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Undergraduate

Green Ammonia Synthesis: An Emerging Source of Renewable Energy

BY ANGENI LIEBEN

Considering that all matter on this planet is made of the same basic elements, the smallest of molecules can have the potential ability to impact our society through the way they interact with the substances around them. One small molecule in this big spotlight is ammonia. Ammonia consists of one nitrogen atom chemically bonded to three hydrogen atoms in a trigonal pyramidal structure (see Figure 1). Most people associate this chemical with their countertop cleaners or stain-removing sprays while others might know that it's sprayed into the soil as fertilizer to help grow crops.¹ While it may seem as though ammonia has already had its fifteen minutes of fame, new research reveals that it could see a whole new era of use as a carbonless source of energy.

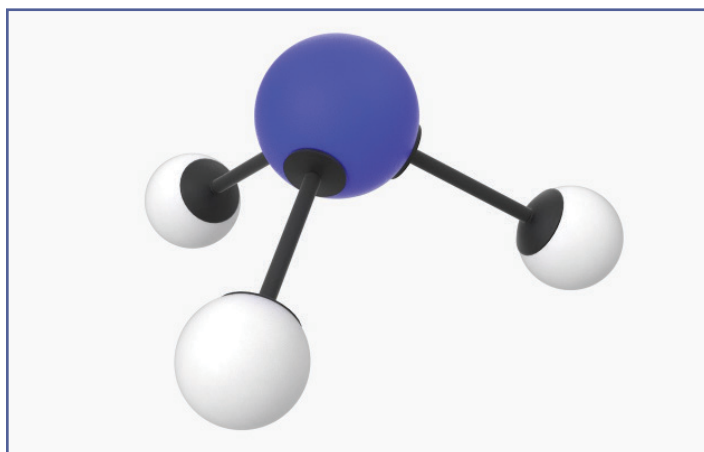


Figure 1: The 3D structure of ammonia.

As atmospheric carbon dioxide (CO_2) levels rise and the Earth's climate and biodiversity begin to experience the consequences of global warming, countries aim to implement substantial changes to reduce CO_2 emissions in the next few decades. This includes the groundbreaking Paris Agreement signed by the United Nations (UN) in 2015 where countries pledged to proactively combat climate change. A global temperature rise of 2.1 to 3.5 °C has been recently projected and UN ambassadors outlined goals of reducing this to 2 or ideally 1.5 °C.² Although this may seem like a small difference, the figures become more alarming when put into context. Based on historical climate data, scientists conclude that the 0.7 °C increase in global temperature over the last 100 years has occurred roughly 8 times faster than the average rate of warming the planet saw after the Ice Ages.³ As the effects of global warming become apparent, many countries promise net zero emissions by 2050.⁴ Governments attempt to accomplish this by passing environmental policies and legislation that regulate pollution, push industries to reduce fossil fuel use, and invest in sustainable energy and products.⁵ Unfortunately, many nations struggle to enact these widespread changes and will not meet these critical goals fast enough to keep up with rapidly rising temperatures.⁶ It will take cutting-edge scientific research to make effective headway. A promising field centers around ammonia as a renewable source of energy. To understand the origin of these ideas, we must consider the role that ammonia currently plays in our daily lives as well as the historic methods of synthesizing it.

THE TRADITIONAL WAY

Ammonia is a noxious and harmful gas at room temperature that can be condensed into a clear liquid under pressure. However, a certain amount is necessary for the processes essential to life.¹ Ammonia can be made naturally by nitrogen-fixing bacteria that use energy from decomposing matter to turn inaccessible nitrogen (N_2) gas into a form that plants can absorb and metabolize.⁷ While nitrogen compounds like ammonia are vital for ecosystems, the natural nitrogen cycle did not evolve as a means to support booming civilizations of people. That is until 1909 when the creation of the Haber-Bosch method (see Figure 2) by two German scientists industrialized a synthetic chemical reaction to produce ammonia for commercial and agricultural use. In it, an iron catalyst promotes a reaction between six hydrogen atoms stripped from coal or natural gas and two nitrogen atoms extracted from the air. This reaction occurs at a high temperature and pressure, yielding two molecules of ammonia.⁸ Due to the reaction's efficiency, current production plants can produce 150 million metric tons of ammonia annually which end up contributing to half the nitrogen in the human body.^{9,10} Since the required hydrogen for the reaction originates from fossil fuels, half of the overall emissions from this process are the leftover CO_2 and hydrogen. Ultimately, the Haber-Bosch method contributes 1% of CO_2 emissions and uses 2% of the world's energy to run it, clouding the hope of a zero-emissions future.¹⁰

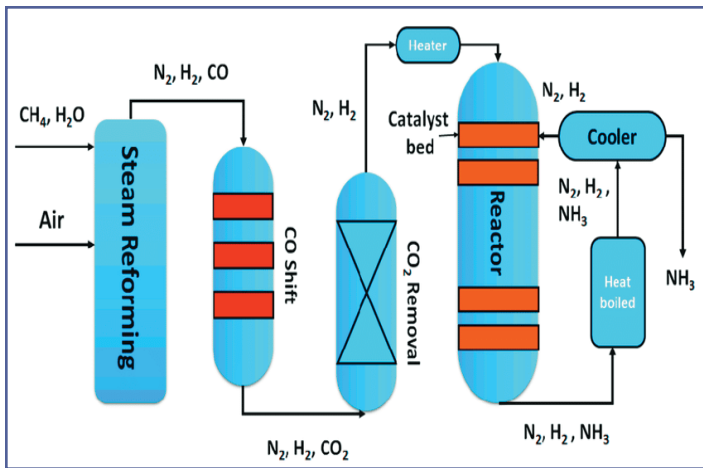


Figure 2: A schematic of the Haber process with all the necessary steps and components.

INNOVATION WITH ELECTROLYTIC CELLS

Although its current form of production is unsustainable, ammonia has potential as a revolutionary renewable fuel and fertilizer. Renewable energy sources are powerful because they can be continuously replenished when consumed. Ammonia can easily liquify under low pressure at $-10\text{ }^\circ\text{C}$, making transport feasible via pipes or ships. What is more, its energy density by volume is nearly double that of pure liquid hydrogen (H_2).¹⁰ Ammonia can also be “cracked” to provide a dependable source of hydrogen—a green fuel dangerous to store because it expands quickly and is highly combustible, though other more economically efficient carbonless processes exist to acquire H_2 such as direct electrolyzation of water.¹¹ With substantial funding, replacing Haber-Bosch ammonia with

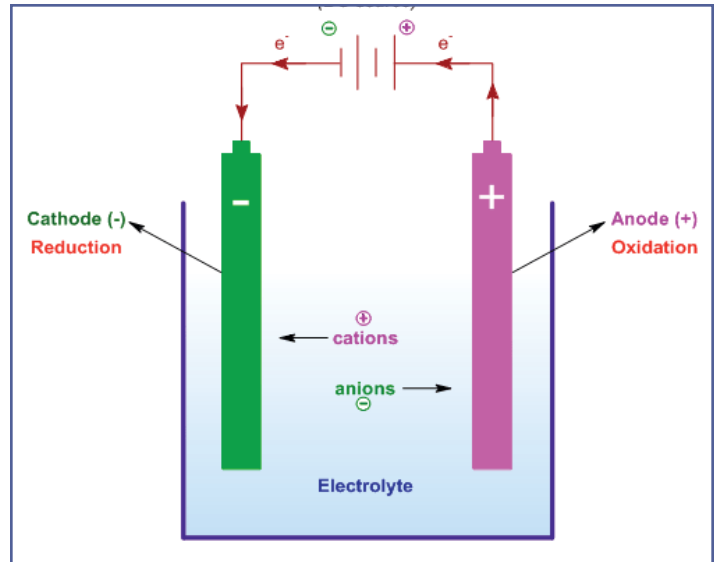


Figure 3: A diagram of how a basic electrolytic cell functions.

green ammonia could result in significant environmental benefits.

Scientists are seeking an alternative synthesis reaction to the Haber-Bosch process in an effort to avoid producing CO_2 as a byproduct. In the last few years, scientists have started using electrolytic cells (see Figure 3) to “naturally” produce ammonia. In chemistry, a cell is a very specific equipment setup allowing for the transfer of electrons in chemical reactions. A cell needs to have an anode, from which electrons leave a chemical compound, connected to a cathode, where another chemical compound accepts them. These electrodes are suspended in a liquid called the electrolyte. The electrolytic cell needed for ammonia production is essentially the reverse of this; it actually requires electricity to run through it to split hydrogen from water and bond it with nitrogen. Since water is part of the electrolyte solution, the extra H^+ ions that lost their electrons will migrate through a permeable membrane in the solution to the cathode where nitrogen gas (N_2) is also added. A key step is adding catalysts that will help split the N_2 and attach the hydrogens to make ammonia (see Figure 4).

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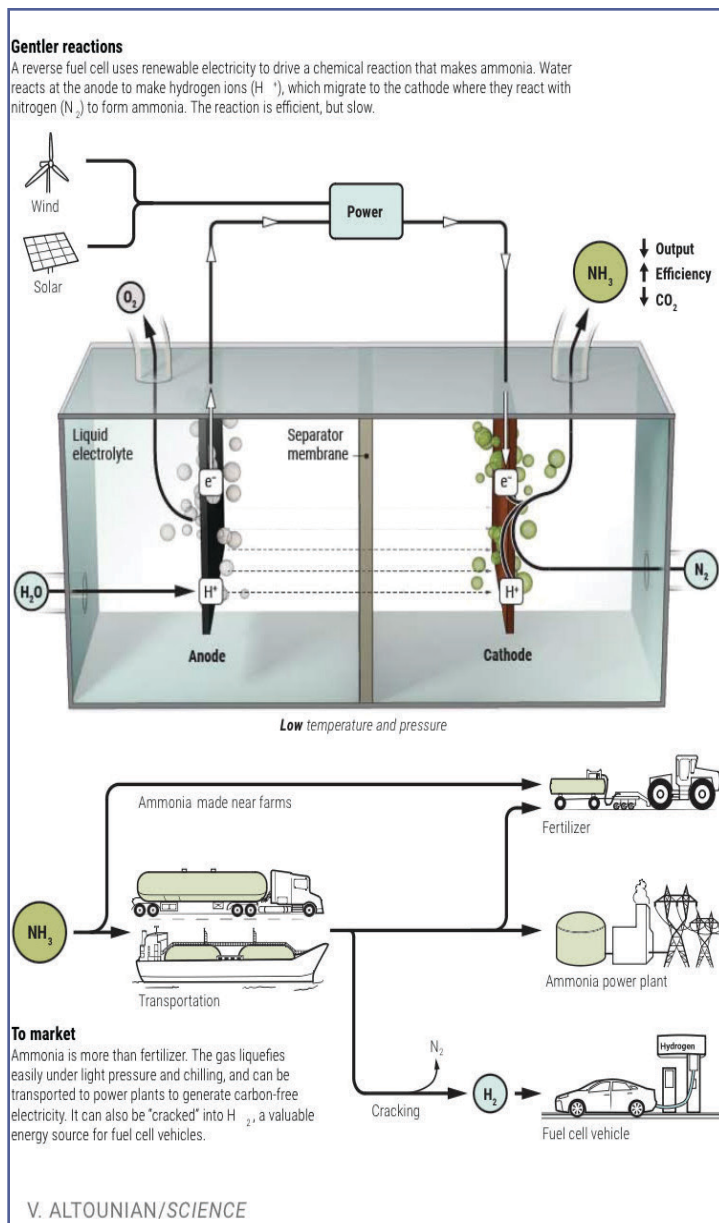


Figure 4: A diagram of the cell framework needed for ammonia synthesis and its uses.

THE DEVIL IS IN THE DETAILS

Despite the requirements of the reaction, there are seemingly endless ways to set up this ammonia-producing electrolytic cell. Most initial experiments were slow at room temperature and pressure with low ammonia yields around 1-15% and a Faraday efficiency around 50%.⁹ Faraday efficiency is another important way to measure the cell's performance because it measures how much of the total electricity input goes into creating the desired product, ammonia. The bulk of research in this area now focuses on a few promising setups with increasing success in getting these processes at an economically feasible level.^{9,12} Through rigorous investigation and tweaking of cell components such as the electrolyte composition, some of these optimized setups have achieved 100% Faraday efficiency and have not gone unnoticed by startup companies.¹² Seeing the promise of scaling up this reaction

for a future green nitrogen-hydrogen economy, scientists focus their efforts on designing an electrolytic cell that can run smoothly, efficiently, and quickly. Ideally, this would be under the low-maintenance environmental conditions where nitrogen is fixated by bacteria: low temperature and pressure with non-metallic electrodes in an aqueous (water-based) electrolyte solution.⁹

“Despite the requirements of the reaction, there are seemingly endless ways to set up this ammonia-producing electrolytic cell.”

The challenge is optimizing this reaction since the efficiency of a cell relies not only on the chemicals chosen for it but also on the nanoscale arrangements of the molecules. This is where the innovation of nanomaterials enters the picture. Recent papers, including from Berkeley researchers, have zoomed in on the cell's workings and devised new nanomaterials for the electrodes and catalysts to maximize the effectiveness of the reaction (see Figure 5).^{13,14} With this technique, there have also been a few reactions that have surpassed the 50% Faraday efficiency mark, but none have reached industrial ammonia formation rates.⁹ While this is a nascent field in need of much more experimentation, the idea of a new renewable energy source entices interested parties around the globe.

THE PATHWAY FORWARD

Potential investors may hesitate to put money into something that has neither proven itself to be profitable nor has an established reputation.¹⁵ The Haber-Bosch infrastructure, on the other hand, is deeply rooted in our industrial economy. Yet, certain countries have already acknowledged the benefits of leaping into this green ammonia market and leading the transition to a carbonless nitrogen-based energy infrastructure. It is one thing to come up with an innovation but another to ensure that the innovation becomes part of our everyday lives. The electricity used to power the ammonia cells could be supplied by renewable sources such as solar or wind power from regions in which it is readily available. For example, Australia boasts 25,000 untapped gigawatts of renewable energy. In 2018, the Australian Renewable Energy Agency donated an initial AU\$20 million to replace coal and natural gas export with renewable energy export. That year, the South Australian government also donated AU\$20 million in grants and loans to ammonia projects, including several pilot plants.¹⁰ Interest is burgeoning in other countries like New Zealand, Canada, Japan, Singapore, and Korea.^{10,16-18}

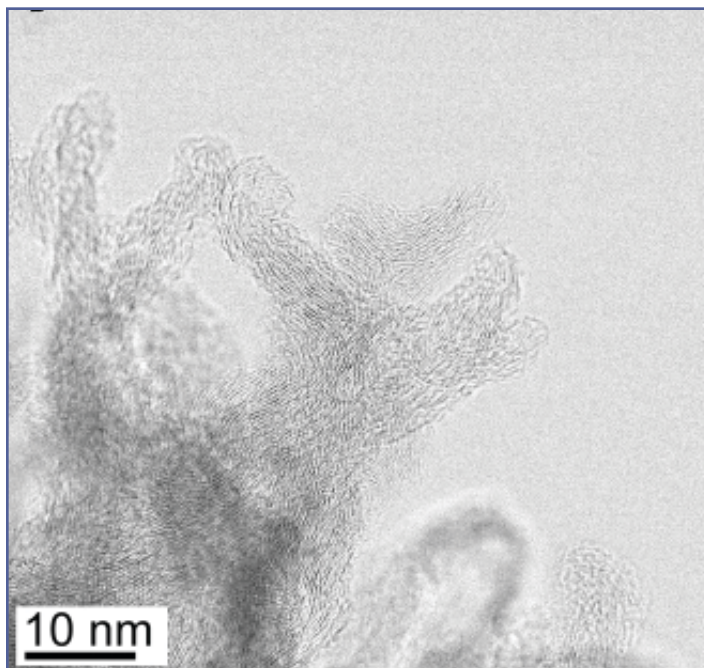


Figure 5: Electron microscopy image of nitrogen-covered carbon nanospike electrodes that were designed to reduce H_2 byproducts and bind well with N_2 .

In just the past few years, research on synthetic ammonia cells has flourished as scientists around the globe continue to test aspects of this chemical pathway, pushing it toward maximum output and potential. This electrochemical wonder is drawing attention from policymakers, shipping company directors, and concerned citizens alike as global warming continues to rear its ugly head. Within the chemical bonds and traveling electrons of this deceptively simple contraption lies a vision. A vision that could change the way human civilization powers its inventions and interacts with the environment. Pure experimental chemistry is needed to unlock this possible future, and it will take the collaboration of many different groups to turn it into a sustainable reality.

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