

# Is lithium the key for nitrogen reduction?

Why lithium appears critical for electrochemical ammonia synthesis remain elusive

By Olivia Westhead<sup>1</sup>, Rhodri Jervis<sup>2</sup>, Ifan E L Stephens<sup>1</sup>

Department of Materials, Imperial College London, UK. Email: i.stephens@imperial.ac.uk

<sup>2</sup>Electrochemical Innovation Laboratory, Department of Chemical Engineering, University College London, London, UK.

The Haber-Bosch process converts nitrogen (N<sub>2</sub>) and hydrogen (H<sub>2</sub>) into ammonia (NH<sub>3</sub>) over iron-based catalysts. Today, 50% of global agriculture uses Haber-Bosch NH<sub>3</sub> in fertilizer. Efficient synthesis requires enormous energy to achieve extreme temperatures and pressures, and the H<sub>2</sub> is primarily derived from methane steam reforming. Hence, the Haber-Bosch process accounts for at least 1% of global greenhouse gas emissions (1). Electrochemical N<sub>2</sub> reduction to make NH<sub>3</sub>, powered by renewable electricity under ambient conditions, could provide a localized and greener alternative. On page xxx of this issue, Suryanto *et al.* (2) report highly efficient and stable electrochemical N<sub>2</sub> reduction based on a recyclable proton donor. This study builds on earlier work showing that an electrolyte containing a lithium salt in an organic solvent with a sacrificial proton donor was unique in its ability to unequivocally reduce N<sub>2</sub> (3, 4). In both studies, it is still unclear why lithium is so critical.

Neighboring fields of homogeneous and bio-catalysis provide insight. The nitrogenase enzyme selectively reduces N<sub>2</sub> to NH<sub>3</sub> with a Faradaic efficiency of 65% at ambient N<sub>2</sub> pressure (5), far higher than has been achieved with heterogeneous catalysts (see the figure). Studies of nitrogenase and homogeneous mimics have revealed the crucial role of proton donation rate to activate N<sub>2</sub>. Nitrogenase moderates access of protons to active sites through internal channels through an anhydrous and hydrophobic protein matrix; electrochemical studies showed that the isolated catalytic cofactor in aqueous solution undergoes a catastrophic loss of efficiency (6). The biomimetic compound reported in 2003 by Yandulov and Schrock (7) could reduce N<sub>2</sub> efficiently only if the proton source and reducing agent were added slowly. Chalkley *et al.* (8) later showed that moderate proton donating ability led to optimal efficiency.

Singh *et al.*'s models predict that inhibiting proton access to the electrode, so that N<sub>2</sub> adsorption is no longer blocked, enhances selectivity (9). Nonetheless complete inhibition of access to protons will prevent NH<sub>3</sub> formation; hence their model implies that moderate access to protons leads to optimum rates, albeit possibly at the cost of selectivity. Aqueous solutions provide unhindered proton access, and so aqueous electrochemical paradigms produce NH<sub>3</sub> in quantities indistinguishable from background contamination (4). However, in 1993, Tsuneto *et al.* reported efficient NH<sub>3</sub> synthesis in an organic electrolyte containing a small amount of ethanol as a proton source and a lithium salt, noting that nonlithium salts yielded negligible NH<sub>3</sub> (3). Later isotopic labeling experiments proved that only a lithium ion (Li<sup>+</sup>) electrolyte could unequivocally reduce N<sub>2</sub> (4).

Under ambient conditions, lithium metal can dissociate the stable N<sub>2</sub> bond (3); however, such strong N<sub>2</sub> binding generally results in even stronger binding to hydrogen (12). Moreover, in the homogeneous systems and nitrogenase, nitrogen hydrogenation precedes N≡N bond scission (7, 11). As such, dissociative N<sub>2</sub> binding may not be a pre-requisite to nitrogen reduction. Rather, we propose that the solid electrolyte interphase (SEI) that is formed via the lithium salt, as observed in Li<sup>+</sup> batteries, is the key. When a Li<sup>+</sup> battery is initially charged, electrolyte decomposition products form a layer on the anode surface. This layer is electronically insulating but Li<sup>+</sup> conducting, and protects the battery from further electrolyte decomposition (13). An SEI layer is also formed in Li<sup>+</sup>-mediated N<sub>2</sub> reduction (10). This layer could mimic the hydrophobic and anhydrous environment housing the catalytic cofactor in nitrogenase.

The lithium-mediated paradigm is the most efficient and reproducible system to date but still has vast scope for optimization. Factors that can improve the efficiency, activity, and stability include N<sub>2</sub> partial pressure (2, 3, 10), choice of proton donor (2, 3), potential cycling (10), electrolyte cation, (14), and use of a gas diffusion electrodes (14) (see the figure). These optimization efforts have resulted in substantial improvements since the verification of the continuous LiClO<sub>4</sub>-based system in 2019 (4). In particular, the work by Suryanto *et al.* represents a crucial step toward longer term stability. The tetraalkyl phosphonium salt stably shuttles protons from the anode as the cation to donate them to nitrogen reduced at the cathode to form an ylide. Critically, this salt is not consumed like the previously reported sacrificial alcohol donor. The salt also enhances ionic conductivity, which allows this system to achieve high NH<sub>3</sub> production rates (60 nmol s<sup>-1</sup> cm<sup>-2</sup>) in 20-hour experiments at 20 bar N<sub>2</sub>.

Despite these advances, no reported system is ideal. The ideal system would operate at negligible overpotential (that is, toward 100% potential efficiency), with high current densities (>1 A/cm<sup>2</sup>) (that is, high turnover frequencies), have a lifetime of at least 5 years and achieve 100% selectivity to NH<sub>3</sub> (see blue stars in the figure). The best turnover numbers are still only ~10<sup>5</sup> per site, well below the ideal of ~10<sup>10</sup> per site. Crucially, the dependence on metallic lithium results in a built-in requirement for high potential losses given the negative reduction potential of Li<sup>+</sup>. The organic electrolyte is also highly resistive, which results in an incredibly low energy efficiency (10,14).

The SEI layer itself could be a source of instability. During NH<sub>3</sub> synthesis, the organic electrolyte continues to undergo reduction and product accumulation on the electrode surface, which increases resistance (10). In battery systems, the SEI composition is tailored through the choice of electrolyte components to protect the system from continued electrolyte decomposition (13). Battery science could provide key insights for improving the stability and effectiveness of the N<sub>2</sub> reduction SEI, which is still uncharacterized and unoptimized. For NH<sub>3</sub> synthesis. An effective SEI may even enable the use of water as a proton donor versus more costly organic molecules.

## REFERENCES AND NOTES

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#### Toward ideal ammonia synthesis

The relative performance of various systems with respect to the “ideal” electrode (blue stars, see text). Filled symbols are for 1 bar N<sub>2</sub> while open symbols are for higher pressures. Circles use a sacrificial proton donor (ethanol) and triangles use a recyclable proton donor ([P<sub>6,6,6,14</sub>][FAP]). Potentials were corrected for Ohmic losses and often become more negative during operation. Nitrogenase data was collated from various sources. See reference 15 for calculation details.

