

Is lithium the secret ingredient for nitrogen electroreduction?

Lithium appears to have a unique ability to mediate nitrogen reduction, but the reason why remains elusive.

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At the turn of the 20th century, Fritz Haber and Carl Bosch developed their catalytic process to synthesise ammonia on an industrial scale, known today as the Haber-Bosch process. This resulted in a revolutionary societal shift, meaning that today 50% of agriculture worldwide uses Haber-Bosch ammonia in its fertiliser. It would seem that the problem of ammonia synthesis was solved. However, today we face the grand challenge of climate change mitigation, requiring another revolutionary shift towards clean energy. Again, ammonia could play a critical role as a hydrogen fuel transportation vector, or even as a carbon free fuel. However, the Haber-Bosch process, while well optimised, is an environmentalist's nightmare; efficient synthesis requires extreme temperatures and pressures, resulting in an enormous power demand. Furthermore, the hydrogen required to form ammonia is primarily derived from methane steam reforming. These issues mean that the Haber-Bosch process alone accounts for at least 1% of global greenhouse gas emissions¹. Electrochemical nitrogen reduction to make ammonia, powered by renewable electricity operating at point of use under mild conditions, could provide the answer. In their work published in this issue, Suryanto, Simonov, MacFarlane and co-workers² report the most efficient and stable electrochemical nitrogen reduction system to date based on a novel recyclable proton donor, as shown in figure 1. This builds on earlier work which established the unique ability of an electrolyte made up of a lithium salt in an organic solvent with a sacrificial proton donor to allow for unequivocal nitrogen reduction^{3,4}. However, it is still a mystery as to exactly why lithium is such a critical component of this system.

The most convenient source of protons for nitrogen reduction would be water, building on the wealth of expertise in traditional aqueous electrochemistry. However, all aqueous paradigms yield negligible ammonia quantities, indistinguishable from background contamination⁴. Virtually all surfaces favour bind to hydrogen more favourably than to nitrogen. Therefore, adsorbed hydrogen will poison nitrogen reduction⁵ and favour the competing reaction, hydrogen evolution. However, lithium could provide hope. In 1993, Tsuneto et al. found that using an organic electrolyte containing a small amount of ethanol as a proton source and a lithium salt resulted in efficient ammonia synthesis, noting that using a non-lithium salt yields negligible ammonia³. Later isotopic labelling experiments proved that Tsuneto et al's lithium based electrolyte was the only system capable of unequivocal nitrogen reduction⁴. Lithium, it seems, is a critical component of a successful nitrogen reduction system.

Nature provides crucial insight. The nitrogenase enzyme has the remarkable ability to selectively reduce nitrogen to ammonia; in the absence of nitrogen, the enzyme will simply evolve hydrogen. When nitrogen is introduced, hydrogen evolution is suppressed, resulting in a Faradaic efficiency of 65% towards ammonia production under 1 bar N₂⁶; far higher than has been achieved heterogeneously, as shown in figure 1. Nitrogenase contains a metal cluster, called the catalytic co-factor, which is the active site for nitrogen fixation and reduction⁷. While the nature of the catalytic co-factor is an important puzzle piece, another critical component is its environment. The co-factor resides in a hydrophobic and anhydrous protein matrix, with proton delivery being strictly regulated along a dedicated channel⁷. Indeed, electrochemical studies in which an isolated catalytic co-factor had unconstrained access to protons in solution resulted in a catastrophic loss of efficiency⁸. It seems,

therefore, that moderating the access of protons to the catalytically active site is critical. The story is similar when examining homogeneous paradigms. In their seminal 2003 work, Yandulov and Schrock reported on the first molecular compound capable of reducing ammonia⁹. Part of the reason for their success was the *slow* addition of the proton source and reducing agent. Indeed, further investigations by Peters and co-workers into the effect of proton donor pK_a value on the efficiency of their molecular complexes shows that a moderate pK_a , and thus moderate proton donating ability, results in optimum efficiency¹⁰. This insight from nature and the neighbouring field of homogeneous catalysis could aid nitrogen fixation over a heterogeneous electrocatalyst. Indeed, Singh et al's models suggest that restricting the access of protons to the electrode surface should also result in more *selective* ammonia synthesis, by facilitating nitrogen adsorption over hydrogen⁵. Even so, we hypothesise that if access to protons is over constrained, then the reaction rate will be limited by nitrogen hydrogenation; the optimum rate is likely when the environment around the catalytically active site provides *moderate* access to protons, as shown schematically in figure 2.

One feature of lithium often touted as the reason for its success is its ability under ambient conditions to spontaneously dissociate the strong dinitrogen triple bond upon adsorption,¹¹. However, dissociative adsorption of nitrogen does not seem to be a prerequisite for nitrogen reduction: on nitrogenase⁷ and the homogeneous catalysts^{9,10}, the scission of the nitrogen-nitrogen bond occurs only once the nitrogen is hydrogenated. Rather, we propose that lithium's uniqueness could lie in its exceptional ability to form a Solid Electrolyte Interphase (SEI), a phenomenon well known to the lithium-ion battery community. When a lithium-ion battery is first charged, a layer is formed on the anode surface from electrolyte decomposition products. This layer is electronically insulating but lithium-ion conducting, protecting the battery from further electrolyte decomposition and ensuring its stability¹². Such an SEI layer is also formed in the lithium-mediated nitrogen reduction system¹³. This layer could mimic the hydrophobic and anhydrous environment housing the catalytic cofactor in nitrogenase, moderately constraining the access of protons to the electrode (see figure 2) and enabling maximal nitrogen reduction activity.

The lithium-mediated paradigm, while the most efficient and reproducible system to date, has vast scope for optimisation. As shown in figure 1, the factors that can improve the efficiency, activity and stability include nitrogen partial pressure^{2,3,14}, choice of proton donor^{2,3}, potential cycling¹⁴, electrolyte cation¹¹ and use of a gas diffusion electrode¹⁵. The optimisation efforts carried out so far have resulted in great leaps forward; figure 1 shows that the metrics have improved enormously since the verification of the continuous LiClO_4 based system in just 2019⁴. In particular, the work by Suryanto et al represents a critical step forward for longer term stability² (figure 1 a). However, as yet, no system is able to operate under 'ideal' conditions, requiring negligible extraneous potential and with high current densities (or turnover frequencies), a 5 year lifetime and 100% selectivity to ammonia (see blue stars in figure 1). Crucially, the dependence on metallic lithium results in a built-in requirement for high potential losses due to lithium's very negative reduction potential. In addition, the organic electrolyte is highly resistive, which results in an incredibly low energy efficiency^{14,15}. Several authors hypothesise that the SEI layer itself is a source of instability.¹⁴ In its current uncharacterised and unoptimised state, organic electrolyte reduction components continue to accumulate on the electrode surface during ammonia synthesis, increasing electrode resistance¹⁴. In battery systems, the SEI composition is tailored by choice of electrolyte components, protecting the system from continued electrolyte decomposition¹². An effective SEI may even eventually enable the use of water as a proton donor. Battery science could provide key insight to improve the stability and effectiveness of the nitrogen reduction SEI. Over one hundred years on since the inception of Haber-Bosch process, nitrogen fixation continues to fascinate the scientific community.

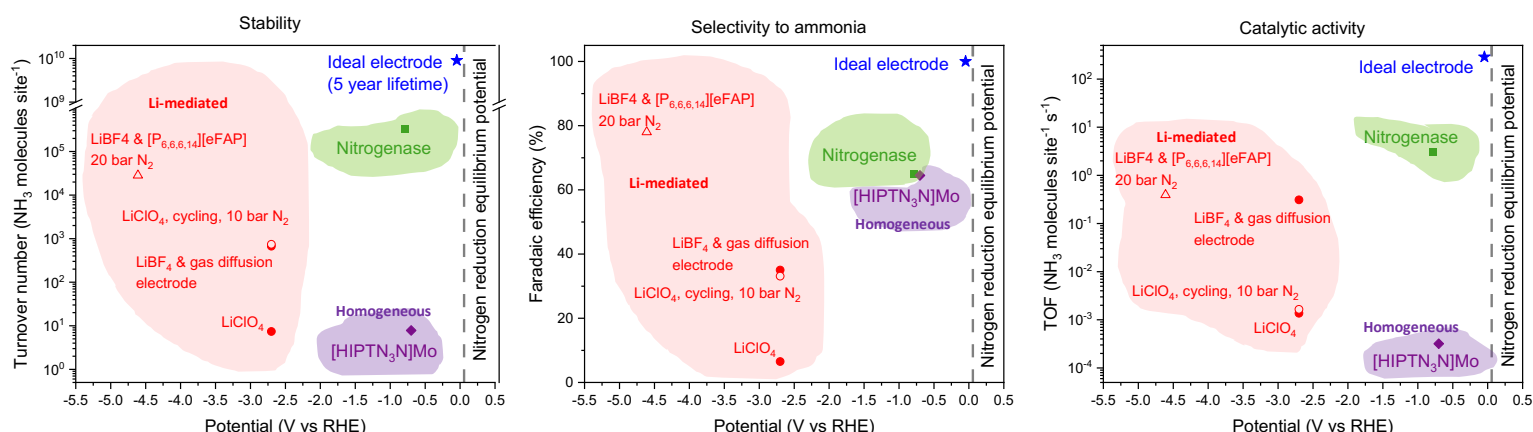


Figure 1 Plots to show the relative performance of various systems with respect to the ideal electrode. The potential is defined on the Reversible Hydrogen Electrode (RHE) scale, corrected for Ohmic losses. The ideal electrode would operate very close to the thermodynamic equilibrium potential for nitrogen reduction with 100% Faradaic efficiency and a current density towards ammonia production of 1 A cm^{-2} with a roughness factor of 33. Points in red represent the lithium mediated heterogeneous electrocatalytic system with tetrahydrofuran as a solvent, the point in purple represents the Schrock homogeneous catalyst⁹ and the point in green is nitrogenase^{6,7,16,17}. Filled points represent work done at 1 bar N_2 . Hollow points represent experimental work done at a higher N_2 pressure. Triangle points represent experimental work done with $[\text{P}_{6,6,6,14}][\text{eFAP}]$ as a proton source (Suryanto et al²), circle points represent work done with ethanol as a proton source. Work done using LiClO_4 was carried out by Chorkendorff and coworkers^{4,14}. Work done using LiBF_4 and a gas diffusion electrode was carried out by Manthiram and coworkers¹⁵. Note that, in many cases, the operating potential shown for the lithium mediated system is a minimum since the potential often becomes more negative over the course of an experiment.

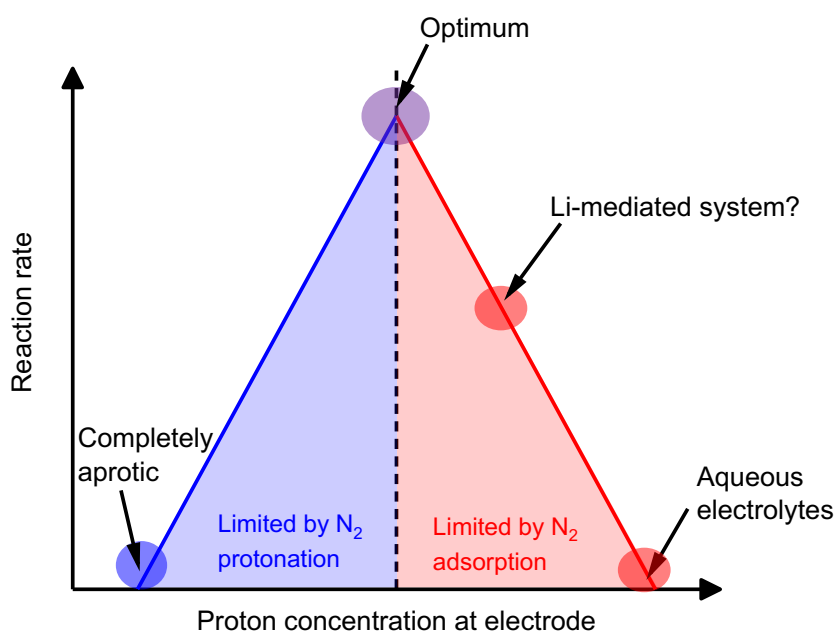


Figure 2 A schematic to show the hypothesised dependence of activity on the concentration of protons at the electrode surface. In the lithium mediated system, this may be controlled by the mobility of protons through the SEI.

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