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Review

Effective N_2 activation strategies for electrochemical ammonia synthesis

Minghang Jiang,[1,2] Xi Chen,[1] Fasheng Chen,[1,4] Mengjun Wang,[1] Xiaojun Luo,[1] Yi He,[1] Caijun Wu,[1] Liyun Zhang,[1] Xiao Li,[3,*] Xuemei Liao,[1,4,*] Zhenju Jiang,[1,4,*] and Zhong Jin[2,*]

[1]Department of Chemistry, School of Science, Xihua University, Chengdu, Sichuan 610039, P.R. China

[2]State Key Laboratory of Coordination Chemistry, MOE Key Laboratory of Mesoscopic Chemistry, MOE Key Laboratory of High Performance Polymer Materials and Technology, Jiangsu Key Laboratory of Advanced Organic Materials, Suzhou Key Laboratory of Green Intelligent Manufacturing of New Energy Materials and Devices, Tianchang New Materials and Energy Technology Research Center, Institute of Green Chemistry and Engineering, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210023, P.R. China

[3]College of Chemistry and Food Science, Yulin Normal University, Yulin, Guangxi 537000, China

[4]School of Food and Biological Engineering, Xihua University, Chengdu, Sichuan 610039, China

*Correspondence: leex211@126.com (X.L.), xmliao@mail.xhu.edu.cn (X.L.), zhjjiang@mail.xhu.edu.cn (Z.J.), zhongjin@nju.edu.cn (Z.J.)

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THE BIGGER PICTURE The exploration of electrochemical ammonia (NH_3) synthesis, utilizing N_2 as the raw material, carries tremendous importance in enabling decentralized production efforts and nurturing sustainable environmental advancements. However, the activation of N_2 molecules continues to pose significant challenges. This review delves into the recent groundbreaking research on effective N_2 activation strategies, encompassing lithium (Li)/ calcium (Ca)-mediated and plasma-assisted technologies for electrochemical NH_3 synthesis. These technologies involve the conversion of inert N_2 into more reactive nitrogen-containing species, which are further converted to produce NH_3. Moreover, we conclude by underscoring the persisting challenges and promising avenues in this domain. Our aim is that this comprehensive review will offer profound insights and spark innovative ideas in the realm of effective N_2 activation strategies, ultimately propelling the field of electrochemical NH_3 synthesis forward.

SUMMARY

Ammonia (NH_3) synthesis using N_2 as reaction raw material powered by renewable electricity provides a promising route to realize artificial N_2 fixation. However, the activation of N_2 molecules, a crucial step in the process, remains challenging. Recently, significant progress has been made in developing effective strategies, including lithium (Li)/calcium (Ca)-mediated and plasma-assisted technologies, to enhance N_2 activation. These technologies involve the conversion of inert N_2 into more reactive nitrogen-containing species, which are further converted to produce NH_3. In this review, we present recent pioneering works on effective N_2 activation strategies, including Li/Ca-mediated and plasma-assisted technologies for electrochemical NH_3 synthesis. Finally, we highlight the remaining challenges and prospects. We hope that this review will provide profound insights and inspire innovative thinking in the area of effective N_2 activation strategies, thereby significantly advancing the field of electrochemical NH_3 synthesis.

INTRODUCTION

Ammonia (NH_3) is one of the most essential chemical feedstocks for fertilizer and pharmaceutical production.[1–4] Currently, the predominant method for producing NH_3 on an industrial scale is the conventional Haber-Bosch (HB) process.[5–7] HB process accounts for 1%–2% of total global annual energy consumption and results in >1% of worldwide greenhouse gas emissions.[8,9] Therefore, it is urgent to develop a green and sustainable NH_3 synthesis technology. For this purpose, an increasing number of researchers are being devoted to developing artificial NH_3 synthesis techniques, including biological enzyme nitrogen fixation,[10,11] photocatalytic nitrogen fixation,[12–14] electrochemical NH_3 synthesis,[15–21] and so on to replace the HB process. Among which, electrochemical NH_3 synthesis using N_2[1,18,22–25] as reaction raw material powered by renewable electricity provides a promising route to realize artificial nitrogen fixation.

Over the past few years, the electrochemical reduction of N_2 reaction (N_2RR) has attracted more attention from researchers. However, the development of electrochemical N_2RR is substantially hindered by a relatively low-energy efficiency,[9,26]

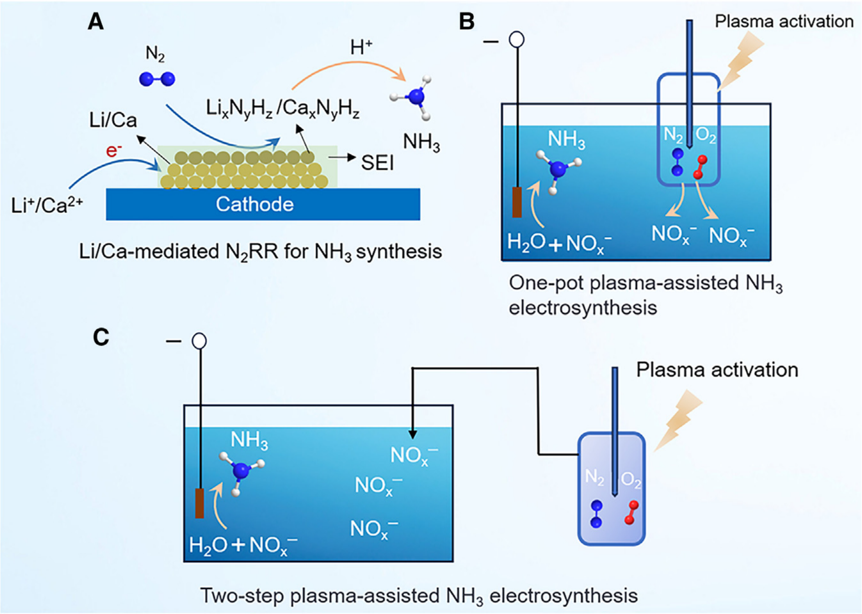

Figure 1. Illustration of various N_2 activation strategies for electrochemical NH_3 synthesis

(A) Li/Ca-mediated electrochemical NH_3 synthesis. SEI represents the abbreviation for solid-electrolyte interphase.

(B) One-pot plasma-electrochemical hybrid technology.

(C) Two-step plasma-electrochemical hybrid technology.

because the high dissociation energy of the N–N triple bond (941 kJ•mol^{-1}),[27–29] the limited N_2 solubility,[21,30,31] and the vigorous competition of the hydrogen evolution reaction (HER) in aqueous solutions.[9,20,26] Moreover, the current NH_3 production level (at a microgram scale) in the realm of electrocatalytic N_2RR presents a significant challenge for both qualitative and quantitative assessment, making it difficult to differentiate genuine activity from contamination.[6,32–34] This contamination may arise from NH_3 present in the air, human breath, ion-conducting membranes, nitrogen-containing compounds commonly found in the N_2 stream, the atmosphere, or even within the catalyst itself.[6,35–38] Therefore, researchers have gradually recognized that the potential impact of designing catalysts to activate N_2 molecules is exceedingly constrained. Developing more effective N_2 activation strategies may be the key to effectively enhancing the performance of electrochemical NH_3 synthesis.

The utilization of effective N_2 activation strategies, such as lithium (Li)/calcium (Ca)-mediated and plasma-assisted technologies, has ignited significant interest. These N_2 activation strategies can initially convert inert N_2 into more reactive nitrogen-containing species (such as $Li_xN_yH_z$, $Ca_xN_yH_z$, or NO_x^-), which are subsequently transformed to produce NH_3 (Figure 1). Specifically, the distinct property of Li lies in its ability to spontaneously cleave N_2, resulting in the formation of $Li_xN_yH_z$. This high-energy intermediate can subsequently react readily with a source of protons to generate product NH_3 (Figure 1A).[39] Aside from Li metal, Ca can effectively function as a mediator in the reduction of N_2 for electrochemical NH_3 synthesis (Figure 1A).[40] Another promising strategy for surmounting the limitations of electrochemical N_2RR involves the conversion of N_2 using plasma technology into a more reactive species, such as NO_x^-, which is then further transformed into NH_3 through electroreduction (Figures 1B and 1C).[4,41,42] By using appropriate catalyst materials, it is possible to selectively convert NO_x^- into NH_3 with an efficiency of approximately 90%.[2,3,28,43–46] Therefore, plasma-assisted electrochemical NH_3 synthesis technology has garnered increasing attention from researchers.[41,47,48] Despite the effective promotion of electrochemical NH_3 synthesis technology by these N_2 activation strategies, it still remains in its initial stage. Therefore, it is highly desirable to comprehensively summarize and analyze the research separately within the realms of Li/Ca-mediated and plasma-assisted electrochemical NH_3 synthesis. This approach would facilitate the categorization of intricate reaction pathways, pinpoint specific bottleneck issues, and ultimately offer insightful guidelines for artificial NH_3 electrosynthesis.

EFFECTIVE N_2 ACTIVATION STRATEGIES

Electrochemical NH_3 synthesis using N_2 as reaction raw material under ambient condition holds great significance in advancing human society and preserving Earth's ecosystem.[49] In the pursuit of developing effective electrochemical N_2RR processes, it is crucial to establish benchmarking protocols for the reaction and to implement a standardized suite of control experiments. These protocols are designed to systematically identify and subsequently remove the potential NH_3 contamination. Adhering to this protocol (Figure 2), no more NH_3 was produced than the background level, which is approximately 10 parts per billion, even when employing the most promising pure-metal catalysts like ruthenium, rhenium, rhodium, and others for this reaction in aqueous media.[6,37] Researchers have increasingly recognized that the potential impact of designing catalysts to activate N_2 molecules is severely limited. The development of more effective N_2 activation strategies may hold the key to significantly enhancing the performance of electrochemical NH_3 synthesis. Here, we present recently published studies indicating that the concentration of NH_3 production from electrochemical NH_3 synthesis using N_2 as reaction raw material, such as Li/Ca-mediated and plasma-assisted electrochemical NH_3 electrosynthesis, significantly exceeds ambient levels of NH_3 pollution. By thoroughly analyzing and comprehensively summarizing the currently effective strategies for N_2 activation, we aim to provide valuable insights and references for the field of

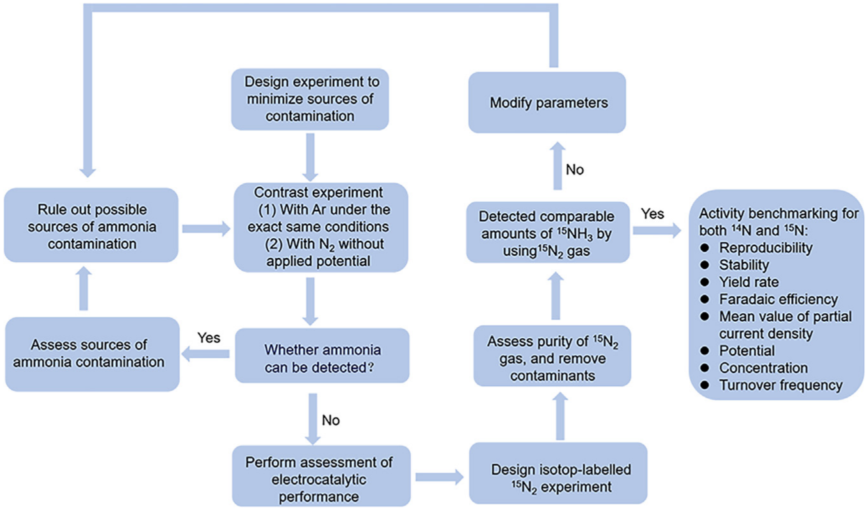

Figure 2. Proposed protocol for conducting rigorous N_2RR control experiments to exclude the possibility of NH_3 contamination

electrochemical NH_3 synthesis, utilizing N_2 as the primary reactant.

Li-mediated N_2RR

The investigation of Li-mediated electrochemical NH_3 synthesis can be traced back to 1930 when Fichter and colleagues conducted a systematic study on this process in an ethanol (EtOH) solution containing LiBr/LiCl (Figure 3).[50] 63 years later, Sakata's team refined the electrolyte composition by utilizing a polar aprotic solvent to prevent metallic Li from being consumed by alcohol. Moreover, they systematically explored the influence of electrode materials, Li salts, pressures, and proton donor on Li-mediated electrochemical NH_3 synthesis.[51] From 1995 to 2018, the progress in Li-mediated electrochemical NH_3 synthesis remained almost stagnant, with only a few studies on Li-mediated N_2RR for NH_3 synthesis through stepwise approach being reported.[52–54] In 2019, Chorkendorff and his team confirmed the effectiveness and reproducibility of Li-mediated N_2RR for electrochemical NH_3 synthesis through a rigorous protocol.[6] Since that time, researchers have increasingly focused on the Li-mediated N_2RR for electrochemical NH_3 production. Utilizing various strategies, such as adjustments to the deposition of metallic Li, solid-electrolyte interphase (SEI) engineering, electrolyte engineering, optimization of operating parameters, and design of reaction devices, to improve the performance of Li-mediated N_2RR for electrochemical NH_3 synthesis.

The deposition of metallic Li

The reaction of Li-mediated N_2RR for electrochemical NH_3 synthesis encompasses three primary steps (Figure 1A)[55–58]: Li^+ is reduced to metallic lithium, metallic lithium can spontaneously react with nitrogen to split the $N \equiv N$ triple bond to form a nitrogenous lithium compound, and this compound is subsequently converted into NH_3 by proton sources. The deposition of metallic Li on the working electrode (WE) is a prerequisite for the entire reaction. The rational design of WE materials can facilitate the uniform deposition of metallic Li on their surface, enabling it to react sufficiently with N_2, thereby promoting the formation of NH_3 molecules. Previous studies investigated several metals (such as iron, titanium, molybdenum, nickel, copper, palladium, and so on) as WE for Li-mediated N_2RR for electrochemical NH_3 synthesis, and as long as the metal does not alloy with Li, it can be used.[51] Currently, Mo[6,59] and Cu[1,55] electrodes have been previously identified as appropriate WE materials for Li-mediated NH_3 synthesis (Table 1). The WE with a greater specific surface area is more conducive to exposing more metallic Li surface, thereby significantly enhancing the NH_3 formation rates per geometric surface area.[62] In addition to adjusting the deposition area and uniformity of Li metal on the WE surface, the effective acceleration of the kinetics process of Li salt reduction to metallic Li may clearly enhance the performance of electrochemical NH_3 synthesis. The reduction of Li^+ represents an endothermic reaction and acts as the rate-determining step.[56] Optimizing the composition of the WE to accelerate the kinetics of Li^+ reduction to metallic Li may significantly enhance the performance of NH_3 synthesis. For instance, when Au-coated carbon paper (Au/CP) is employed as the WE, the presence of Au profoundly augments electron transfer kinetics, thereby promoting the catalysis of metallic Li formation, which considerably accelerates the spontaneous N_2RR.[56] Moreover, the interaction between the WE and plated Li could potentially influence the performance of Li-mediated N_2RR.[80] However, further study is still needed to investigate the interaction between them and its mechanism to improve the performance of Li-N_2RR. The performance of Li plating can also be improved by incorporating additives into the electrolyte. For instance, the mere inclusion of cesium salt into a traditional organic electrolyte substantially boosted the performance of Li plating.[53] This enhancement was predominantly attributed to alterations in the morphology of the Li deposit induced by cesium, resulting in the mitigation of unwanted side reactions between metallic Li and propylene carbonate. In the future, identifying abundant, low-cost, and non-toxic additives to promote the deposition of metallic Li may be an effective approach to enhance Li-mediated N_2RR for NH_3 electrosynthesis.

SEI engineering

The SEI layer (Figure 4) on the electrode surface is mainly comprised of electrolyte decomposition products, including a variety of inorganic and organic components.[63] The SEI serves as an electrically insulating passivation layer, effectively limiting additional electrolyte degradation.[64] It facilitates the conduction of Li ions and allows the passage of protons, nitrogen, and NH_3, significantly influencing the relative diffusion rates of these reactive species.[63,65] Therefore, the SEI layer plays a

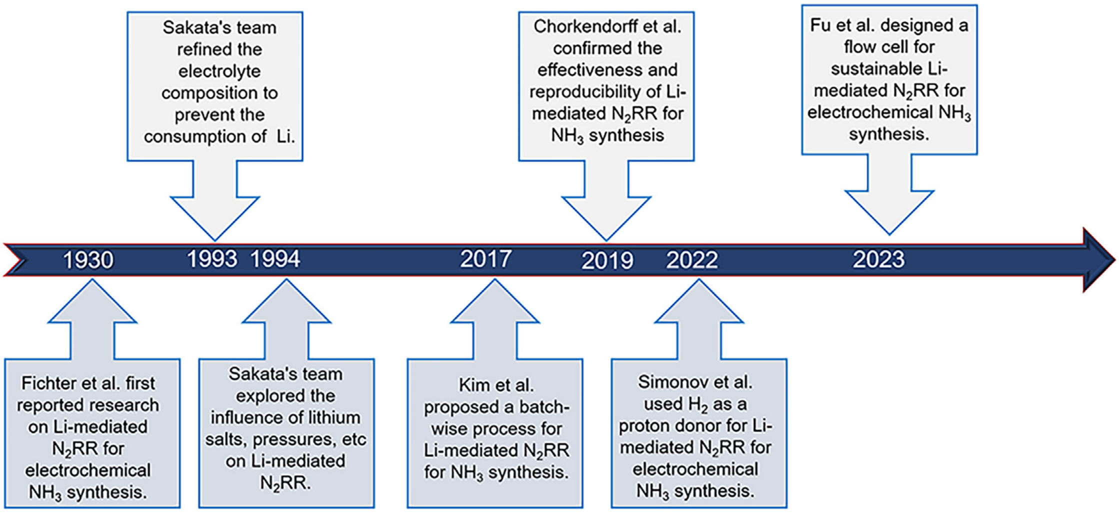

Figure 3. Development timeline of Li-mediated N_2RR
The development history of Li-mediated N_2RR for electrochemical NH_3 synthesis

critical role in influencing the activity of the Li-mediated electrochemical NH_3 synthesis process.[63,65,66,81] The microstructure and physicochemical properties of the SEI can be effectively modified by using appropriate Li salts[63] as well as the introduction of additives, including dimethyl sulfide (DMS)[67] and oxygen-containing species.[65,66] Specifically, fluorine-based electrolytes are advantageous for achieving a high FE_{NH3}.[63] This is because SEI layers enriched with LiF reduce the rate of Li^+ diffusion, resulting in fewer electrons being "lost" during Li deposition compared with those utilized in reducing N_2. Furthermore, LiF promotes uniform Li plating and establishes a more effective interface to suppress unwanted reactions between deposited Li and the electrolyte, as well as electrolyte decomposition. The above studies underscore the relationship between the efficacy of the Li-mediated N_2RR and the physicochemical properties of the SEI. However, further investigation is needed into the exact composition and functionality of the SEI layer in the Li-mediated N_2RR for electrochemical NH_3 synthesis process. Delving into the diffusion kinetics of reactive species, including Li^+, H^+, and N_2, within the SEI involves conducting controlled experiments that employ the single factor variable method to screen and identify key influencing factors. Additionally, *in situ* characterization techniques, such as cryogenic transmission electron microscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, and others, are utilized to further comprehend their behavior. This will be beneficial for providing guidance on the composition and microstructure construction of the SEI in the future. Apart from choosing the suitable Li salt, the concentration of the Li salt also notably affects the composition ratio of the SEI, thereby influencing the performance of Li-mediated N_2RR in synthesizing NH_3.[82]

In addition to screening suitable Li salts, introducing certain additives, including DMS[67] and oxygen-containing species,[65,66,68] can effectively modify the SEI. The physical structure of the SEI can be regulated by the introduction of DMS, changing it from a film to a net-like configuration.[67] This is primarily attributed to the significant impact of DMS addition on the deposition size and uniformity of metallic Li on the WE. Meanwhile, the incorporation of Li_2SO_4 and Li_2S into the SEI improved both ion conductivity and electron insulation properties, resulting in improved uniformity in Li plating and decreased electrolyte decomposition. Except for adding sulfides, the SEI can be modified by introducing small amounts of oxygen-containing species such as O_2[66] and water.[65,68] The inclusion of minute quantities of oxygen-containing species can serve as a beneficial SEI additive or modifier, significantly enhancing the apparent stability and FE_{NH3} of the Li-mediated N_2RR system.[66] This is mainly attributed to oxygen-containing species influencing the deposition of Li by modifying the SEI layer. The influence of oxygen-containing species addition on the structure and composition of SEI requires further investigation, which may be achieved through advanced techniques such as isotope labeling and *in situ* characterization. Given the high sensitivity of Li-mediated N_2RR to oxygen-containing species, future research should aim to accurately quantify the content of oxygen-containing species such as O_2 and water to provide precise guidance for subsequent studies. Moreover, the SEI membrane plays a crucial role in Li metal batteries, protecting the Li electrode and stabilizing battery performance.[83] Perhaps improvement strategies in the field of Li metal batteries,[84,85] such as introducing specific functional groups or catalysts, could be applicable to the Li-mediated N_2RR for NH_3 synthesis. This interdisciplinary inspiration may facilitate the sharing of experiences and technologies across different fields, advancing Li-mediated N_2RR technology.

Electrolyte engineering

The electrolyte used for Li-mediated N_2RR for electrochemical NH_3 synthesis typically consists of a Li-containing salt (such as $LiClO_4$,[51,53,57] $LiBF_4$,[55,60,69] Li trifluoromethanesulfonate [LiOTf],[68] and Li bis(trifluoromethanesulfonyl)imide ($LiNTf_2$)[64,70,86]), an

Table 1. Performance comparison of reported Li-mediated N_2RR for electrochemical NH_3 synthesis

Ref	Reaction devices	Cathode	Anode	Li source	Solvent	Proton donor	N_2 pressure	NH_3 yield rate	FE_{NH3} (%)	Current density	Test time
Suryanto et al.[1]	single-compartment cell	Cu disk	platinized titanium grid	$LiBF_4$	THF	H_2	20 bar	53 ± 1 nmol s^{-1} cm^{-2}	69 ± 1	−27.9 mA cm^{-2}	93 h
Lazouski et al.[55]	two-compartment cell	Cu foil	Pt foil	$LiBF_4$	THF	ethanol	ambient	(7.9 ± 1.6) × 10^{-9} mol cm^{-2} s^{-1}	18.5 ± 2.9	N/A	2 min
Tsuneto et al.[51]	single-compartment cell	Cu wire	Pt wire	$LiClO_4$	THF	ethanol	50 atm	N/A	42	−2.0 mA cm^{-2}	N/A
Lazouski et al.[60]	three-compartment cell	SSC	Pt/SSC	$LiBF_4$	THF	H_2	1.9 ± 0.2 kPa	8.7 ± 1.4 μmol cm^{-2}	35 ± 6	8.8 ± 1.4 mA cm^{-2}	1 h
Fu et al.[61]	three-chamber flow cell	SSC	PtAu/SSC	$LiBF_4$	THF	H_2	1 bar	N/A	61 ± 1	−6 mA cm^{-2}	350 min
Gao et al.[56]	single-compartment cell	Au/CP	Pt wire	$LiClO_4$	THF	ethanol	ambient	47.2 mg h^{-1} cm^{-2}	34 ± 4.5	N/A	100 min
Schwalbe et al.[57]	single-compartment cell	Mo rod	Pt wire	$LiClO_4$	THF	ethanol	ambient	N/A	∼10	−0.08 mA cm^{-2}	2 h
Andersen et al.[59]	single-compartment cell	Mo foil	Pt mesh	$LiClO_4$	THF	ethanol	10 bar	N/A	33.1 ± 1.3	−2 mA cm^{-2}	125 h
Li et al.[62]	single-compartment cell	HBTCu	Pt mesh	$LiClO_4$	THF	ethanol	20 bar	46.0 ± 6.8 nmol s^{-1} cm_{geo}^{-2}	13.3 ± 2.0	−100 mA cm^{-2}	N/A
Li et al.[63]	single-compartment cell	porous Cu/SS	Pt mesh	$LiBF_4$	THF	ethanol	20 bar	2.5 ± 0.1 nmol s^{-1} cm_{geo}^{-2}	71 ± 3	−1 A cm^{-2}	20 min
Du et al.[64]	single-compartment cell	Ni wire	Pt wire	$LiNTf_2$	THF	ethanol	15 bar	150 ± 20 nmol s^{-1} cm_{geo}^{-2}	98 ± 2	N/A	96 h
Spry et al.[65]	single-compartment cell	Mo foil	Pt mesh	$LiClO_4$	THF	ethanol	Ambient	N/A	27.9 ± 2.5	N/A	1.4 h
Li et al.[66]	single-compartment cell	Mo foil	Pt mesh	$LiClO_4$	THF	ethanol	20 bar	N/A	78 ± 1.3	4 mA cm^{-2}	2 h
Lim et al.[67]	single-compartment cell	Mo foil	Pt foil	$LiClO_4$	THF	ethanol	20 bar	390 ± 50 μg h^{-1} cm^{-2}	46 ± 6	–4 mA cm^{-2}	21 h
Cherepanov et al.[68]	single-compartment cell	Cu wire	Pt wire	LiOTf	THF	ethanol	2 bar	1 nmol s^{-1} cm^{-2}	60	N/A	60 h
Cai et al.[69]	three-compartment cell	SSC	Pt foil	$LiClO_4$	THF	ethanol	ambient	0.41 ± 0.038 μg s^{-1} cm^{-2}_{geo}	39.5 ± 1.7	20 mA cm^{-2}	500 s
Du et al.[70]	single-compartment cell	Ni wire	Pt wire	$LiNTf_2$	THF	i-PrOH	15 bar	430 nmol s^{-1} cm_{geo}^{-2}	96 ± 1	N/A	24 h
Li et al.[71]	three-chamber flow cell	SSC	PtAu/SSC	$LiBF_4$	diethylene glycol dimethyl ether	H_2	ambient	N/A	64 ± 1	N/A	300 h
Cai et al.[72]	three-compartment cell	SSC	Pt plate	$LiBF_4$	THF	ethanol	ambient	N/A	58.5 ± 6.1	–5 mA cm^{-2}	33 min
Fu et al.[73]	three-chamber flow cell	SSC	PtAu/SSC	$LiBF_4$	THF	H_2	ambient	N/A	72 ± 3	N/A	∼2.5 h
Lazouski et al.[74]	Two-compartment cell	SSC	Pt foil	$LiBF_4$	THF	1-butanol	Ambient	N/A	40.3 ± 3.9	25 mA cm^{-2}	N/A
Kani et al.[75]	single-compartment cell	Ni foam	Pt	$LiBF_4$	THF	1-butanol	20 bar	N/A	∼70	–100 mA cm^{-2}	N/A
Li et al.[76]	three-compartment cell	SSC	Pt sheet	$LiClO_4$	THF+ DEE	*n*-pentanol	ambient	19.92 ± 0.58 nmol s^{-1} cm_{geo}^{-2}	54.78 ± 1.6	–10 mA cm^{-2}	N/A
Krishnamurthy et al.[77]	two-compartment cell	stainless-steel foil	Pt foil	$LiBF_4$	THF	1-butanol	ambient	N/A	15.6	N/A	N/A
Cai et al.[78]	MEA	SSC	Pt/C	$LiBF_4$	PEO	H_2	N/A	2.41 ± 0.14 μmol h^{-1} cm_{geo}^{-2}	8.9 ± 1.7	N/A	20 h
McShane et al.[79]	single-compartment cell	Cu	Pt mesh	$LiClO_4$	THF	ethanol	ambient	N/A	20	N/A	N/A

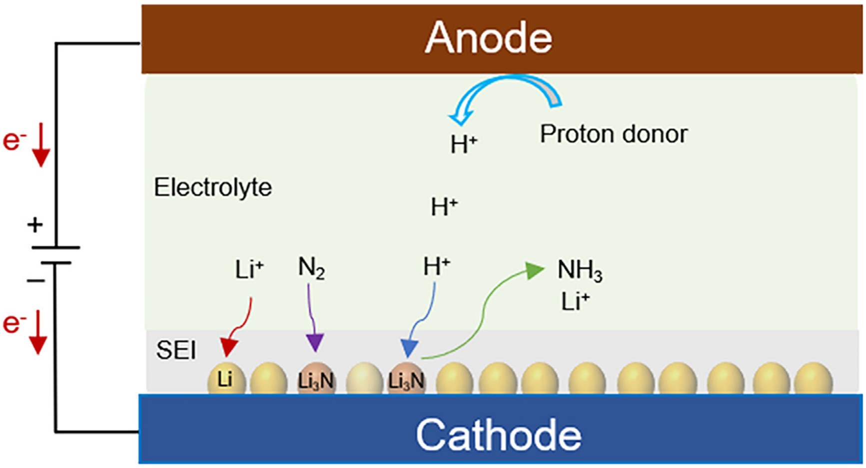

Figure 4. Reaction schematic of Li-mediated N_2RR for NH_3 synthesis

Li-mediated N_2RR for NH_3 synthesis is indeed a complex reaction comprising several crucial steps. Initially, lithium salts deposit as metallic lithium at the cathode. Subsequently, certain electrolyte decomposition products accumulate on the surface of the metallic lithium, forming a SEI layer. N_2 then diffuses through this SEI from the electrolyte, making contact with the metallic lithium, and triggers a reaction leading to the formation of $Li_xN_yH_z$. Concurrently, at the anode, a proton donor (such as EtOH, H_2, and so on) undergoes oxidation, releasing protons. These protons migrate toward the cathode, where they protonate the $Li_xN_yH_z$, ultimately resulting in the production of NH_3.

organic solvent (such as cyclic ether[51,71,80] and chain ether[71,72]), and a proton donor (such as EtOH,[51,55,57] phenol,[73] n-butanol,[74] and isopropanol[70]). Currently, $LiClO_4$ is commonly used as the Li source[75,82] (Table 1). The chosen Li salt should facilitate the uniform deposition of metallic Li on the cathode. Additionally, the Li salt has a significant impact on the structural modification of the SEI, as mentioned in the section on SEI engineering.

Organic solvent, as a crucial element in nonaqueous electrolytes, plays a vital role in determining electrochemical interface stability.[76] An ideal solvent for Li-mediated N_2RR should possess the following attributes[72]: exceptional solubility for Li salts, the capacity to provide sufficient conductivity, reliable stability to endure reactive metallic Li, and the capability to encourage the generation of a beneficial SEI layer for nitrogen reduction. These traits directly influence the performance of Li-mediated N_2RR, including factors such as NH_3 yield rate, FE_{NH3}, stability, and so on. To date, the majority of studies have utilized tetrahydrofuran (THF) as the solvent[55–57,59,69,72,77] (Table 1). However, THF hinders sustained NH_3 production in Li-mediated N_2RR due to issues related to polymerization and volatility. In addressing this concern, a chain-ether-based electrolyte has been developed to facilitate sustained and continuous NH_3 synthesis.[71] This enhancement is credited to the non-polymerizing properties and elevated boiling point (162°C) of the chain ether solvent, which allows for the creation of a dense SEI layer on the gas diffusion electrode (GDE). The aforementioned characteristics of the chain-ether-based electrolyte facilitate long-term continuous NH_3 synthesis, enabling it to operate for over 300 h.[71] Moreover, Cai et al. observed that linear ether-based electrolytes generally exhibit higher conductivity compared with cyclic ether-based ones, attributed to more thorough solvation of conductive ions.[72] SEI formation in linear ether-based electrolytes contains a higher proportion of inorganic and heavier organic compounds compared with cyclic ether-based ones. This feature enhances their resistance to EtOH corrosion and consequently enhances NH_3 entrapment in deposits. Their work provides valuable insights into the subsequent effects of solvents on SEI formation and morphological changes. To clearly distinguish the characteristics of each solvent, the above studies focus on single-solvent electrolytes.[71,72] However, optimizing the solvent by using two or even three different solvents may effectively enhance the stability of the reaction system while also improving the selectivity of NH_3 synthesis. For instance, due to its structural similarity and ready availability, diethyl ether was chosen as the co-chain solvent to be paired with THF.[76] The introduction of chain ethers improves the coordination between Li^+ and anions within the solvation shell. This reinforced solvation structure enhances the electrolyte's resistance to reduction, thus inhibiting excessive SEI generation at the reaction interface and reducing mass transfer impedance for active species. Moreover, such a ring-chain coupling electrolyte also enhances nitrogen diffusion kinetics, thereby facilitating the reaction between nitrogen and metallic Li. There is a need for more in-depth research on aspects such as solvent structure, the synergistic effects between different solvents, and the identification of more abundant, inexpensive, non-toxic, and stable solvents to further enhance the performance of Li-mediated N_2RR.

A proton donor is crucial for facilitating the protonation of reduced nitrogen species (e.g., Li nitride) to produce NH_3 while simultaneously enabling the recovery of Li ions.[51,77,87] The efficiency of NH_3 formation relies heavily on both the type and quantity of proton source introduced into the electrolysis medium.[51] When employing 2-propanol or EtOH as the proton supplier, a significant rise in both the concentration of produced NH_3 and the current efficiency is observed, in contrast to alternative proton sources like 2-methyl-2-propanol, 1-propanol, methanol, water, and acetic acid. This improvement is attributed to the predominance of the HER in the presence of highly protic compounds acting as proton donors. Subsequent studies mostly utilize EtOH as the proton donor for Li-mediated N_2RR in electrochemical NH_3 synthesis[55–57,59,68,69] (Table 1). Even minor alterations in the structure of the proton donor can have a considerable influence on the NH_3 yield. Moreover, the majority of active proton donors demonstrate a threshold behavior concerning their concentration, whereby the selectivity toward NH_3 experiences a sharp increase beyond a specific concentration of the

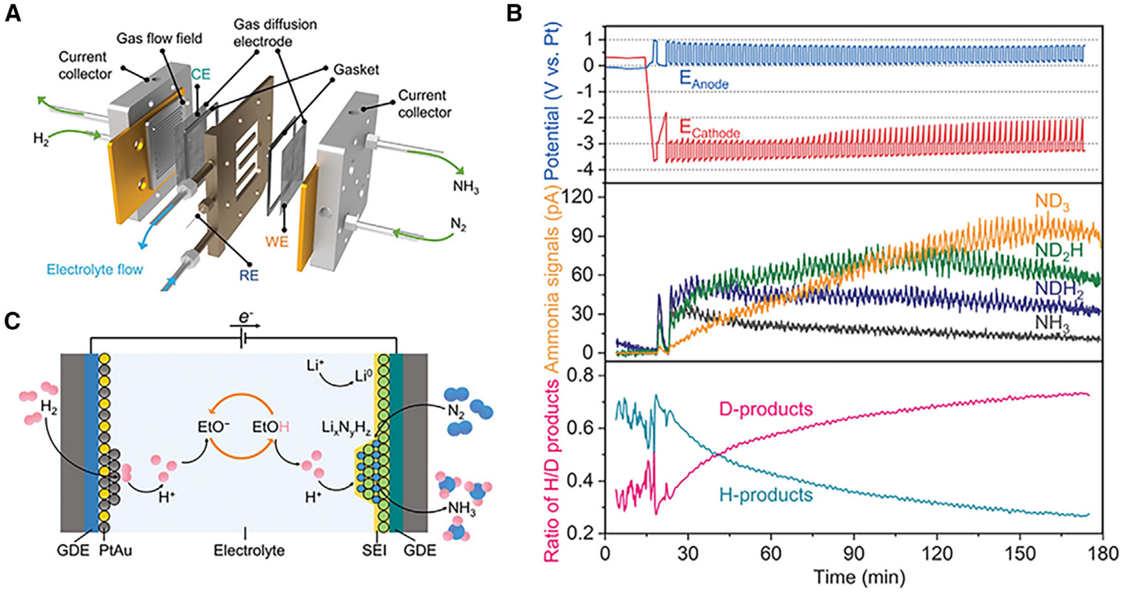

Figure 5. Continuous-flow electrosynthesis of NH_3 by nitrogen reduction and hydrogen oxidation

(A) Expanded view of the continuous-flow electrolyzer configurations for Li-mediated N_2RR.

(B) Operando mass spectrometry of cathodic NH_3 gas products during Li-mediated N_2RR by isotope-labeled deuterium.

(C) Schematic process of the Li-mediated N_2RR in a continuous-flow electrolyzer.

(A)–(C) reprinted with permission from Fu et al.[61] Copyright 2023, American Association for the Advancement of Science.

proton donor.[74] The proposed Kamlet-Taft parameters could be employed as descriptors to elucidate the activity of proton donors in NH_3 production.[77] Nevertheless, the recyclability of the suggested proton donors in this system remains unclear and necessitates further assessment, including their stability toward oxidation at the anode.

The aforementioned proton donors (such as EtOH, etc.) are sacrificed to supply protons for the protonation of Li nitride. However, to achieve scalability, the protons must originate from sustainable proton donors (such as H_2[1,60,61,73]). Upon thorough consideration, the hydrogen oxidation reaction (HOR) has emerged as a promising anode process in the Li-mediated N_2RR, with the ultimate goal of ensuring a sustainable supply of protons.[60] For instance, Lazouski et al. using a Li-mediated N_2RR paired with the HOR, where the H_2 originated from water-splitting. However, in their study, there is no evidence provided to demonstrate that the hydrogen present in product NH_3 originates from the HOR.

In 2023, a continuous-flow electrolyzer incorporating GDEs was designed for Li-mediated N_2RR, wherein Li-mediated N_2RR is paired with the HOR (Figure 5A)[61]. Operando mass spectrometry investigations, along with D_2 isotope analysis, suggest that the hydrogen present in product NH_3 derived from the HOR occurring at the anode (Figure 5B). Furthermore, the authors claimed that the protons produced during HOR are transported from the anode to the cathode by proton shuttles (such as $C_2H_5O^-$), facilitating the protonation of Li nitride to form NH_3 (Figure 5C). However, there is a lack of definitive evidence suggesting that the protons generated during the HOR are indeed transported from the anode to the cathode via proton shuttles.

In addition to $C_2H_5O^-$, a phosphonium salt also possesses the functionality of acting as proton shuttles.[1] Moreover, the phosphonium-based salts are capable of re-protonating the phosphonium cation through reaction with acetic acid, but this was not confirmed in the actual Li- mediated N_2RR process. Recently, Fu et al., to verify PhOH as a proton shuttle, substituted PhOH with Li phenoxide (PhOLi) to assess its activity in the Li-mediated N_2RR process.[73] In contrast to PhOH, the FE_{NH3} remained unaffected by the concentration of PhOLi, indicating that the concentration of protons available in the electrolyte was exclusively constrained by the current density of the HOR. Moreover, at a PhOLi concentration of 50 mM, a FE_{NH3} was attained, closely rivaling the performance achieved at the optimal concentration of PhOH. Therefore, they demonstrated that PhO^- functions as the proton shuttle, facilitating proton transfer during Li-N_2RR process. However, this also does not seem to rule out the possibility of protons generated by HOR being transferred individually from the anode to the cathode without relying on a shuttle agent at a constant potential. If the protons generated by HOR at the anode combine with shuttle agents (such as $C_2H_5O^-$ and PhO^-) to form C_2H_5OH or PhOH, then electrically neutral C_2H_5OH or PhOH is unlikely to transfer from the anode to the cathode under negative potential. Instead, protons with positive charges are more likely to move from the anode to the cathode under constant potential. Further confirmation is needed through *in situ* characterization and isotopic labeling techniques to ascertain whether protons

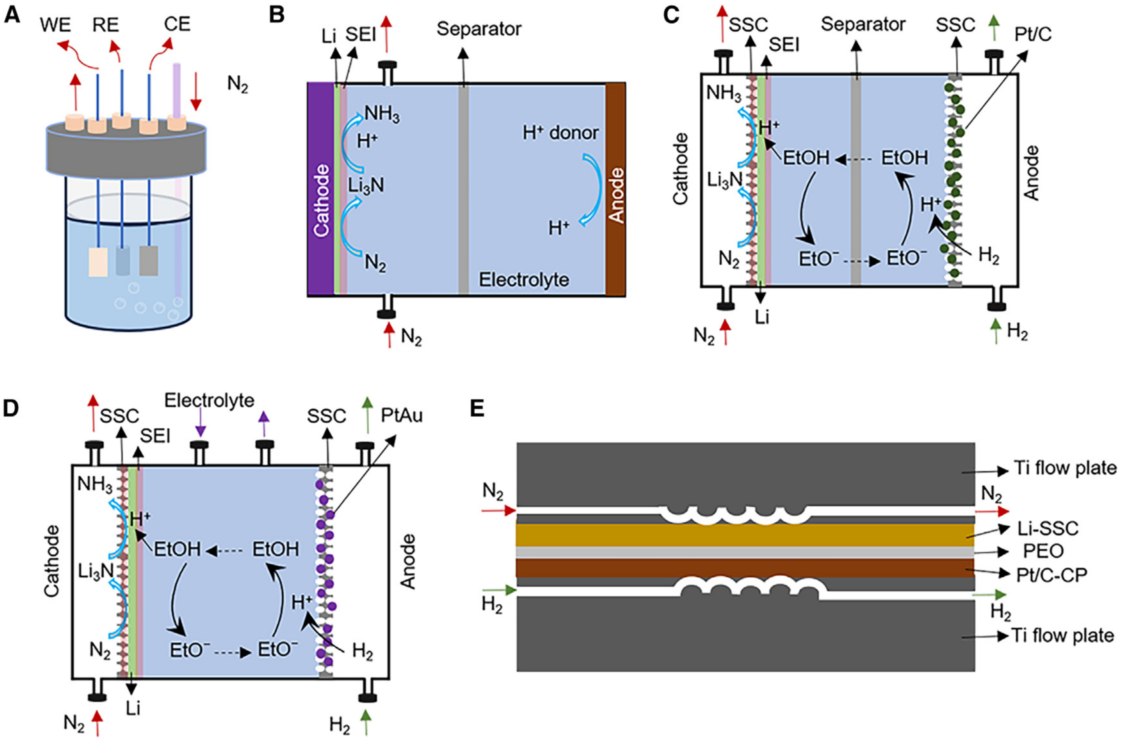

Figure 6. Diagram of an electrochemical reactor for Li-mediated N_2RR

(A) A single-compartment cell.

(B) Two-compartment electrochemical cell with a continuous N_2 purging setup.

(C) Three-compartment cell, utilizing SSC as GDE for the anode and cathode.

(D) Continuous-flow electrolyzer where an SSC-based GDE was placed between a gas flow field and an electrolyte chamber. This setup allowed gaseous reactants to be supplied directly to one side of the SSC electrode, while electrolyte was supplied to the other side.

(E) Structural diagram of MEA for Li-mediated N_2RR.

generated by HOR truly need to be transported to the cathode via proton shuttle.

Optimization of operating parameters

Some parameters, such as N_2 pressure[68,75,88] and electrode potential,[68,89] can have a significant influence on the activity of Li-mediated N_2RR for electrochemical NH_3 synthesis. The influence of N_2 pressure on Li-mediated N_2RR is primarily attributed to the fact that an elevated pressure enhances the solubility of N_2 in the electrolyte solution, leading to a higher concentration of dissolved N_2. Subsequently, this dissolved N_2 reacts with the electrodeposited Li to form $Li_xN_yH_z$, ensuring an ample supply of $Li_xN_yH_z$ due to the increased pressure.[75] However, once the N_2 pressure surpasses a certain threshold, while the production of $Li_xN_yH_z$ may increase, the rate of protonation may become constrained due to limitations in the mass transport of protons. This phenomenon appears to be consistent with the theoretical model proposed by Andersen and colleagues earlier.[59] Future research may be able to further improve the performance of Li-mediated N_2RR for NH_3 synthesis by balancing the solubility of N_2 in the electrolyte and the proton concentration. Moreover, it is essential to investigate whether N_2 pressure affects the structure and composition of the SEI, as well as the deposition behavior of Li on the WE.

Besides the impact of N_2 pressure on performance, optimizing electrode potential can also significantly improve the performance of Li-mediated N_2RR. Depositing Li on the WE needs to be done under the condition of applying a negative potential. However, continuous deposition of Li at around -3.0 V vs. standard reference electrode also leads to a significant decrease in the overall energy efficiency. Regarding this issue, Andersen et al. have devised a strategy to enhance the FE_{NH3} by cycling the applied potential between a regime that favors Li deposition and one that favors Li dissolution.[59] This approach results in a substantial improvement in both the system's stability and catalytic efficiency.[59,71] By optimizing the potential application method to regulate the energy loss issue caused by excessive Li deposition on the WE surface, it is expected to further significantly enhance the FE_{NH3}. Moreover, a stable electrochemical potential is also crucial for achieving long-term stable NH_3 production in Li-mediated N_2RR operation. Until now, researchers in this field have primarily employed Pt or Ag wires as reference electrode (RE).[1,64,66] However, these metals lack a clearly defined redox couple in this environment, and the equilibrium that determines their redox potential remains unascertained.[90] Consequently, there is an absence of independent regulation of each electrode's

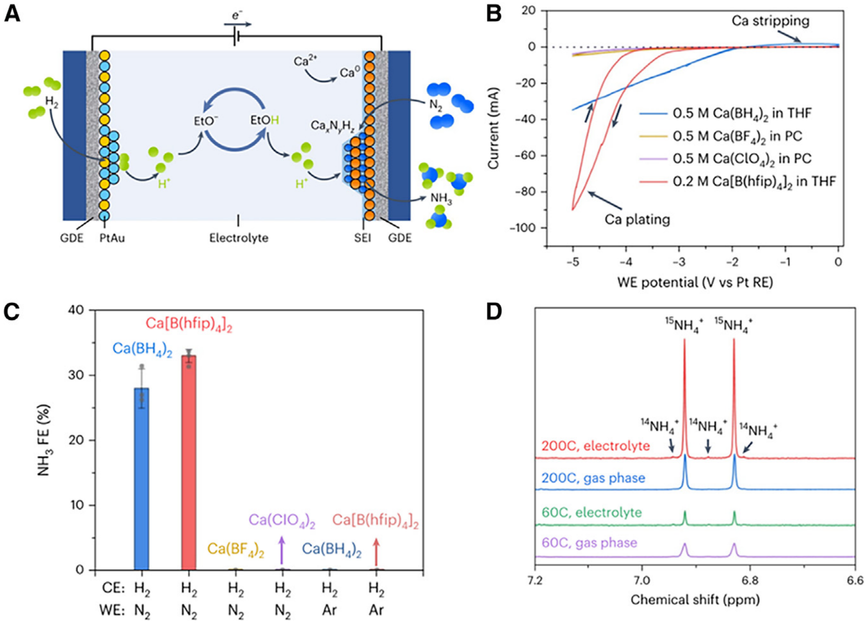

Figure 7. Ca-mediated N_2RR for electrochemical NH_3 synthesis

(A) Schematic of the Ca-mediated N_2RR in a flow cell.

(B) CV curves recorded between 0 and −5 V vs. Pt at a scan rate of 20 mV s^{-1} without iR correction (i, current; R, resistance).

(C) FE_{NH3} values of the different Ca salts under control experimental conditions.

(D) ^{15}N-isotope labeling experiments for Ca-mediated N_2RR.

(A)–(D) reprinted with permission from Fu et al.[40] Copyright 2024, Springer Nature.

potential, as opposed to the total cell voltage, which can obviously affect the reaction outcome.[89]

Designing electrochemical reactors

The rational design of reaction devices plays a crucial role in determining system efficiency, stability, and scalability.[88] Currently, the reaction devices used for Li-mediated N_2RR are mainly divided into batch reactors,[1,51,55] flow reactors,[60,61,71,73] membrane electrode assembly (MEA) configuration reactor.[78] Batch reactors, such as single-compartment cells[1,51,66] are frequently employed to assess the activity of Li-mediated N_2RR (Table 1). In a single-compartment cell, the WE, counter electrode (CE), and RE are all positioned within the one-compartment cell (Figure 6A).[88] Single-compartment cells are often utilized for initial exploration and mechanistic studies in the field of Li-mediated N_2RR owing to their uncomplicated configuration and ease of operation.[51] However, their primary challenge lies in the limited mass transfer of the reactants (such as N_2, H^+, and electrolyte ions) and the oxidation of the product NH_3.[88,91] Separating the cathode and anode regions may effectively prevent the diffusion of the product NH_3 to the anode, thereby avoiding the oxidation losses of product NH_3 and the generation of other byproducts. For instance, Lazouski et al. designed a two-compartment cell separated by a microporous polyethylene (Daramic 175) for Li-mediated N_2RR in electrochemical NH_3 synthesis (Figure 6B).[55] While the design of the two-compartment cell effectively prevents the diffusion of product NH_3 to the anode for oxidation, the limited mass transfer of the reactants still remains a challenge to address. Furthermore, the low solubility of gas reactants (such as N_2 and H_2) in the electrolyte is also a key limiting factor for performance.

To enhance the solubility of gas reactants, such as N_2 and H_2, within the electrolyte, a three-compartment cell incorporating a Daramic 175 separator (depicted in Figure 6C) was devised. This cell utilizes stainless-steel cloth (SSC) as a GDE for both the anode and cathode, ensuring optimal contact between the gas reactants and the electrode surface, thereby facilitating the dissolution process.[60] In their experiment, while the use of GDE increased the contact between gas reactants and the active sites on the electrode surface, the electrolyte was not flowing. Therefore, the slow mass transfer of reactive species in the electrolyte remained unresolved. To overcome the limitation of mass transfer for reactants within the electrolyte, a continuous-flow reactor, incorporating an SSC-based GDE positioned between a gas flow field and an electrolyte chamber, was devised for Li-mediated N_2RR (Figure 6D).[61] This setup facilitated the direct supply of gas reactants to one side of the SSC electrode, while the electrolyte was fed to the opposing side. This design enhanced the transfer of Li ions from the electrolyte into the SEI. Within the SEI, these ions undergo electrochemical reduction into metallic Li on the electrode, leading to a continuous reaction with N_2 to produce NH_3. Moreover, this design enhances the transport of gaseous species (such as N_2) in electrolytes by facilitating efficient gas-liquid contacting in the vicinity of the electrode, thereby improving the performance.[60] Recent studies have employed a similar continuous-flow setup for Li-mediated N_2RR, with all achieving FE_{NH3} exceeding 60%.[71,73] In their continuous-flow reactor, they opted not to utilize a separator between the cathode and anode. In such a scenario, the product NH_3 at the cathode may migrate to the anode and undergo oxidation, causing losses. Additionally, the hydrogen entering the anode may diffuse through the electrolyte to the cathode and react with Li, forming LiH, which could result in the consumption of metallic Li. To date, there is no corresponding research work to exclude the possibility of adverse outcomes that may arise from not using a separator as described above.

To address the mass transfer constraints, reliance on organic solvents, and substantial voltage loss, Cai et al. introduced an MEA setup consisting of a cathode made of Li-deposited SSC, a polymer electrolyte of Li-doped polyethylene oxide (PEO), and an anode composed of CP loaded with Pt/C catalyst (Figure 6E).[78] The MEA achieves a more streamlined setup by combining the electrode and electrolyte

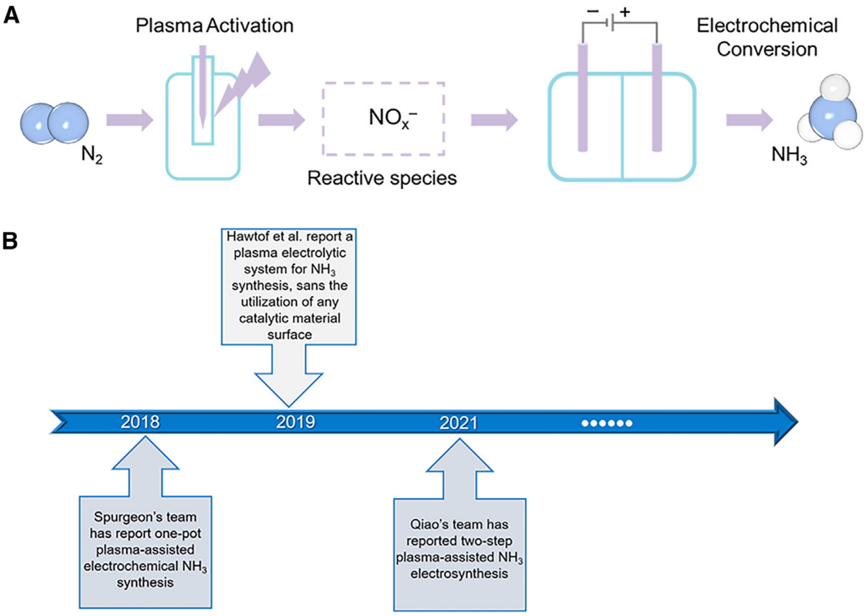

Figure 8. Plasma-assisted electrochemical NH_3 synthesis

(A) Schematic illustration of plasma-electrocatalysis system for NH_3 synthesis.

(B) The development history of plasma-assisted electrochemical NH_3 synthesis.

into a thin film. This advantageous feature helps reduce voltage drops due to its significantly shortened distance between the cathode and anode compared with traditional reactors. Meanwhile, substituting polymer electrolytes for organic liquid electrolytes may effectively address issues such as poor stability caused by organic solvent degradation, polymerization, and volatility. However, whether reactive species (such as Li^+ and H^+) exhibit more favorable mass transfer characteristics in the polymer electrolyte of the MEA compared with organic electrolytes needs further in-depth investigation from a kinetic perspective.

Ca-mediated N_2RR

Aside from Li metal, Fu et al. have recently reported that Ca can effectively function as a mediator in the electrochemical N_2RR for NH_3 synthesis (Figure 7A).[40] They discovered that electroplating and stripping of Ca could be obtained in electrolytes containing Ca borohydride ($Ca(BH_4)_2$) in THF (Figure 7B). They successfully conducted a Ca-mediated N_2RR using $Ca(B(hfip)_4)_2$ or $Ca(BH_4)_2$ dissolved in THF with the addition of EtOH (at 0.25 vol %) as a proton shuttle. In the case of $Ca(B(hfip)_4)_2$ and $Ca(BH_4)_2$ electrolytes, the FE_{NH3} values were 40 ± 2% and 28 ± 3%, respectively, under 1 bar pressure and room temperature (Figure 7C). Control experiment and quantitative $^{15}N_2$ isotope measurements provided confirmation that the synthesized NH_3 originated from the reduction of N_2 (Figures 7C and 7D). Ca boasts a copious reserve compared with Li, being the fifth most abundant element in the Earth's crust, with a prevalence of 4.7%.[40] These findings present a promising avenue for harnessing abundant materials in the electrochemical synthesis of NH_3. Moreover, this study serves as motivation for the further investigation of other cost-effective and readily available metal alternatives (such as Mg, Sr, Ba, and so on) to Li for facilitating the reduction of N_2 into NH_3. Since they belong to the same family as Ca, they exhibit certain similarities in terms of their physical and chemical properties. However, currently, research on Ca-mediated N_2RR for NH_3 synthesis is still in its early stages. The exploration of the SEI layer on the surface of Ca, particularly its stability, cation conductivity, and insulating characteristics, remains an uncharted territory. Furthermore, the selection and design of electrode materials, as well as the optimization and modification of electrolyte solutions, in the Ca-mediated N_2RR reaction system, require further in-depth research.

Plasma-assisted electrochemical NH_3 synthesis

Plasma technology is increasingly gaining attention as an effective approach for the activation of inert molecules, such as CO_2 and N_2.[92–94] Specifically, the supplied electrical energy will selectively raise the temperature of the electrons, owing to their relatively low mass. As a result, these energized electrons will come into collision with inert gas molecules, including CO_2 or N_2, leading to processes of excitation, ionization, and dissociation. The excited species, ions, and/or radicals will then promptly engage in further reactions, generating fresh reactive species.[93] Previous studies[92,95] have reported on the reaction mechanism of plasma-activated N_2, as follows:

$$N_2 + e^- \rightarrow e^- + N_2^* \quad \text{(Equation 1)}$$

$$O_2 + e^- \rightarrow e^- + O_2^* \quad \text{(Equation 2)}$$

$$e^- + N_2^* \rightarrow N^* + N^* \quad \text{(Equation 3)}$$

$$e^- + O_2^* \rightarrow O^* + O^* \quad \text{(Equation 4)}$$

$$N^* + O_2 \rightarrow NO + O^* \quad \text{(Equation 5)}$$

$$O^* + N_2 \rightarrow NO + N^* \quad \text{(Equation 6)}$$

$$NO + O^* \rightarrow NO_2 \quad \text{(Equation 7)}$$

$$NO + 1/2O_2 \rightarrow NO_2 \quad \text{(Equation 8)}$$

In light of the aforementioned factors, certain research endeavors have put forth a plasma-electrochemical hybrid technology as a promising approach for the efficient electrochemical synthesis of NH_3[41,47,48,96] (Figure 8A). Compared with the high-energy consumption of thermal plasmas, nonthermal plasmas with relatively lower energy consumption can efficiently convert inert N_2 molecules into active NO_x (such as NO and NO_2, and so on) in the presence of oxygen.[97,98] It is worth that the NO_x species are involved in the electroreduction in the forms of as NO_x^- (NO_2^-/NO_3^-) ions.[99] This is because, in the quantitative detection of NO_x, it is usually need to first use an alkaline medium to absorb and convert NO and NO_2 into NO_2^- and NO_3^-. This is based on their spontaneous reactions with OH^-, as follows:

$$NO + NO_2 + 2OH^- \rightarrow 2NO_2^- + H_2O \qquad \text{(Equation 9)}$$

$$2NO_2 + 2OH^- \rightarrow NO_2^- + NO_3^- + H_2O \qquad \text{(Equation 10)}$$

According to the operational procedure, plasma-assisted NH_3 electrosynthesis is primarily categorized into one-pot (Figure 1B) and two-step approaches (Figure 1C).[100]

One-pot approach

The plasma system is combined with the electroreduction system within a single reactor (Figure 1B), where NO_x^- formation occurs through the plasma process, and the generated NO_x^- is subsequently converted into NH_3 through electroreduction. For example, one-pot plasma-electrochemical hybrid technology was proposed for NH_3 production[48] (Figure 8B). This innovative approach begins with the application of non-thermal plasma-assisted technology to activate N_2 from the air, leading to the generation of NO_x^- in solution. The acquired NO_x^- is subsequently utilized in the electrocatalytic reduction process to yield NH_3.[41] The plasma-electrochemical hybrid technology for NH_3 production makes use of readily available resources, such as air and H_2O, as cost-effective reactants for NH_3 production. This presents a significant advantage for process scalability, as this NH_3 synthesis technology does not necessitate ultra-pure N_2. This stands in contrast to the HB process, where even the slightest contamination by oxygen can be detrimental to the catalyst. However, the residual O_2 feedstocks in the electrolyte may interfere with the electroreduction of NO_x^- to NH_3 when utilizing the one-pot approach.[100] This is because the reduction potential of O_2 is more positive than that of NO_x, leading to a decrease in energy efficiency. By optimizing reaction parameters, including adjusting the oxygen content within the reactants and incorporating an efficient NO_x^- separation technology from the O_2/NO_x^- mixture into the system, it could potentially mitigate or eradicate the interference of residual O_2 in the electrolyte during the electroreduction process of NO_x^- to NH_3.

Two-step process

To alleviate the interference of residual O_2 feedstocks in the electrolyte on the electroreduction of NO_x^-, Qiao's research group has reported a two-step process for N_2-to-NH_3 conversion, which involves sequentially integrating plasma-driven N_2 oxidation with the electrocatalytic reduction of nitrogen oxyanions to NH_3.[47] Firstly, they activate N_2 into NO_x^- using a non-thermal plasma technique, followed by purging with Ar gas into the electrolyte to eliminate any remaining dissolved O_2. Subsequently, they selectively convert NO_x^- into NH_3 through electrocatalytic reduction (Figure 1C). Similarly, Wu et al. presented a plasma-electrocatalysis approach in their research to extract NH_3 from the atmosphere.[101] During a stable operation spanning over 50 h at −0.33 V vs. reversible hydrogen electrode, they attained a nearly 100% FE for NH_3 production. Except as optimizing the reaction steps, experimental parameters such as the distance of spark discharge, discharge power, the O_2 volumetric content in the feeding gas, and gas flow rate also have a significant influence on plasma-assisted electrochemical NH_3 synthesis.[95,99] Currently, the reported plasma-electrochemical hybrid technology shows FE_{NH3} close to 100% for NH_3 electrosynthesis (Table 2). However, previous studies have indicated that even in the absence of an electrocatalyst, NH_3 can be generated during the plasma activation of N_2 in an aqueous solution.[92,96,97] This NH_3 may be formed from excited N_2 species dissociating water molecules at the Nafion membrane surface, rather than as a result of an electrochemical reaction.[48] Consequently, in utilizing the plasma-electrochemical hybrid technology to synthesize NH_3 and assess electrochemical NH_3 production performance (such as FE_{NH3}), the NH_3 formed during the N_2 activation process should be subtracted to accurately evaluate the selectivity of catalyst for the electroreduction of NO_x^- to NH_3. More importantly, when calculating the FE_{NH3}, the electrical energy loss in the plasma-activated N_2 process should also be considered as part of the total energy consumption. Previous studies indicated that the theoretical energy consumption for plasma-based N_2 fixation is significantly lower, exceeding a 2.5-fold reduction compared with the HB process.[47,92,93] The tech-economic model analysis[112] of target NH_3 production for plasma-assisted electrochemical NH_3 synthesis needs to be conducted to guide future research directions and industrial applications.

CHALLENGES AND PERSPECTIVE

While there have been notable advancements in the realm of electrochemical NH_3 synthesis by utilizing techniques like Li/Ca-mediated or plasma-assisted N_2 activation, several obstacles remain to be addressed. To advance the development in the realm of Li/Ca-mediated or plasma-assisted nitrogen-to-NH_3 conversion, we outline the challenges impeding the use of Li/Ca-mediated or plasma-assisted N_2RR for electrochemical NH_3 production and propose some perspectives.

Enhancing the performance of Li/Ca-mediated or plasma-assisted electrochemical NH_3 synthesis

Currently, Li/Ca-mediated electrochemical NH_3 synthesis is still in the initial exploration stage. More researchers will need to focus on the formation and stability of SEI, enhancing the stability of electrolytes, developing affordable and sustainable proton donors, optimizing the reactor designs, and studying the kinetics of various reactive species in the reaction system. Through future research establishing correlations between these processes, it will provide guidance for the development of efficient Li/Ca-mediated electrochemical NH_3 synthesis systems. Although plasma-assisted electrochemical NH_3 synthesis technology can effectively activate N_2 molecules, the reported concentration of synthesized NH_3 is still very low (Table 2). It may be possible to activate N_2 molecules by designing a more efficient and low-energy consumption plasma system. Furthermore, the development of highly efficient electrocatalysts is also of paramount importance in the implementation of this

Table 2. Performance comparison of reported plasma-assisted electrochemical NH_3 synthesis

Ref	Operation process	Type of plasma	Energy consumption	Electrocatalyst	NH_3 yield rate	FE_{NH3} (%)	Current density	Test time
Sun et al.[41]	two-step process	a custom plasma bubbler	253 kW h kg^{-1} NH_3	Cu nanowires	45 nmol s^{-1} cm^{-2}	~100	–45 mA cm^{-2}	8 h
Li et al.[47]	two-step process	nanosecond pulsed discharges	N/A	$Ni_3B@NiB_{2.74}$	198.3 μmol h^{-1} cm^{-2}	96.7	N/A	3 h
Kumari et al.[48]	one-pot approach	a custom-built plasma jet reactor	8.4 W	Pt/C	5.3×10^{-11} mmol s^{-1} cm^{-2}	N/A	N/A	~1 h
Wu et al.[101]	two-step process	rotating gliding arc plasma	51.8 MWh/t-NH_3	Co SAs/N-C	1.43 ± 0.05 mg_{NH3} cm^{-2} h^{-1}	98	N/A	50 h
Liang et al.[95]	two-step process	dielectric barrier discharge (DBD)	25.5 MJ/mol	$Co(OH)_2$	16.23 mg h^{-1}	82	N/A	8 h
Hawtof et al.[96]	one-pot approach	N/A	N/A	N/A	N/A	~100	–1 mA	45 min
Ren et al.[99]	two-step process	spark discharges	N/A	Cu nanoparticles	40 nmol s^{-1} cm^{-2}	~90	N/A	210 min
Cui et al.[102]	one-pot approach	N/A	N/A	$LaFeO_3$ and MOF-400	3.0 mg h^{-1} cm^{-2}	83.2	N/A	N/A
Liu et al.[103]	two-step process	spark discharges	18.36 MJ mol^{-1} NH_3	$Ni(OH)_x/Cu$	1.25 mmol h^{-1} cm^{-2}	92	–240 mA cm^{-2}	100 h
Meng et al.[104]	two-step process	jet-type plasma generator	11.18 kW h mol^{-1}	oxygen vacancy-rich Co_3O_4 NPs	39.60 mg h^{-1} cm^{-2}	96.08	376.48 mA cm^{-2}	20 h
Yang et al.[105]	two-step process	N/A	N/A	Cu^0 nanoparticles	4.5 mg cm^{-2} h^{-1}	84.7	N/A	20 cycles
Kang et al.[106]	two-step process	jet-type plasma	N/A	CoW/CF	N/A	N/A	N/A	120 min
Guo et al.[107]	one-pot approach	gliding arc discharge plasma	–N/A	$La_{1.5}Sr_{0.5}Ni_{0.5}Fe_{0.5}O_4$ perovskite oxide	N/A	80	N/A	100 h
Shen et al.[108]	one-pot approach	DBD	10.1 kWh mol NO_x^{-1}	Cu@hNCNC	2.44 mol h^{-1} g^{-1}	90.5	N/A	30 min
Gao et al.[109]	owo-step process	non-thermal plasma jet system	3.85 kWh mol NO_x^{-1}	$CuCo_2O_4/Ni$	6.1 mol h^{-1} g^{-1}	94.2	N/A	N/A
Meng et al.[110]	two-step process	N/A	N/A	$Co\text{-}_1/CNT@CP$	$10.2mg_{NH3}$ h^{-1} $mg_{Cat}{}^{-1}$	89	N/A	12 h
Shen et al.[111]	one-pot approach	DBD	N/A	$Ag_1/NOCNT$	~41.5 mol h^{-1} g_{Ag}	85.2	N/A	120 min

strategy.[104–111] At the same time, it is also possible to increase the amount of activated N_2 molecules per unit time by optimizing the contact area between reactants (such as N_2 and air) and the plasma system. Moreover, there is an urgent need to minimize the energy consumption of the reaction system through the optimization of the reaction conditions and parameters. For example, by optimizing the parameters of the plasma system, such as the plasma discharge distance, input voltage, frequency, duration, gas type and flow rate, as well as the liquid type (i.e., electrolyte/water) and its flow rate, it may effectively reduce the energy consumption of the reaction system.[41,99]

The development of more effective strategies for N_2 activation

Developing more effective N_2 activation strategies is crucial for advancing the electrochemical NH_3 synthesis. Metallic Ca exhibits a positive activation effect on N_2 molecules.[40] Inspired by this, other alkaline earth metals such as Mg, Sr, and Ba may also possess the ability to activate N_2 molecules. Since they belong to the same family as Ca, they share some similar physical and chemical properties. Moreover, previous literature has demonstrated that metal hydrides (such as lithium hydride,[113] alkaline earth metal hydrides,[114,115] and sodium hydride[116]) and aluminum[117] can also effectively mediate the activation of N_2 under certain conditions. Recently, Cao et al. demonstrated that lasers can effectively activate N_2 molecules,[118] so combining laser technology with electrochemical technology may effectively enhance the performance of electrochemical NH_3 synthesis. However, there have been no reports of experimental studies introducing laser-activated N_2 molecules in the electrochemical synthesis of NH_3. The electrocatalytic N_2 oxidation reaction (N_2OR) to form nitrogen oxides is thermodynamically more favorable than the electrocatalytic N_2RR process, especially under neutral/alkaline conditions.[119–123] Therefore, the electrocatalytic oxidation of N_2 to NO_x^- at a positive potential, followed by the reduction of the formed NO_x^- to NH_3 at a negative potential, has the potential to effectively improve the electrochemical NH_3 synthesis performance.

Broadening the realm of N_2 reduction products

The integration of C-sources, notably CO_2, into the standalone electrochemical N_2RR system facilitates the synthesis of organonitrogen compounds, such as urea, via C–N coupling reactions.[124–129] This strategy combines the benefits of standalone electrochemical N_2RR reduction with the potential to synthesize products of greater value and broaden the scope of available product categories.[130] Considering the significant achievements of Li/Ca-mediated or plasma-assisted N_2 activation strategies in electrochemical NH_3 synthesis, applying these N_2 activation strategies to the electrochemical co-reduction of N_2 and CO_2 for the synthesis of high-value organic nitrogen compounds offers great potential for improving N_2 reduction efficiency and expanding the range of high-value products. In addition to CO_2, it is worth considering the incorporation of other carbon-containing precursors such as CO, formic acid, methanol, etc., into the Li/Ca-mediated or plasma-assisted N_2RR system. These strategies hold the potential to produce a variety of high-value organonitrogen compounds, including urea, methylamine, ethylamine, acetaldoxime, and so on.

A profound comprehension of the reaction mechanism

Attaining a thorough understanding of the reaction pathways is imperative for advancing Li/Ca-mediated or plasma-assisted N_2RR systems. However, there are still certain aspects of the reaction pathways involved in the Li/Ca-mediated or plasma-assisted N_2RR to produce value-added NH_3 that remain unclear and require further exploration. Steinberg et al. exhibited that in the absence of EtOH, the SEI layer renders the Li metal inactive for nitrogen reduction by passivating it. However, the introduction of EtOH disrupts this passivation layer, facilitating sustained reactivity at the surface of the Li metal.[131] Given that the Li/Ca metal surface is shielded by an SEI layer, it is essential to comprehend the transport mechanisms of reactive species (such as N_2, H^+, NH_3, etc.) within the SEI. Utilizing techniques like isotope tracing, constructing theoretical models, and other techniques is crucial for improving performance. Moreover, researchers have utilized various methods to probe the reaction pathways of electrochemical conversion of N_2 to NH_3. These methods include theoretical calculations like density functional theory calculation,[132–134] molecular dynamics simulations,[22,25] and so on), and diverse *in situ* spectroscopic characterization methodologies (such as Fourier transform infrared spectroscopy,[22,25] Raman spectroscopy,[21] and so on) have been employed. However, the signals emanating from these pivotal active intermediates, captured through *in situ* spectroscopy, are frequently feeble and pose challenges in achieving distinct visibility. Herein, it is crucial for researchers to devote more efforts to the development of comprehensive *in situ* spectroscopy techniques and corresponding surface signal enhancement methods.[135] These advancements will enable effective detection of signals from key intermediates.

Challenges in large-scale application of Li/Ca-mediated and plasma-assisted NH_3 electrosynthesis

For the Li/Ca-mediated N_2RR, the energy consumption can be more than 10 times higher than that of the HB process, even with 100% FE_{NH3} and zero overpotentials.[136] Only electrosynthesis with a cell voltage below 0.38 V may have the potential to compete energetically with the HB process. Therefore, when evaluating the performance of Li/Ca-mediated N_2RR, energy efficiency should be reported as a key indicator. Another potential challenge arises from the competition for limited Li resources, exemplified by Li-based batteries,[40] the continuous requirement for adding Li salts during the reaction process limits its industrial applicability. The heightened demand for lithium across diverse industries may give rise to supply chain bottlenecks, causing possible disruptions in the production process.[91] Moreover, the issue of cost associated with Li resources is also a key consideration, necessitating a techno-economic analysis (TEA) to assess the Li-mediated N_2RR for NH_3 synthesis. The objective of this analysis is to ensure that the economic costs are kept below those of the traditional HB process, thereby providing significant guidance for the practical implementation of future technologies. On the other hand, developing abundant and inexpensive metals like Ca to mediate N_2RR for electrochemical NH_3 synthesis might be a promising direction. However, the economic feasibility of utilizing more abundant and cost-effective metals, such as Ca, warrants further exploration. Moreover, most HOR catalysts currently utilize precious metals.[40],[61],[71] Cost-effective and stable HOR electrocatalysts need to be designed and integrated into the continuous-flow reactor.[137] Currently, in the Li/Ca-mediated N_2RR system, the majority of research works have reported durability testing time is within a few tens of hours (Table 1), severely limiting its practical application. Perhaps enhancing its stability through SEI and electrolyte engineering could be effective.[71] Regarding plasma-assisted electrochemical NH_3 synthesis, compared with two-step approaches, the one-pot approach is more conducive to the continuous industrial synthesis of NH_3 demand. However, the interference issue of residual O_2 in the electrolyte on the electroreduction of NO_x^- to NH_3 urgently needs to be addressed. It may be possible to mitigate or eliminate the interference of residual O_2 in the electrolyte on the electroreduction of NO_x^- to NH_3 by optimizing reaction parameters, such as adjusting the oxygen content in the reactants and integrating efficient NO_x^- separation technology from the O_2/NO_x^- mixture into the system. In addition, the introduction of advanced MEA in the plasma-assisted electrochemical NH_3 synthesis reaction system can overcome the problem of slow mass transfer and significantly improve the NH_3 yield.[107]

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AUTHOR CONTRIBUTIONS

Conceptualization, M.J. and Z. Jin; writing – original draft, M.J., X.C., and F.C.; writing – review & editing, M.J., M.W., X. Luo, Y.H., C.W., and L.Z.; supervision, X. Li, X. Liao, Z. Jiang, and Z. Jin.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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