


Ammonia synthesis takes NO for an answer

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Electrochemical methods are emerging as potential ways to electrify the production of ammonia (NH_3). Now, researchers have discovered a copper–tin electrocatalyst that can efficiently and selectively achieve high production rates of ammonia from nitric oxide (NO) feedstocks, marking a key step forward in decarbonizing ammonia synthesis.

Ammonia, a critical component in fertilizers, has long been at the heart of modern agricultural practices, underpinning the global food supply chain¹. It is also being discussed as a potential energy carrier. Currently, ammonia production is reliant on the Haber–Bosch process, an energy-intensive method with a large carbon footprint that is a substantial contributor to global carbon dioxide emissions. With increasing global demand for crops and sustainable practices, substantial effort has been devoted to minimizing the footprint of ammonia production. Electrochemical approaches to ammonia synthesis have been touted as a cleaner alternative, because they can be driven by renewable energy sources and lessen the emission of carbon dioxide².

Many studies have focused on the electrochemical production of ammonia starting directly from nitrogen gas (N_2). This strategy,

however, struggles with low selectivity and scalability, primarily owing to the competing hydrogen evolution reaction³. In recent years, researchers have turned to an alternative two-stage pathway beginning with the oxidation of N_2 , breaking its strong $\text{N} \equiv \text{N}$ triple bond, followed by reduction of the resultant NO_x species to ammonia (Fig. 1). For such a strategy to work, breakthroughs are needed in the design of both N_2 oxidation and NO_x reduction processes. Now, new research has taken a step towards achieving the latter: writing in *Nature Energy*, Guoxiong Wang, Jianping Xiao and colleagues at the Dalian Institute of Chemical Physics, University of Chinese Academy of Sciences and Shanghai Institute of Applied Physics report the design of a copper–tin (Cu_6Sn_3) electrocatalyst that can efficiently produce ammonia from nitric oxide⁴.

Numerous electrochemical ammonia-synthesis studies have focused on the reduction of nitrite (NO_2^-) and nitrate (NO_3^-), which are pervasive groundwater contaminants⁵. Yet it remains unclear whether the recovery of NO_2^- and NO_3^- from disparate and dispersed sources is economically feasible⁶. Wang, Xiao and colleagues have targeted electrochemical NH_3 synthesis from NO as an alternative approach. NO electrochemical reduction has been studied for decades⁷, but has recently received increased attention because it can potentially achieve high selectivity and activity, requiring fewer elementary steps compared to the reduction of other NO_x molecules. There have also been recent advances in NO production from N_2 oxidation via non-thermal plasmas⁸, which provides additional motivation for using NO as a feedstock for ammonia synthesis.

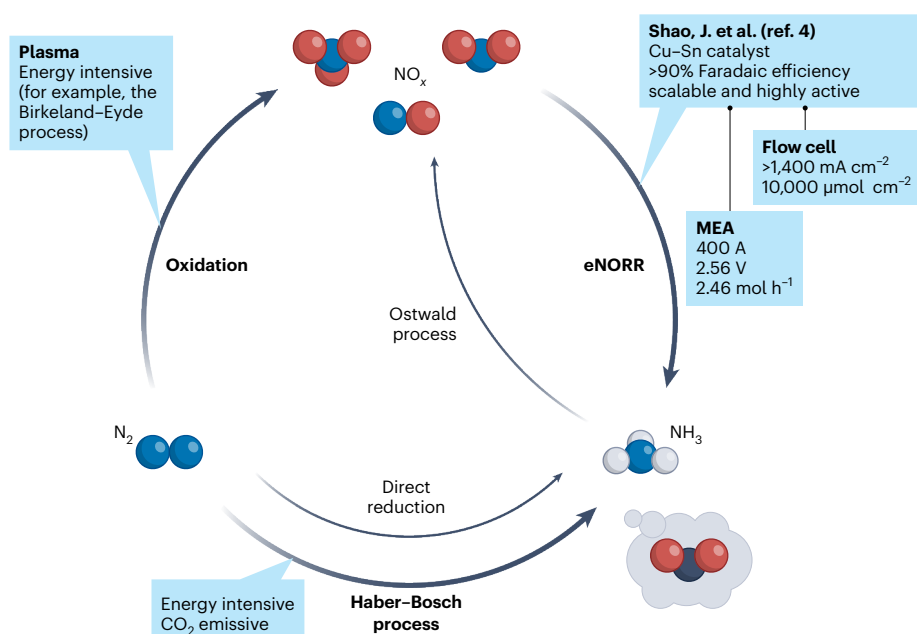


Fig. 1 | Pathways to ammonia. The traditional route to ammonia is the Haber–Bosch process. Wang, Xiao and colleagues demonstrate an alternative based on electrochemical reduction of nitric oxide (eNORR). For eNORR, key performance indicators of the newly reported Cu–Sn catalyst in a flow cell and membrane electrode assembly (MEA) are highlighted.

Wang, Xiao and colleagues⁴ pursued Cu-based catalysts for NO reduction: previous studies have shown that Cu ought to be a near-optimal catalyst for this task because it achieves the right balance of binding energies for key NH_x^* and H^* surface intermediates⁹. The team employed a computational catalyst design workflow that identified Cu-Sn alloys as promising candidates. Indeed, the synthesized Cu_6Sn_5 catalyst demonstrated an ammonia-production rate of $10 \text{ mmol cm}^{-2} \text{ h}^{-1}$ with a current density exceeding $1,400 \text{ mA cm}^{-2}$ and a Faradaic efficiency of over 95% in a flow cell. To place this in context, prior state-of-the-art catalysts achieved ammonia-production rates of about $5 \text{ mmol cm}^{-2} \text{ h}^{-1}$. Employing this catalyst in a scaled-up membrane electrode assembly reactor yielded a production rate of 2.47 mol h^{-1} at about 90% Faradaic efficiency with a current of 400 A at 2.56 V.

The researchers estimated that the cost of ammonia production, based on their flow cell performance, approaches the current market price, albeit making assumptions regarding the cost of electricity, thus demonstrating the potential economic viability of the process.

Beyond demonstrating impressive catalytic performance, Wang, Xiao and colleagues also offer fundamental insight into why their Cu_6Sn_5 catalyst works as well as it does. The researchers explored the thermodynamics of NO reduction across five metals (Ag, Cu, Pd, Rh and Sn) with density functional theory, building a reaction phase diagram that predicted activity trends and favoured reaction mechanisms amongst possible reaction pathways. The catalyst's increased activity and Faradaic efficiency for ammonia synthesis was credited to lower barriers in the reaction steps leading to NH_3 and its better resistance to oxidation when compared to pure Cu and Sn, respectively. This study shows how a close coupling of theoretical and experimental efforts has great potential for materials discovery for NO-conversion applications. Rational catalyst design can help to navigate the vast compositional space of candidate metal alloys.


Achieving an ammonia-synthesis pathway via the two-stage N_2 -to-NO-to- NH_3 process requires consideration both of N_2 oxidation to NO and of NO oxidation to NH_3 . Although this work from Wang, Xiao and colleagues⁴ represents a step forward for the latter, far less is known about the viability of the former. At present, the Ostwald process is a major industrial source of NO as an intermediate during

nitric acid (HNO_3) production, but this process relies on ammonia as a feedstock. Non-thermal plasma catalysis is an emerging and promising possibility to produce NO (refs. 8,10), but such plasma-based processes remain in their infancy and are not yet economically competitive. The researchers acknowledge this limitation in their assessment of the ultimate commercial viability of a N_2 -to-NO-to- NH_3 process, because any techno-economic analysis is subject to the inevitable uncertainties of early-stage technologies. Nevertheless, reports describing advances in the process of N_2 oxidation to NO in the recent literature⁸ are a promising sign.

As for NO reduction, further materials design and device assembly improvements will be required to achieve stable operation under the high current densities required, beyond the 135 hours reported by Wang, Xiao and colleagues⁴. Device stability and long-term durability must be a focal point of future efforts. Ultimately, forging an NO-based pathway towards ammonia synthesis will require a combination of materials discovery and device engineering, and it will critically depend on innovation in the production of NO from N_2 .

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Competing interests

The authors declare no competing interests.