Abstract

Ammonia, produced *via* the Haber-Bosch process for more than $150 \cdot 10^6$ tons per year, is responsible of around 1.4% of the global greenhouse gas emissions. It is a fundamental building-block for fertilizers and could represent a future H_2 carrier, but it is still dependent from fossil fuels. Finding a delocalized electrochemical process complementary to the Haber-Bosch one could be a key solution to move towards a renewable-driven NH_3 production.

Nowadays, the lithium-mediated pathway represents the most promising solution in the N_2 reduction reaction challenging field, achieving the highest Faradaic efficiency (FE) and NH_3 production rate. Different strategies exploiting the ability of this metal to bind N_2 even in standard conditions are under evaluation. They could be divided into continuous or stepwise strategies.

In the first strategy, 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. On the plated lithium, a solid electrolyte interphase (SEI) layer unavoidably forms due to electrolyte degradation on the interface, determining both the selectivity towards NH_3 formation and the stability of the process.

In the second case, the electroreduction of N_2 at the cathode has been proposed to form Li_3N as a key intermediate, then protonated into ammonia in a second step. The exploitation of a Li-N_2 galvanic cell, inspired by lithium-air batteries, could maximize Li_3N formation.

In both cases, a critical eye on interferents and impurities should be adopted to ensure a correct NH_3 quantification. Moreover, the quantification methodology should be adapted to the specific lithium-mediated strategy studied, as the high concentration of the electrolytes used, together with the aprotic solvent matrices adopted, could interfere with a correct and reproducible measurement.

This dissertation first discusses preliminary tests to select a reproducible quantification methodology, and the lithium reactivity with N_2 is investigated. Subsequently, two different strategies for N_2 electroreduction are studied.

The first strategy is a stepwise process in which the formation of the intermediate, *i.e.*, Li_3N, is assessed in a separate step through a Li-N_2 Galvanic cell.

In this case, the characterization of the cell through different electrochemical techniques is critically evaluated. Moreover, a few innovative materials, as an abundant and cheap catalyst, *i.e.*, MoS_2, are tested to increase both the stability and the activity of the cell. Lithium, used as anodic material, was also observed as an element leading to false-positive results.

The second strategy tested is a discontinuous lithium-mediated process. In this case, a multivariate approach, combining the Doehlert design of experiments with response surface methodology, allowed to optimize the electrolyte composition, with the aim of tailoring the SEI layer composition and improve the FE of the process. The two most significant factors for this strategy, *i.e.*, lithium salt and ethanol concentrations, are investigated. Lithium tetrafluoroborate ($LiBF_4$), a commonly-used salt, was used to validate the methodology, then applied to a newly proposed salt, *i.e.*, lithium difluoro oxalate borate (LiFOB). With this statistical analysis, the optimal electrolyte composition was identified with only 7 experimental points and 3 replicates of the central one.

The collected results highlight the importance of a correct balance of the different components of the system, confirming the key role of the SEI layer. A correct tailoring of this element opens to an improved stability and efficiency of NH_3 electrosynthesis devices.