

Lithium-mediated pathways towards ammonia electroproduction

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Significance and Relevance

The proposed work focuses on the electrochemical synthesis of ammonia through lithium-mediated processes inspired by battery technologies. This approach addresses the pressing need for sustainable ammonia production, reducing reliance on energy-intensive Haber-Bosch processes. By integrating advancements in battery science, the study aims to enhance efficiency and scalability, contributing to global efforts in green chemistry and energy transition. The relevance lies in its potential to revolutionize industrial ammonia synthesis, making it more environmentally and economically viable.

Preferred and 2^{nd} choice for the topic: H_2 storage and transportation, green H_2 production, hydrogen vectors / Sustainable and clean energy production and transport

Preferred presentation: Oral only

Introduction and Motivations

Ammonia, produced via the Haber-Bosch process for more than 150 10^6 t per year, is responsible of around 1.5% of the global greenhouse gas emissions [1]. It is a fundamental building-block for fertilizers and could represent a future H₂ carrier, but it is still dependent from fossil fuels. To find a delocalized electrochemical process complementary to Haber-Bosch could be a key solution to move towards a renewable-driven NH₃ production.

Nowadays, the lithium-mediated pathway represents the most promising solution in the N_2 reduction reaction challenging field, achieving the highest Faradaic efficiency and NH_3 production rate [2,3]. Different strategies are under evaluation in literature, all exploiting the ability of this metal to bind N_2 even in standard conditions. They could be divided into continuous or step-by-step strategies. In the first, Li⁺ ions from the aprotic electrolyte are electrodeposited on the cathode, where N_2 is reduced and protonated into NH_3 , directly and in the same environment [4]. In the second case, the electroreduction of N_2 at the cathode has been proposed, and the formation of an intermediate product containing fixated nitrogen is the key step. Only in a second separate step, this intermediate should be protonated into NH_3 . To achieve the first step of N_2 activation, the exploitation of a Li- N_2 galvanic cell, inspired by lithium-air batteries, has been proposed in literature to optimize the process efficiency and allow the direct protonation with H_2O [5,6].

Materials and Methods

In both cases, is crucial to study the phenomena at the cathodic electrode-electrolyte interphase, as the aprotic electrolyte inevitably reacts on the active sites, forming a solid electrolyte interphase. This component of the system determines both the selectivity towards NH₃ formation and the stability of the process. Due to the dynamicity of this layer, a critical eye should be adopted for a correct electrochemical characterization and NH₃ quantification of the systems. Our laboratory is currently addressing these challenges within the SuN₂rise project, applying also statistical methods as the design of experiment to optimize the studied factor with a restricted number of experiments.

Results and Discussion

To fasten the comprehension and optimization of the complex lithium-mediated nitrogen reduction system, for the first time a multivariate approach is proposed as a powerful tool to reduce the number of experiments in comparison with the classical one-factor-at-a-time approach. Doehlert design and surface response methodology are employed to optimize the electrolyte composition for a batch



autoclaved cell. The method is validated with the common LiBF₄ salt, and the correlations between the FE and the amount of lithium salt and ethanol as proton donor are elucidated, also discussing their impact on the solid electrolyte interphase (SEI) layer. Moreover, a new fluorinated salt is proposed (*i.e.*, lithium difluoro(oxalate) borate (LiFOB)), taking inspiration from lithium batteries. This salt is chosen to tailor the SEI layer, with the aim of obtaining a bifunctional interfacial layer, both stable and permeable to N₂, the latter being an essential characteristic for batch systems. The SEI layer composition is confirmed strategic and its tailoring with LiFOB boosts FE values even at considerably high water content (*i.e.*, 600 ppm).

References

- [1] G. Soloveichik, Nat. Catal, 2, 377–380, 2019.
- [2] X. Fu et al., Science, **379**, 707–712, 2023.
- [3] N. Lazouski et al., ACS Catal., 12, 9, 5197–5208, 2022.
- [4] S. Li et al., Nature, 629, 8010, 2024.
- [5] A. Mangini et al., Adv. Energy Mater., 14, 2400076, 2024.
- [6] Z. Zhang et al., Angew. Chem. Int. Ed., 58, 17782–17787, 2019.

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