Electrochemical Reduction of Nitrogenous Compounds to Ammonia and Organonitrogen Fertilizers

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The constant growth of food production demand is inevitably recalling an increase in requests for fertilisers, which are mainly produced starting from ammonia (NH_3). The Haber-Bosch (HB) process is the leading technology for NH_3 production, sustaining 90% of the global NH_3 synthesis. The increasing attention on the environmental impact of all industrial processes reached also this field, for which carbon dioxide (CO_2) emissions account for 1.6% on a global basis. Indeed, high temperatures and pressures are essential to break the N_2 triple bond and catalyse the reaction to NH_3. To reduce the HB process carbon footprint, several alternatives have been evaluated in recent years. Among them, the most appealing and challenging ones are the "green" approaches, which include the electrochemical N_2 reduction reaction (E-NRR) - both in aqueous and in the lithium-mediated pathways – and the electrochemical nitrate (NO_3^-) reduction reaction (E-NO_3RR) starting from polluted wastewaters, groundwaters, or nuclear wastes. All these technologies exploit the presence of a catalyst and the application of an external potential supply to carry out the reaction. To reduce the process environmental impact in terms of greenhouse gas emissions, power supply can be guaranteed by renewable energies.

In this PhD Thesis, E-NRR in aqueous media and E-NO_3RR in low-NO_3^- concentration ranges are explored as alternative ways for the production of NH_3. Regarding the E-NRR, a bismuth catalyst with excellent performance according to the literature is synthesised and tested in a three-phase-interface system, where liquid electrolytes and gas stream are continuously recirculated. The pitfalls in the E-NRR are thoroughly investigated and the biggest sources of contamination and experimental errors leading to false positives are carefully scrutinised. Among them, detection methods and membrane influence are discussed. Specifically, the interaction between different types of membranes and NH_3 leads to the conclusion that, in the case of E-NRR, anionic exchange membranes are the safest option, with a lower risk of false positives caused by contaminations.

E-NO_3RR is studied for a commercial MoS_2 commercial catalyst in a flow cell reactor. The specific setup used is optimised to evaluate the effect of the operational parameters on the NH_3 Faradaic efficiency (FE) and productivity (P). The considered variables are supporting salt concentration, catalyst loading, applied potential, liquid flow rate, binder and gas diffusion layer (GDL) types, and cation species in the supporting electrolyte. The effect of the first 3-factors is studied using the Doehlert design of experiments and response surface methodology (DoE-RSM) in a precisely selected investigation domain. Varying those factors, both FE and P were maximised to 60% and 200 μg h^{-1} cm^{-2}, respectively, in 500 mg L^{-1} NO_3^- initial concentration. The system durability was assessed for 150 and 100 h in the optimal conditions obtained and electrode integrity was demonstrated through chemical characterisations. Further optimisation was obtaining changing the GDL support to a more wettable one.

Finally, the last part of the Thesis introduces the possibility of directly producing urea or other organonitrogen compounds through the electrochemical CO_2 and NO_x coupling. In this experimental campaign, Cu, Sn, and Cu/Sn catalysts synthesised through the electrodeposition method are tested in different electrolyte conditions to evaluate the production of organonitrogen products, especially formamide, and the detection method based on proton nuclear magnetic resonance (^{1}H-NMR) was refined to increase reliability in the quantification.