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Co-designing Electrocatalytic Systems with Separations To Improve the Sustainability of Reactive Nitrogen Management

V. A. Niemann, P. Benedek, J. Guo, Y. Xu, S. J. Blair, E. R. Corson, A. C. Nielander, T. F. Jaramillo,* and W. A. Tarpeh*

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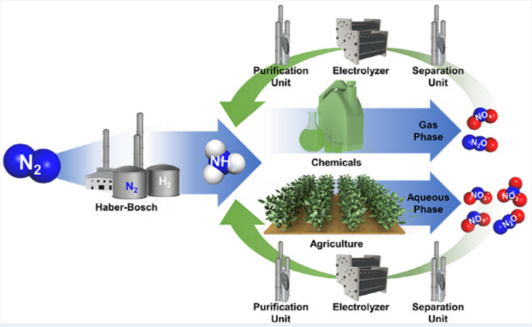
ABSTRACT: Humans have altered the nitrogen cycle to produce nitrogen commodities like fertilizers and chemicals while releasing anthropogenic reactive nitrogen (N_r) contaminants into the environment. These contaminants endanger human and environmental health, but nitrogen commodities are necessary for quality of life. One approach to solving this global challenge is to remove and recover N_r contaminants as commodities; this approach has caught the attention of the electrocatalysis and separations communities alike. In this perspective we propose co-design, or the integration of typically disparate N_r separations and electrocatalytic technologies. We consider real N_r contaminant waste streams and N_r commodity purity requirements. Considering these criteria in electrocatalytic system design reveals fundamental gaps in understanding as well as opportunity for developing co-designed technology that is uniquely tailored to address a challenge in nitrogen management. We focus on three representative challenges in nitrogen management (nitrate, nitrogen oxides, and nitrous oxide), identify their sources and conditions, highlight accomplishments in the fields of electrocatalysis and separations, and explore ways to address each challenge with a co-design approach. We note that this approach will benefit from advancements in related fields such as nitrogen sensing and environmental policy, especially because transformative solutions for the nitrogen challenge lie at the confluence of multiple fields. The final goal is to transition to a circular nitrogen economy that secures a food-safe, environmentally friendly future.



KEYWORDS: *electrocatalysis, nutrient removal, reactive nitrogen, reactive separations, resource recovery, nitrogen cycle*

■ INTRODUCTION

In pursuit of food, raw materials, and energy, humans have doubled the amount of reactive nitrogen in the environment over the past century.[1−4] Nitrogen is a critical building block in living organisms but is difficult to access from inert molecular nitrogen (N_2). N_2, however, can be converted into usable forms as reactive nitrogen (N_r).[1] There are a variety of natural processes that form N_r from N_2, including bacterial nitrogen fixation,[1,2,5,6] volcanic eruptions,[1,2] and lightning;[1,2] these processes combined release ∼203 Mt N_r per year[2] into the environment (Figure 1a). This N_r is reconverted into N_2 in soils (∼100 Mt)[2,7] and aquatic systems (∼140 Mt)[2,7] via aerobic and anaerobic processes, contributing to the maintenance of a balanced nitrogen cycle. However, human activity in the past century has led to a significant increase in N_r released into the environment (Figure 1b).[1−5] The Haber−Bosch (HB) process is one major N_r source, developed in the 1910s to artificially fix N_2 in the form of ammonia (NH_3).[1] NH_3 is a key nitrogen commodity that has become critical to supporting global population growth, with more than 80% of this NH_3 being used to produce fertilizers.[8−12] These fertilizers are applied to crops in excess, largely in the form of the commodity chemical urea, with as much as 50% being wasted and ultimately resulting in nitrogenous pollution.[8,10,13] Furthermore, industrial combustion processes and chemical factories produce N_r (e.g., NO_x via oxidation of N_2 at elevated temperatures[14] and N_2O via byproduct formation of nitrogen-containing compounds).[3] The growth of such industrial processes has led to a combined annual anthropogenic contribution of 210 Mt N_r, a quantity that far exceeds the ability of the environment to maintain N equilibria.[1,2,4,5] Such excesses lead to eutrophication of water sources, upsetting delicate ecosystems with the growth of dead zones and leading to human health concerns, including cancer, methemoglobinemia in infants, and respiratory issues via particulate inhalation.[1−5,15,16] Despite these adverse effects, the growing human population drives an increase in need for HB NH_3; while the market size is currently at 175 million tons, it is expected to increase to between 220 million to 402 million

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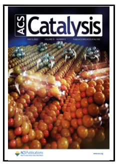

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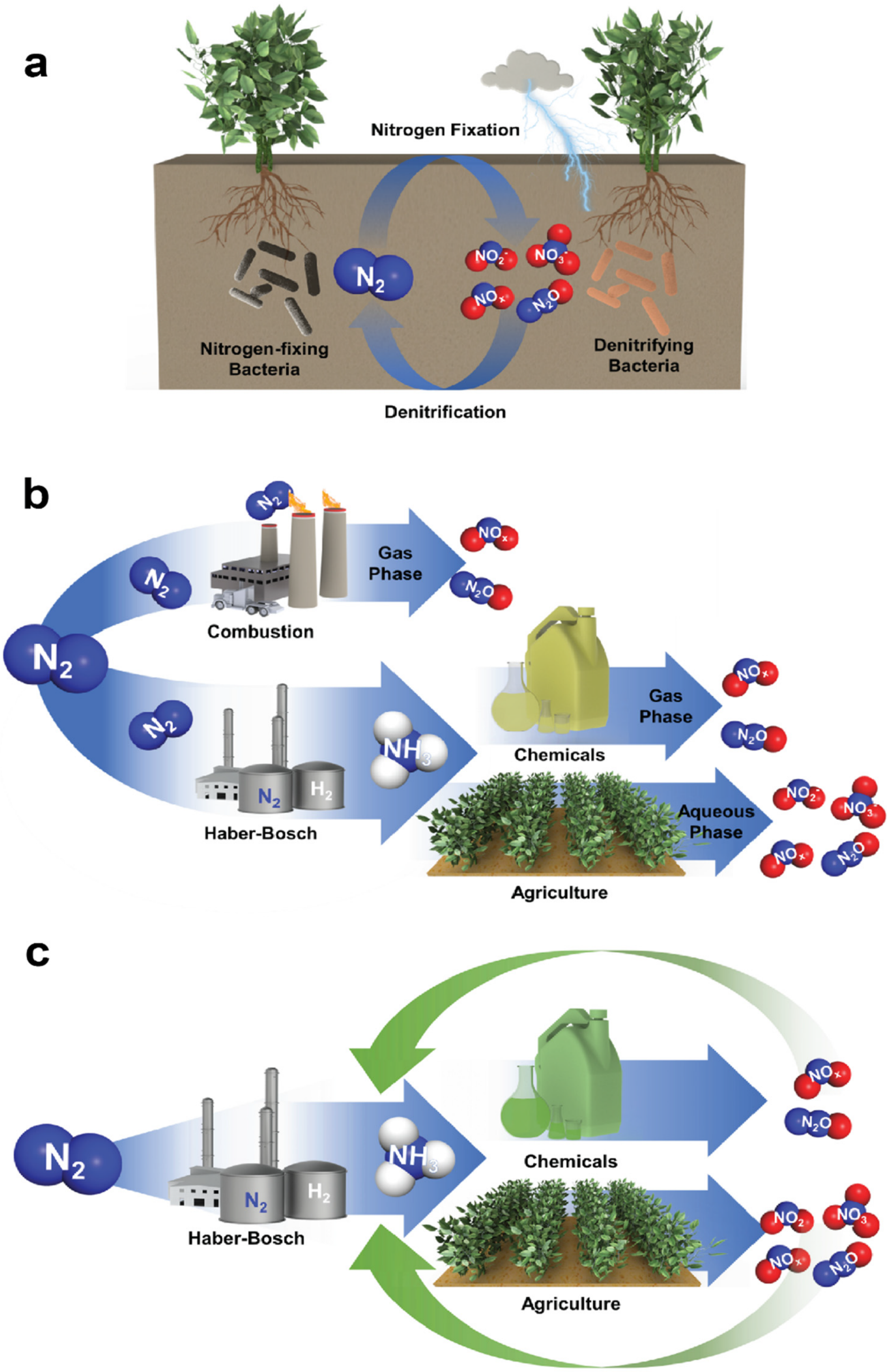

Figure 1. Three versions of the nitrogen cycle: (a) the natural nitrogen cycle, (b) the anthropogenic nitrogen cycle that doubles reactive nitrogen inputs to the environment, and (c) the remedied nitrogen cycle, recycling N_r pollutants into commodities.

tons by 2050.[17] There is consequently a need to reduce the quantity of N_r being released into the environment while providing sufficient N_r to support growing demand.

Thus far, most N_r management has been policy-driven and preventative. Examples include reductions in N_r fertilizer application via nitrogen taxes or charges, direct environmental regulation (e.g., permissible limits of N_r emission), educational efforts in the agriculture industry, and the use of public budgets to encourage better N_r management practices.[15] Meanwhile, remediation of existing N_r in the environment remains a challenge with limited solutions. One method to remediate N_r in the environment could be the collection of N_r pollution and conversion of N_r contaminants into nitrogen-based commodities such as NH_3, urea, and C—N products. Indeed, N_r recovery and conversion into useful commodities has captured the interest of both the separations and electrocatalysis communities. These communities have complementary expertise that, when working in concert, may expedite the

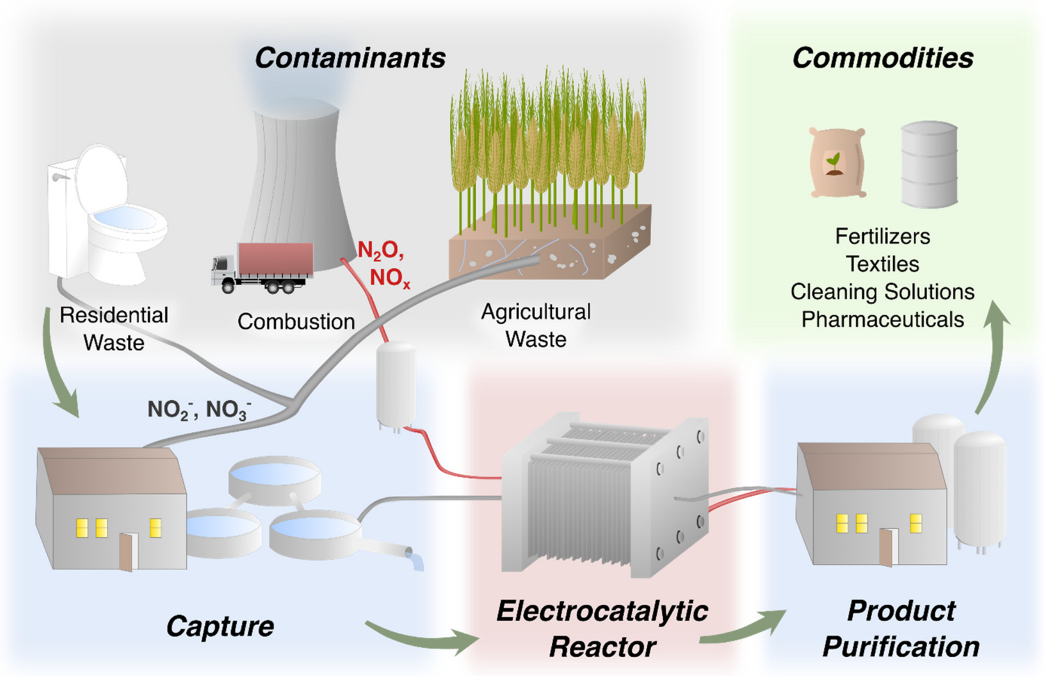

Figure 2. Process scheme for converting nitrogen contaminants into nitrogen commodities. Capture and product purification are primarily separation steps (blue) that enable electrocatalysis (red).

development of effective N_r solutions for a circular nitrogen economy (Figure 1c). N_r solutions will require contributions from multiple fields because of the complexity of the challenges associated with N_r pollution.

WHY IS N_R REMEDIATION A DIFFICULT PROBLEM?

The term "N cascade" encapsulates the primary challenge associated with N_r pollution: discharged N_r molecules can sequentially convert into different contaminants that damage human and environmental health.[1,10] For example, incomplete denitrification of NO_3^- and N_2 oxidation during combustion processes emits nitrogen oxides (NO_x) and nitrous oxide (N_2O), two key contributors to the depletion of the ozone layer.[2,4,18,19] In addition, NO_x is a precursor for atmospheric particulate formation and acid rain and is cited as one of six regulated criteria air pollutants by the U.S. Environmental Protection Agency.[20] This unique cascade effect of the nitrogen cycle means that effective N_r mitigation and sequestration efforts must consider a wide variety of reaction pathways and systems-level approaches. Remediation strategies currently implemented often address the removal of one N_r species while unintentionally releasing another. For instance, while wastewater treatment plants often utilize bioreactors to remove NO_3^- from wastewater, these reactors can convert NO_3^- to unwanted N_2O, a greenhouse gas (GHG) with a global warming potential 300 times greater than that of CO_2 over a 100 year period.[21] One study across 12 wastewater treatment plants found that up to 7% of the influent NO_3^- is converted to N_2O.[22] Similarly, selective catalytic reduction (SCR) systems are used in diesel-powered engines to minimize NO_x emissions but require NH_3 as a reducing agent, thus increasing demand for HB NH_3 production.[23] Although such strategies have been quite effective for environmental mitigation of certain N_r species, there remains a need for technologies that holistically address N_r pollutants and rebalance the nitrogen cycle.

Another major challenge is the legacy of N_r pollution. Mismatches in N flux mass balances have been attributed in part to the difficulty of tracking denitrification, but increasingly, the incomplete mass balances have been attributed to accumulation in the environment.[24,25] Past studies have indicated an increase of subsurface nitrogen in soils and aquifers, projecting that this accumulation would result in significant time lags between changing management practices and measurable improvement in N_r levels.[24,25] In the case of the Mississippi River Basin, even if emissions were halted, organic nitrogen storage in the root zone of soils could persist for 35 years before any measurable improvement in N_r concentration.[25]

Coupling renewably powered electrocatalytic methods with separation processes can provide a new avenue to sustainably close the nitrogen cycle. N_r species have been electrocatalytically converted into not only inert N_2 but also value-added products such as ammonia, urea, hydroxylamine, and hydrazine under a wide variety of electrochemical conditions.[6,26,27] The applicability of such transformations to large-scale N_r remediation is limited, however, by the generally dilute concentrations of N_r in relevant feedstocks.[27] At the same time, the separations research community has developed methods to remove and recover N_r from waste streams into highly concentrated effluent streams.[28−31] Thus, there is a clear opportunity to couple electrocatalysis and separations in tandem to enable the simultaneous separation and remediation of N_r pollutants into usable products. This approach is a key part of the path toward modular, local, and accessible electrification of chemical manufacturing.[32]

In this perspective, we promote the co-design of electrocatalysis and separation technologies to convert N_r contaminants into commodities (Figure 2). Co-design is the integration of two or more separate fields for tailored solutions to complex challenges. To demonstrate a co-design approach, we discuss three representative challenges in nitrogen management, and for each challenge, we identify the associated N_r contaminant, its source conditions, and relevant developments in electrocatalysis and separations. We also acknowledge the importance of sensor development for understanding source conditions with high spatiotemporal resolution. We provide insights into how separations and electrocatalytic systems can work in concert to valorize the contaminant waste streams. In turn, these insights justify the importance of addressing fundamental knowledge gaps for integrating electrocatalytic processes with separations processes. We identify opportunities from state-of-the art CO_2 reduction and capture research that could possibly be applied toward N_r pollution. We also consider the policy support necessary to drive these advances and ensure a sustainable future nitrogen economy.

CHALLENGE 1: VALORIZING WATERBORNE NO_3^- FROM WASTEWATER AND AGRICULTURAL SOURCES

Source and Conditions for the NO_3^- Contaminant. NO_3^- is a contaminant found in multiple wastewater sources, including municipal wastewater,[27] nuclear wastewater, ion exchange brine, and reverse osmosis retentate.[27] Nitrate is also the leading nitrogen contaminant in agricultural runoff,[33,34] which occurs when excess fertilizer is solubilized and ends up in groundwater and aquatic ecosystems.[35] Estimates indicate that 48 Mt of nitrogen contaminants are released into the environment from agricultural runoff, while 20 Mt end up in the environment from human sewage.[33] Current strategies to mitigate these discharges are preventative, such as fertilizer management to limit fertilizer application, livestock management to minimize animal waste N_r contributions, and the use of plant buffers to uptake excess N_r.[34] These preventative measures do not address the NO_3^- already in the environment, such as in polluted groundwater, where it exhibits concentrations of 0.88−1.26 mM NO_3^-.[27] This concentration range contrasts with the ranges often used in catalytic studies, ranging from 10 mM to 1 M,[36−39] but highlights the importance of separations to preconcentrate NO_3^- before catalysis. Complementing preventive measures with remediation measures requires understanding the source and conditions for NO_3^- contaminants in the environment, which could be advanced via improved longevity and reliability of NO_3^- sensors applied in various scenarios.[40]

Feed Requirements for NO_3^- Conversion to NH_3. Electrocatalytic strategies to mitigate NO_3^- pollution have been demonstrated, including NO_3^- reduction (NO_3^-R) to inert N_2 or recovery as NH_3; however, most studies have been performed with synthetic NO_3^- solutions (i.e., produced in laboratories, and often simplified to only nitrate and a countercation). Some pioneering studies have begun to add common contaminants to the laboratory solutions.[41] Additional work is needed to understand how such systems perform with dilute NO_3^- and the presence of multiple co-contaminants, including sulfates, phosphates, carbonates, chloride, arsenic, and organic compounds.[27,42]

Meanwhile, separations research has demonstrated the ability to remove and recover NO_3^- from real waste streams (i.e., produced in practice). Techniques include reverse osmosis (RO), capacitive deionization (CDI), and electrodialysis (ED). RO separates NO_3^- from a feed stream into a concentrated waste stream and produces purified water but does not separate NO_3^- from other co-contaminants. Understanding how co-contaminants may affect NO_3^- conversion to NH_3 from an electrocatalysis perspective could enable the use of the RO concentrate as a fertilizer source. There are also electrochemical separation methods that may pair well with electrocatalytic technologies. For example, in electrodialysis, ions move through ion exchange membranes via migration and diffusion under an applied potential. One study found that this technique can remove up to 99% of NO_3^- ions in real brackish feeds of 1−50 mg/L (0.02−0.6 mM) NO_3^-.[43] CDI uses the electrosorption of NO_3^- onto electrodes with an applied potential and regenerates the electrode by reversing the potential bias. An example of CDI capabilities demonstrated a 48% removal efficiency with a starting concentration of 72 mg/L (1.2 mM) NO_3^- and 21% recovery efficiency of NO_3^- in synthetic wastewater without the presence of competitive ions.[44] The presence of Cl^- and SO_4^{2-} ions in the synthetic wastewater led to an almost 10% decrease in removal efficiency due to adsorption competition.[44]

Several key parameters must be considered when addressing real wastewater conditions of NO_3^- in the environment with respect to electrocatalytic remediation: What is the dilute limit of NO_3^- concentration at which NO_3^- can be feasibly and efficiently reduced to NH_3? What are the co-contaminants, at what concentrations are they present, and how do they modify or inhibit catalyst performance? Do any co-contaminants need to be removed from the feed stream entering an electrocatalytic N-valorization reactor that would convert N_r contaminants into commodities? NO_3^- reduction studies in dilute and mixed streams will help answer these questions and enable the co-design of electrocatalysts with separations technologies.

One example for electrocatalysis and separations co-design centers on the use of ion exchange resins, which have demonstrated an ability to separate NO_3^- from real wastewater sources at concentrations as low as 1.0 mM.[42,45,46] A previous study confirms the performance and benefits of coupled separations and electrocatalysis for alleviating the long-term risk of brine disposal in an ion exchange process, demonstrating 90% removal from the starting NO_3^- concentration of 81 mM along with converting the separated NO_3^- to N_2.[45] To valorize NO_3^-, brine from exchange resins could be fed into the electrolyte feed of a reactor that converts NO_3^- to NH_3. The selectivity of the ion exchange resins can mitigate the poisoning effects of co-contaminants of the downstream catalyst. Similar considerations can be made for CDI, which also removes NO_3^- from dilute sources in groundwater;[47] one study demonstrates 98% NO_3^- removal from a real groundwater source feed with 223 mg/L (3.6 mM) nitrate.[48] The resulting concentrate can be valorized by pairing with a catalytic process that converts NO_3^- into value-added NH_3. These proof-of-concept systems motivate investigations that address more systematic and coordinated questions relevant to catalysis and separations. For example, is NO_3^- reduction to NH_3 possible at these source concentrations with co-contaminants? How can NO_3^- reduction be paired with separation technologies to enable the valorization of groundwater contaminants? If electrocatalytic NO_3^-R is selective toward NH_3 even in mixed, real-world streams, then it could offset separation costs. In the case of ion exchange resins, it would decrease costs associated with energy- and chemical-intensive regeneration, which can contribute the majority of energy and emissions associated with nitrogen separation from wastewaters.[49]

NO_3^- Conversion to NH_3: Co-design Framework. To illustrate the benefit of electrocatalysis and separations co-design, we calculated the cost of electricity for concentrating a typical NO_3^- contaminated stream (0.5 mM NO_3^-)—e.g., from groundwater,[50] fertilizer runoff,[51,52] or municipal wastewater sources[53]—and electrochemically converting it to NH_3 (Figure 3). We estimated potentials and currents required to concentrate nitrates from a 0.5 mM feed to 1, 2, 10, 50, and 100 mM based on a previous electrodialysis study (Figure 3a).[54] As expected, increasing the final concentration of NO_3^- from an initially dilute source requires more electrical energy and therefore higher cost. Figure 3b shows the Faradaic efficiencies of selective copper nickel ($Cu_{0.5}Ni_{0.5}$) alloy catalysts as a function of NO_3^- inlet concentration, which approach 100% with increasing NO_3^- concentration.[37] Using 1 kg NH_3 per day as a target for the reactor, we estimated total current and used reported cell potentials to calculate the energy needed to reach the target (see the Supporting Information).[37] Notably, the cost decreases to a local minimum with increasing selectivity of catalyst. By adding the electricity costs for NO_3^- concentration and NO_3^-R, we find that there is a total cost local minimum at 10 mM NO_3^- as the reactor inlet concentration (Figure 3c). This finding from an illustrative pairing of one electrocatalyst and one separation process highlights the interplay between electrocatalysis and separations—electrocatalyst selectivity and activity drive the optimal concentration target for separations processes to condition the feed stream into the reactor.

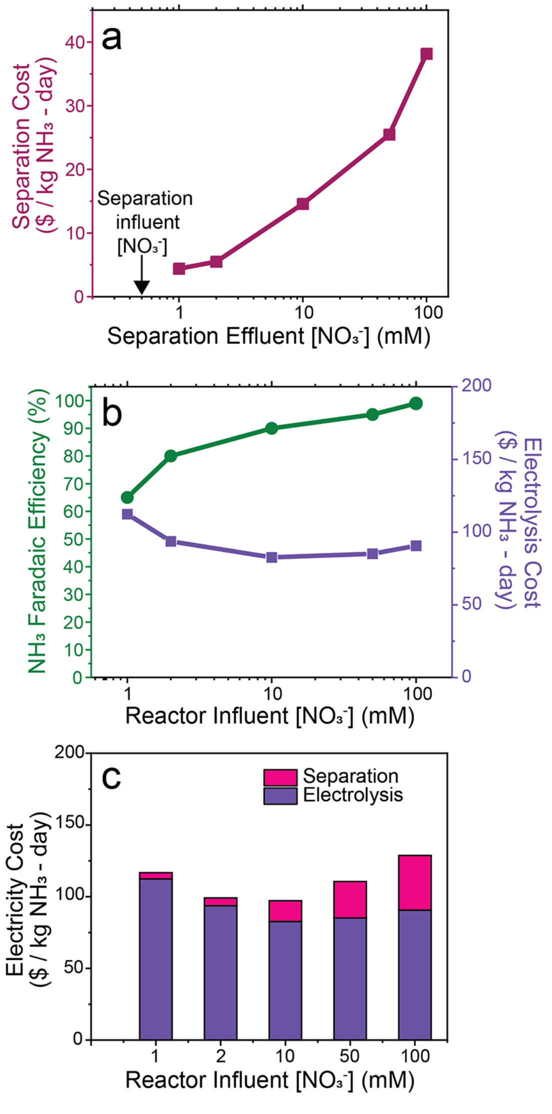

Figure 3. (a) Costs of concentrating NO_3^- from 0.5 mM (arrow) to 1, 2, 10, 50, and 100 mM via electrodialysis where 0.5 mM is in a typical NO_3^- concentration range for contaminated water sources. (b) NH_3 Faradaic efficiency (green) [Reproduced with permission from ref 37. Copyright 2020 American Chemical Society.]. Associated electricity costs per kg NH_3 per day (purple) of electrocatalytic NO_3^-R to NH_3 based on selective $Cu_{0.5}Ni_{0.5}$ alloy catalyst performance. (c) Cost of electricity per kg of NH_3 per day to convert 0.5 mM NO_3^- to NH_3 as a function of reactor influent nitrate concentration.

Product Purification To Yield NH_3. Understanding the effects of varying reactant concentration and co-contaminants is critical to enable electrocatalytic technologies that valorizes nitrate pollution. This understanding would allow for the co-design of catalytic technologies with separations technologies to condition the reactor feed and purify the valuable products leaving the reactor. Recent bimetallic catalyst design has made impressive gains on selectivity.[37,55] Even with a Faradaic efficiency approaching 100%, however, NH_3 would have to be separated out of solution and from unreacted NO_3^- in a commercial device. The ideal catalyst would also lower the activation energy of the rate-determining step, which in NO_3^-R is the reduction of NO_3^- to NO_2^-.[56,57] In other systems there may be multiple species in the outlet stream, including NO_3^-, NO_2^-, and H_2 from the hydrogen evolution reaction (HER) and perhaps co-contaminants in the electrolyte from which aqueous total ammonia (NH_4^+/NH_3) in solution would need to be separated and purified.[6] Gaseous products, including NH_3, N_2, N_2O, and NO_x, would have to be detected and separated if cogenerated as products. Methods to detect the gaseous products, especially NO_x, are critical, and novel detection methods will inform process monitoring and control. Strategies to separate NH_3 include leveraging pH, volatility, and potential bias.[58] One potential scheme incorporating these co-design considerations would be an electrochemical reactor that converts NO_3^- to NH_3 and then collects and purifies the NH_3 by leveraging potential bias for NH_4^+ mobility and pH for NH_4^+ volatilization to NH_3. This technology exemplifies reactive separations, in which chemical reactions and separations take place in one unit. Tuning reaction conditions, such as pH, could enable more NH_3 in the gas phase and thereby facilitate separations. Understanding selectivity and phase of the product presents another opportunity for the electrocatalysis community to interface with separations research in both fundamental and applied studies to realize deployable nitrogen recycling schemes.

C−N Bonds from CO_2 and NO_3^-: A Unique Feed Conditioning and Product Purification Problem. The formation of carbon−nitrogen (C−N) containing products, most notably urea, from mixed carbon and nitrogen feedstocks via electrocatalysis has recently gained renewed attention.[13] Conventional urea production requires the use of fossil fuels in centralized facilities with large energy requirements. Instead, electrochemistry may provide a means for producing urea in decentralized locations from anthropogenic emissions containing NO_3^- and CO_2. The coreduction of CO_2 and NO_3^- is far from reaching 100% Faradaic efficiency toward urea, with one pioneering study reporting FE_{urea} = 35%.[59] Selectivity is likely impacted by other ionic species present in the electrolyte, although such effects are not currently well understood. The increased complexity of the reactant stream also expands the range of possible products beyond nitrogenous products (NO_2^-, NO_x, N_2O, N_2, N_2H_4) to the range of carbon products possible during CO_2 reduction (CO, CH_4, C_2H_4, C_2H_6, etc.) and products containing C−N bonds in aqueous electrolyte.[60,61] This field merits even more careful consideration of mixed stream effects on reaction selectivity. Strategies for designing selective catalysts include designing bimetallic alloys, which have demonstrated improved selectivity from their single-metal components.[62] Indeed, a recent study provides a framework for designing metal alloy catalysts for NH_3 production from NO_3^- by connecting the electronic structure of metals to selectivity mechanisms.[57] Separation units that can handle these numerous (undesired) N- and C-products will be necessary to realize CO_2 and NO_3^- valorization to urea fertilizer or other desired C−N products, such as acetamide[63] and methylamine,[64] which will need to be separated from waste streams after production. The CO_2 capture and electrocatalysis fields provide a foundation for C−N product purification including a bipolar membrane electrode assembly able to capture and convert CO_2 in seawater to purified CO.[65] Other work has shown possible processes and predicted energy costs for separating key electrochemical CO_2R products.[66] Carbon dioxide electrocatalysis and capture could condition CO_2 feedstocks into N_r reactive separations schemes to form numerous high-value organic nitrogen products. This challenge will require a high product selectivity and processing rate. C−N bond formation studies will require advancing these separations schemes to condition contaminant feedstocks CO_2 and N_r as well as purify C−N products.

CHALLENGE 2: REMEDIATING N_2O EMISSIONS FROM AGRICULTURAL AND WASTEWATER SOURCES

Source Conditions of the Gaseous N_2O Contaminant. N_2O is present in the atmosphere at an average concentration of 331 ppb with a lifetime of over 100 years.[18,67] It is the leading contributor to ozone depletion and accounts for 6% of greenhouse gas contributions to global warming, making it the third largest greenhouse gas contributor behind CO_2 and methane (CH_4).[18] The use of nitrogen-based fertilizers has contributed 52% of anthropogenic N_2O emissions.[67] While contributing less N_2O emissions overall, conventional stationary combustion outlet streams have concentrated N_2O emissions ranging from 1 to 5 ppm.[68,69] In fluidized bed combustion reactors, N_2O emissions range from 20 ppm to as high as 150 ppm depending on temperature, O_2 concentration, and fuel properties.[68] Wastewater treatment is another source of N_2O emissions. Domestic wastewater contains 20−70 mg/L of nitrogen, usually in the form(s) of ammonium, nitrate, and/or nitrite.[21] To remove these aqueous N_r species, wastewater treatment plants employ biological nutrient removal (BNR) systems, in which wastewater after activated sludge undergoes reaction with nitrogen-metabolizing bacteria.[21] BNR plants, depending on their design, can emit 0.001%−6.6% of the influent N as N_2O.[21,70] One BNR study quantified N_2O emissions at different stages of a two-step feed, plug-flow reactor, showing an average daily N_2O emission rate of 62.3 kg N/day, with emissions of 12.5 kg N/day emitted in the first step and 49.8 kg N/day in the second step.[71] With 16,000 wastewater treatment plants in the United States, wastewater treatment emits about 1 kiloton/day of N_2O emissions.[72] This estimate does not account for the 25% of the population serviced by on-site wastewater treatment (e.g., septic tanks), which are associated with less controlled and more variable N_2O emissions.[73] Thus, N_2O emissions arise even from N_r remediation systems, highlighting the need for increased focus on developing N_2O mitigation technologies. We note that a crucial part of developing mitigation technology will be working with the sensor community to develop reliable, selective N_2O sensors that operate on land as well as in water- and airsheds.[74]

Feed Requirements for N_2O Remediation. Current capabilities in electrocatalysis and separations suggest that electrochemical N_2O remediation to N_2 is feasible in pure N_2O and synthesized mixed streams.[60,75,76] Previous work in electrocatalysis has demonstrated that N_2O readily reduces to N_2 even when CO_2 is in excess.[76] This result is consistent with the thermodynamic favorability for N_2OR to N_2 ($E°$ = 1.75 V vs RHE, compared to CO_2R and HER (0 V vs RHE). N_2OR is even more thermodynamically favorable than ORR (1.23 V vs RHE). Thus, a pure stream of N_2O may be unnecessary to achieve N_2O remediation. Building off this work, we must understand performance under realistic conditions; the lower limit of N_2O concentration in an air-like stream that can be reduced to N_2 must be found and demonstrated to be converted to N_2 at a high conversion rate and selectivity. This lower limit of N_2O concentration for electrocatalysis will inform the separations community of the selectivity needed for N_2O capture. Even further, these studies at dilute amounts of N_2O could assist the sensor community in developing robust, reliable sensors to more accurately quantify N_2O emissions.[74]

The electrocatalysis community also benefits from understanding N_2O separations capabilities. Considerable progress has been made in pressure-swing adsorbent materials including zeolites, and one study demonstrates an adsorbed amount of 4.1 mmol N_2O per gram of adsorbent from an air stream, which can later be desorbed.[77] Metal−organic frameworks (MOFs) can also be used to adsorb N_2O. Chromium-based MOFs have shown 5.78 mmol N_2O/g MOF and 1000 N_2O/N_2 selectivity from mixtures of N_2 and N_2O.[78] Further development in functional site design has rendered improvements in N_2O/CO_2 selectivity, resulting in a factor of 28 from a CO_2 and N_2O 50%/50% feed stream.[79] We note that the selectivity of N_2O/CO_2 remains a significant challenge for gas phase adsorbent separations. Other technologies can be used to address N_2O-saturated aqueous solutions such as those resulting from wastewater treatment processes, such as the coupled aerobic−anoxic nitrous decomposition operation (CANDO).[80,81] These technologies also include the use of separation membrane contactors, which in one case demonstrated 90% removal from an aqueous N_2O feed with a starting concentration of 3.2 mM.[82] The separations community has developed some promising avenues for N_2O separations from both the gas and liquid phases, although more study is necessary to concentrate it from atmospheric and aqueous environments. In either phase, if separations technology can concentrate N_2O from atmospheric or combustion sources, it can facilitate selective, active, and stable N_2O reduction to N_2.

N_2OR Value-Added Product Discovery. While it is typically reported that N_2O electroreduction produces only N_2 in aqueous electrochemical systems,[60] a promising research direction is to form value-added products from N_2O, either from reduction or oxidation. What are the kinetic limitations that prevent N_2O from forming products other than N_2? How might N_2 reduction studies inform value-added product formation from N_2O? If other products could form (e.g., NH_3), then separations would likely play a large role in both preconcentrating the feed stream and purifying the value-added product.

N$_2$OR: Learning from CO$_2$ Reduction. We compare the challenges and opportunities for N_2O and CO_2 conversion, because both are atmospheric gases contributing to global warming. Indeed, the climate crisis and the central role of CO_2 have ushered in a concentrated effort to close the carbon cycle. The N_2O potential for large GHG contributions and its central role as an ozone depletor calls for similar attention. Electrochemical N_2O reduction could benefit from CO_2RR gas diffusion electrode and vapor-fed cell studies to decrease mass transport limitations on observed electrocatalytic remediation rates. Further, N_2OR may have fundamental insights to offer, since it does not form a buffer in water like CO_2 and occurs at potentials less negative than HER in alkaline electrolytes. Its solubility in water at 1 atm and 20 °C is 2.6×10^{-2} mol/L·atm, which is similar to CO_2 (3.8×10^{-2} mol/L·bar) and higher than other atmospheric gases O_2 (1.3×10^{-3} mol/L·bar), N_2 (1.1×10^{-3} mol/L·bar), and CH_4 (1.4×10^{-3} mol/L·bar).[83,84] These properties would facilitate pH control and less competition with HER in aqueous electrolyte, thereby serving as a model system to study electrochemical mass transport and kinetic phenomena. Meanwhile, CO_2 capture has attracted great interest in literature and industry, but attention to N_2O capture is lacking, especially in feed streams with atmospheric conditions. In tackling the global problem of N_2O emissions, there is an opportunity for the separations and electrocatalysis communities, of both the nitrogen and carbon fields, to coordinate for maximal impact.

N$_2$O Mitigation and Valorization Using Co-design. We have discussed the ability for electrocatalytic systems to reduce N_2O to N_2 in mixed streams even when other gaseous components are greatly in excess. Thus, we envision that N_2O separation processes that concentrate N_2O from atmospheric or other dilute mixtures need not concentrate to a pure N_2O inlet stream in order to deploy electrocatalytic N_2O mitigation reactors. Determining the desired or optimal concentration after separation and before reaction is a critical outcome from the co-design of electrocatalysis and separations. Regulatory N policies would provide economic incentive for processes that produce N_2O (e.g., wastewater treatment) to reduce their greenhouse gas contributions by using this approach. Further study is necessary to understand the valorized products that may be accessed from N_2O—from either its reduction or oxidation. Discovery of valorized products formed from N_2O would be a great advancement for the field, provide economic incentive for N_2O recycling, and enable co-design for N contaminant valorization to diverse commodity portfolios.

CHALLENGE 3: RECYCLING NO$_X$ FROM STATIONARY COMBUSTION AND AGRICULTURAL SOURCES

Source Conditions of the Gaseous NO$_x$ Contaminant. Nitrogen oxides (NO_x) comprise a set of reactive compounds such as NO, NO_2, and N_2O_5. Their reactivity precludes long atmospheric lifetimes; instead, they typically arise from point sources and mainly affect the surrounding airshed. The leading contributor to NO_x emissions is combustion, contributing ~62% to global NO_x emissions.[85] This contribution includes combustion from both stationary and mobile sources. In stationary combustion, outlet streams can reach up to hundreds of ppm at high temperatures and pressures.[86] The exhaust from heavy-duty diesel engines, the primary mobile source of NO_x emissions, can achieve similar concentrations with temperatures above 250 °C.[87] We note that these vehicles also emit NO_x at temperatures below 250 °C during the cold start period of vehicle operation, and typical NO_x control technology does not operate at these temperatures.[87]

In recent years, researchers have identified agriculture as a major source of NO_x emissions, contributing 24% of global NO_x emissions.[85,88] In California, it is estimated that 161,100 t of NO_x-N/year are emitted, with 79% coming from cropland.[88] NO_x emissions from agriculture, while major in their effects, are likely to be dilute, and work is ongoing to understand the fate of this NO_x.

Another contributor to NO_x emissions according to recent studies is the burning of biomass for energy production, which contributes ~13% of global NO_x emissions.[85] This source may not be a viable feedstock because the pollutants are openly released to the atmosphere from large areas at high temperatures; other feedstocks have an exhaust or occur at temperatures that are more amenable for technology implementation.

A variety of metal-oxide-based, semiconductor NO_x sensors are available commercially and employed in industry, but they typically operate at elevated temperatures.[89] Electrochemical sensors have also been developed but require the optimization of selectivity, long-term stability, and low-concentration detection.[90] In order to design and optimize these sensors, molecular relationships between surface structure and reactivity must be better understood.[90] Finally, there is a need to sense NO_x originating from agriculture and biomass sources to better monitor and understand NO_x emission conditions in the environment.

Feed Requirements for NO$_x$ Remediation and Valorization. The sources of NO_x are dilute in both agricultural and industrial settings, and the nature of these sources opens interesting questions for the electrocatalysis community to consider. In agricultural settings, NO_x conversion would need to be targeted close to the point source. Further studies are needed to determine NO_x capture capabilities such that tandem electrochemical separation and conversion methods could be used. In industrial settings, selective catalytic reduction is widely employed as a reactive separations method, but co-contaminants like sulfur oxides, heavy metals, and alkali metals are known to poison catalyst active sites, leading to performance degradation.[23] Often, sulfur oxides are removed in separate desulfurizer stages.[23] These challenges require optimizing reactant selectivity and/or catalyst stability. Technoeconomic analyses could analyze the trade-offs of adding a pretreatment sulfur oxide removal step with a NO_x reactive separations step.

Because NO_x species, especially nitric oxide, spontaneously react with surrounding species like O_2 and coexist with co-contaminants such as sulfur oxides, the overall longevity of electrochemistry processes will be the key parameter to consider. The high temperatures and pressures of many NO_x sources as well as the reactivity of NO_x compounds will require a focus on catalyst and separations stability. We note that in vehicular NO_x sources, current technologies such as selective catalytic reduction and nonselective catalytic reduction do not operate below 250 °C, opening an opportunity to methods at milder conditions to remove and recycle NO_x contaminants.[87]

Techniques for NO_x separations include using wet scrubbers and contact absorbers, but recent advances have been made in electrochemical separations.[91−93] These methods have used mediator complexes to separate NO_x and sulfur from model flue gas streams, and they have accomplished up to 97.5% removal efficiency.[93] Engineering electrochemical, solution-based separations techniques may allow for continual regeneration, and they may immediately pair with electrocatalytic processes to achieve NO_x remediation and value-added product formation in one step. The major limit for solution-based separations techniques, however, would be the low solubility of NO_x compounds in water and the operation of these processes at elevated temperatures.

Product Purification To Yield NH_3. NO reduction to NH_3 has been demonstrated in multiple electrocatalytic reactors and reactive separations schemes.[92,94,95] Additionally, NO is an intermediate for NO_3^-R to NH_3, and its formation is the selectivity-determining step in the overall NO_3^-R mechanism.[56,60,62] Understanding how to steer selectivity starting with NO reduction would therefore inform NO_3^-R selectivity. Mechanistic studies that explain NO reduction selectivity toward NH_3 versus N_2O as an end product would benefit the NO_3^-R field.

C−N Bonds from CO_2 and NO_x: Mechanistic Studies To Understand C−N Coupling. Stationary combustion sources of NO_x may not be feasible for C−N forming reaction schemes because of their high temperatures. Milder conditions during cold start heavy duty vehicle operation may be amenable to NO_x and CO_2 recycling to urea but would be highly intermittent. It is also questionable as to whether dilute, agricultural sources of NO_x would feasibly serve as a feedstock for making C−N bonds. We suggest that such studies using NO as a nitrogen source can inform how more stable nitrogen species (e.g., NO_3^-) can be coreduced with CO_2 to form C−N products via the NO intermediate. Since NO reduction is the selectivity-determining step in NO_3^-R, it may be important in steering selectivity in C−N coupling reactions involving NO_3^- as the nitrogen source. Steering selectivity with the NO intermediate would inform approaches to maximize selectivity for coupled NO_3^- and CO_2 feedstocks.[56,60] In exploring value-added product formation, we again observe the opportunity for the carbon and nitrogen fields to work together, but in the case of NO, the coupling would also advance mechanistic understanding of steering selectivity toward desired C−N products.

NO_x Mitigation and Valorization Using Co-design. Co-design of NO_x separation and catalysis technology would take into account the separation of common co-contaminants (e.g., sulfur oxides) before electrocatalysis to valorize NO_x to products like NH_3 or urea. Additionally, a co-designed approach would consider the temperatures and pressures at which NO_x contaminants are evolved, conditioning the feed accordingly to facilitate active, selective, and stable conversion to NH_3. For example, NO_x could be absorbed into a solution phase that is compatible with a downstream electrochemical reactor. Further study on realistic conditions for NO_x conversion to NH_3 or urea would enable the use of the co-design framework in Figure 3 to evaluate NO_x valorization schemes.

■ CONCLUSIONS AND OUTLOOK

Electrocatalysis that seeks to mitigate and recycle anthropogenic N_r, specifically NO_3^-, N_2O, and NO_x, requires a better understanding of source conditions and how they affect catalyst performance (activity, stability, and selectivity). At the outlet of the reactor, in-line product detection methods are necessary to understand the full range of nitrogen species that are formed in each reduction process and to inform product purification requirements in postreaction separations. By understanding feed conditions and product purity from the inlet and outlet of advanced electrochemical reactors, electrocatalysis can interface with the separations community to co-design processes or reactive separation units that recycle N_r into valuable commodities. We note that for each N_r type, advancing its sensor technology will enable a better understanding of concentrations and conditions that require separations or can be fed directly to the electrochemical reactor. In addition, benchmarking these co-designed technologies will be necessary to drive their progress and serve as a basis for technoeconomic analyses.[96] The results of technoeconomic analyses could then serve as feedback for electrocatalytic systems and separations development.[97] Altogether, these considerations will also involve dedicated efforts toward scaling up processes and ensuring durable performance to meet the urgent needs associated with mitigating waterborne and atmospheric emissions.

Advances in electrochemistry are necessary but not sufficient for impacting the global nitrogen cycle—adoption and implementation through policy is crucial for necessary impact. Policies will need to be implemented at multiple scales and across industries to match the multiple length scales as well as types and conditions of N_r emission sources. N_r pollution often does not abide by municipal, state, regional, or even national boundaries. Thus, solutions to these problems must not only be multidisciplinary but also consistent across a large number of governing bodies, with a commitment to widespread and tunable N_r mitigation being a common goal.[15]

Nitrogen management on the global scale can borrow insights from efforts to manage the carbon cycle. Anthropogenic carbon emissions have increased the atmospheric carbon content by 50% since before the Industrial Revolution.[98] The resulting negative observed environmental impacts have led to concentrated efforts in catalysis research, carbon capture, and carbon policy. Meanwhile, in the past four decades, anthropogenic N_2O emissions have increased by 30%, and the atmospheric concentration of N_2O is expected to rise 2% per decade.[67] Furthermore, N_r flux has increased by 100% since the Industrial Revolution and is expected to increase by at least another 102% by 2050 unless ambitious N_r regulation protocols are designed and implemented.[99,100]

While there are similar motivations, N_r pollution is also distinct from carbon pollution in some ways. First, N_r pollution exists largely in the aqueous phase as NO_3^-, NH_4^+, and dissolved N_2O, presenting opportunities to leverage solution-based electrochemistry, reactive separations, and separations techniques. Although carbon pollution also exists in the aqueous phase, most electrochemistry, reactive separations, and separations techniques have addressed it in the gas phase. Second, N_r presents the issue of the nitrogen cascade, in which N_r species interconvert to harm the environment in both aqueous and gaseous phases. Efforts to mitigate N_r pollution are not as extensive as those to mitigate carbon emissions. We give a call to action to increase effort in N_r sensing, regulation, and mitigation, building from lessons learned from sensing, regulating, and mitigating carbon emissions. With these parallels established, policymakers could adapt technological and political strategies that have been effective in mitigating carbon emissions toward N_r emissions.

Electrochemical methods to mitigate N_r pollution have thus far provided understanding in pure, controlled feeds. The next step is to understand how real conditions affect the electrochemical reactor systems as well as consider how to purify desired products. With this understanding, the co-design of reactors with separations requirements becomes possible. Investigations and deployment of this technology, together with policy, will enable the meeting of human needs (e.g., food security, access to commodity chemicals) while mitigating the deleterious effects of N_r. Ultimately, sustainably managing the nitrogen cycle by capturing and valorizing N_r pollutants could safeguard human livelihoods and environmental quality.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.3c00933.

Calculations to co-design a process to separate and convert nitrate (contaminant) into ammonia (commodity) (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

W. A. Tarpeh − *Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States; SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States;* orcid.org/0000-0002-2950-526X; Email: wtarpeh@stanford.edu

T. F. Jaramillo − *Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States; SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States;* orcid.org/0000-0001-9900-0622; Email: jaramillo@stanford.edu

Authors

V. A. Niemann − *Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States; SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States;* orcid.org/0000-0002-9565-022X

P. Benedek − *Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States; SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States*

J. Guo − *Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States;* orcid.org/0000-0002-8775-3085

Y. Xu − *Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States; SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States*

S. J. Blair − *Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States; SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States;* orcid.org/0000-0001-6680-0199

E. R. Corson − *Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States; SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States;* orcid.org/0000-0003-2722-674X

A. C. Nielander − *SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States;* orcid.org/0000-0002-3639-2427

Complete contact information is available at: https://pubs.acs.org/10.1021/acscatal.3c00933

Notes

The authors declare no competing financial interest.

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