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News & Highlights Most Efficient Reaction Bolsters Prospects for Low-Carbon Ammonia Mitch Leslie

Senior Technology Writer

At first glance, the 10 cm \times 10 cm stainless steel box that Douglas MacFarlane, professor of chemistry at Monash University in Clayton, Australia, and his colleagues designed does not look like anything special (Fig. 1). Four thin plastic tubes plug into ports on the box, and electrical wires connect to either side. But in 2022, MacFarlane and his team used the nondescript device to achieve a chemical first that may one day help clean up one of the dirtiest industrial processes. Inside the box was a unique mix of chemicals, including a type of electrolyte known as an imide. When the researchers pumped in nitrogen gas and water (which provides the hydrogen) and turned on an electrical current, the device produced ammonia with 99% efficiency, a breakthrough that beat the record for any electrochemical reaction, all at room temperature [1,2].

"We showed that it is fundamentally possible" to make ammonia in this way with a rapid reaction rate and high efficiency, said MacFarlane. The device is also significant because unlike the large factories that produce almost all of the world's ammonia (Fig. 2), it does not require fossil fuels as raw materials or generate carbon dioxide. Jupiter Ionics, a spinoff company in Melbourne co-founded by MacFarlane, is now working to scale up the device to yield one kilogram of ammonia per day. If it can achieve that goal, MacFarlane and his colleagues want to go even bigger, building a shipping container-sized reactor that could supply one tonne of ammonia per day, he said.

Their strategy is one of many novel approaches to shrink the enormous carbon footprint of ammonia production, which is about the same as that of the aviation industry [3,4]. Like their work, some of these approaches are still under development, but others have emerged from the lab. A handful of reduced-emission ammonia plants are operating at a relatively small scale [5]. And facilities under construction or planned in Saudi Arabia, Australia, and other locations will soon be producing millions of tonnes of low-carbon, "green" ammonia every year, potentially demonstrating that these alternatives are feasible and commercially viable [6,7].

Ammonia is a little-recognized culprit in climate change. Most people do not think of it as a major contributor, but its production accounts for about 2% of the world's total energy use and 1%–2% of carbon emissions [3,8]. About 70% of the roughly 1.8×10^8 tonnes of ammonia manufactured every year becomes fertilizer, with the rest going into plastics, explosives, and other products [8,9]. The need for ammonia will soar in the coming decades because it is

gaining new uses, experts say. The electrical power and shipping industries are eying ammonia as a cleaner-burning alternative to fossil fuels, for instance [10]. Because ammonia is relatively easy

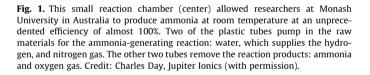




Fig. 2. Like almost every other ammonia plant in the world, this one in Brunei burns fossil fuels to produce ammonia via the Haber–Bosch process. The facility, which opened in 2022, produces 2200 tonnes of ammonia daily. Credit: DeltaSquad833, Wikimedia Commons (CC BY-SA 4.0).

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to transport and store, it could also serve as a carrier molecule for the hydrogen needed by the fuel cells expected to power larger electric vehicles such as trucks, buses, trains, and ships [9,11–13].

Ammonia's climate impact stems from how it is manufactured. Almost all of the world's supply is produced through the Haber-Bosch process, in which nitrogen from the air combines with hydrogen [8]. Developed more than a century ago, the process requires large amounts of energy-more than 30 GJ t^{-1} of ammonia-to reach the necessary temperatures of 400-500 °C and pressures of 150–300 bar (1 bar = 10^5 Pa) [14]. This energy typically comes from fossil fuels, and the Haber-Bosch process is dependent on them for another reason. These fuels-most often natural gas-also usually furnish the hydrogen required as a raw material [8]. Amplifying the climate impact, some Haber–Bosch process chemical reactions, including the ones that separate hydrogen from fossil fuels, also emit CO₂ [8]. Overall, the process generates more than two tonnes of CO_2 for every tonne of ammonia and is responsible for more carbon emissions than any other chemicalproducing industrial process [8,14]. With demand rising, the effect of ammonia production on climate change "is only going to get worse," said MacFarlane.

Many of the strategies for reducing ammonia's carbon emissions target steps of the Haber–Bosch process. A huge facility under construction at the planned city of NEOM in Saudi Arabia, for instance, will use solar and wind power to make hydrogen gas through electrolysis of water, thus eliminating fossil fuels as a hydrogen source [15]. Wind and solar will also furnish the power to operate the plant that, when it opens in 2026, will turn out about 1.2×10^6 tonnes of ammonia per year [6]. Another massive project, which will use renewable energy to produce hydrogen for fuel and for ammonia production, is being built in northwestern Australia [7,16].

A 2023 paper by Benjamin Snyder, assistant professor of chemistry at the University of Illinois, Urbana-Champaign, IL, USA, and colleagues in the laboratory of Jeffrey Long at the University of California, Berkeley, CA, USA, suggests a possible way to reduce the carbon emissions of another step in the Haber-Bosch process [17]. After nitrogen and hydrogen react, the resulting gas is chilled to allow ammonia to condense out [18]. But cooling requires a substantial amount of energy and chemical infrastructure. Snyder and his colleagues had been experimenting with a metal-organic framework-a porous, crystalline material composed of copper and the molecule trans-1,4-cyclohexanedicarboxylate-when they noticed that it avidly and selectively absorbed ammonia. "It is almost like a sponge" for the gas, Snyder said. The material undergoes a structural change when it absorbs ammonia, and then reverts to its original structure when it frees the ammonia. This flexibility promotes the binding and release of ammonia at temperatures up to 185 °C, the researchers found. Snyder cautioned that the discovery is "more conceptual than practical," and researchers will still "need to find out how [the framework] would stand up to industrial conditions." Still, the work raises the possibility of using similar metal-organic frameworks to capture ammonia under more moderate reaction conditions.

Instead of revamping the Haber–Bosch process, another approach seeks to trap its emissions. So-called blue ammonia comes from facilities that use fossil fuels but capture and store the resulting CO_2 [19], a scheme now also being applied in other industrial settings [13,20]. Unlike green ammonia, blue ammonia is already on the market, with Saudi Arabia and the United Arab Emirates exporting it to Europe and Asia [21]. In addition, several projects are planned to produce it in the United States [22].

Some researchers, including MacFarlane and his team, want to go further and dispense with the Haber–Bosch process. They are not the first scientists to produce ammonia through electrochemical reactions. Researchers first showed that lithium electrodes can generate the gas more than a century ago, MacFarlane said. However, previous efforts were slow and yielded little ammonia. MacFarlane and his team suspected they could do better by using a different electrolyte. The one they chose, bis(trifluoromethylsulfonyl)imide, appears to coat the cathode in their setup and promotes the reaction between lithium ions and nitrogen gas that is necessary to generate ammonia. The best efficiency achieved by prior studies that generated ammonia electrochemically was 78%, so the team's results represent a dramatic step forward. Another advantage is that their reactions run at room temperature. If they can scale up their reactor, it might reduce the need for large, polluting factories by allowing individual growers or farms to produce their own ammonia for fertilizer.

That step would be only one of many needed to diminish ammonia's carbon output, according to a plan laid out by MacFarlane and his colleagues in 2020 [23]. Low-carbon alternatives for manufacturing ammonia will eventually replace the Haber–Bosch process, MacFarlane said, albeit slowly. "It will happen, but probably not in my lifetime," he said.

References

- Du HL, Chatti M, Hodgetts RY, Cherepanov PV, Nguyen CK, Matuszek K, et al. Electroreduction of nitrogen with almost 100% current-to-ammonia efficiency. Nature 2022;609(7928):722–7.
- [2] Boerner LK. Chemists make N₂ into NH₃ in most efficient electrochemical reaction ever [Internet]. Washington, DC: Chemical & Engineering News; 2022 Aug 4 [cited 2023 Apr 15]. Available from: https://pubs.acs.org/doi/10. 1021/cen-10027-scicon1.
- [3] Ammonia technology roadmap [Internet]. Paris: International Energy Agency; 2021 Oct [cited 2023 Apr 15]. Available from: https://iea.blob.core.windows. net/assets/6ee41bb9-8e81-4b64-8701-2acc064ff6e4/AmmoniaTechnology Roadmap.pdf.
- [4] International Energy Agency (IEA). Aviation [Internet]. Paris: International Energy Agency; 2022 Sep [cited 2023 Apr 15]. Available from: https://www. iea.org/reports/aviation.
- [5] Jones N. From fertilizer to fuel: can 'green' ammonia be a climate fix? [Internet]. New Haven: Yale Environment 360; 2022 Jan 20 [cited 2023 Apr 15]. Available from: https://e360.yale.edu/features/from-fertilizer-to-fuel-cangreen-ammonia-be-a-climate-fix.
- [6] Ornes S. Green ammonia could produce climate-friendly ways to store energy and fertilize farms. Proc Natl Acad Sci USA 2021;118(49):e2119584118.
- [7] Low M. Project sets sights on hydrogen to produce green ammonia [Internet]. Adelaide: Cosmos; 2022 Dec 12 [cited 2023 Apr 15]. Available from: https://cosmosmagazine.com/science/engineering/hydrogen-produces-greeenammonia/.
- [8] Boerner LK. Industrial ammonia production emits more CO₂ than any other chemical-making reaction. chemists want to change that [Internet]. Washington, DC: Chemical & Engineering News; 2019 Jun 15 [cited 2023 Apr 15]. Available from: https://cen.acs.org/environment/green-chemistry/ Industrial-ammonia-production-emits-CO2/97/i24.
- [9] Tullo AH. Is ammonia the fuel of the future? [Internet]. Washington, DC: Chemical & Engineering News; 2021 Mar 8 [cited 2023 Apr 15]. Available from: https://cen.acs.org/business/petrochemicals/ammonia-fuel-future/99/ i8.
- [10] Crownhart C. How ammonia could help clean up global shipping [Internet]. Cambridge: MIT Technology Review; 2022 Aug 31 [cited 2023 Apr 15]. Available from: https://www.technologyreview.com/2022/08/31/1058791/ ammonia-fuel-clean-up-global-shipping.
- [11] Palmer C. Hydrogen power focus shifts from cars to heavy vehicles. Engineering 2020;6(12):1333–5.
- [12] Palmer C. Hydrogen-powered trains starting to roll. Engineering 2022;11:9–11.
- [13] Derouin S. Hydrogen fuel prospects rise with governmental support and green production. Engineering 2023;24:3–6.
- [14] Ghavam S, Vahdati M, Grant Wilson IA, Styring P. Sustainable ammonia production processes. Front Energy Res 2021;9:580808.
- [15] Nereim V. Saudi Arabia to start building green hydrogen plant in NEOM [Internet]. New York City: Bloomberg; 2022 Mar 17 [cited 2023 Apr 15]. Available from: https://www.bloomberg.com/news/articles/2022-03-17/ saudi-arabia-to-start-building-green-hydrogen-plant-in-neom#xj4y7vzkg.
- [16] Bearak M. Inside the global race to turn water into fuel [Internet]. New York City: The New York Times; 2023 Mar 11 [cited 2023 Apr 15]. Available from: https://www.nytimes.com/2023/03/11/climate/green-hydrogen-energy.html.
- [17] Snyder BER, Turkiewicz AB, Furukawa H, Paley MV, Velasquez EO, Dods MN, et al. A ligand insertion mechanism for cooperative NH₃ capture in metalorganic frameworks. Nature 2023;613(7943):287–91.

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- [18] Smith C, McCormick AV, Cussler EL. Optimizing the conditions for ammonia production using absorption. ACS Sustain Chem Eng 2019;7(4):4019–29.
 [19] Ammonia: zero-carbon fertiliser, fuel and energy store [Internet]. London:
- [19] Ammonia: zero-carbon fertiliser, fuel and energy store [Internet]. London: Royal Society; 2020 Feb 19 [cited 2023 Apr 15]. Available from: https:// royalsociety.org/topics-policy/projects/low-carbon-energy-programme/greenammonia/.
- [20] Leslie M. Construction industry innovation takes aim at reducing carbon emissions. Engineering 2022;19:7–10.
- [21] Ratcliffe V. Europe hunts for clean energy in the Middle East, but how clean is it? [Internet]. New York City: Bloomberg; 2022 Sep 28 [cited 2023 Apr 15].

Available from: https://www.bloomberg.com/news/articles/2022-09-28/ europe-s-blue-ammonia-cargoes-from-saudi-arabia-uae-won-t-be-carbonfree#xj4y7vzkg.

- [22] Tullo AH. Chemical makers plan blue ammonia projects [Internet]. Washington, DC: Chemical & Engineering News; 2022 May 5 [cited 2023 Apr 15]. Available from: https://cen.acs.org/business/Chemical-makers-planblue-ammonia/100/i16.
- [23] MacFarlane DR, Cherepanov PV, Choi J, Suryanto BHR, Hodgetts RY, Bakker JM, et al. A roadmap to the ammonia economy. Joule 2020;4 (6):1186–205.