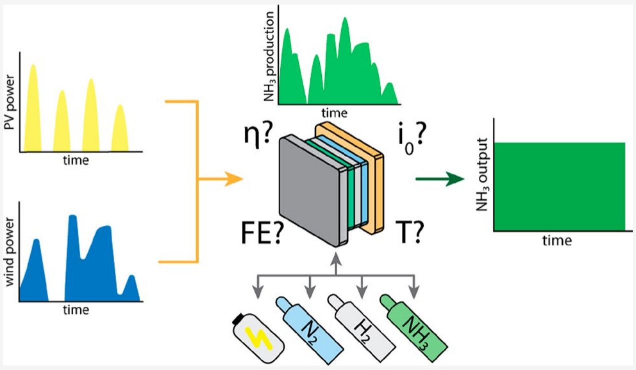
Nikifar Lazouski, Aditya Limaye, Abhishek Bose, Michal L. Gala, Karthish Manthiram,* and Dharik S. Mallapragada*

Cite This: *ACS Energy Lett.* 2022, 7, 2627−2633

Read Online

ACCESS | Metrics & More | Article Recommendations | * Supporting Information

ABSTRACT: Methods to produce ammonia from air, water, and renewable electricity are necessary to transition ammonia production away from the CO_2-emitting Haber−Bosch process. In this vein, a fully electric process in which water-splitting-derived hydrogen and air-separation-derived nitrogen are reacted in an electrochemical process to produce ammonia is attractive. Herein, we evaluated the cost-effectiveness of large-scale fully electric ammonia production relying on renewable electricity sources in conjunction with different types of storage and flexible operation using a mixed-integer linear programming framework. We found that ammonia can be produced in an economically competitive manner, i.e., at costs < 1 \$/kg, at large scales if the electrochemical reactor can produce ammonia at partial currents exceeding 400 mA cm^{-2}, energy eficiencies exceeding 30%, and process lifetimes of several years. In light of this, alternative chemistries that can reduce nitrogen at high rates and moderate (<2.5 V) overpotentials are necessary for economical, fully electrochemical ammonia production.

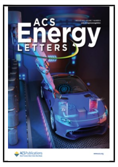


Owing to its high volumetric energy density and facile liquefaction at moderate temperature and pressure conditions,[1] renewably generated ammonia is a compelling low-carbon fuel for the heavy transportation sector.[2] The conventional method for producing ammonia, the Haber−Bosch process, however, consumes fossil fuels and emits CO_2. On the other hand, fully electrified ammonia synthesis approaches utilizing electrochemical nitrogen reduction present a viable, emission-free alternative. These processes, consuming only nitrogen, water, and renewable electricity, have received a great deal of recent interest in academic research, as they can operate at near-ambient conditions and respond dynamically to power supply intermittencies.[3,4]

However, despite laboratory-scale reports of fully electrochemical ammonia generation processes of all stripes,[5−17] these approaches are nearly universally assessed to lack the efficiency and robustness required to produce ammonia economically at scale in their present form. Techno-economic analyses of renewable ammonia production have been performed, though most focus on thermochemical ammonia synthesis using hydrogen derived from renewable-energy-powered electrolysis.[18−22] Far fewer analyses have assessed the techno-economic fundamentals of fully electrochemical ammonia production which utilizes electrochemical nitrogen reduction to produce ammonia;[3] those that have either assume continuous operation or model intermittent operation under heavily simplifying assumptions.[4]

In this work, we carry out a holistic techno-economic analysis (TEA) of the cost-optimal design and operation of a fully electrochemical ammonia generation process that utilizes intermittent renewable energy sources, setting out to identify key productivity metrics that are necessary for economic viability. These metrics are used to motivate a discussion of key operating parameters and concrete technical goals for researchers working on electrochemical nitrogen reduction efforts.

Received: May 23, 2022
Accepted: July 13, 2022
Published: July 19, 2022



https://doi.org/10.1021/acsenergylett.2c01197
ACS Energy Lett. 2022, 7, 2627−2633

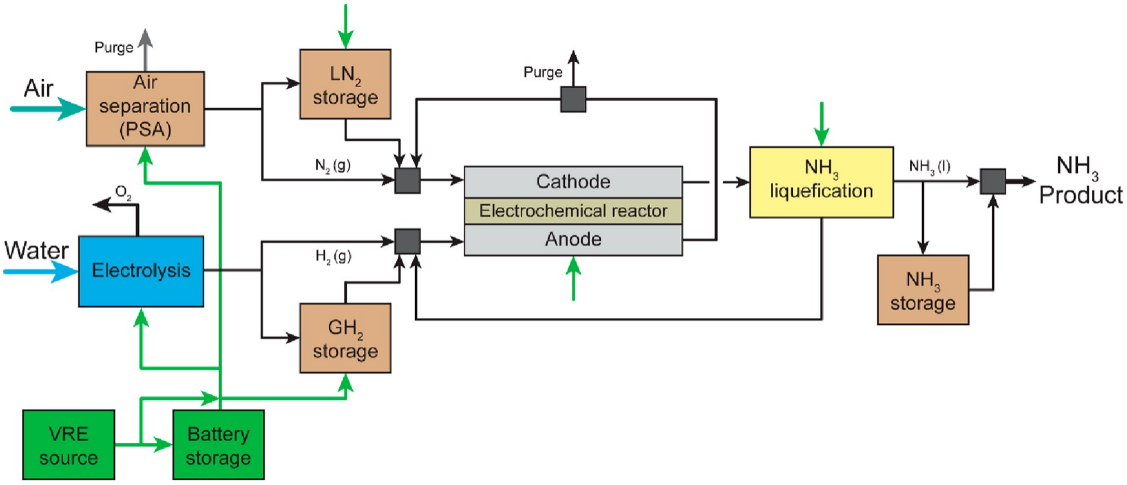


Figure 1. Process flow diagram of the fully electric ammonia production process evaluated in this study. Major unit operations and their mass connections are depicted. Most units have an electrical energy input, depicted by a green arrow. The full length of some electrical connections is omitted for clarity. Reproduced with permission from ref 27. Copyright 2021 Massechusetts Institute of Technology (MIT).

First, we will describe some of the assumptions made to model the process. Fully electrochemical ammonia production from air, water, and renewable electricity can, in theory, be modeled in a single unit operation. However, due to the difficulty of electrochemical nitrogen reduction, especially in the presence of water,[23] and for reasons discussed in detail in the Supporting Information, we believe that a practical fully electrochemical ammonia production process would need a minimum of four unit operations: separation of N_2 from air, synthesis of H_2 from water, synthesis of NH_3 from N_2 and H_2, and separation of NH_3 from side products. Following this, technologies for the unit operations were selected on the basis of a combination of projected costs and technological maturity; the full selection process is described in the Supporting Information. Briefly, H_2 is produced using proton exchange membrane (PEM) water electrolysis, N_2 is produced from air via pressure swing adsorption (PSA), and NH_3 is purified from unreacted N_2 and H_2 via low-temperature liquefaction. Because the ammonia synthesis unit is the one being studied in detail in this work, a chemistry-agnostic black-box model was used, the main governing equations of which are described in the Supporting Information (SI). A process flow diagram for the ammonia production process considered here is depicted in Figure 1. By recycling the anode and cathode streams, higher mass conversion of N_2 and H_2 to ammonia can be achieved even at low Faradaic efficiencies.[19]

We formulated the least-cost design and operation of the ammonia production process as a mixed-integer linear programming (MILP) model, which is described in detail in the Supporting Information. The goal of the model is to minimize the levelized cost of ammonia production by determining optimal sizing and utilization of process components such that hourly variations in electricity supply and annual and hourly plant-level production requirements are respected. Thus, our design optimization approach allows us to estimate the least-cost plant design for ammonia production for varied input power availabilities and electrochemical ammonia productivity metrics.

The model seeks to maintain a constant 250 tonnes of NH_3 day^{-1} outflow from the plant while allowing intermittent operation of all unit operations and storage of energy and materials. The plant capacity chosen stores energy in the form of NH_3 at a rate of ∼60 MW; this power is comparable to the power generation of large-scale renewable energy projects being developed for hydrogen and ammonia synthesis in 2021–2026.[24] This is a relatively small scale plant when compared to conventional thermochemical ammonia synthesis plants, which have scales of 600–3300 tonnes day^{-1}.[25] However, we believe modeling larger scales of production above a certain threshold is unlikely to change the conclusions of the study, as the costs of most parts of a fully electrochemical ammonia synthesis plant increase linearly with scale: additional identical electrolysis or power production units are deployed at larger scales instead of scaling up single unit operations.[26]

The electrochemical reactor was modeled by two compartments representing the electrodes of the cell. In the anode compartment, hydrogen gas is removed (i.e., oxidized) and transferred to the cathode. The reaction of hydrogen oxidation at the anode was assumed to occur with unity Faradaic efficiency. In the cathode compartment, the transferred hydrogen reacts with nitrogen gas to produce ammonia with some Faradaic efficiency, λ^{FE}, which is one of the parameters that is varied throughout the study. The remainder of the Faradaic efficiency, $1 - \lambda^{FE}$, is assumed to go toward hydrogen gas, which can be modeled as unreacted gas transferred from the anode.

The power consumption of the ammonia-producing electrochemical is assumed to be the product of the current passing through the reactor, which is a proxy for the production rate, and from the voltage drop across the electrodes of the reactor.

The voltage drop is assumed to consist of thermodynamic, overpotential, and resistive contributions. The thermodynamic contribution is affected by stream composition, operating conditions, and the chemistry but is relatively constant in this study. The overpotential contribution is a combination of Butler–Volmer kinetic overpotentials and first-order reaction transport overpotentials. In these contributions, the exchange limited current density, the transport limited current density, and resistivity of the electrolyte arise as important variable parameters. Equations detailing the mass balance and costing of the electrochemical reactor, as well as more detailed derivations of the power consumption terms, can be found in the Supporting Information.

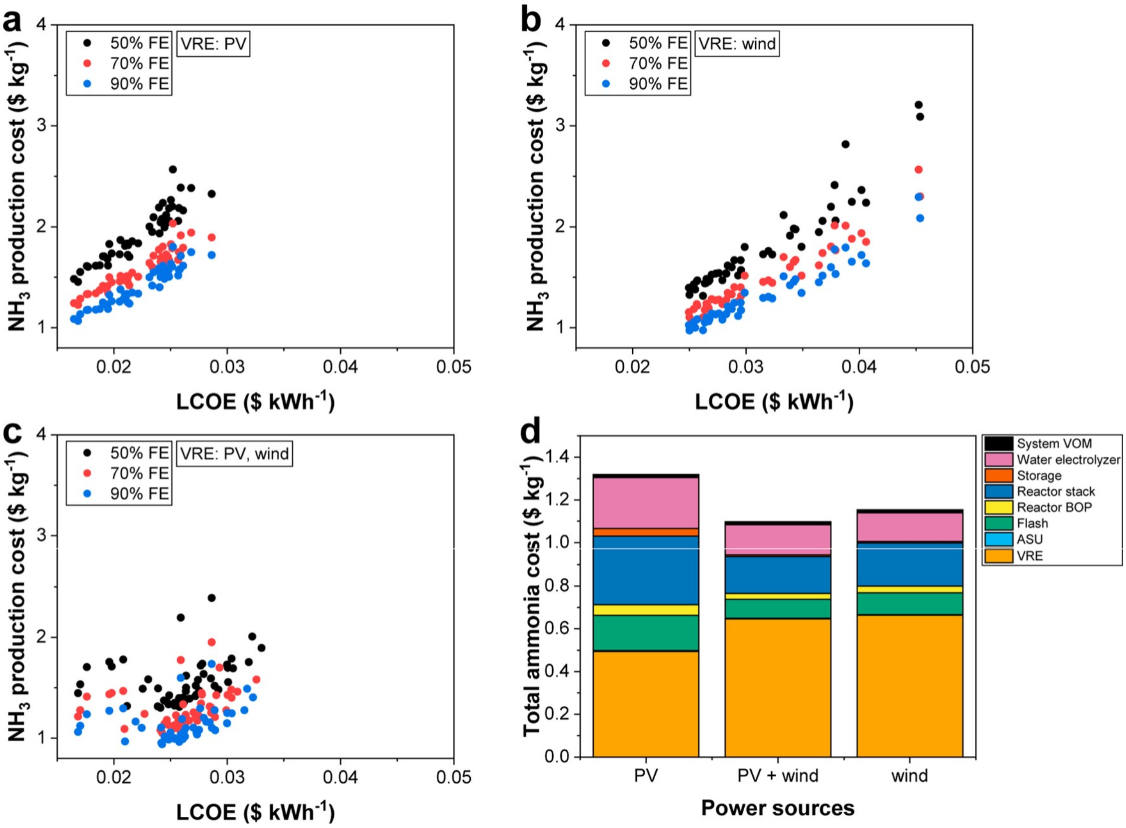


Figure 2. Cost of ammonia production as a function energy sources available and location based on base case parameters defined in Tables S1 and S2. (a−c) Relationship between the levelized cost of electricity (LCOE) from renewable power installations and levelized cost of ammonia (LCOA) production cost for 50 locations in the contiguous United States. The data assume that (a) only PV is used, (b) only wind is used, or (c) both PV and wind can be used. (d) Breakdown of plant components to the overall cost of ammonia when using different energy sources in West Texas.

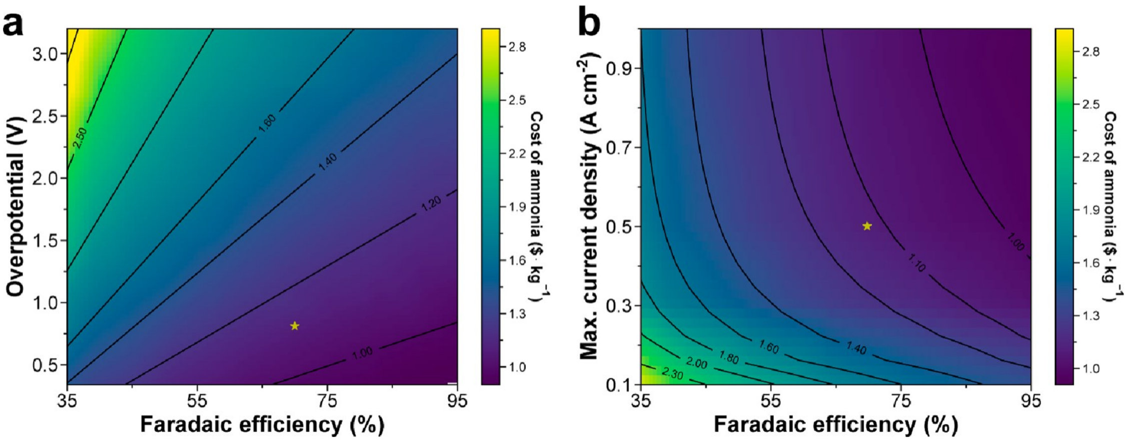


Figure 3. Effects of electrochemical reactor parameters on ammonia cost. (a) Effect of Faradaic efficiency and cell overpotential on the cost of ammonia. At low overpotentials, there is some cost tolerance for low Faradaic efficiencies. (b) Effect of Faradaic efficiency and maximum possible current density on the cost of ammonia. While the Faradaic efficiency consistently decreases the cost of ammonia, the current density does not significantly affect ammonia cost above ∼700 mA cm^{-2}.

Our model estimates that the levelized cost of ammonia (LCOA), defined as the ratio of the annualized system cost and the annualized production amount, is strongly dependent on the specific mix of renewable power sources available at the plant location (Figure 2). In general, using multiple renewable energy sources (e.g., both wind and PV) lowers the LCOA; this is likely due to higher capacity factors for electricity production, which lead to less oversizing of unit operations and lower capital costs for ammonia production (see SI Figure S1). In light of this, we analyzed the effect of electrochemical reactor parameters on the LCOA while using both PV and wind for a plant located in West Texas, which has some of the highest power availability for both wind and solar energy in the U.S., to assess the best-case, "lowest cost" ammonia production. Higher costs for producing electricity will increase

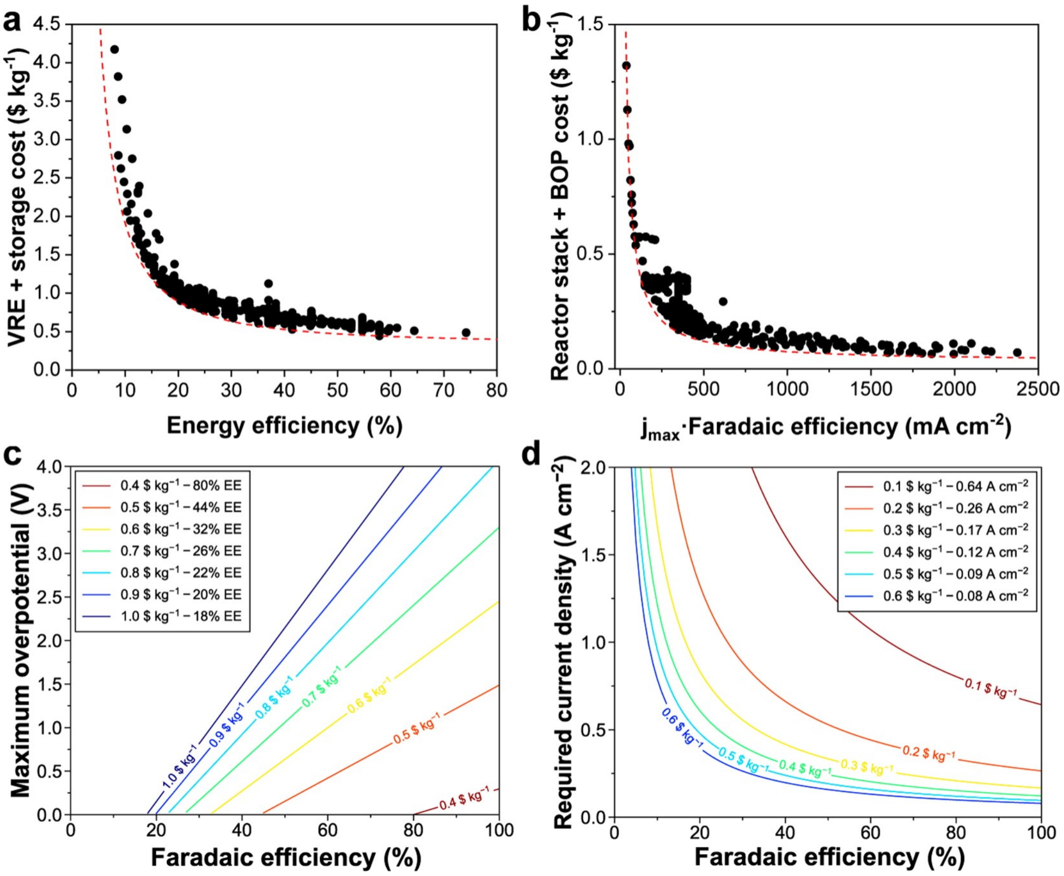


Figure 4. Metrics to estimate the contributions to the cost of ammonia. (a) Correlation between combined VRE generation and storage costs and the energy efficiency of the ammonia production reactor. (b) Correlation between the product of the maximum partial current density toward ammonia and the contribution of the ammonia reactor capital cost. (c) Maximum allowable overpotential in the ammonia production reactor as a function of reactor Faradaic efficiency to allow a given combined VRE generation and storage cost. (d) Minimum required total current density of the ammonia production reactor as a function of reactor Faradaic efficiency to allow a given reactor capital cost. The red lines in panels a and b are meant to represent lower bounds for the cost contributions at given parameter values and are used to compute the curves in panels c and d.

the cost of ammonia, as VRE contributes 40–60% of the total cost of ammonia (Figure 2d).

Decreases in the electrochemical overpotential and improvements in the Faradaic efficiency have a strong correlation with decreases in LCOA (Figure 3a). The impact of decreasing FE on LCOA is less pronounced at lower overpotentials, which suggests that efficient kinetics could accommodate a less selective reaction system without a major impact on the total cost. Therefore, any technological improvements that mitigate the kinetic overpotential or increase the Faradaic efficiency, such as more selective catalysts or decreased proton availability[23] are desirable.

We also observe diminishing returns to increases in the maximum current density (Figure 3b). At low maximum current densities, the capital cost of the electrochemical reactor is large, as it must have a large total electrode area to match a fixed ammonia production rate. At large maximum allowable current densities, the capital cost reduction is low and the plant tends to not run at maximum production rate. We predict an optimum point of ∼700 mA cm^{-2} total applied current density, above which increases in the maximum current density do not appreciably impact the production cost of ammonia; this value is a possible target for economical electrochemical ammonia production.

On the basis of the above results, we sought to outline key targets for the economic viability of an electrochemical ammonia synthesis process. The cost target used for economic comparisons was one for ammonia produced via the thermochemical Haber–Bosch process using water-splitting-derived hydrogen as a feedstock; the cost of this ammonia is 0.8–1.0 $/kg.[28] The flexible, fully electrochemical approach utilizes little high-cost battery and hydrogen storage, instead utilizing inexpensive ammonia storage to counter the intermittent nature of renewable electricity generation.

We found that the LCOA can be broadly split into three contributions: energy-consumption-related (VRE and energy storage) capital costs, ammonia-producing reactor capital and operating costs, and capital and operating costs of other unit operations. The water electrolysis, ammonia liquefaction, and air separation units are mostly unaffected by changes in the operating parameters of the chemical reactor or contribute little to the final ammonia cost (Figures S6–S8). In total, these units consistently contribute 0.2–0.25 $/kg to the final cost of ammonia when both PV and wind can be used as power sources; the contribution is higher when a single power source is used (Figure 2d).

Changes in the total energy consumption are dominated by differences in the consumptions of the ammonia synthesis reactor (Figures S6–S8). A simple metric to predict the reactor energy consumption that is often quoted in the nitrogen reduction literature is the effective energy efficiency of the electrochemical reactor.[13,16,29] This metric captures losses due to non-unity Faradaic efficiency and excess overpotential necessary to drive the reaction:

$$EE_R = FE_{NH_3} \frac{V_{NH_3,\mathrm{ideal}}}{V_{NH_3,\mathrm{ideal}} + \eta_R}$$

where $V_{NH_3,\mathrm{ideal}}$ is a free-energy-based potential for ammonia synthesis from air and water, assumed to be 1.18 V, and η_R is the overpotential in the reactor. Given the necessity of energy storage, especially for energy-intensive ammonia production, we include the cost of energy storage in the total cost of energy when making the cost-efficiency correlation.

This energy efficiency can be correlated to the total cost of energy generation and storage in the plant (Figure 4a). We find that at low energy efficiencies (<30%), the cost of energy necessary for the plant increases dramatically with losses in efficiency. We found that an energy cost contribution of 0.6 $/kg is necessary for viable ammonia production (i.e., total cost <1 $/kg), keeping in mind all assumptions made in the present work.

For the energy costs to contribute ≤0.6 $/kg, the energy efficiency of the ammonia production reaction must be ≥32% (Figure 4c). In order to achieve this energy efficiency, the Faradaic efficiency toward ammonia must be ≥32% in the absence of any overpotentials. This result implies that many reported chemistries utilizing aqueous electrolytes, while claiming low overpotentials,[30−32] cannot be used for economically viable fully electrochemical ammonia production due to low FEs alone. At unity (100%) Faradaic efficiencies, the overpotential of the reaction must be ≤2.45 V to maintain energy efficiencies ≥ 32%. This finding implies that lithium-mediated nitrogen reduction, which often demonstrates high FEs but requires overpotentials in excess of 3 V,[7,13,17,20,33] also requires fundamental modifications to decrease the overpotential for economic viability of the chemistry.

While the simple definition of energy efficiency as described above can be correlated to the energy cost for producing ammonia relatively well, it may not capture all sources of energy loss. An example of modified energy efficiency which appears to more accurately predict energy costs (Figure S15) is described in the Supporting Information.

We found that the capital cost of the electrochemical reaction, while being a more complex function of parameters, can be bound by the product of the maximum obtainable current density and Faradaic efficiency, i.e., the maximum partial current density for ammonia production (Figure 4b). If the reactor experiences a large amount of resistive losses at high current densities, the total capital cost will be elevated, which may explain the observed spread in reactor capital costs (Figure 4b). At partial current densities above ⍰400 mA cm^{-2}, the capital cost contribution of the reactor does not change as significantly as at lower production rates (Figure 4b,d) and reaches a value of 0.1−0.2 $/kg. In light of this, we suggest that an approximately 400 mA cm^{-2} ammonia partial current density is likely necessary for economic viability of electrochemical ammonia production. At the moment, no nitrogen reduction chemistry has reported production rates of this magnitude. This suggests that breakthrough improvements to the electrolyte, chemistry, and architectures are critical for the electrochemical nitrogen reduction approach to be economically viable.

Taken together, the cost of ammonia for a system that reaches the above-mentioned minimum viable production metrics can approach 0.9−1.0 $/kg when using both PV and wind power in West Texas. These costs are competitive with second generation, semielectrochemical ammonia synthesis methods.[4]

The plant lifetime was assumed to be 20 years when computing the capital cost of the electrochemical reactor (Table S2). If parts of the reactor require replacement at more rapid intervals, then the capital cost of the reactor will increase proportionately. The lifetime of the reaction is important to consider in electrochemical nitrogen reduction, as few reports report operation for longer than a few hours.[13,16,34,35] In light of this, significant improvements must be made to the lifetime of the process for economic viability of fully electrochemical nitrogen reduction.

It is important to note that the present analysis assumes low-cost yet intermittent renewable electricity sourced in West Texas. The cost of ammonia may be lower when using electricity sources with higher capacity factors such as hydroelectric or nuclear power due to a lower need for oversizing of unit operations (see Figure S1), assuming the overall cost of electricity is lower. On the other hand, if PV- or wind-based electricity is used in areas with lower power availability, the costs of ammonia may be significantly higher (Figure 2a−c). For this reason, the productivity metrics outlined in the present work should be treated as minimum economic viability targets for use with intermittent power sources, as they may be more stringent under harsher conditions.

In summary, we developed a model to assess the costs of producing ammonia at large scales in a centralized process using a flexible, fully electric method utilizing wind and PV energy resources. Using the model, we found that the energy efficiency and partial current density toward ammonia are key parameter groupings that can be used to assess the viability of electrochemical methods for producing ammonia. The energy efficiency must be >30% for cost-competitive ammonia production. An ammonia partial current density of approximately 400 mA cm^{-2} is necessary for economical ammonia production. In addition, the lifetime of the reaction must exceed several years, based on the assumptions made when obtaining cost estimates. In light of this, radical changes to either the chemistries currently studied or the approach to ammonia synthesis are likely necessary for fully electrochemical ammonia production to be economically competitive in a large-scale centralized process.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.2c01197.

Detailed descriptions of the model assumptions and analysis, description of model variables, parameters, and equations, and figures supporting the claims of the work (PDF)

AUTHOR INFORMATION

Corresponding Authors

Dharik S. Mallapragada – *MIT Energy Initiative, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States;* orcid.org/0000-0002-0330-0063; Email: dharik@mit.edu

Karthish Manthiram – *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States;* orcid.org/0000-0001-9260-3391; Email: karthish@caltech.edu

Authors

Nikifar Lazouski – *Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States;* orcid.org/0000-0002-4655-2041

Aditya Limaye – *Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States;* orcid.org/0000-0003-0639-4154

Abhishek Bose – *MIT Energy Initiative, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States;* orcid.org/0000-0003-4358-8601

Michal L. Gala – *Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsenergylett.2c01197

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The findings reported here are adapted from a dissertation submitted by N.L.; previous versions of these case study results are archived in the MIT thesis repository. N.L., M.L.G., A.L., and K.M. gratefully acknowledge support by the National Science Foundation under Grant No. 2204756. N.L. and A.L. acknowledge the support by the National Science Foundation Graduate Research Fellowship under Grant No. 1745302. A.B. acknowledges funding from the Energy Fellowship program at the MIT Energy Initiative. D.S.M. acknowledges support from the Future Energy Systems Center at the MIT Energy Initiative.

REFERENCES

(1) Davis, S. J.; et al. Net-zero emissions energy systems. *Science* 2018, *360*, No. eaas9793.

(2) International Maritime Organization. *Adoption of the Initial IMO Strategy on Reduction of GHG Emissions from Ships and Existing IMO Activity Related to Reducing GHG Emissions in the Shipping Sector. Note to the UNFCCC Talanoa Dialogue*, International Maritime Organization, April 13, 2018; https://unfccc.int/sites/default/files/resource/250_IMO%20submission_Talanoa%20Dialogue_April%202018.pdf (accessed 2022-06-27).

(3) Ganzer, C.; Mac Dowell, N. A comparative assessment framework for sustainable production of fuels and chemicals explicitly accounting for intermittency. *Sustain. Energy Fuels* 2020, *4*, 3888−3903.

(4) MacFarlane, D. R.; et al. A Roadmap to the Ammonia Economy. *Joule* 2020, *4*, 1186−1205.

(5) Kyriakou, V.; Garagounis, I.; Vourros, A.; Vasileiou, E.; Stoukides, M. An Electrochemical Haber-Bosch Process. *Joule* 2020, 142−158.

(6) Skodra, A.; Stoukides, M. Electrocatalytic synthesis of ammonia from steam and nitrogen at atmospheric pressure. *Solid State Ionics* 2009, *180*, 1332−1336.

(7) Kim, K.; et al. Electrochemical Synthesis of Ammonia from Water and Nitrogen: A Lithium-Mediated Approach Using Lithium-Ion Conducting Glass Ceramics. *ChemSusChem* 2018, *11*, 120−124.

(8) Shah, J. R.; Gorky, F.; Lucero, J.; Carreon, M. A.; Carreon, M. L. Ammonia Synthesis via Atmospheric Plasma Catalysis: Zeolite 5A, a Case of Study. *Ind. Eng. Chem. Res.* 2020, *59*, 5167−5176.

(9) Peng, P.; et al. Atmospheric Plasma-Assisted Ammonia Synthesis Enhanced via Synergistic Catalytic Absorption. *ACS Sustain. Chem. Eng.* 2019, *7*, 100−104.

(10) Li, F. F.; Licht, S. Advances in understanding the mechanism and improved stability of the synthesis of ammonia from air and water in hydroxide suspensions of nanoscale Fe_2O_3. *Inorg. Chem.* 2014, *53*, 10042−10044.

(11) Yang, X.; et al. Mechanistic Insights into Electrochemical Nitrogen Reduction Reaction on Vanadium Nitride Nanoparticles. *J. Am. Chem. Soc.* 2018, *140*, 13387−13391.

(12) Qing, G.; et al. Recent Advances and Challenges of Electrocatalytic N_2 Reduction to Ammonia. *Chem. Rev.* 2020, *120*, 5437−5516.

(13) Lazouski, N.; Chung, M.; Williams, K.; Gala, M. L.; Manthiram, K. Non-aqueous gas diffusion electrodes for rapid ammonia synthesis from nitrogen and water-splitting-derived hydrogen. *Nat. Catal.* 2020, *3*, 463−469.

(14) Zhou, F.; et al. Electro-synthesis of ammonia from nitrogen at ambient temperature and pressure in ionic liquids. *Energy Environ. Sci.* 2017, *10*, 2516−2520.

(15) Schwalbe, J. A.; et al. A Combined Theory-Experiment Analysis of the Surface Species in Lithium Mediated NH_3 Electrosynthesis. *ChemElectroChem* 2020, *7*, 1542−1549.

(16) Andersen, S. Z.; et al. Increasing stability, efficiency, and fundamental understanding of lithium-mediated electrochemical nitrogen reduction. *Energy Environ. Sci.* 2020, *13*, 4291−4300.

(17) McEnaney, J. M.; et al. Ammonia synthesis from N_2 and H_2O using a lithium cycling electrification strategy at atmospheric pressure. *Energy Environ. Sci.* 2017, *10*, 1621−1630.

(18) Hochman, G.; et al. Potential Economic Feasibility of Direct Electrochemical Nitrogen Reduction as a Route to Ammonia. *ACS Sustain. Chem. Eng.* 2020, *8*, 8938−8948.

(19) Hollevoet, L.; De Ras, M.; Roeffaers, M.; Hofkens, J.; Martens, J. A. Energy-Efficient Ammonia Production from Air and Water Using Electrocatalysts with Limited Faradaic Efficiency. *ACS Energy Lett.* 2020, *5*, 1124−1127.

(20) Gomez, J. R.; Garzon, F. Preliminary economics for green ammonia synthesis via lithium mediated pathway. *Int. J. Energy Res.* 2021, *45*, 13461−13470.

(21) Wang, M.; et al. Can sustainable ammonia synthesis pathways compete with fossil-fuel based Haber−Bosch processes? *Energy Environ. Sci.* 2021, *14*, 2535−2548.

(22) Zhang, H.; Wang, L.; Van herle, J.; Maréchal, F.; Desideri, U. Techno-economic comparison of green ammonia production processes. *Appl. Energy* 2020, *259*, 114135.

(23) Singh, A. R.; et al. Electrochemical Ammonia Synthesis—The Selectivity Challenge. *ACS Catal.* 2017, *7*, 706−709.

(24) Interatomic Energy Agency (IEA). *Renewables 2021: Analysis and Forecasts to 2026*; IEA: Paris, 2021; p 167.

(25) Interatomic Energy Agency (IEA). Ammonia Technology Roadmap; Towards more Sustainable Nitrogen Fertilizer Production; IEA: Paris, 2021; p 163.

(26) Osman, O.; Sgouridis, S.; Sleptchenko, A. Scaling the production of renewable ammonia: A techno-economic optimization applied in regions with high insolation. *J. Clean. Prod.* 2020, *271*, 121627.

(27) Lazouski, N. Development of a lithium-mediated nitrogen reduction process. Doctoral thesis, Massechusetts Institute of *4*, Technology (MIT), Cambridge, MA, USA, 2021.

(28) Bose, A.; Lazouski, N.; Gala, M.; Manthiram, K.; Mallapragada, D. S. Spatial variation in cost of electricity-driven continuous ammonia production in the United States. *ChemArXiv Preprint (Energy)*, 2022. DOI: 10.26434/chemrxiv-2022-kdd5s.

(29) Lazouski, N.; Schiffer, Z. J.; Williams, K.; Manthiram, K. Understanding Continuous Lithium-Mediated Electrochemical Nitrogen Reduction. *Joule* 2019, *3*, 1127−1139.

(30) Song, Y.; et al. A physical catalyst for the electrolysis of nitrogen to ammonia. *Sci. Adv.* 2018, *4*, No. e1700336.

(31) Zhao, H.; et al. High-performance nitrogen electroreduction at low overpotential by introducing Pb to Pd nanosponges. *Appl. Catal. B Environ.* 2020, *265*, 118481.

(32) McPherson, I. J.; Sudmeier, T.; Fellowes, J.; Tsang, S. C. E. Materials for electrochemical ammonia synthesis. *Dalt. Trans.* 2019, *48*, 1562−1568.

(33) Suryanto, B. H. R.; et al. Nitrogen reduction to ammonia at high efficiency and rates based on a phosphonium proton shuttle. *Science (80-.)* 2021, *372*, 1187−1191.

(34) Li, K.; et al. Enhancement of lithium-mediated ammonia synthesis by addition of oxygen. *Science (80-.)* 2021, *374*, 1593−1597.

(35) Nash, J.; et al. Electrochemical Nitrogen Reduction Reaction on Noble Metal Catalysts in Proton and Hydroxide Exchange Membrane Electrolyzers. *J. Electrochem. Soc.* 2017, *164*, F1712−F1716.