Abstract

Electrochemical processes are gaining recognition as a transformative alternative to conventional chemical manufacturing, which remains one of the most carbon-intensive industrial sectors due to its reliance on fossil fuels as both feedstocks and energy sources. By contrast, electrochemical pathways can directly leverage renewable electricity (*e.g.*, wind, solar) and abundant, low-carbon feedstocks (*e.g.*, water, CO_2), offering a viable route toward sustainable chemical production.

Significant progress has already been made in fundamental electrochemical transformations such as water splitting for green hydrogen production and CO_2 reduction (CO_2RR), with several systems advancing toward industrial implementation. Building on these advances, current efforts focus on complex electrosynthetic reactions that enable the carbon-heteroatom bonds formation. In this context, the catalytic electrosynthesis of C-N bonds has emerged as a particularly promising direction, with urea representing a key target molecule due to its high global demand and potential for carbon-neutral production. Currently, urea is the most widely used synthetic nitrogen fertilizer, and its conventional synthesis occurs *via* the Haber-Bosh and Bosh-Meiser processes, energy-intensive and fossil fuel-based reactions, accounting for more than 2% of global energy consumption. Therefore, the Electrochemical Urea Synthesis (EUS), through the co-reduction of waste-derived carbon sources and nitrogen species, could provide a novel and sustainable alternative.

Progress in EUS research is hindered by the lack of rigorous and reproducible experimental protocols. Most of the findings supporting the feasibility of EUS, using the most common co-reduction approach (typically, the combination of CO_2RR and nitrate reduction reaction, NO_3RR) have been achieved in limited and non-scalable systems (*i.e.*, the use of H-cell, in which CO_2RR is intrinsically limited) and not in an industrially relevant configuration and environment. Furthermore, since the reported results are derived from analytical methodologies susceptible to inaccuracies, not only is there a lack of protocols for the precise quantification of urea, and consequently for the assessment of the faradaic efficiency of the systems, but also of reliable benchmarks (*e.g.*, the EUS activity/selectivity of basic catalytic systems like zero-valent metals).

This PhD thesis has two main objectives: to develop and validate a reliable analytical protocol for the accurate detection and quantification of EUS systems, and to identify and evaluate the operational conditions under which urea could be feasibly synthesized electrochemically.

To achieve the first objective, an in-depth analysis of the methods currently employed for urea detection and quantification in EUS was carried out. These techniques were found to suffer from major limitations, including inaccuracy and poor reproducibility, susceptibility to interferers and high limit of detection or long acquisition times. To overcome these drawbacks, a robust, interference-free, and time-efficient chromatographic method was developed as an *ad hoc* analytical procedure, specifically designed to minimize false positives and negatives.

Building on this analytical foundation, the second objective focused on investigating the feasibility of EUS itself. The newly established quantification protocol was coupled with electrochemical testing to reassess the EUS activity, *via* CO_2 + NO_3^- co-reduction, of polycrystalline Cu, the first EUS-active catalyst reported by Shibata et al. back in 1995, under near-neutral pH conditions (*i.e.*, $KHCO_3$ + KNO_3 aqueous electrolyte) in both static H-cell and three-compartment flow-cell setups. The results revealed that GDE-based setup enhanced EUS efficiency.

To further explore the reaction landscape, Cu, Ag, and Au gas diffusion electrodes (GDEs) were also tested in flow-cells under alkaline conditions (*i.e.*, KOH + KNO_3 aqueous electrolyte), where the hydrogen evolution reaction (HER) is suppressed, thereby promoting CO_2RR and NO_3RR and their potential coupling. However, even under these optimized conditions, no traces of urea were detected, demonstrating the infeasibility of EUS *via* CO_2 and NO_3^- co-reduction under the experimental conditions applied in this study.

Based on these results, the final stage of the project explored an alternative, anodic (oxidative) pathway for urea synthesis. In this approach, C-N coupling is envisioned to occur through the oxidation of ammonia into reactive nitrogen intermediates under controlled anodic potentials, while CO serves as the carbon source for subsequent coupling.