



VIAS ELETROQUÍMICAS EMERGENTES PARA A PRODUÇÃO DE AMÔNIA VERDE: UMA REVISÃO CRÍTICA

EMERGING ELECTROCHEMICAL ROUTES FOR GREEN AMMONIA PRODUCTION: A CRITICAL REVIEW

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RESUMO

A amônia (NH_3) é essencial para a indústria química global, principalmente na produção de fertilizantes, e tem emergido como um promissor vetor de energia carbono-neutro. O processo Haber–Bosch (HB) convencional, responsável por mais de 90% da produção mundial, é altamente intensivo em energia e responde por 1–2% do consumo energético global e até 1,8% das emissões de CO_2 . Para atender às metas de neutralidade carbônica, alternativas baseadas em eletricidade renovável vêm sendo desenvolvidas. Esta revisão examina vias eletroquímicas emergentes para a síntese de amônia verde, incluindo o Haber–Bosch eletroquímico (e-HB), a redução de nitrogênio (eNRR), a redução de nitrato (NO_3^- -RR) e a redução de óxidos de nitrogênio (NO_x -RR). São destacados os avanços (2020–2025) em catalisadores, eletrólitos e design de células, bem como desafios como a baixa eficiência faradaica (FE) e a competição com a reação de evolução de hidrogênio. O e-HB apresenta o maior grau de maturidade (FE de até 99%, TRL 8–9), enquanto a eNRR e a rota mediada por lítio (Li-NRR) oferecem alta seletividade, mas com limitações de eficiência energética e escalabilidade. A NO_x -RR se destaca por sua seletividade superior a 90% e pela integração com processos de tratamento de resíduos. De forma geral, o e-HB permanece como a rota mais viável no curto prazo, enquanto a eNRR e a NO_x -RR apresentam potencial de longo prazo para uma produção descentralizada e sustentável, desde que sejam alcançados ganhos em eficiência, escalabilidade e políticas de apoio.

Palavras-chave: Amônia Verde; Síntese Eletroquímica; Redução de Nitrogênio; Haber–Bosch Eletrificado; Análise de Rentabilidade.

ABSTRACT

Ammonia (NH_3) is essential to the global chemical industry, primarily for fertilizer production, and is emerging as a promising carbon-neutral energy carrier. The conventional Haber–Bosch (HB) process, which supplies over 90% of global production, is energy-intensive and accounts for 1–2% of global energy use and up to 1.8% of CO_2 emissions. To meet carbon-neutrality goals, renewable electricity-based alternatives are under development. This review examines emerging electrochemical pathways for green ammonia synthesis, including electrochemical Haber–Bosch (e-HB), nitrogen reduction (eNRR), nitrate reduction (NO_3^- -RR), and nitrogen oxides reduction (NO_x -RR). Advances (2020–2025) in catalysts, electrolytes, and cell design are highlighted, along with challenges such as low Faradaic efficiency (FE) and competition with hydrogen evolution. e-HB shows the highest maturity (FE up to 99%, TRL 8–9), while eNRR and Li-mediated NRR offer high selectivity but limited energy efficiency and scalability. NO_x -RR stands out for its >90% selectivity and integration with waste treatment. Overall, e-HB remains



the most viable near-term route, whereas eNRR and NO_xRR hold long-term potential for decentralized and sustainable production, contingent on efficiency gains, scalability, and supportive policy measures.

Keywords: Green Ammonia; Electrochemical Synthesis; Nitrogen Reduction; Electrified Haber–Bosch; Profitability Analysis.

1 INTRODUCTION

Ammonia (NH₃) is among the most widely produced synthetic chemicals, with global capacity reaching 236 million tons in 2021 and projected to approach 290 million tons by 2030 [1,2]. Approximately 85% of this output is used in fertilizer production, while increasing attention has turned to NH₃ as a carbon-neutral energy carrier, particularly for hydrogen storage and transport. Compared with liquefied hydrogen, liquefied ammonia provides higher volumetric energy density, offering advantages for large-scale energy logistics [3–5].

Industrial production remains dominated by the Haber–Bosch (HB) process, developed over a century ago, which operates under harsh conditions of 400–500 °C and 150–350 bar [3,6]. This fossil fuel–dependent route is highly energy-intensive, accounting for ~1.8% of global CO₂ emissions and ~2% of global energy consumption [1,6,7].

The urgency to decarbonize the chemical and energy sectors has spurred interest in “green ammonia,” synthesized from renewable energy [8–10]. Among third-generation technologies, electrochemical routes are particularly promising, enabling NH₃ production from air and water under ambient conditions powered by solar and wind energy [9–11].

The main pathways under investigation include: (i) electrochemical Haber–Bosch (e-HB), replacing fossil H₂ with green H₂ from water electrolysis; (ii) the electrochemical nitrogen reduction reaction (eNRR), directly converting N₂ and protons into NH₃ in a single cell; and (iii) the electrochemical reduction of nitrate/nitrogen oxides (NO_xRR), which valorizes pollutants into NH₃ [4,7,10,12,13].

This review critically assesses these routes, focusing on reaction mechanisms, catalytic advances, technological barriers, and prospects for decentralized and sustainable ammonia production.

2 METHODOLOGY

This review critically analyzes recent scientific literature (2020–2025), selected from indexed databases (Scopus, Web of Science) using keywords such as “*electrochemical ammonia synthesis*,” “*green ammonia*,” “*nitrogen reduction*,” and “*nitrate reduction*.” The analysis focused on: (i) reaction mechanisms for eNRR and NO_xRR, including dissociative, associative, and Mars–van Krevelen pathways [3,9,14]; (ii) catalytic materials, from noble and transition metals to SACs, MXenes, and defect-engineered systems [11,13–15]; (iii) cell configurations and electrolytes, comparing H-type, flow cells, MEAs, and aqueous, molten-salt, and solid-state systems [14,16,17]; (iv) performance metrics such as ammonia yield, Faradaic efficiency, and techno-economic case studies (e.g., landfill biogas) [3]; and (v) comparative energy efficiency, assessing round-trip efficiency (RTE) of ammonia versus hydrogen [5].

3 RESULTS AND DISCUSSION

3. 1. Electrochemical Routes for Green Ammonia Synthesis



3.1.1. Electrochemical Haber–Bosch (e-HB).

The e-HB pathway is the most mature and technically feasible option for large-scale green ammonia production [4,5,7]. It substitutes fossil H_2 with green H_2 from water electrolysis (AWE, PEM, SOE), powered by renewable electricity, while N_2 is supplied via air separation [4]. Its main advantage is leveraging the existing HB infrastructure, enabling up to an eightfold reduction in CO_2 emissions [19,20]. However, the high cost of green H_2 , dependence on renewable prices, and intermittency limit widespread adoption [7,19]. Case studies show current non-viability without subsidies >50%, though cost parity with conventional ammonia may be achievable around 2030 if renewable power drops below USD 20/MWh [3,4,7].

3.1.2. Electrochemical Nitrogen Reduction (eNRR).

eNRR directly reduces N_2 and protons to NH_3 in a single cell [9,10], making it attractive for modular applications [7,10]. The challenge is the strong $N\equiv N$ bond (941 kJ/mol) and competition with HER [9,12,14]. Pathways include associative and dissociative mechanisms [3,9,14]. Catalysts such as Ru/Mo [13,15], CoS_2/MoS_2 (FE 20.8%) [18], Fe–N/C SACs (FE 39.6%) [14], and MXenes/MOFs (FE ~25–31%) [14] have shown promise. Still, overall FE (<20%) and production rates ($\sim 10^{-7} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$) remain far below industrial targets, and contamination control is critical [1,14,15].

3.1.3. Lithium-Mediated Reduction (Li-NRR).

Li-NRR proceeds via Li deposition, Li_3N formation, and protonation to regenerate Li^+ [3,19]. It suppresses HER and achieves high FE (up to ~100%) with ionic liquids (69% FE) [2,3,10]. Yet, high overpotentials, SEI formation, solvent degradation, and low energy efficiency (<3%) severely limit scalability [4,10]. Mitigation strategies include O_2 addition and potential cycling [3,10].

3.1.4. Nitrate/Nitrogen Oxide Reduction (NO_x RR).

NO_x RR converts NO_3^- and NO_x pollutants into NH_3 , benefiting from weaker $N=O$ bonds (204 kJ/mol) [12,21]. Cu-based catalysts show high selectivity via an eight-electron pathway [21], with CuNi/CuPd alloys and SACs achieving FE >95% and current densities $>100 \text{ mA} \cdot \text{cm}^{-2}$ [13,21]. Bi nanocrystals with K^+ reached FE 90.6% [2]. However, selectivity strongly depends on pH, potential, and catalyst structure [12,21], while by-product formation and stability in real effluents remain challenges. Hybrid plasma– NO_x RR processes show higher efficiency [9,12].

3.2. Comparative Analysis and Future Perspectives

3.2.1. Ammonia as an Energy Carrier

Beyond being a key chemical feedstock, NH_3 is also a promising energy carrier. Round-trip efficiency (RTE), which accounts for losses from production to reconversion, reaches $28 \pm 5\%$ when NH_3 is decomposed and used in solid oxide fuel cells (SOFCs) over 30 days of storage—comparable to the best hydrogen pathways [5]. For longer storage (>30 days), ammonia is superior to H_2 due to lower boil-off losses, making it suitable for seasonal storage and global energy transport. Sensitivity analyses highlight electrolysis and reconversion efficiencies as decisive factors [5].

3.2.2. Techno-Economic Comparison.

To enable a direct comparison among different green ammonia production routes, **Table 1** summarizes their key techno-economic indicators, including Faradaic efficiency, production rate, energy efficiency, technology readiness level (TRL), and projected relative cost.



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Table 1. Comparative techno-economic indicators of electrochemical routes for green ammonia production.

Parameter	e-HB	eNRR	Li-NRR	NO _x RR
Faradaic Efficiency (FE)	~95–99% (via electrolysis)	< 20% (up to 39.6% in SACs)	~70–100% (in optimized systems)	> 90% (Cu, Bi, alloys)
NH ₃ Production Rate	High (industrially viable)	Low ($\ll 10^{-7}$ mol·cm ⁻² ·s ⁻¹)	High (in laboratory systems)	High (up to >100 mA·cm ⁻²)
Energy Efficiency	Moderate (~30–40%)	Very low (< 1–2%)	Very low (< 3%)	Moderate (~20–40%)
Technology Readiness Level (TRL)	8–9 (near-commercial)	3–4 (laboratory/early pilot)	3–4 (laboratory)	5–6 (pilot development)
Projected Relative Cost	Medium (declining toward 2035)	High (due to low efficiency)	High (electricity and lithium costs)	Variable (may be competitive if integrated with waste treatment)

Source: Authors.

These data confirm that e-HB is currently the most mature and competitive option, especially where renewable electricity is inexpensive. Projections suggest it could reach cost parity with conventional NH₃ by 2035, particularly under carbon pricing policies [4]. Li-NRR achieves the highest Faradaic efficiencies and laboratory-scale production rates but is hindered by low energy efficiency, stability concerns, and high lithium costs [4,10]. eNRR and NO_xRR are attractive for decentralized and modular production; in particular, NO_xRR adds value through wastewater and flue gas treatment, though major breakthroughs in catalyst design remain necessary [7].

Common Challenges.

Across all routes, key bottlenecks include: (i) improving energy efficiency by reducing overpotentials and side reactions [10,16]; (ii) developing stable and selective catalysts [8,21]; (iii) advancing reactor engineering with flow cells and GDEs to overcome mass transport limits [14,17]; (iv) adopting rigorous experimental protocols for reproducibility [1,2,9]; and (v) addressing economic barriers, as case studies (e.g., landfill biogas) show limited profitability without more efficient catalysts and milder operating conditions [3].

3.2.3. Engineering and Scalability Challenges.

While laboratory metrics are encouraging, scaling to pilot and industrial plants involves complex engineering hurdles often overlooked in fundamental studies [7,16]. Challenges include designing continuous-flow, pressurized reactors with large surface areas, ensuring uniform flow distribution, thermal management, sealing of membranes, and efficient separation/purification of NH₃ [1,16].

For e-HB, the main challenge is not the reactor itself but integrating the entire chain (electrolyzer, air separation, synthesis reactor) under intermittent renewables, demanding advanced process control [4,7]. eNRR requires high current densities with selectivity, driving research on 3D porous electrodes [1,10,14]. Li-NRR faces intrinsic efficiency limits and safety risks from metallic lithium handling [10,19]. NO_xRR scalability depends on logistics and pretreatment of variable feedstocks, avoiding catalyst poisoning [12,21].

4 CONCLUSION



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The production of green ammonia through electrochemical pathways represents a decisive technological frontier for achieving deep decarbonization in agriculture and for consolidating ammonia as a strategic clean energy vector. Among the options evaluated, the electrochemical Haber-Bosch process (e-HB) stands out as the most immediately viable route, leveraging an established industrial framework while replacing fossil-derived hydrogen with green H_2 . Nevertheless, its long-term competitiveness critically depends on the sustained reduction of renewable electricity and electrolysis costs.

Emerging technologies such as the direct electrochemical reduction of N_2 (eNRR) and the reduction of nitrates/nitrogen oxides (NO_x RR) hold transformative potential for decentralized, modular, and fully electrified production. The lithium-mediated pathway (Li-NRR) demonstrates near-total Faradaic efficiency under laboratory conditions but remains hindered by poor energy efficiency and stability constraints. Transition metal-based strategies have advanced through innovative catalytic platforms, including SACs, MXenes, and defect engineering, which continue to expand the design space for selective and durable catalysts. Beyond electrochemical approaches, photocatalysis and biocatalysis are emerging as complementary technologies capable of operating under mild environmental conditions, thereby broadening the portfolio of sustainable solutions toward carbon neutrality.

Looking ahead, the future of sustainable ammonia production will likely involve the integration of multiple technological routes, strategically adapted to regional resources and application scales. Realizing this vision requires not only continued fundamental research into reaction mechanisms but also disruptive advances in catalyst innovation and reactor engineering. Together, these developments will be essential to overcome current barriers and to enable ammonia to play a central role in the emerging global clean energy economy.

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