Efficient nitrate-to-ammonia conversion for circular nitrogen economy

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Abstract

The development of an economically feasible system for the electrochemical treatment of nitrate-rich wastewater is hampered by the complexity of the matrices. The use of membrane-free systems can be beneficial to avoid contamination by organic impurities and dissolved salts, but their implementation is challenging considering that ammonia is susceptible to anodic oxidation. This article previews a new approach that maximizes ammonia recovery by integrating a nitrate electrochemical reduction cell with a UV-assisted stripping unit that converts over 70% of nitrate into ammonia chloride.

Although several studies suggest the electrocatalytic nitrate (NO_3^-) reduction reaction (ENRR) to ammonia (NH_3) as an alternative to Haber-Bosch,[1] a significant portion of the production of NO_3^- relies on the NH_3 oxidation process (Ostwald method).[2] For this reason, Zhang and co-workers invite us to assess this research field through the lens of a circular economy.[3] There are several industrial processes that generate residues rich in nitrate, such as chemical synthesis, military enterprise and fertilizer production.[4] The excess of NO_3^- in industrial wastewater increases the expenses of waste disposal and offers risk in terms of groundwater contamination.[5] In this context, the ENRR would enable not only the recovery of NH_3 but also the mitigation of the costs of wastewater treatment, and the decrease of the carbon footprint of NH_3 Haber-Bosch synthesis.[6]

In a recent article published in Nature Sustainability,[3] Zhang *et al.* study the ENRR under some key aspects that are crucial to make it a viable technology for nitrate-rich wastewater treatment. From the catalyst point of view, they fabricated a porous Cu-Ni alloy that offers high efficiency, stability over several hours and high surface area. Regarding the

electrolytic system, the authors developed a proton-exchange membrane (PEM) free electrochemical NO_3^- conversion synchronized with NH_3 recovery (ECSN) system, which integrates a flow-through cell with a photo-irradiation in situ stripping, minimizing the oxidation of NH_3 to N_2 from anodic reactions. Looking at more fundamental aspects of the reaction, the authors conducted in situ Fourier transform infrared spectroscopy (FTIR) and online differential electrochemical mass spectrometry (DEMS) experiments to get information about the reaction mechanism. From the economic point of view, Zhang *et al.*[3] present a preliminary technoeconomic analysis (TEA) and life-cycle analysis (LCA) to assess the viability of their ECSN system for wastewater management. We will describe in this preview some of their findings that allow us to be one significant step closer to the application of electrochemical systems for nitrate-rich wastewater treatment.

Zhang *et al.*[3] fabricated a 3D-printed electrode with a porous microstructure of Cu-Ni (MPCN) that makes it feasible to be employed in flow-through reactors (Figure 1a). They demonstrated that the MPCN performance for ENRR to NH_3 overcomes printed Cu or Ni electrodes, in terms of both activity and stability, confirmed by post-mortem Raman spectra of the electrodes (Figure 1b). Additionally, the MPCN electrode held an industrial current density (200 mA cm^{-2}) for over 1,000 hours under batch operation mode.

The authors also investigated the ENRR mechanism through in situ FTIR and online DEMS experiments to get a better understanding of the improved performance of the MPCN electrode to produce NH_3. In situ FTIR spectra (Figure 1c) revealed that adsorbed $*NO_3$ (positive peaks at 1350 and 1392 cm^{-1}) deoxygenates to $*NO_2$ (1633 cm^{-1}) and *NO (negative peak at 1234 cm^{-1}). At more negative potentials, they assign the formation of N−H bonds to the rise of a negative peak at 1110 cm^{-1}. Online DEMS results (Figure 1d) detected the potential-dependent formation of both NO and NH_3 by the variation of mass-charge ratio (m/z) 30 and 17 respectively. Combining these results, the authors proposed the following ENRR pathway for the MPCN electrode: $NO_3^- \rightarrow *NO_3 \rightarrow *NO_2 \rightarrow *NO \rightarrow *NOH \rightarrow *NHOH \rightarrow *NH_2OH \rightarrow *NH_2 \rightarrow *NH_3$.

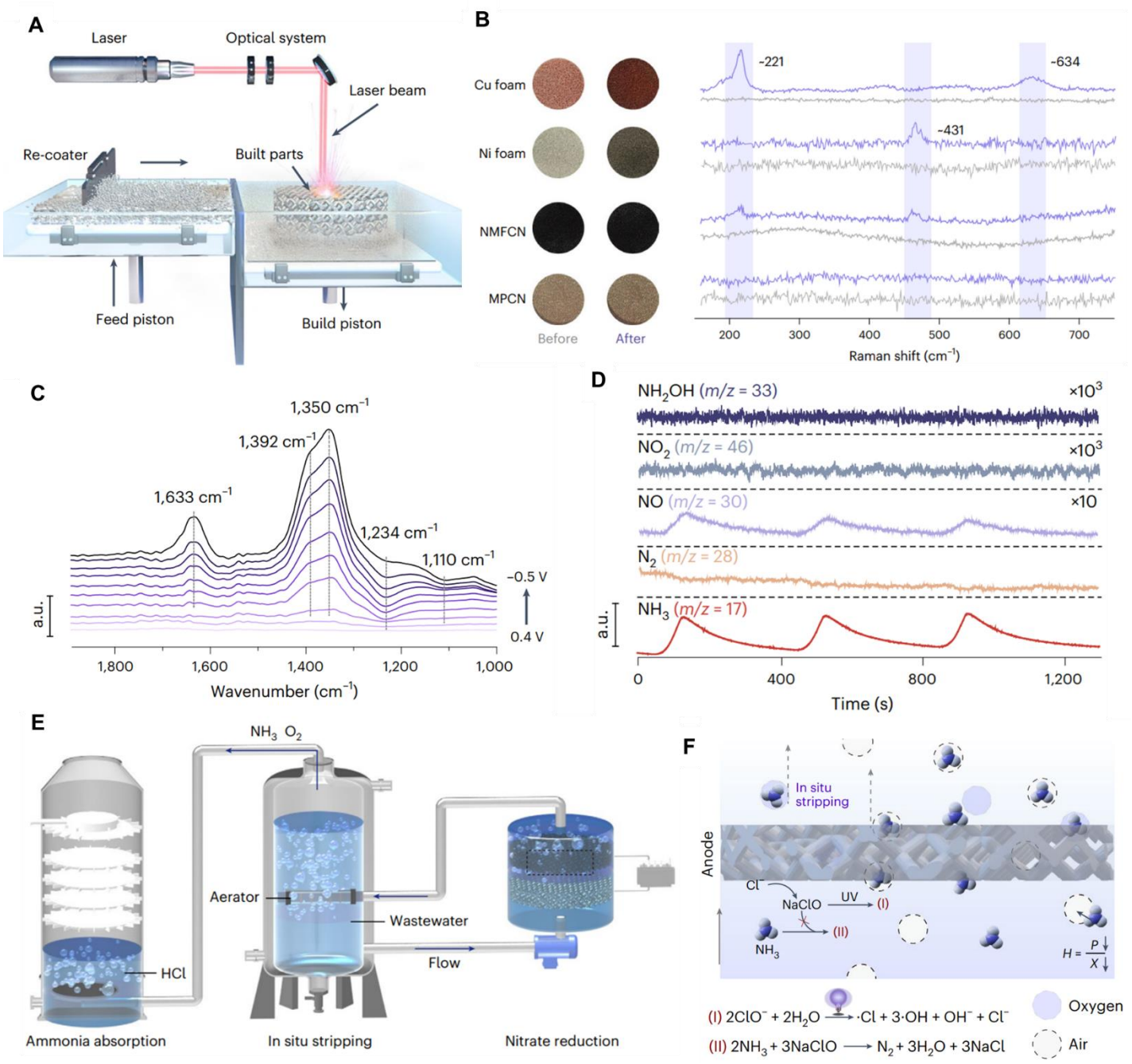

Figure 1. Preparation of Cu-Ni catalyst, stability and, mechanistic results and application. (a) Scheme for the experimental setup of the 3D-printed MPCN electrode. (b) Optical images of Cu, Ni, nanostructured MG-free Cu-Ni (NMFCN) and MPCN electrodes with the corresponding Raman spectra before and after nitrate reduction using real wastewater. (c) Electrochemical in situ FTIR spectra and (d) online DEMS measurements using the MPCN electrode. (e) ECSN recovery system and (f) scheme representing the side reactions in the anodic side. Reproduced from [3].

To maximize the recovery of NH_3 using a PEM-free electrochemical cell, the authors developed the ECSN system (Figure 1e). They used an anode consisting of IrO_2-Ta_2O_5 coated with Ti that presents an adequate lifetime under complex water conditions. They also employed

an in-situ stripping technique to collect NH_3 coupled with ultraviolet (UV) irradiation to avoid the oxidation of NH_3. Considering that wastewater presents chloride ion concentrations of thousands of ppm, the system operating at a current density of 200 mA cm^{-2} produces hypochlorite at a rate of 0.5 mmol min^{-1}.[7] The irradiation of UV light cleaves the hypochlorite into chlorine and hydroxyl radicals. Then, the authors could reduce the oxidation of NH_4^+ by lowering the interfacial concentration of hypochlorite, favoring the competing oxidation of chloride ions, according to Le Chatelier's principle (Figure 1f). This enhanced recovery of NH_3 was validated by the results reported by Zhang *et al.*[3] that showed an increase of the conversion rate of NO_3^--to-NH_3 from 37% to 50%.

The authors conducted TEA and LCA to assess the economic feasibility of the system that they have developed. They demonstrated that by employing the ECSN system in comparison with the conventional evaporation-crystallization-solidification-landfill (ECSL), the cost for the wastewater treatment decreases from US$193.50 to US$116.30 per m^3 of wastewater. This cost decreases to US$105.00 when they consider the profit of the recovered ammonia. From the environmental point of view, the authors demonstrated that their reported ECSN system would result in a mitigation of of 207 million tons of CO_2 emissions annually by reducing the emissions of both wastewater treatment and Haber-Bosch process.

The recent publication of Zhang and co-workers[3] represents a significant breakthrough in the field of the development of electrochemical alternatives for nitrate-rich wastewater streams. The authors thoughtfully address many aspects of the nitrate reduction reaction that represent bottlenecks for its application, such as the use of a two-electrode-PEM-free setup, the feasibility of employing the system with a chloride-rich feedstock, and the optimization of the stability of Cu-based catalysts. Furthermore, their economic and environmental analyses motivate the electrochemistry community to continue efforts toward implementing new technologies for the treatment of nitrate-rich wastewater sreams.

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