

Towards sustainable metal-mediated ammonia electro-synthesis

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Ammonia is a key component of fertilizers, a crucial industrial chemical and a carbon-free fuel. Electro-synthesis of ammonia from nitrogen under ambient conditions presents an attractive alternative to the centralized Haber–Bosch process. Although lithium- and calcium-mediated nitrogen reduction (Li-NRR and Ca-NRR) show promise, long-term continuous ammonia electro-synthesis at high rates will be needed for industrial application. In this Perspective we argue that for Li-NRR and Ca-NRR to operate sustainably, the use of continuous-flow reactors—in which NRR is coupled with the hydrogen oxidation reaction, avoiding non-sustainable proton sources and electrolyte oxidation—is essential. Providing the necessary protons via hydrogen oxidation is vital for the sustainable production of ammonia and long-term system stability. We propose strategies such as optimizing the solid–electrolyte interphase design, refining the electrode and reactor engineering to enhance the system stability and ammonia production rate. We also strongly advocate the exploration of electrocatalytic routes for surpassing the theoretical energy efficiency limit of Li/Ca-NRR.

Ammonia (NH₃) plays a vital role in the fertilizer and chemical industries and is considered a carbon-free fuel^{1–3}. The dominant method for NH₃ production, the Haber–Bosch process, reacts dinitrogen (N₂) and hydrogen gas (H₂) over an iron-based catalyst at high temperatures (350–450 °C) and pressures (150–200 bar)⁴. Given its high energy consumption, substantial carbon dioxide emissions and capital-intensive nature, there is a growing urgency to explore alternative solutions. Electrochemical NH₃ synthesis is emerging as a promising option^{5,6}, enabling electrification through coupling with renewable energy sources.

Many claims have been put forward regarding the electrochemical synthesis of NH₃ from N₂ in aqueous electrolytes. However, the credibility of most of these accounts has been questioned⁷, primarily due to the absence of rigorous quantitative measurements with ¹⁴N₂ and ¹⁵N₂ isotopes, essential for proving that the NH₃ produced (which currently is typically present at microgram levels) indeed originates from N₂ instead of nitrogen oxides⁸. Only when the concentration of NH₃ produced exceeds the milligram range may isotopic proofs become unnecessary.

Currently, the only known reliable method of electrochemical NH₃ synthesis at ambient temperature is via the metal-mediated nitrogen reduction reaction (NRR), including lithium- and calcium-mediated nitrogen reduction (Li-NRR and Ca-NRR)^{8–11}. Although the precise reaction mechanisms involved are not yet understood, the consensus is that both Li-NRR and Ca-NRR processes rely on the lithium or calcium metal reduced from Li⁺ or Ca²⁺ present in an electrolyte to dissociate N₂ followed by a series of electron and proton transfers to form NH₃ (refs. 12–14). Li-NRR in non-aqueous electrolytes was first reported in 1930 (ref. 10) and was later investigated in 1993 (ref. 11), and Ca-NRR in non-aqueous electrolytes was first reported in 2023 (ref. 9). Batch and continuous-flow reactors can use identical electrodes and electrolyte components (such as solvents and proton shuttles) and are compatible with both Li-NRR and Ca-NRR. However, the batch reactor relies on sacrificial proton donors, whereas the continuous reactor uses proton shuttles and sustainable proton sources (that is, H₂). It has also been noted that electrodeposited magnesium has been used for reaction with N₂, followed by protonation to produce ammonium¹⁵. Although this two-step process was

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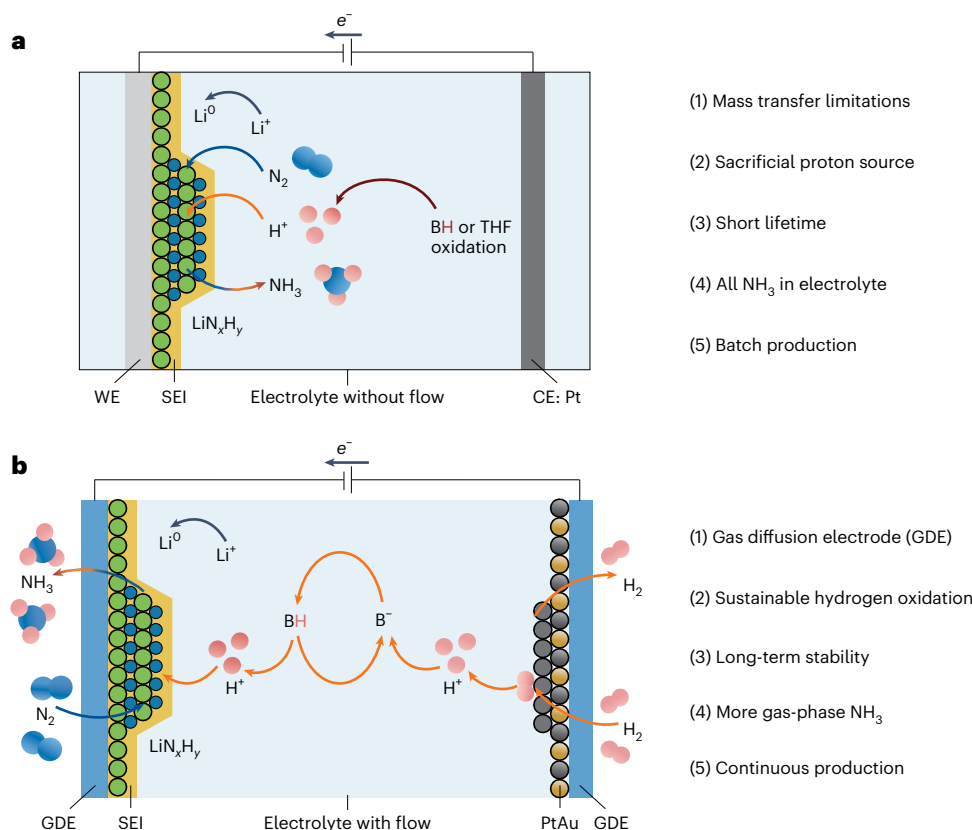


Fig. 1 | Overcoming limitations of the batch reactor by combining HOR and NRR. a, b, Schematic processes of Li/Ca-NRR in a batch reactor (a) and in a continuous-flow reactor (b). BH denotes the proton shuttle and B⁻ is the deprotonated form of the proton shuttle. Atom colours: Li, green; N, blue; H, pink; Pt, dark grey; Au, orange. WE, working electrode; CE, counter electrode; THF, tetrahydrofuran.

demonstrated in batch reactor separately, it shows the potential to run in a continuous-flow reactor and produce NH_3 directly.

Since the introduction of rigorous control procedures⁸, various strategies have been reported for increasing the NH_3 Faradaic efficiency (FE)^{16–18}, current density^{19,20} and stability¹² of Li-NRR. In particular, close to a 100% FE has been reported using a LiTFSI-based electrolyte (that is, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$) under 15 bar N_2 (ref. 16), and a current density of -1.0 A cm^{-2} has been demonstrated by combining a fluorine-based electrolyte with a high-surface-area copper electrode under 20 bar N_2 (ref. 20). Nearly all Li-NRR investigations have been conducted using batch reactors, which poses challenges associated with the use of non-sustainable proton sources and the scaling up of production.

A promising approach to creating sustainable hydrogen sources for NH_3 synthesis involves incorporating a hydrogen oxidation reaction (HOR) at the anode^{18,21,22}. Platinum-coated stainless steel cloth has been reported as the counter electrode for the HOR, coupled with Li-NRR in a three-compartment cell²¹. This approach resulted in an NH_3 FE of 35%, with an operation time of between 5 and 8 min and a passed charge of less than 10 C. Some recent studies have emphasized the use of a bimetallic catalyst^{22,23}, as opposed to a conventional platinum anode, for the HOR in organic electrolytes. Using a platinum–gold alloy (PtAu) catalyst and a continuous-flow reactor, a continuous operation lasting 10 h has been demonstrated with an NH_3 FE of 61% at 1 bar and room temperature²². Importantly, the origin of hydrogen in the produced NH_3 was validated in this work through operando mass spectrometry coupled with isotope-labelling studies, confirming its derivation from the HOR at the anode rather than the electrolyte²².

Previous studies have struggled to achieve long-term continuous-flow NH_3 electrosynthesis beyond 10 h and to demonstrate gram-scale production. As previously stated, whereas a 100% FE¹⁶ and a -1.0 A cm^{-2} current density²⁰ have been reached, these goals have not been achieved

simultaneously. Electrolyte oxidation on the anode, rather than the HOR, presents a challenge for comparing batch and continuous-flow reactors effectively. This introduces complications, as electrolyte decomposition products may seriously influence the HOR catalyst, proton shuttle and reactor. Such differences not only create confusion in assessing the technology's progress but also impede researchers in evaluating new materials and obscure the allocation of resources to the most promising systems.

In this Perspective we contend that use of the HOR is essential for sustainable NH_3 electrosynthesis via Li-NRR and Ca-NRR. We discuss the limitations of batch reactors and the importance of using the HOR in terms of it providing sustainable proton sources and enabling the long-term stability of the system. We also propose strategies to enhance the stability and NH_3 production rate and consider other candidates beyond lithium and calcium towards sustainable NH_3 electrosynthesis.

The limitations of batch reactors

Figure 1 illustrates the Li-NRR in a batch reactor and in a continuous-flow reactor that combines Li-NRR and HOR. There are three main limitations of batch reactors for NH_3 synthesis (Fig. 1a): mass transfer limitations, sacrificial proton sources and scaling up.

First, in a batch reactor for Li-NRR, it is essential that nitrogen is dissolved in the electrolyte for it to participate in the reaction. This configuration is mass-transport-limited due to the low solubility of N_2 in non-aqueous electrolytes^{12,13}.

Second, Li-NRR suffers from using sacrificial proton sources, such as ethanol and solvents (for example, tetrahydrofuran, THF), which results in severe electrolyte oxidation due to the high anode potential associated with these sources. In a batch reactor, severe solvent oxidation and the resulting electrolyte discolouration have also been widely observed across various electrolytes and at different

current densities^{20,24}. The high anode potential in a batch reactor can also induce increased ring-opening polymerization of THF^{25,26}, a commonly used solvent in Li-NRR. This, in turn, can lead to increased viscosity of the electrolyte and destabilization of the entire system.

Using H₂ as a sustainable proton source in a batch reactor poses challenges due to its competition with N₂ for reaction with metallic lithium, forming lithium hydride (LiH). When H₂ was introduced into a batch reactor for use at the anode¹⁸, this strategy faced limitations due to mass transfer challenges and LiH formation, hindering the ability to activate nitrogen under ambient conditions. It is noteworthy that increasing the reactor pressure aids in increasing the solubility of N₂ in the electrolyte and improving the NH₃ FE^{11–13}, although it does not address the limitations related to proton sources.

Third, the challenges of long-term NH₃ production and obtaining a considerable gas-phase yield of NH₃ are evident obstacles for scaling up the batch reactor process. For example, two experiments exceeding 90 h have been reported: one involved a 96 h experiment conducted using a batch reactor at 15 bar (with a 0.05 cm² electrode for the cathode)¹⁶, resulting in the production of a total NH₃ yield of 0.0647 g in the electrolyte; the other, lasting 93 h (ref. 18), was performed using a batch reactor at 20 bar (with a 0.012 cm² electrode for the cathode), giving a total NH₃ yield in the electrolyte of 0.0026 g. In both studies, the tiny electrode area and the limited production of NH₃ relative to the electrolyte volume probably contributed to the observed long-term stability.

The essentiality of using sustainable proton sources

In a continuous-flow reactor (Fig. 1b), the NRR is coupled with the HOR, supplying N₂ and H₂ directly to the interface of the electrolyte and the gas diffusion electrode (GDE), thereby reducing mass transfer limitations²². Pairing Li-NRR with HOR not only eliminates sacrificial solvent as the proton source but also reduces the cell voltage, thereby increasing the NH₃ FE and the energy efficiency (EE).

Li-NRR in a continuous-flow reactor typically involves a number of steps²². Lithium ions (Li⁺) diffuse from the bulk electrolyte through the solid–electrolyte interphase (SEI) layer on the electrode surface; the SEI layer comprises electrolyte decomposition products, including various inorganic and organic components, and exhibits ion-conducting but electron-insulating properties. The Li⁺ are electrochemically reduced to metallic lithium (Li⁰) on the electrode, which then reacts with N₂ to produce lithium nitride. Subsequently, the lithium nitride is protonated by a proton shuttle (for example, ethanol), leading to the continuous release of NH₃. The sustainable proton sources are derived from the HOR at the anode²². It is also worth highlighting here that the source of hydrogen atoms in NH₃ production is a critical factor in determining the overall sustainability of the process: for the NH₃ produced to be sustainable, its hydrogen atoms must come from a sustainable hydrogen supply.

Figure 2a shows the typical anode and cathode potentials ($E_{CE,anode}$ and $E_{WE,cathode}$, respectively) during NH₃ electrosynthesis using chronopotentiometry. Although they depend on the applied current density, the electrolyte formulation and the reactor design, the reported anode potential and total cell voltage of the batch reactor are much higher than those in most continuous-flow reactors (Fig. 2b). It is worth noting that Lazouski et al. were the first to propose the use of a stainless steel cloth as the GDE²¹. However, the high cell voltage that ranges from 20 to 30 V limits the lifetime of this three-compartment system. The high anode potential indicates the severe electrolyte oxidation and the associated destabilization of cathode potential and entire system. Therefore, the combination of HOR with NRR is not only important to allow the use of sustainable proton sources but also essential to the stability of the system.

Furthermore, conclusions derived from observations in a batch reactor may not be universally applicable to continuous-flow reactors due to the local environment and mass transfer differences.

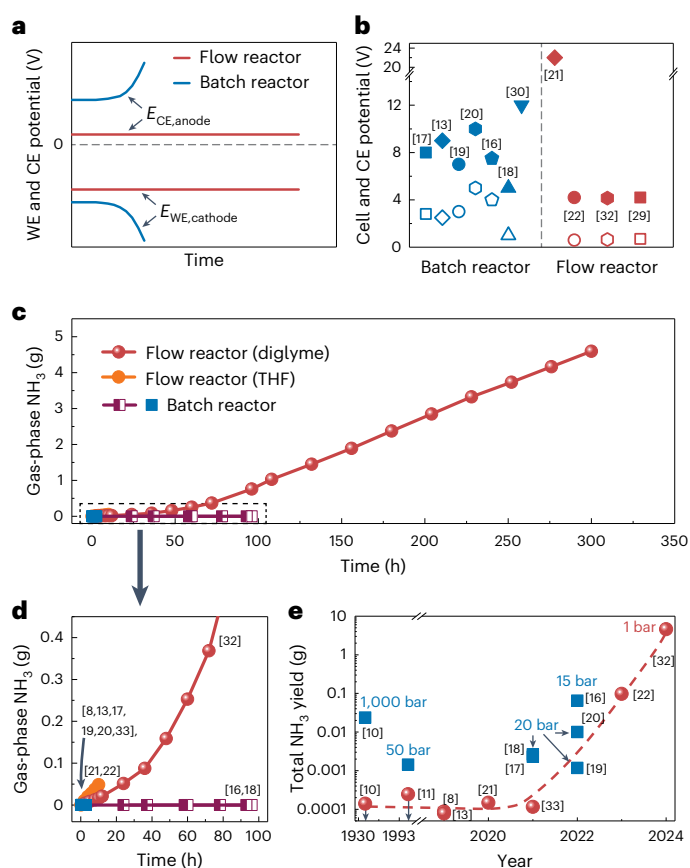


Fig. 2 | Electrochemical performance in batch reactors and continuous-flow reactors. **a**, Schematic illustration of chronopotentiometry in a batch reactor and a continuous-flow reactor. **b**, Anode potential (open symbols) and cell potential (closed symbols) of Li/Ca-NRR in a batch reactor (blue symbols) and in a continuous-flow reactor (red symbols)^{8,13,16–22,30,32}. References are indicated in square brackets. **c, d**, Gas-phase NH₃ versus time of Li/Ca-NRR in a batch reactor and in a continuous-flow reactor^{8,13,16–22,32,33} (**c**), where an expanded version of the data for the first 100 h is shown (**d**). Diglyme, diethylene glycol dimethyl ether. **e**, Produced NH₃ yields reported in the literature for Li-NRR from 1930 onwards^{8,10,11,13,16–22,32}. All red spheres represent the condition at 1 bar. The red dashed line in **e** is a guide to the eye. All data are taken from the cited literature and their respective Supplementary Information.

This aspect warrants particular attention, especially when using different electrolytes, as the impacts on the HOR catalyst and proton donor/shuttle need to be thoroughly examined and understood. For example, when sulfur-containing lithium salts or solvents are used, the resulting decomposition product may poison the HOR catalyst. Moreover, the optimized parameters, such as the lithium salt concentration and the proton donor/shuttle concentration, may vary between batch and continuous-flow reactors^{20,22}.

Validating that the protons in the NH₃ produced are truly from the H₂ feed is essential, which is not only crucial for screening different proton shuttles^{24,27–29} but also important for investigating various solvents and lithium salts^{30–33}. Without confirming that H₂ serves as the proton source, the investigated proton shuttles may simply serve as proton sources, and the high anode potential could have unknown effects on the solvent oxidation. Operando mass spectrometry, combined with isotope-labelling studies, has proved to be an effective method for validating the origin of hydrogen in the produced NH₃ and identifying the genuine proton shuttle. For example, the operando mass spectrometry of deuterium oxidation has both demonstrated that the HOR can supply protons for NH₃ synthesis and confirmed the recyclability of ethanol and phenol as a proton shuttle^{22,29,32}.

The chemical and electrochemical stability of the solvents and proton shuttles further determine the long-term stability of the system. THF has been used widely as a solvent for Li-NRR since 1993 (ref. 11), in contrast to the alcohol-based solvents reported in 1930 (ref. 10). One of the main reasons for the absence of long-term operation in a continuous-flow reactor is the polymerization and volatility of the THF, which has a low boiling point of 66 °C. The low boiling point of THF leads to solvent evaporation, which occurs through natural volatilization and accelerated volatilization on the GDE with continuous gas flow.

An ideal solvent for a continuous-flow reactor should exhibit high lithium salt solubility and electrochemical stability and resist polymerization. The solvent should be compatible with the proton shuttle and the metallic lithium, to form a suitable SEI layer and to balance the delivery of Li⁺ and the protons generated from the HOR. To produce more NH₃ in the gas phase, the solvent-induced SEI on the GDE must be compact, ensuring that it does not impede the release of NH₃ into the gas phase. Having NH₃ present in the gas phase is highly desirable as it facilitates separation—improving the cost-effectiveness—compared with NH₃ produced in the electrolyte. Finally, to enhance long-term stability, the solvent should resist polymerization to prevent electrolyte degradation and have a high boiling point to prevent electrolyte evaporation. Figure 2c,d underscores the significance of using a continuous-flow reactor with a chain ether-based solvent, such as diethylene glycol dimethyl ether (boiling point, 162 °C). This approach not only ensures long-term stability, lasting up to 300 h, but also facilitates the production of NH₃ in the gas phase, reaching 98% (ref. 32). The total NH₃ produced is 4.6 g (Fig. 2e), which is an order of magnitude higher than the previous best results (<0.1 g). This solvent also exhibits non-polymerization properties and forms a compact SEI layer on the GDE, facilitating NH₃ release in the gas phase and ensuring electrolyte stability.

Efficient proton shuttles are also highly desirable for Li-NRR in a continuous-flow reactor, and the specific role and reactions of proton shuttles dictate certain requirements and design principles²⁹. First, the proton shuttle should incorporate a functional group, such as –OH or/and –COOH, that is capable of donating/accepting a proton with an appropriate pK_a value in the electrolyte. The optimal pK_a strikes a balance between its protonation ability and minimizing side reactions, particularly the hydrogen evolution reaction (HER). Second, the proton shuttle needs to be compatible with metallic lithium and the solvent. It must maintain a certain diffusion rate to regulate the availability of protons on the electrode surface. In addition, its deprotonated form should exhibit both good chemical and electrochemical stability. In the final aspect, all components of the electrolyte, including the solvent, proton shuttle and salt, must exhibit excellent compatibility with each other and the NRR–HOR system in the continuous-flow reactor²⁹. For example, the electrolyte and the potentially existing decomposition product should not deteriorate the activity and stability of the HOR catalyst.

Towards commercially relevant ammonia electro-synthesis

While the HOR coupled with NRR has been demonstrated to sustainably produce NH₃ in a continuous-flow reactor without using a sacrificial solvent as the proton source, the cost-effective and industrial-scale production of NH₃ remains challenging. Achieving NH₃ electro-synthesis at costs below US\$1 per kg at an industrial scale requires a high NH₃ partial current density that exceeds 400 mA cm⁻², an EE above 30% and a process lifetime of several years³⁴.

Two strategies for achieving a high current density in NH₃ electro-synthesis are increasing the electrochemical surface area (ECSA) of the electrodes, such as constructing high-surface-area GDEs (Fig. 3a); and minimizing the ohmic drop by improving the electrolyte conductivity and reducing the distance between cathode and anode.

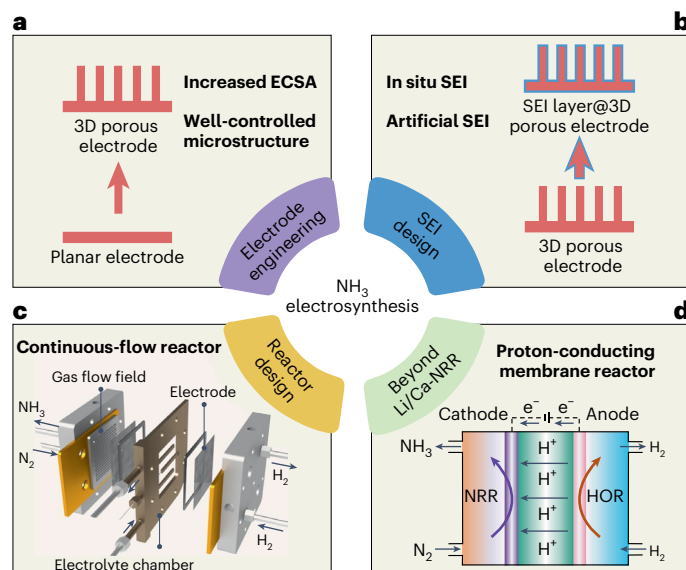


Fig. 3 | Strategies towards high-performance Li/Ca-NRR and next-generation NH₃ electro-synthesis. a,b, Strategies for achieving high current densities via electrode engineering (a) and high FE values through rational SEI design (b). 3D, three-dimensional. **c,d**, Configurations of the continuous-flow reactor for Li/Ca-NRR (c) and the proton-conducting membrane reactor (d).

The anodic HOR must efficiently meet the high current density demands of the cathodic NRR. Developing HOR catalysts with high activity, stability, selectivity and cost-effectiveness in the organic electrolyte (for example, using non-precious metal catalysts) is crucial to prevent the HOR from becoming a bottleneck in the system's performance and economic feasibility. Insights from the fuel cell community, particularly regarding the anode catalyst for direct methanol fuel cells, can inspire advancements in the HOR process in the organic electrolyte. Increasing the number of active sites and their intrinsic activity can boost the activity of HOR catalysts. Theoretical calculations are crucial for screening and predicting non-precious metal catalysts in the organic electrolyte and for understanding the mechanisms and kinetics of various HOR catalysts. These investigations aid in designing and optimizing electrocatalysts^{9,22} and electrolytes^{17,20} for Li/Ca-NRR, advancing NH₃ electro-synthesis.

Mass transport is crucial for preventing concentration polarization and ensuring that reactant concentrations at the electrode surface remain sufficient compared with the bulk solution. The SEI layer has been shown to control transport selectivity of ions and species^{12,20,35}. An optimized SEI layer can improve ion transport^{16,17,20,33}, enhancing the reaction kinetics and overall efficiency in Li/Ca-NRR (Fig. 3b). Inspiration for improved SEI designs in Li/Ca-NRR can be drawn from the artificial SEI (intentionally designed using specific additives or compounds) developed in battery research. However, the SEI needed for Li/Ca-NRR differs from that in batteries as we require an SEI that balances the transport of reactants and products and supports the reactivity of metallic lithium for NH₃ synthesis. In addition, the presence of nitrogen and protons/proton shuttles in Li/Ca-NRR leads to a distinct SEI structure and chemistry compared with that in batteries. Theoretical studies have revealed the critical role of the SEI layer in determining the Li-NRR performance^{12,17,20,31,32}. Tuning the ionic conductivity and explaining changes in the SEI enhance our understanding of Li/Ca-NRR mechanisms and the design of effective SEI layers for achieving high FE values^{9,17,20,32}.

Operating conditions such as temperature and pressure significantly affect the HOR and NRR kinetics. A higher temperature generally increases diffusion rates, whereas an increased pressure can enhance the reaction rate between N₂ and metallic lithium or calcium

by increasing the coverage of N_2 on Li or Ca surfaces. Raising the reactor temperature boosts the electrolyte ionic conductivity, reducing the ohmic drop; however, careful management is necessary as higher temperatures may not only accelerate electrolyte degradation but also affect the rate of lithium deposition and consumption, as well as the proton flux. In addition, higher pressures and temperatures necessitate more robust, expensive equipment with complex designs. Efficient proton transfer ensures an ample supply of protons at the cathode for NH_3 synthesis, which aligns with the NRR rate (that is, the proton consumption rate) at high current density and low cell voltage. However, controlling the proton availability is crucial as excess protons can trigger the HER and reduce the FE³⁶. Thus, optimizing the mass transport of reactants and products is essential for meeting the demands of high current densities. At the same time, the heat management should be considered at high current density to avoid equilibrium issues at high temperature.

In industrial settings, processes not only need to be efficient and cost-effective but also reliable and durable over extended periods (several years). The long-term stability of the NH_3 electrosynthesis system is crucial for its viability in industrial applications. Factors such as the HOR catalyst, solvent, proton shuttle and SEI layer each play a vital role in ensuring the durability of the system. For example, HOR catalysts must resist degradation over time to maintain their activity in facilitating H_2 oxidation.

The reactor design profoundly affects NH_3 electrosynthesis, notably impacting the EE and overall feasibility (Fig. 3c). Shortening the distance between anode and cathode can decrease cell resistance, improving the EE. However, it may also lead to challenges such as H_2 diffusion to the cathode and LiH formation. Lowering the cell voltage is essential for improving the EE, which translates to lower energy consumption and costs. Achieving this entails optimizing the composition of the electrolyte, the electrode materials and the reactor design.

In pilot-scale flow cells, the production capacity is often boosted by arranging the cells in stacks. The stack design, including the cell arrangement and reactant distribution, significantly impacts the performance. Ensuring a uniform current distribution and minimizing the overpotential requires efficient electrolyte and gas distribution within the stack. By optimizing the reactor design, more efficient, cost-effective and scalable units can be achieved for sustainable NH_3 production. However, maintaining stability during scale-up poses challenges such as aggravating the degradation of the electrolyte and SEI, the mechanical stability of the electrode, catalyst poisoning and process control difficulties. Addressing these requires a comprehensive understanding of processes, advanced reactor designs, robust electrode and catalyst materials, and tailored control strategies for industrial-scale operation. In addition, system stability and reproducibility across various manufacturing conditions must be ensured.

Whereas Li-NRR holds promise for sustainable NH_3 synthesis, its maximum theoretical EE using H_2 is about 28% (ref. 22), and experimental results have so far reached 17% (ref. 32). (It is important to note that this calculated EE accounts for the theoretical energy required for H_2 production.) By contrast, current commercial NH_3 synthesis achieves an EE of 62–65%, with potential to surpass 70% using solid oxide electrolysis cells for water splitting^{37,38}.

The electrocatalytic reduction of N_2 to NH_3 shows promise for addressing the EE limitations of the Li/Ca-NRR system. However, it faces challenges from the competing HER, which reduces the selectivity of the NRR process by consuming protons and electrons on the catalyst surface³⁶. Strategies such as managing the proton availability and controlling the electron transfer are needed if the FE is to be improved. The question is whether we can achieve a favourable balance through artificial SEI layers or alternative approaches that are similar to the Li-mediated system. Weng et al. introduced an electrochemical proton-conducting membrane reactor for NH_3 production at 350 °C (ref. 39). In this set-up (Fig. 3d), H_2 is initially converted into protons on

the anode side via a platinum catalyst. These protons are then transported through the solid membrane, ultimately contributing to the synthesis of NH_3 on the cathode side along with N_2 , using a ruthenium catalyst. Although this approach seems promising, as it is operated at 350 °C and it is possible that the observed NH_3 production may result from thermal processes instead of electrochemical processes. Therefore, it is imperative to explore lower operating temperatures, such as 150–200 °C, to clarify this aspect.

Conclusion

In this Perspective, we emphasize the importance of coupling the NRR with the HOR in continuous-flow reactors to ensure sustainable proton sources and improve the stability of the system. We propose strategies such as SEI design, electrode engineering and reactor design to enhance the production rates and stability. We strongly encourage the exploration of new metal mediators (for example, metals with low reduction potentials) and alternative electrochemical routes (for example, electrocatalytic N_2 reduction) to raise the theoretical EE above 28%. We hope that our recommendations will contribute to realizing commercial NH_3 electrosynthesis from nitrogen and water, fostering a more sustainable and carbon-neutral future.

Data availability

Source data are provided with this paper.

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Competing interests

The authors declare no competing interests.

Additional information

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