Ambient lithium-mediated ammonia synthesis

Nikifar Lazouski[1] and Karthish Manthiram[1,*]

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

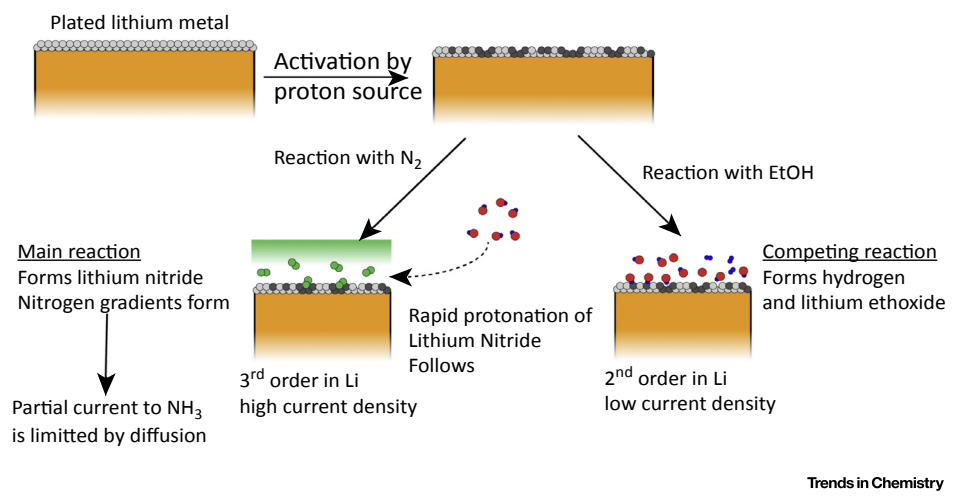
$$N_2 + 3EtOH + 3e^- \xrightarrow[\text{ambient conditions}]{Li^+,\ THF} NH_3 + 3EtO^-$$

ORIGIN

Ammonia is traditionally synthesized thermochemically via the Haber-Bosch process, where nitrogen gas and fossil-fuel derived hydrogen react at high temperatures and pressures over iron catalysts.[2] Lithium-mediated routes allow for replacing costly temperature/pressure with voltage in an electrochemical reactor. Lithium-mediated routes allow for replacing costly temperature/pressure with voltage in an electrochemical reactor. Lithium-mediated routes allow for replacing costly temperature/pressure with voltage in an electrochemical reactor.

REACTION MECHANISM

In lithium-mediated nitrogen reduction, current passed at the cathode is used directly to plate lithium metal, which is then responsible for further reduction reactions. In the absence of a proton source, in this case ethanol, lithium metal is unreactive and does not react with nitrogen to form lithium nitride. Only once a critical concentration of ethanol is reached does the lithium react with nitrogen and ethanol rapidly. Beyond this critical concentration, ethanol competes with nitrogen for the available lithium, such that ammonia yields decrease rapidly with increasing ethanol concentration due to generation of hydrogen and lithium ethoxide. The reactions to reduce nitrogen and ethanol have different orders with respect to lithium: nitrogen is third order in lithium, while ethanol is second order. This suggests that more lithium is needed to reduce nitrogen than ethanol. It also allows to increase the specificity towards ammonia by applying a higher current density. The achievable partial current densities toward ammonia, however, are limited by nitrogen diffusion limitations. The optimal Faradaic efficiency towards ammonia is achieved at one third of the transport limited current density, which is in turn achieved at high applied current densities. The optimal Faradaic efficiency towards ammonia is achieved at one third of the transport limited current density, which is in turn achieved at high applied current densities.



IMPORTANCE

While the individual bulk reactions between lithium, nitrogen, and ethanol may be well known and used for batchwise lithium-mediated synthesis, the mechanistic details and competition between these reactions is not well understood in continuous processes that operate at ambient conditions. This mechanism shows that it is possible to promote ammonia formation over hydrogen formation, as well as points out potential issues that will need to be overcome in future work.

*Correspondence: karthish@mit.edu (K. Manthiram).

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Literature

1. Chen, J.G. *et al.* (2018) Beyond Fossil Fuel–driven Nitrogen Transformations.. *Science* 80, eaar6611
2. Ertl, G. (2008) Reactions at Surfaces: From Atoms to Complexity (Nobel Lecture). *Angew. Chemie Int. Ed.* 47, 3524–3535
3. McEnaney, J.M. *et al.* (2017) Ammonia Synthesis from N_2 and H_2O Using a Lithium Cycling Electrification Strategy at Atmospheric Pressure. *Energy Environ. Sci.* 10, 1621–1630
4. Lazouski, N., Schiffer, Z.J., Williams, K., Manthiram, K. A Mechanistic Study of Continuous Lithium-Mediated Electrochemical Nitrogen Reduction. *Submitted; Draft available upon Request*.
5. McFarlane, E.F. and Tompkins, F.C. (1962) Nitridation of Lithium. *Trans. Faraday Soc.* 58, 997
6. Kim, K. *et al.* (2018) Electrochemical Synthesis of Ammonia from Water and Nitrogen: A Lithium-Mediated Approach Using Lithium-Ion Conducting Glass Ceramics. *ChemSusChem* 11, 120–124

  https://doi.org/10.1016/j.trechm.2018.08.001