New Ways To Nab Nitrogen

Stephen K. Ritter

More sustainable approaches to synthesizing ammonia could re-revolutionize agricultural fertilizer production.

British chemist Humphry Davy is best known for being the first person to isolate several elements, including sodium and calcium. Davy carried out his work electrolytically more than 200 years ago as an early experimenter with batteries. Less known about Davy is that during experiments on water electrolysis, in which water is split into hydrogen and oxygen, he found that ammonia formed on the cathode in his electrolysis cell. Davy had unexpectedly coupled N₂ dissolved in the water from the air with the H₂ being formed to make NH₃.

Scientists and engineers have been fixated on this so-called nitrogen-fixing process ever since, primarily as a means to make NH₃ to prepare fertilizer. We now know that bacteria in the soil produce nitrogenase enzymes to pull N₂ from the air to make NH₃. The ammonia is subsequently converted to nitrate by other bacteria in the soil so that it can be used by plants.

A new set of NH₃ production strategies now combines the best of both these worlds: Davy’s electrochemical observation and nature’s enzymatic approach. If these experimental technologies prove successful on a larger scale, they could one day usher in a new revolution in agricultural fertilizer production, much in the way that the Haber−Bosch−Ostwald pathway has ushered in a fertilizer revolution when it was developed 100 years ago.

In one example, postdoctoral researcher Ross D. Milton and chemistry professor Shelley D. Minteer of the University of Utah and co-workers have developed a bioelectrochemical process in which an enzyme-based fuel cell produces NH₃ from N₂ and H₂ at room temperature and pressure. In another example, chemistry professor Daniel G. Nocera at Harvard University, biochemistry professor Pamela A. Silver at Harvard Medical School, and co-workers are developing engineered bacteria that incorporate H₂ from water electrolysis with N₂ from the air to produce NH₃.

Minteer and Nocera presented details of their research in April at the American Chemical Society national meeting in San Francisco.

Following Davy’s discovery, chemists began trying to develop electrosynthesis procedures to produce ammonia on a large scale. And with an understanding of the biological nitrogen-fixing process, chemists have been trying to develop metal catalysts that mimic enzymes. But researchers have not quite figured out how to make these approaches work efficiently on a large enough scale to be practical.

For that, we have the Haber−Bosch chemical synthesis process. This brute-force industrial method employs a metal catalyst to couple H₂ with N₂ at high temperature and pressure to prepare NH₃. Much of the NH₃ is then converted to nitric acid by the Ostwald process to make the fertilizer ammonium nitrate.

The Haber−Bosch−Ostwald pathway requires a substantial industrial infrastructure that consumes massive amounts of energy and creates great volumes of carbon dioxide and other pollutants. Researchers have therefore sought out environmentally friendlier and more sustainable approaches to producing ammonia, ranging from thermal solar reactors to engineered plants that make their own ammonia. The new strategies from Minteer and Nocera could be part of the solution everyone is looking for.

“Inter electrolysis should become a viable strategy for nitrogen fixation, it could be a means of circumventing the...
Haber–Bosch and Ostwald processes,” says chemistry professor Robert H. Crabtree of Yale University, who specializes in catalytic strategies for alternative energy generation.

Last year, Crabtree and chemistry intellectual property specialist Michael Jewess published a perspectives paper recounting Davy’s discovery and proposing that scientists ramp up efforts to develop sunlight-driven bioelectrochemical systems for making NH₃. In a big picture way, electrocatalytic nitrogen fixation for distributed fertilizer production would be a more sustainable method for individual farms to harvest N₂ from the air and make their own fertilizer, bypassing the current industrial production and distribution systems, Crabtree suggests.

“This is leading the chemical side of the nitrogen-fixation problem to progress beyond prior mechanistic and biomimetic concerns and take on real practical significance, as the recent work of the Minteer and Nocera groups shows,” Crabtree says.

Although many researchers have explored enzymatic approaches to NH₃ production, Minteer’s group at Utah has provided the first evidence for bioelectrochemical NH₃ production by a complete nitrogenase, rather than just one subunit of the enzyme. The Utah team’s enzymatic fuel cell consists of two compartments. On one side, a hydrogenase enzyme oxidizes H₂ supplied to the cell to form hydrogen ions and electrons. Because the enzyme is not efficient at directly interacting with the electrode, the researchers need to provide a redox-active compound as a go-between to pick up and drop off the electrons. They chose methyl viologen, a versatile compound often used for this electrochemical role.

In the other compartment of the fuel cell, they use a nitrogenase enzyme to reduce N₂ from the air to make NH₃, using electrons supplied from the hydrogenase side of the cell through an external circuit. Methyl viologen again acts as a redox mediator to shuttle the electrons between the electrode and the enzyme. The hydrogen ions, needed to form NH₃, migrate through a membrane separating the two compartments. As a bonus, the overall reaction generates a small excess of electricity.

There are a few catches to the bioelectrochemical system, Minteer explains. Nitrogenases are not commercially available, and when isolated from cultured bacteria they must be handled with care because the enzymes can be irreparably damaged by oxygen. In addition, nitrogenases require the coenzyme adenosine triphosphate (ATP) to operate; ATP undergoes hydrolysis to mediate energy transfer for nitrogen reduction. Minteer’s group had to devise a way to continuously supply ATP to the enzyme, which the researchers did by adding creatine phosphate to recycle adenosine diphosphate (ADP) into more ATP.

The team has been able to produce small amounts of NH₃ so far, Minteer says, and several challenges remain before scaling up. But she thinks those will be mostly related to materials design and enzyme engineering. One challenge is to address the oxygen sensitivity of nitrogenase and the lifetime of the enzymes. Another is to develop a workaround to avoid the need for ATP.

Looking to the future, Minteer is thinking about small-scale systems in which every farmer could use a solar cell to run an enzymatic bioelectrosynthesis cell or set of cells to make ammonia, rather than buying it delivered in trailer-mounted tanks as many currently do. Farmers could use the excess electricity to help power their operations, or they could sell it to the power grid.

“We generally think of Haber–Bosch as an intensive process that consumes energy. But with the right catalytic system design, we can actually generate energy,” she says. “Our technology would definitely enable us to decentralize fertilizer production and avoid building and running large industrial plants.”

Nocera’s group is already known for developing an "artificial leaf," a wireless solar-cell device that mimics a...
natural leaf by splitting water into H₂ and O₂. The H₂ can be stored and used as needed to run fuel cells to generate electricity. The team has recently been taking the concept a step further to develop systems for making liquid fuels, and now a hybrid artificial leaf-microbial system to produce NH₃.

The new approach, a construct called a “bionic leaf,” is actually an engineered bacterium that effectively carries out Haber–Bosch in a single microbial cell. The researchers designed a Xanthobacter species to take H₂ from the artificial leaf and use a carbohydrogenase enzyme to couple it with CO₂ from the air to make the bioplastic polyhydroxybutyrate. A number of bacteria are known to produce such bioplastics that they store as a fuel source, like people store fat. But the team also integrated the ability for the microbe to absorb N₂ from the air and use its nitrogenase to couple it with H₂ from the polyhydroxybutyrate to make NH₃. This trick replaces the need for ATP to power the enzyme.

The researchers spray a solution containing the polyhydroxybutyrate-storing bacteria onto the soil like a nutrient, where NH₃ is produced and expelled into the ground, reminiscent of the way farmers apply liquid ammonia to fields. Natural bacteria in the soil do the rest, converting the NH₃ into nitrate that plants can absorb through their roots. Nocera’s group tested the strategy on radishes, showing that plants treated with the bacteria weigh 150% more than untreated plants. “We can grow big radishes, really big radishes,” Nocera exclaims.

The technology is still at an early stage and nowhere near being put into practical use, Nocera stresses. “I just wanted to find out if we could actually do it,” he says. “The answer is yes.”

Nocera’s team is now exploring ways to speed up NH₃ production. The proof of concept also points to the possibility of modifying the microbes to synthesize other compounds. “One day we might be able to make everything we need by tailoring these bugs,” Nocera says. “You would have a solar-based manufacturing lab.”

Nocera notes the primary beneficiaries of the Haber–Bosch process have been people living in developed countries with established infrastructure. He views the bionic leaf instead as a means of boosting agriculture and food production in developing regions. In fact, the strategy assumes developing an infrastructure won’t be needed at all.

“The Haber–Bosch process is one of the greatest scientific achievements in the 20th century,” says John J. Watkins, chief executive officer of Fulcrum Biosciences. “Industrial-scale nitrogen fixation allowed agriculture production to increase enormously and feed an ever-increasing world population. However, there has been a growing interest in alternative, greener methods that move away from centralized ammonia production.”

Watkins’ company is working toward increasing the nitrogen-fixation rate of algae biofilms using genetic modification and electrochemical methods. Part of his evaluation includes looking at the dynamics of the fertilizer market.

“The current system of purchasing fertilizer is straightforward for farmers: Fertilizer is purchased, delivered, and then applied,” Watkins says. Because agriculture operates on narrow margins, farmers must balance increased yields against increased cost to remain profitable, he adds. That means any new production process, like the technologies being developed by the Minteer and Nocera groups, must be cost competitive, Watkins says. And they must be simple to operate with low maintenance demands. “Growing up in Iowa, I never knew any farmers with an abundance of free time or money.”

Stephen K. Ritter is a senior correspondent at Chemical & Engineering News, the weekly news magazine of the American Chemical Society. This story first appeared in C&EN.