

LOWERING BARRIERS TO CLEANER AMMONIA PRODUCTION

TODAY, roughly half of the world's population relies on crops grown with the aid of synthetic fertilizers composed primarily of nitrates and ammonia. As such, global production of ammonia alone exceeds 150 million tons annually.

Most industrial ammonia is produced through the Haber-Bosch process, a century-old approach using thermochemical reactions to convert atmospheric nitrogen into ammonia through reaction with hydrogen and a metal catalyst at high temperature and pressure. Consequently, the method is resource intensive. To meet current global demand, roughly 2 percent of the world's energy output and 5 percent of its natural gas resources are devoted to producing ammonia this way, releasing more than 500 million tons of carbon dioxide each year. In addition, the method can introduce toxic compounds into natural environments, requiring costly remediation efforts. "Ammonia production has a massive impact, touching billions of lives and consuming enormous resources," says staff scientist Jeremy Feaster. "Instead of taking incremental steps to make Haber-Bosch cleaner, we're proposing a radically different approach that uses electrochemical systems under near-ambient conditions."

Staff scientist Jeremy Feaster holds a palm-sized ammonia reactor prototype. Feaster's team is researching the catalysis of atmospheric nitrogen using electricity to produce ammonia from air—a major departure from today's standard, carbon-intensive route. By constructing prototype reactors with 3D-printing technology, the team can rapidly iterate on reactor designs and maximize performance prior to scale-up.

Out with the Old, In with the N₂

Feaster is the principal investigator on a project to pioneer an ammonia production method that circumvents the Haber-Bosch process altogether. The team's research efforts represent Livermore's growing expertise in electrocatalytic reactor systems, initially spurred by a 2019 Laboratory Directed Research and Development-funded project aimed at transforming waste carbon dioxide into hydrocarbon feedstocks for 3D printing.

"What also makes our approach unique is how we're adapting aspects of fuel cell technology and applying it to

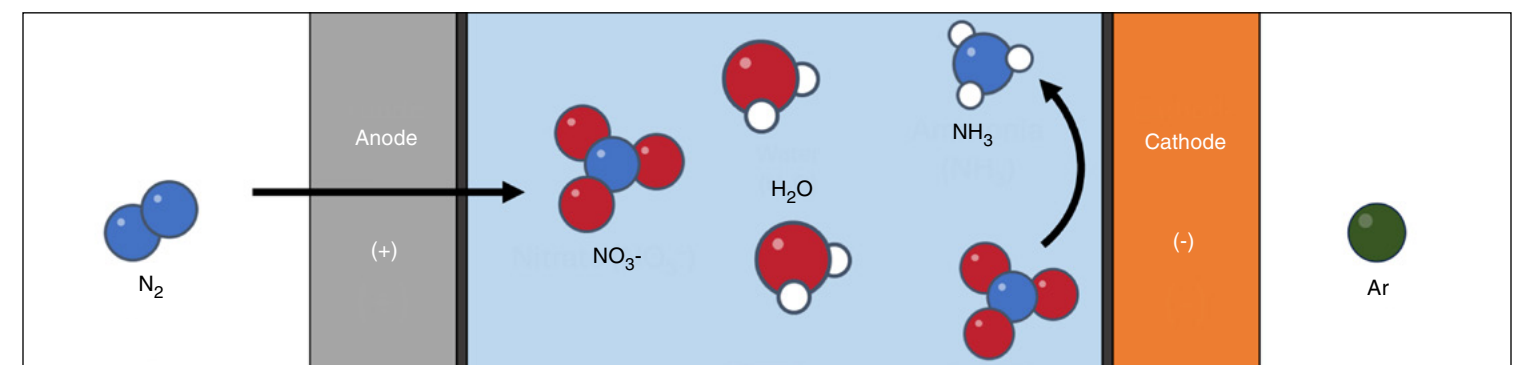
nitrogen chemistry in a way that has never been done before," says staff scientist Jack Davis. Rather than rely on the inefficient, pollutive methods for sustaining the environments needed for Haber-Bosch reactions, Feaster's team aims to harness energy from renewable sources such as solar and wind to power an electrolytic system that sets the ammonia-producing chemical reactions in motion. The team proposes simultaneous, partnered reduction-oxidation (redox) reactions to produce ammonia from the nitrogen present in air. Feaster explains, "Most electrocatalytic reactors carry out the reaction of interest on just one electrode while the other electrode idles. The positively and negatively charged electrodes hardly 'talk to' each other. Our team aims to make each electrode work in unison to perform both steps of the ammonia production process."

The final conversion of nitrate to ammonia—reduction—is well established in scientific literature, so the team is now concentrating on the more challenging first phase: oxidation of nitrogen into nitrate. Air is pumped into the reactor, and the nitrogen gas present adsorbs onto the surface of the positively charged anode. Electricity surging through the anode catalyzes the transformation of nitrogen to nitrate by lowering the activation energies of the string of oxidation reactions. The anode contacts an electrolyte solution—water and potassium carbonate—which cycles through the central chamber to enhance reaction efficiency. Over time, nitrogen's oxidation state increases from zero to +5 (in nitrate), indicating fewer electrons are associated with the molecule's nitrogen atom. Once nitrate forms, it will undergo reduction at the cathode, located on the opposite face of the chamber, to yield ammonia.

"Considering how the different factors interact with one another—the reaction pathways, the effect of the solvent, and the applied potential—is a defining feature of this research effort," says staff scientist Sneha Akhade.

To progress from theory to implementation, the team is determining the optimal chemical reaction pathway and selecting the best-suited mix of reactor materials to maximize nitrate production. Similar to traveling across a city, many potential routes exist to reach a final destination—some direct, others, a detour. The researchers are seeking the simplest, most energy-efficient route to convert nitrogen into nitrates (and later ammonia). Although initially splitting nitrogen would free up nitrogen atoms to interact with oxygen, the nitrogen molecule's triple bond is among the strongest in nature; therefore, more applied energy is required to break the bond, which raises the experimental difficulty. "It's incredibly hard for scientists to force nitrogen to do what we want it to do experimentally," says Davis.

Using computational techniques, the team predicted that electrocatalysis makes nitrogen more likely to accept an oxygen atom—oxidizing to form nitrous oxide—than having its bond split. Their follow-on laboratory experiments supported this finding. Akhade says, "At first, we were skeptical that any route other than initial separation of nitrogen would be energetically preferable because the number of follow-on reactions needed to obtain nitrate would have to increase in number. Yet, when adding up the thermodynamics of subsequent steps, we found that beginning with oxidation requires less energy input overall, despite representing the longer route."



This cross-section schematic depicts the high-level reactions that transform atmospheric nitrogen (N₂) into nitrate (NO₃⁻) in an electrocatalytic cell. Air is pumped into the cell at the left, and nitrogen adsorbs onto the anode (gray), which is made of a metal catalyst. Electrical current runs through the anode, initiating oxidation reactions that proceed in the middle chamber (blue) filled with water (H₂O) and electrolyte. These reactions raise nitrogen's oxidation state until nitrate forms. Then, at the cathode (orange), nitrate is reduced to ammonia (NH₃). Argon (Ar), an inert gas, is present to prevent unforeseen reactions at the cathode.

Advanced Catalyst Screening

To ensure maximum product for minimum energy input, the team seeks an ideal material for electrodes to catalyze chemical reactions. Candidates include metals such as platinum, cobalt, palladium, or iridium. Each one responds characteristically to applied voltage based on its atoms' electronic structures, in turn dictating how reactants and intermediate species form and break molecular bonds on its surface.

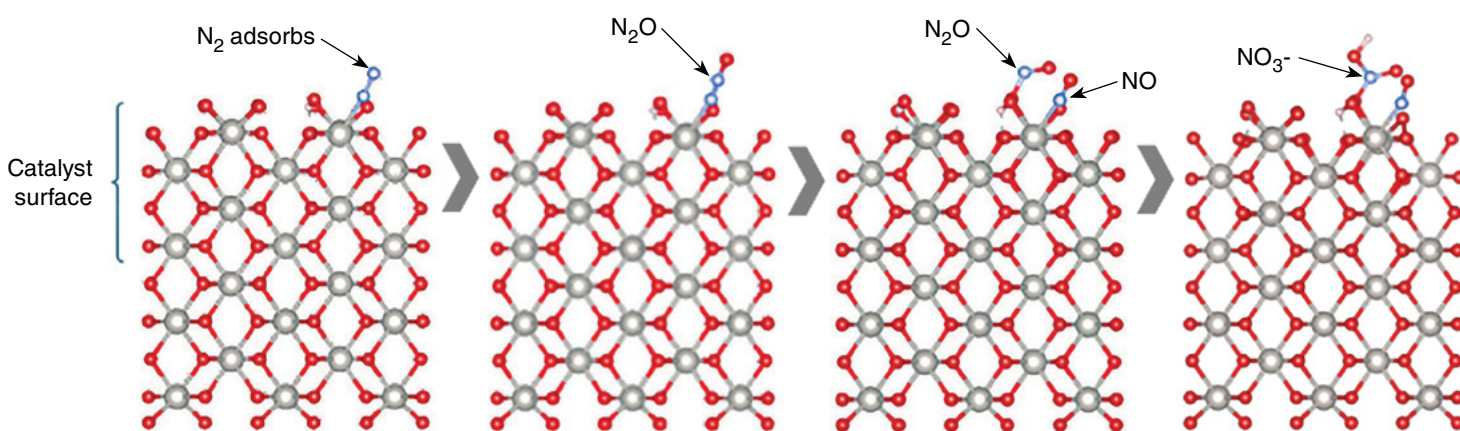
To expedite catalyst selection, the group uses high-performance computing to simulate how each catalyst will interact with nitrogen throughout the ensuing reactions. Postdoctoral researcher Alexandra Zagalskaya explains, "The predominant method in computational electrochemistry is ab initio thermodynamics, but research indicates that this approach alone may be insufficient for accurate predictions due to the kinetic limitations of real-world reactions." Thermodynamic methods can determine which chemical reactions are favored energetically given a system's initial and final states; kinetics provide insight into the reaction mechanism and the achievable conversion rate. "In catalysis, once we show the reaction is possible, the challenge lies in understanding molecular kinetics."

Carrying out these reactions in the same reactor is particularly challenging due to the multiple phases of matter present: solid catalyst, liquid electrolyte, and gaseous nitrogen. By employing additive-manufacturing methods, the team devised printed structures that drive air directly to the catalyst while confining water to the interior chamber, limiting nitrogen dissolution that would otherwise reduce nitrate yield (as it

does in the Haber–Bosch process). Nitrogen must also oxidize without triggering the electrolysis of water, which can split into oxygen and hydrogen under similar conditions and contaminate the reaction. "Ten coupled electron–proton reactions stand between nitrogen and nitrate, and the intermediate species can disrupt other reactions. We need to identify the steps with the highest kinetic barriers and make them more favorable while also minimizing competing reactions," says Zagalskaya. In accordance with the team's earlier findings concerning reaction pathways, the ideal catalyst must also enable the reactor to transform nitrogen into nitrous oxide early on yet maintain the conditions necessary for the remaining reactions.

3D-Printed Process

Once the team identifies a promising combination of reactor parameters, postdoctoral researcher Aditya Prajapati performs laboratory experiments to evaluate their practical performance. "The process is a feedback loop," he says. "We build the reactor with the selected catalyst, run the reactions, and analyze the products. This allows us to refine our mechanistic understanding and improve reactor design." The team uses a range of diagnostic tools to assess reactor performance. Having multiple means of measurement is essential for validating the operation of the novel catalysis setup. Because the primary product of interest, nitrate, has negatively charged regions, the team detects it using ion chromatography. They measure the remaining species using a combination of gas chromatography, mass spectrometry, and nuclear magnetic resonance. Understanding the relative levels of products and reactants at



This computer simulation of molecular behavior shows initial adsorption and repeated oxidation of nitrogen on a platinum catalyst surface (the anode), eventually yielding nitrate. Nitrogen atoms are shown in blue, oxygen in red, and platinum in gray. These reactions occur at a triple-phase point where solid catalyst, liquid electrolyte, and gaseous nitrogen meet.



Feaster's group uses additively manufactured components to rapidly iterate through reactor design changes. Stereolithography (SLA) 3D printing is a quick and inexpensive additive-manufacturing process in which a laser focuses on a vat of photosensitive polymer to solidify print layers one by one. SLA is also ideal for fabricating the structures needed to deliver nitrogen directly to the anode.

each reaction step helps reveal any process bottlenecks and inform the next reactor modifications to be made.

At this stage of the project, test reactors fit within the palm of a hand. Their miniature size is not a limitation, but a feature of the team's methodology. The team can rapidly implement necessary design changes thanks to additive-manufacturing methods. They use a stereolithography setup that 3D prints clear acrylic components by focusing a laser onto a vat of resin to harden it into shape. New reactor designs are manufactured in a matter of hours, and the acrylic used is inexpensive. To convert enough nitrogen gas into nitrate—and ultimately ammonia—to be economically viable, the reactors will have to scale significantly. "The process eventually becomes engineering optimization. We consider how to bump up the system's selectivity and efficiency, and we need to assess how behavior changes when scaling up to a larger platform," says Prajapati. Once the researchers settle on a combination of parameters, they can physically enlarge the reactors and shift the construction to machined metal components. These upgrades will bring the effort one step closer to large-scale reactors and pilot plants that could begin producing fertilizer ingredients closer to home.

Although the United States does have ammonia production facilities, primarily in Texas and Louisiana, most ammonia production occurs in China and Russia. Relying too heavily on imported ammonia has direct economic and security

consequences. For instance, following Russia's invasion of Ukraine, fertilizer prices quadrupled in less than one month. Using simple, ubiquitous ingredients—air, water, and electricity—would empower more communities to produce ammonia and related products that are customized to the needs of local growers while reducing reliance on distant, potentially unstable supply chains. Localized production could also give communities greater control over ammonia's additional uses, chiefly, as an energy carrier much like hydrogen fuel.

Through collaboration with the Laboratory's Innovation and Partnerships Office, the research group has been investigating what real-world deployment of larger scale reactors could look like, starting with neighbors in California's Central Valley, the state's breadbasket. "This team realizes that we don't do research in a silo. If science is a service to society, we need to make sure we're talking with people to meet their needs," says Feaster. He and the project's collaborators have been in talks with the region's farmers to understand the benefits and obstacles to deploying such a system. Meanwhile, device optimization research and technoeconomic analysis continues to maximize the energy efficiency, affordability, safety, and impact of electrochemical reactors for the ammonia industry.

— Elliot Jaffe

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