

Ambient lithium-mediated ammonia synthesis

Nikifar Lazouski,¹ and Karthish Manthiram^{1*}

¹Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

*Correspondence: karthish@mit.edu

Abstract

Electrochemical nitrogen reduction enables ammonia synthesis under ambient conditions. Here, the mechanism of lithium-mediated nitrogen reduction is described, which offers critical insights for future increases in rates and efficiencies.

Origin

Ammonia is traditionally synthesized thermochemically via the Haber-Bosch process,¹ where nitrogen gas and fossil fuel-derived hydrogen react at high temperatures and pressures over iron catalysts.² Electrochemical routes for producing ammonia allow for replacing costly temperature/pressure with voltage in an electrochemical reactor.³ Lithium-mediated electrochemical approaches have been shown to produce ammonia both continuously⁴ and in a batch-wise fashion.^{5,6}

Reaction Mechanism

In lithium-mediated nitrogen reduction, current passed at the cathode goes towards plating of lithium metal, which facilitates further reduction reactions.⁵ In the absence of a proton source, here ethanol, the lithium metal is unreactive.⁷ Ethanol is used as a model proton source, which is useful from the standpoint that ethanol is a renewable feedstock, although eventual work will need to transition towards more cost-effective hydrogen sources such as water. Only once a critical ethanol concentration is reached does the lithium react with nitrogen and ethanol (Steps I, II).⁷ Beyond this critical concentration, ethanol competes with nitrogen for available lithium (Step II), such that ammonia yields decrease rapidly with increasing ethanol concentration due to generation of hydrogen and lithium ethoxide. Reduction of nitrogen (Step I) and ethanol (Step II) exhibit different orders with respect to lithium: nitrogen is third order in lithium concentration, while ethanol is second order; the orders correspond to the number of lithium atoms required to produce a molecule of ammonia and hydrogen, respectively. The reaction between lithium and nitrogen to form lithium nitride (Step II) is followed by rapid protonation of the nitride by ethanol, forming ammonia (Step III). As more rapid plating increases the amount of available lithium, increased selectivity towards ammonia is achieved by applying a higher current density. However, the achievable partial current densities toward ammonia are limited by nitrogen diffusion. The optimal Faradaic efficiency towards ammonia is realized at one third of the transport-limited current density, which is achieved at high applied current densities.

Importance

While the individual bulk reactions between lithium, nitrogen, and ethanol are well known and used for batch-wise lithium-mediated synthesis,^{5,6,8} the mechanisms of these reactions are not well studied in continuous processes that operate at ambient conditions. This mechanism indicates that

it is possible to promote ammonia formation over hydrogen formation and highlights potential future issues that must be overcome, such as transport limitations.

References

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Figure 1



Full Figure

