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Li⁺

N₂

Proton donor

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Protonation

Electrode

REVIEW ARTICLE
Leiduan Hao, Zhenyu Sun *et al.*
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REVIEW

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Lithium-mediated electrochemical dinitrogen reduction reaction

Muhammad Saqlain Iqbal,†[b] Yukun Ruan,†[a] Ramsha Iftikhar, [iD][c] Faiza Zahid Khan,[d] Weixiang Li,[a] Leiduan Hao,*[a] Alex W. Robertson, [iD][e] Gianluca Percoco[f] and Zhenyu Sun [iD]*[a]

The Haber–Bosch process is the dominant approach for NH_3 production today, but the process has to be maintained at energy-intensive high temperatures and pressures. Li-mediated electrocatalytic dinitrogen reduction reaction (eN_2RR) could instead enable sustainable and green NH_3 production at ambient conditions. Lithium mediators realize the synthesis of NH_3 *via* the formation of Li_3N, and thus lower the energy required for the direct cleavage of N_2. There has now been a surge of interest in devising approaches to optimize the NH_3 yield rate and faradaic efficiency of the eN_2RR process by employing different catalysts as well as electrolytes. This review discusses the recent advances in the field of the Li-mediated eN_2RR along with the latest insights into the proposed catalytic mechanisms. Moreover, it also highlights the state-of-the-art reported electrocatalysts and electrolytes that have revolutionized the field of the Li-mediated eN_2RR. In addition to the above, our review provides a critical overview of certain limitations and a future prospectus that will provide a way forward to explore this area.

1 Introduction

Ammonia (NH_3) is a crucial chemical fertilizer for crop development that has supported the rapid increase in our global population. It has high hydrogen content, a large gravimetric energy density comparable to methanol, and is easy to liquefy for storage and transit, among other beneficial properties. The global production of NH_3 is expected to increase to about 290 million tons by 2030. In 2022, the global ammonia market was valued at USD 78.26 billion and is expected to reach USD 129.63 billion by 2030, with a projected compound annual growth rate (CAGR) of 6.51% during the forecast period from 2022 to 2030 (Fig. 1).[2] Table 1 provides an overview of the global NH_3 market from

2021 to 2030, including the market size in 2022 and the projected market size by 2030, with a forecasted CAGR of 6.51% from 2022 to 2030. The report studied different global regions, and found that the Asia-Pacific region is the largest market for ammonia products, followed by North America. The report also accounted for different segments of the ammonia market, including the product form and application.[2] The large-scale centralized Haber–Bosch (HB) process is the current favored industrial technique for realizing this sizeable international demand and delivering the mass production of NH_3. In the HB process N_2 reacts with H_2 ($N_2 + 3H_2 \rightarrow 2NH_3$) on an Fe-based catalyst, and is typically operated at high temperatures (400–500 °C) and high pressure (150–250 bar), resulting in high energy use and cost.[1] Due to the combination of high and growing demand for NH_3, and the high temperature requirements of the HB process, it is urgent to develop new catalysts and procedures for NH_3 synthesis that can reduce the energy required and the carbon footprint.

In order to find alternatives to the energy-intensive H–B process, scientists have searched for catalysts that might avoid the direct cleavage of the dinitrogen triple bond and that can produce NH_3 when powered by electricity.[3,4] The reduction of dinitrogen (N_2) by electrocatalysis has been studied extensively over the past few years using a variety of electrocatalysts. However, it has been revealed that even the best reported catalysts could only use 1% of the electrons to

[a] *State Key Laboratory of Organic–Inorganic Composites, College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China. E-mail: haold@buct.edu.cn, sunzy@mail.buct.edu.cn*

[b] *Department of Electrical and Information Engineering, Polytechnic University of Bari, Via E. Orabona 4, 70125 Bari, Italy*

[c] *School of Chemistry, University of New South Wales, 2033 Sydney, Australia*

[d] *Institute of Chemistry, Rheinische Friedrich-Wilhelms-Universität Bonn, 53113 Bonn, Germany*

[e] *Department of Physics, University of Warwick, Coventry CV4 7AL, UK*

[f] *Department of Mechanics, Mathematics and Management, Polytechnic University of Bari, Via E. Orabona 4, 70125 Bari, Italy*

† These authors contributed equally to this work.

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Review

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produce NH_3 in aqueous solutions because of the competitive hydrogen evolution reaction (HER). Recently, the lithium-mediated N_2 reduction reaction (Li-eN_2RR) has been found to be a promising route for electrochemical NH_3 synthesis at ambient conditions. The Li-eN_2RR was first attempted in an alcoholic solution of lithium halide in 1930 by Fichter and coworkers.[5] Tsuneto et al. further improved the faradaic efficiency (FE) by employing an electrolyte with tetrahydrofuran (THF) mixed with ethanol (EtOH) and increasing the N_2 pressure.[6] Lee et al.[7] reported that lithium used along with the electrolyte solution acted as a mediator, as the Li^+ ions after reduction allow for the conversion of N_2 gas into Li_3N. Moreover, this Li-mediated system can be modified with superhydrophobic metal organic frameworks (MOFs) to suppress the competing HER and enhance the eN_2-RR. The greatest advantage of Li-eN_2RR is that the active Li and inert proton source can promote N_2 activation and hinder H_2 evolution, respectively. However, a majority of Li-eN_2RR studies have the limitation of using a sacrificial solvent as a proton donor, prohibiting the scale up synthesis in batch cells.

2 Li-mediated eN_2RR

For NH_3 synthesis, a wide range of different catalytic materials and systems have been investigated. It has been suggested that Li in particular holds the potential of producing NH_3 at ambient pressure. The rate-determining step in the synthesis of NH_3 is often the adsorption and activation of N_2.[8–14] Li has an extraordinarily low work

Muhammad Saqlain Iqbal has earned his Master's degree from COMSATs University Islamabad (2021) and is currently pursuing his Ph.D. from Politecnico di Bari. He is working under the supervision of the distinguished Professor Gianluca Percoco, a renowned expert in the field of materials science and engineering.Mr. Iqbal has a keen interest in the development of 3D printed batteries, with a particular focus on lithium and solid-state batteries. His research is motivated to improve energy storage, he explores innovative techniques and materials to enhance battery performance, including energy density, power density, and cycle life while ensuring efficiency, affordability, and sustainability.

Muhammad Saqlain Iqbal

Yukun Ruan received his BS degree in Beijing University of Chemical Technology in 2020. He is pursuing his MS degree in Beijing University of Chemical Technology under the supervision of Prof. Zhenyu Sun. His current research interest is N_2 reduction reaction.

Yukun Ruan

Dr. Leiduan Hao received her PhD in materials science at Institute of Chemistry, Chinese Academy of Sciences in 2016. From 2017 to 2021, she worked at Washington State University as a postdoctoral research associate to study the design of novel porous materials for green catalysis. Then she joined the Sun group at Beijing University of Chemical Technology (China) as an associate professor. Currently, her research mainly focuses on CO_2 and N_2 conversion.

Leiduan Hao

Zhenyu Sun completed his PhD at the Institute of Chemistry Chinese Academy of Sciences in 2006. He carried out postdoctoral research at Trinity College Dublin (Ireland, 2006–2008), Ruhr University, Bochum (Germany, 2011–2014), and the University of Oxford (UK, 2014–2015). He is currently a full professor at the College of Chemical Engineering at Beijing University of Chemical Technology (China). He was awarded a Humboldt Research Fellowship for Experienced Researchers (Germany). His current research focuses on energy conversion reactions including N_2 reduction reaction and CO_2 reduction reaction.

Zhenyu Sun

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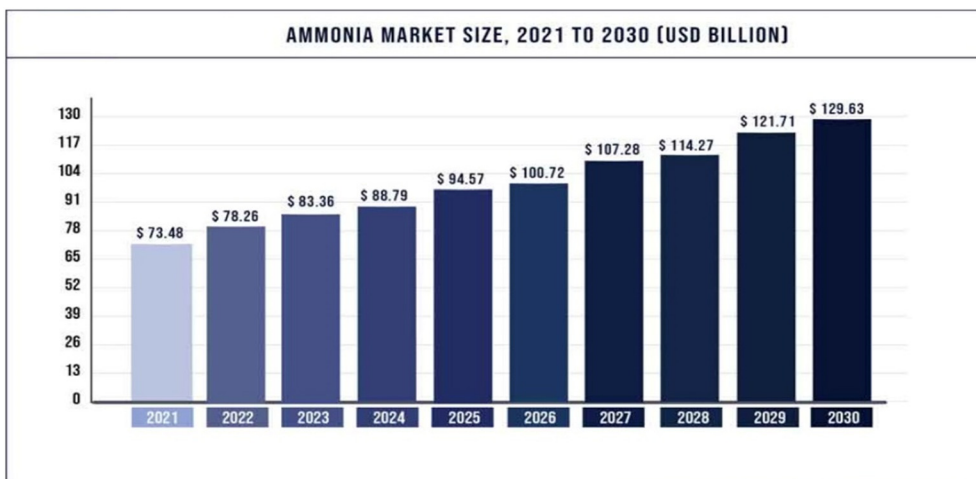
Fig. 1 Projected global ammonia demand growth from 2021 to 2030.[2] Copyright 2023, Precedence Research.

Table 1 Overview of global ammonia market (2021–2030)[2]

Report coverage	Detail
Market size in 2022	USD 78.26 billion
Market size by 2030	USD 129.63 billion
Growth rate from 2022 to 2030	CAGR of 6.51%
Largest market	Asia-Pacific
Second largest market	North America
Base year	2021
Forecast period	2022 to 2030
Segments covered	• By product form
	• By application
Regions covered	• North America
	• Europe
	•Asia-Pacific
	• Latin America
	•Middle East & Africa

function and high reactivity for this process. Li can therefore be used to break the strong N≡N triple bond and fix N_2 as Li_3N, which subsequently converts to NH_3. Additionally, Li^+ ions have been shown to disrupt the water molecule, which lowers the rate of water splitting.[15] According to the study by McEnaney et al., Li may undergo electro-cycling to create NH_3 in a molten electrolyte at atmospheric pressure with an extremely high NH_3 FE of 88.5%.[1] A larger applied energy (potential) is required for the electrodeposition of Li at the cathode, which stabilizes N_2 in the form of Li_3N. This study further demonstrated that Li^0 can facilitate the electrochemical reduction of N_2 to NH_3. An NH_3 FE of 57.7% was attained with an Fe electrode using 0.2 M $LiClO_4$ in THF as the electrolyte and 0.18 M ethanol as the proton source while operating under high pressure (50 atm) of N_2.[6] Li^+ ions were found to inhibit the competitive HER on the surface of Pt while promoting the HER on Au.[16] As opposed to this study, Suo et al. instead attributed the suppression of the HER to the decomposition of the TFSI anion in the formed lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) salt. Due to the electrodes' weak selectivity for N_2 reduction,

ambient eN_2RR in an aqueous electrolyte remains a difficult task.[17,18] Since the standard potential needed for the eN_2RR is close to that of the HER, the N_2 reduction reaction in aqueous electrolytes is usually accompanied by the HER.[19] Therefore, approaches that either hamper the HER by changing to an electrocatalyst with weak H^+ adsorption, or by changing the electrolyte (for instance, to non-aqueous systems) are required to be developed.[20]

The Li-mediated eN_2RR for NH_3 synthesis driven by renewably generated electricity has garnered a lot of recent scientific interest.[21–23] Due to competition with HER and the high stability of the N≡N triple bond, the key challenge is to significantly improve efficiency and the rate of NH_3 generation. Ethanol is frequently applied as the local proton source, which however may deteriorate in the reaction environment. In a THF solution containing 1% ethanol, Lazouski et al. attained an NH_3 production rate of 7.9×10^{-9} mol cm^{-2} $s^{-1}$and a maximum NH_3 FE of 18.5% via the Li-mediated eN_2RR.[11] A more encouraging result was achieved in a phosphonium salt in place of ethanol, with an NH_3 production rate approaching approximately 6.0×10^{-8} mol cm^{-2} s^{-1} and an NH_3 FE of roughly 69% for 20 h under 0.05 MPa H_2 and 1.95 MPa N_2.[24]

In order to alleviate the unwanted HER and achieve an initial current efficiency of 88.5%, electrochemical lithium cycling was proposed as an effective method for manufacturing NH_3, which requires independent steps of LiOH electrolysis, direct nitridation of Li, and release of NH_3 from Li_3N. However, this multi-step process is difficult to operate, and the step that involves LiOH electrolysis for Li regeneration is particularly challenging. Jain et al. synthesized NH_3 through hydrolysis of Li_3N at 80 °C in a closed cycle and Li-metal was reproduced at the end of the reaction.[25] In addition to using Li–Sn alloys for breaking the N≡N triple bond to produce Li_3N, which was subsequently used for NH_3 synthesis below 500 °C under 0.5 MPa, Yamaguchi et al. also reported the use of pure Li to fix N_2. The same research group has recently established a three-

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step pseudo-catalytic method for the production of NH_3 below 400 °C under 0.1 MPa by reacting solid Li–Sn alloy with N_2 and H_2 consecutively, followed by regeneration of the initial alloy in a chemical loop. The maximum molar proportion of NH_3 is equivalent to one-tenth of the composition at thermodynamic equilibrium. The Li–Sn catalyst system's stability, however, was not the subject of a thorough study. Since the solid Li–Sn alloy, as well as the produced Li_3N and LiH, are sensitive to O_2 and H_2O, its deactivation is a significant problem.[26] Additionally, the scaling relationship between the activation barrier for N_2 dissociation and the N_2-binding energy limits Li, much like it does for transition metals (TMs). In Li_3N, nitrogen is strongly bound to lithium. Li_3N can react with H_2 to produce a mixture of $LiNH_2$, Li_2NH, and LiH at relatively low temperatures, but it is difficult to further hydrogenate $LiNH_2$ and Li_2NH to produce LiH and NH_3 for both thermodynamic and kinetic reasons.

The question of how to overcome Li's scaling relation is an enormous challenge but has been rarely studied. One method discussed by McEnaney calls for separate N_2 fixation stages in the absence of a proton source and the subsequent exothermic release of NH_3 by exposing the solid Li_3N to H_2O rather than H_2.[1] While TMs offer insights into catalyst design, further work has been reported on circumventing the scaling relation imposed on TMs. For instance, introducing alkali metals or oxides as promoters resulted in an increased NH_3 synthesis rate and mitigated the well-known pure-TM scaling relation by creating local electrical fields.[27,28] Wang et al. also found that employing LiH to mediate N_2 transfer and NH_3 production broke the scaling relation on TMs. Instead of using Li's high activity to fix N_2, LiH's negatively charged hydrogen ions can serve as potent reducing agents when reacting with N_2 atoms that have been activated by the right solid-state transition metal to create $LiNH_2$. Then, H_2 and $LiNH_2$ interact to form NH_3 and regenerate LiH. The LiH and TM work together to overcome the scaling relation on TMs and enable an energy-efficient NH_3 production.[29] Additionally, NH_3 synthesis was demonstrated to be mediated by alkali or alkaline earth metal hydride/imide pairings (e.g., LiH/Li_2NH, $BaH_2/BaNH$) with an ability to disrupt the scaling relation comparable to Fe, Co, and Ni in the N_2 fixation stage.[30]

The most commonly used aqueous electrolytes in NH_3 synthesis include alkaline electrolytes (KOH and $KHCO_3$),[31,32] acidic electrolytes (HCl and H_2SO_4), and $LiClO_4$- and Li_2SO_4-based neutral electrolytes.[3,33] These Li-mediated aqueous electrolytes have been identified as promising potential electrolytes due to the improved interaction between Li^+ and N_2.[34,35] Because large cations include core electrons, the stabilizing impact of the electrostatic and induction effects on the total energy is constrained, leading to the conclusion that Li^+ is more effective than Na^+ for N_2 adsorption.[36] An order of $Ca^{2+} > Na^+ > Li^+$ was proposed, in which the adsorption energies for N_2 decrease.[35] Chen et al. recently employed the Li^+ incorporation approach, which not only

resulted in slow kinetics and a higher energy barrier for the generation of H_2, but also provided suitable eN_2RR sites. $LiClO_4$ has been demonstrated to deliver better NH_3 FE and yield rate compared to $NaClO_4$ and $KClO_4$ electrolytes because of the improved interactions between Li^+ and N_2.[32]

The performance of eN_2RR is dependent on the electrolysis current and the freshness of lithium deposits. A higher current results in fresher lithium deposits, which exposes more active lithium to nitrogen and enhances eN_2-RR. In contrast, a low current leads to passivation of lithium, deteriorating its reactivity towards eN_2RR. Strategies such as retarding passivation or creating a protective layer may be employed to improve N_2RR efficiency. One approach is to use electrolyte additives to engineer the solid-electrolyte interphase to create a protective layer that is impervious to electrolyte but penetrable by nitrogen and proton source.[37]

Although there are still obstacles to the practical viability of lithium-mediated ammonia synthesis, such as the need for a replacement for the sacrificial proton source, a promising alternative to N_2 pressure for independently increasing the mass transport of N_2 relative to protons could be the use of gas diffusion electrodes. According to the model by Andersen,[38] a higher rate at a similar FE could be achieved if the transfer rate of N_2 to the surface were to be increased proportionally. This model highlights the unique features of the lithium-mediated process. Lithium has a strong binding affinity for nitrogen and a low barrier for N_2 dissociation,[1] similar to early transition metals and nitrides.[19,39] However, only lithium has been shown to develop a protective solid electrolyte interphase (SEI) layer. This passivating layer plays a crucial role in determining the system's function and catalytic performance.

2.1 Reaction mechanisms of Li-mediated N_2 reduction

2.1.1 Chemical N_2 splitting and chemical protonation. Tsuneto et al.[6] first proposed a Li-mediated route, which involves three processes (eqn (1)): (1) Li^+ ions are reduced to metallic Li; (2) metallic Li reacts with N_2 and breaks the robust triple bond of N_2 (through a dissociative mechanism) and forms Li_3N; (3) Li_3N reacts with an aprotic additive such as EtOH and forms NH_3 and Li^+ ions that dissolve back into solution.

$$Li^+ \xrightarrow{e^-} Li \xrightarrow{e^-} Li_3N \xrightarrow{3EtOH} NH_3 + 3EtOLi \qquad (1)$$

There are two major steps involved for N_2 reduction to synthesize NH_3, i.e., the activation of N_2 followed by its protonation. A spontaneous chemical interaction takes place between split N_2 and electrodeposited Li to generate lithium nitride in the chemical N_2 splitting and chemical protonation model (Fig. 2). This suggests that interactions between N_2 and the electrons of metallic Li take place. Additionally, the release of Li^+ into the solution occurs concurrently with the chemical protonation of activated lithium nitride to create NH_3. Activation of N_2 is mainly affected by the different characteristics of Li deposition. As long as there is still active Li
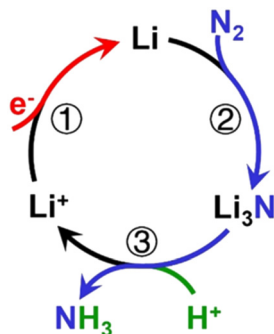
Fig. 2 Mechanism of catalytic recycling of lithium intermediates. Reproduced with permission.[23] Copyright 2021, Wiley-VCH.

on the electrode, N_2 reduction and NH_3 synthesis can continue even after the current is switched off.[6,11,23] In this mechanism, N_2 is activated and protonated mainly through chemical reactions. The only electrochemical step in this route is Li deposition. The rate-determining step was claimed to be the reaction of Li with N_2.

Likewise, Cai *et al.* provided a detailed mechanisms of eN_2RR where the majority (>99%) of the electrochemical reaction is Li deposition, while the subsequent chemical reactions of N_2 activation and protonation are primarily chemical in nature (Fig. 3). They further demonstrated that another significant competing reaction is the interaction between Li deposits and THF. Substantial reactivity for N_2 activation is only present in recently deposited Li. After being deactivated by THF, the newly deposited Li gradually loses its ability to reduce N_2. Therefore, protecting "fresh" metallic Li is essential to enhancing N_2 reduction performance. This "fresh Li" technique also explains how performance is influenced by current density. A high level of NH_3 FE and NH_3 yield rate were obtained through this mechanism.[40]

2.1.2 N_2 activation and pronation through an associative mechanism. High energy electrons are also easily accessible at the Li-plating potential and may theoretically electrochemically convert dissolved N_2 and protons into NH_3. A Li layer might support coupled proton–electron transfers in a heterogeneous catalytic cycle. As protons and electrons are transferred in tandem, metallic Li^+ should not dissolve. N_2 activation and protonation can be controlled by altering the electrode surface or the applied potential when N_2 activation and protonation are both electrochemical processes.[40,41]

Schwalbe and coworkers[41] combined experiment with density functional theory (DFT) modeling and revealed that plated Li could react with N_2 and ethanol to form Li_3N and LiH, and that the active centers on the surfaces of Li, Li_3N, and LiH are the long-bridge site, the nitrogen vacancy, and the hydrogen vacancy, respectively.[41] Based on DFT calculations, they inferred that $Li-eN_2RR$ could follow a heterogeneous mechanism (Fig. 3a). N_2 is first adsorbed onto the solid surface composed of Li, Li_3N, and LiH. It is then activated on the surface and the activated N_2 is protonated stepwise to form NH_3. They also showed that Li_3N is kinetically stable but not thermodynamically stable. There could therefore be a bottleneck in the diffusion of vacancies from the bulk to the surface, which limits the decomposition of Li_3N to Li and NH_3. The authors proposed plausible pathways on the surfaces of Li, Li_3N, and LiH, depicted in Fig. 3b. The necessary limiting potentials on the corresponding surfaces are −0.76, −1.33, and −1.53 V against the reversible hydrogen electrode (RHE), respectively. Before the formation of NH_3, all routes pass through absorbed NH_x. It is essential to remember that the determination of the limiting potential makes use of the computational hydrogen electrode (CHE) assumptions.[42] The CHE assumes the pH of the aqueous electrolyte is known. They employed onset potential for ethanol reduction from the trials as a baseline to account for the nonaqueous electrolyte present in this experiment. The results showed that under the conditions of these trials, all three surfaces are capable of assisting in the production of NH_3.[41]

2.1.3 Chemical N_2 splitting and electrochemical protonation. An alternative $Li-eN_2RR$ mechanism involves a

Fig. 3 (a) A 'Heterogeneous mechanism', in which there is a stable amount of lithium on the electrode at all times; (b) free energy diagram of NH_3 formation on the surfaces of Li, Li_3N, and LiH. The free energy diagram is represented through dash lines when the limiting potential is switched on. All of these surfaces are active for NH_3 synthesis.[41]
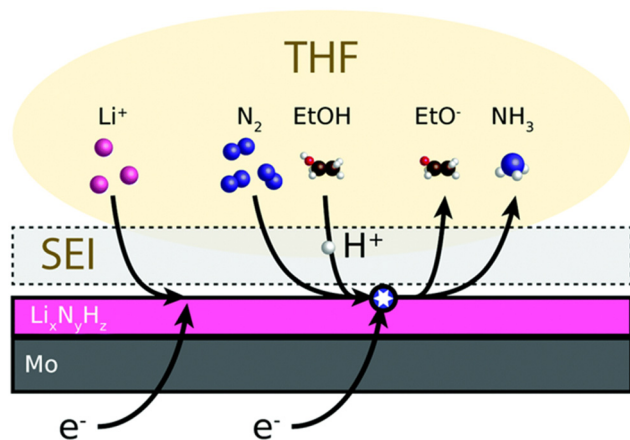
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Fig. 4 Schematic of the mechanism for Li-eN$_2$RR to NH$_3$. A non-aqueous electrolyte (THF) contains lithium salt which is electrodeposited onto a metal electrode (Mo) as metallic Li.[38]

chemical process of Li$_3$N and an electrochemical process from Li$_3$N back to metallic Li, as presented in Fig. 4. Andersen and coworkers claimed that the active surface site of Li (Li$^•$) can react with ethanol and activate N$_2$. Li$^•$ was not consumed throughout the process.[38] This kinetic model of Li-eN$_2$RR is consistent with the observation of a variation in NH$_3$ yield rate and FE with the change of external conditions. To explain the mechanism of Li-mediated N$_2$ reduction reaction toward NH$_3$, the authors created a basic kinetic model. They proposed that the following fundamental actions take place during lithium deposition.

$$Li^+ \xrightarrow{r_{Li}} Li^+_{(s)} \quad \text{(slow step)} \tag{2a}$$

$$Li^+_{(s)} + e^- \xrightarrow{k_{Li}} Li^• \quad \text{(fast step)} \tag{2b}$$

$$H^+ \xrightarrow{r_H} H^+_{(s)} \quad \text{(slow step)} \tag{2c}$$

$$Li^• + \left(H^+_{(s)} + e^-\right) \xrightarrow{k_{H-1}} Li^•H^* \quad \text{(fast step)} \tag{2d}$$

$$Li^•H^* + \left(H^+_{(s)} + e^-\right) \xrightarrow{k_{H-2}} Li^• + H_2 \quad \text{(fast step)} \tag{2e}$$

$$N_2 \xrightarrow{r_N} N_{2(s)} \quad \text{(slow step)} \tag{2f}$$

$$Li^• + 1/2N_{2(s)} \xrightarrow{k_{N-1}} Li^•N^* \quad \text{(fast step)} \tag{2g}$$

$$Li^•N^* + \left(H^+_{(s)} + e^-\right) \xrightarrow{k_{N-2}} Li^•NH^* \quad \text{(fast step)} \tag{2h}$$

$$Li^•NH^* + \left(H^+_{(s)} + e^-\right) \xrightarrow{k_{N-3}} Li^•NH^*_2 \quad \text{(fast step)} \tag{2i}$$

$$Li^• + \left(H^+_{(s)} + e^-\right) \xrightarrow{k_{N-4}} Li^• + NH_3 \quad \text{(fast step)} \tag{2j}$$

∴ s = close to surface species
∴ Li$^•$ = active surface site of Li

∴ Li$^•$X* = surface bound X species

Here eqn (2a) and (2b) describe the slow steps of Li-deposition, while eqn (2c)–(2e) and (2f)–(2j) show the catalytic formation of H$_2$ and NH$_3$, respectively.

There have been several computational studies on the reaction mechanism of Li-mediated N$_2$ reduction and understanding the factors that influence the efficiency and selectivity of this process. These studies have used a variety of computational techniques, including DFT calculations, to examine the reaction pathways and intermediate species involved in the reduction of N$_2$ to NH$_3$ using lithium as a mediator. Some of the key findings from these computational studies include the importance of the choice of electrocatalyst, as different electrocatalysts have been found to have a significant impact on the reaction mechanism and efficiency of the Li-mediated N$_2$ reduction process. The formation and stability of intermediate species, such as lithium nitride and lithium amide, have been found to play a key role in the reaction mechanism of Li-mediated N$_2$ reduction. The influence of electrolytes also has significant impact on the reaction mechanism.[40,43–46]

Maniscalco *et al.* employed a Car–Parrinello molecular dynamics (CPMD) method to simulate the first step of Li-mediated NH$_3$ synthesis. CPMD, a type of *ab initio* molecular dynamics method (AIMD), is a classical technique, which is well known from classical molecular dynamics (or force-field) calculations, to address the challenge of how to characterize nuclear motion in a simple manner. The DFT method was employed for the studies of electronic structure and the motions in the system, which were further characterized through CPMD.[47]

At every step, the electronic cloud tracks the nuclei's movement. The dynamics of molecular systems on the size of a few ps and a few NH$_3$ can be described using a time interval of around 0.1 fs. Since chemical reactions are infrequent events, it is challenging to meaningfully simulate them. Before monitoring reactions, it is especially preferable to build an equilibrium system with a precise temperature. Such equilibrated systems are difficult to obtain or perhaps unattainable. The molecules of N$_2$ were those that interact with the surface the most firmly. In contrast to how molecules behave when they come in contact with oxide surfaces,[48,49] Maniscalco *et al.* observed that the N$_2$ molecules are quickly "swallowed" by the metallic-Li surface. Typically, this causes the nitrogen–nitrogen bond to lengthen. Most simulations showed at least one N$_2$ molecule completely dissociating.[50] To evaluate the eN$_2$RR route on lithium, lithium nitride, and lithium hydride surfaces, Schwalbe *et al.* employed DFT calculations and limiting potential analysis.[41] Both lithium that is electrochemically attached to the electrode and lithium that is separated, where the dissolution is triggered by the loss of lithium metal to lithium ions, will be affected by this. The experimental results indicate that only a tiny portion of the lithium that is plated will react to generate a species that contains N$_2$, which is why lithium was chosen. The thermodynamic justification

used to select nitride and hydride is described above. The final assumption from these studies is that all three surface species have plausible routes. According to previous research on nitride materials, the active site for the nitride and hydride is a vacancy.[51,52]

Despite their usefulness, computational methods have several limitations in understanding Li-mediated N_2 reduction. One major limitation is the accuracy of the computational models and the assumptions made during the simulations. These assumptions can lead to errors and inaccuracies in the results. Additionally, some of the simulations may not capture the full complexity of the reaction mechanism or may oversimplify the system. Another limitation is the computational cost of the simulations, which can be significant, especially for large systems or long time scales. Finally, the results of computational simulations may not always be directly applicable to experimental systems, as experimental conditions may differ from the simulated conditions.

2.2 Cathode catalysts reported for Li-mediated N_2 reduction

The fixation and optimization of N_2 to yield NH_3 at ambient conditions is a key challenge for the field of chemical engineering. N_2 fixation by several chemical as well as electrochemical systems has been employed to realize the synthesis of NH_3 at mild conditions. Li metal catalysts are now well known for the electrochemical reduction of N_2 to NH_3 at ambient conditions.[53,54] The spontaneous reaction of Li with N_2 yields Li_3N, and subsequent protonation of the Li_3N realizes the synthesis of NH_3. However, it is a challenge to employ Li catalysts in an aqueous solution during Li-mediated eN$_2$RR. When a lithium mediator is used in an aqueous solution, the competitive HER occurs at a more positive potential than that of the reduction of Li^+ to Li.[55–57]

In 1930, Fichter et al.[5] for the first time described the Li-mediated eN$_2$RR. It was further extended and explored by Tsuneto et al. in the early 1990s. The reduction of N_2 was carried out in the presence of $LiClO_4$ (0.2 M) as an electrolyte, THF and ethanol (volume ratio of 99 : 1) as protic solvents and N_2 at 1 atm. Different metal electrodes such as Al, Ti, Mo, Fe, Co, Ni, Cu, Ag, etc. were explored. The process achieved a maximum current efficiency of 8% at 1 atm. The current efficiency of the process was demonstrated to be increased up to 59% by raising the pressure of N_2 to 50 atm. Moreover, the study revealed that NH_3 could be generated by taking the air as the source of N_2 with a current efficiency of 3.7%. The lower current efficiency was attributed to the side reaction of Li metal with O_2 present in the air.[6]

The current efficiency of the electrochemical process was found to rely on the metals used for electrodes (especially the cathode) in addition to electrolytes, protic additives, temperature, and pressure conditions.[38] For practical applications, the efficiency of the Li-eN$_2$RR process can be enhanced by the introduction of alternative cyclic strategies, surface engineering of the electrode's reactive interface, use

of gas diffusion electrodes for efficient catalysis, the possible use of ionic liquids as proton shuttles, or addition of oxygen species.[22,24,38,58,59] In the following section, we only focus our discussion on the state-of-the-art contributions that have demonstrated exceptional activity by optimization of the Li-mediated electrocatalytic reduction process.

2.2.1 Noble metal catalysts for Li-mediated eN$_2$RR

2.2.1.1 Li–Ru composite. Ma et al.[60] investigated eN$_2$RR based on a Li–N$_2$ battery using carbon-supported Ru nanoparticles as a cathode catalyst in the presence of water as a proton source. LiOH and NH_3 were produced by passing N_2 through the water/Ru cathode interface via discharge–charge cycling. The water also played an additional role in the film formation and decomposition reaction at the cathode. The Li–N$_2$ battery process provided an NH_3 yield of 2.66 mg, with an NH_3 FE value of 4.2% at 0.1 mA cm^{-2}, while an NH_3 yield of 4.46 mg and an NH_3 FE value of 1.4% at 0.5 mA cm^{-2} after discharging for 2 h. This study suggested the novel application of Li–N$_2$ batteries for continuous Li-mediated production of NH_3 and highlighted the optimal ternary role of water as a proton source.[60]

2.2.1.2 Ag wire. In 1993, Tsuneto et al.[61] tested 12 different metal wire cathodes for N_2 reduction reaction using a single compartment cell under 1 atm N_2 in a solution of $LiClO_4$ (0.2 M) in tetrahydrofuran/ethanol (99 : 1 v/v). Ag wire electrode was found to display the best activity with a current efficiency of about 8.4% toward NH_3 formation. Larger current efficiency (48.7%) was achieved when the electrolysis was performed under a high pressure of N_2 (50 atm).

2.2.1.3 Au-coated carbon fibrous paper (Au/CP) catalyst. Gao et al.[23] employed Au/CP as a model catalyst to investigate its electrocatalytic activity for the nonaqueous Li-mediated eN$_2$-RR process. In situ XRD confirmed the transformation of lithium intermediates during the eN$_2$RR (Fig. 5). A faster Li electro-reduction kinetics was observed on Au/CP compared to CP cathodes. The Li_3N(100) peak gradually emerged after bubbling N_2 for 5 min with Au/CP (Fig. 5e), whereas no obvious signal of Li_3N appeared with a bare CP electrode (Fig. 5k). Rapid depletion of Li and Li_3N took place (Fig. 5f) after addition of EtOH, probably resulting from NH_3 formation, which was corroborated by UV/vis absorption spectroscopy and nuclear magnetic resonance measurements. Au/CP demonstrated superior activity compared with CP because Au possessed higher adsorption energy than the carbon surface. Owing to higher adsorption energy, the effective transfer of electrons from Au to Li^+ lowered the catalytic barrier for Li reduction. Au/CP significantly enhanced the kinetics of Li reduction, resulting in the formation of metallic Li that critically influenced the spontaneous eN$_2$RR process by the formation of Li_3N and NH_3. The heterogeneous catalysis by Au/CP achieved an NH_3 FE of 34.0% and NH_3 yield rate of 50 μg h^{-1} cm^{-2}.[23]

2.2.2 Nonprecious metal catalysts for Li-mediated eN$_2$RR

2.2.2.1 Copper-based materials. Cu does not react with Li and has been demonstrated to be a suitable cathode for Li-mediated eN$_2$RR. Recently, a highly structured Cu electrode

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Fig. 5 *In situ* XRD contour maps of (a) and (d) Au/CP and; (g) and (j) CP under Ar atmosphere; (b) and (e) Au/CP and (h) and (k) CP under N_2 atmosphere without EtOH; (c) and (f) Au/CP and (i) and (l) CP under N_2 atmosphere with EtOH.[23]

on Ni foam substrates was fabricated by Li and coworkers through a hydrogen bubble template (HBT) method (Fig. 6a).[58] An NH_3 formation rate of 46 ± 6.8 nmol s^{-1} cm$_{geo}^{-2}$ with a corresponding FE and energy efficiency (EE) of $13.3 \pm 2.0\%$ and $2.3 \pm 0.3\%$ was attained at a current density of -100 mA cm$_{geo}^{-2}$ under 20 bar N_2 using 2 M $LiClO_4$ in THF as an electrolyte and 1 vol% of EtOH as a proton source. The NH_3 FE and EE for HBT Cu were shown to be comparable to Cu foil (NH_3 FE: $13.6\% \pm 1$; EE: $3.9 \pm 0.3\%$), while the NH_3 formation rate of HBT Cu was over 45 times that of Cu foil (1.0 ± 0.1 nmol s^{-1} cm$_{geo}^{-2}$). It is worth noting that the synthesized HBT Cu electrode shows a great potential for scale up application compared to previously reported electrodes in terms of current density (Fig. 6b). Furthermore, an increase in salt concentration in the electrolyte was observed to lead to improved stability of the system, which may be due to suppressing the formation of a passivating decomposition layer, or it otherwise altering the SEI layer composition.

Zhang *et al.*[14] embedded Cu particles into lithium by sample rolling. They found that the Li in the resulting Cu/Li composite provided a reaction rate over 1000 times faster than bare Li for the lithium nitridation process (Fig. 7a and b). This was attributed to the alteration of nitrogen adsorption and decrease in the total energy required for the nitridation reaction. Reaction of Cu/Li_3N with deionized water ($2Li_3N + 3H_2O \rightarrow 2NH_3 + 6LiOH$) yielded NH_3 (Fig. 7c), which was validated by infrared spectroscopy (Fig. 7d) and Nessler's reagent spectrophotometry. The authors further compared this work with the traditional H–B process in terms of energy consumption for production of 1 kg of NH_3 (Fig. 7e). Taking into account that Li, Cu, and HCl are not consumed, only the costs of industrial-grade H_2O and N_2 and the electricity employed for Li-ion reduction were considered in the calculation. The use of H_2O as a hydrogen source instead of H_2 provides benefits for eliminating the amount of consumed fossil fuels for yielding H_2, thus substantially reducing CO_2 emissions. The FE of this eN_2RR

Fig. 6 (a) Illustration of Cu foil and HBT Cu for Li-mediated eN_2RR; (b) comparison of HBT Cu and previously reported electrode materials in terms of current density and NH_3 FE.[58]
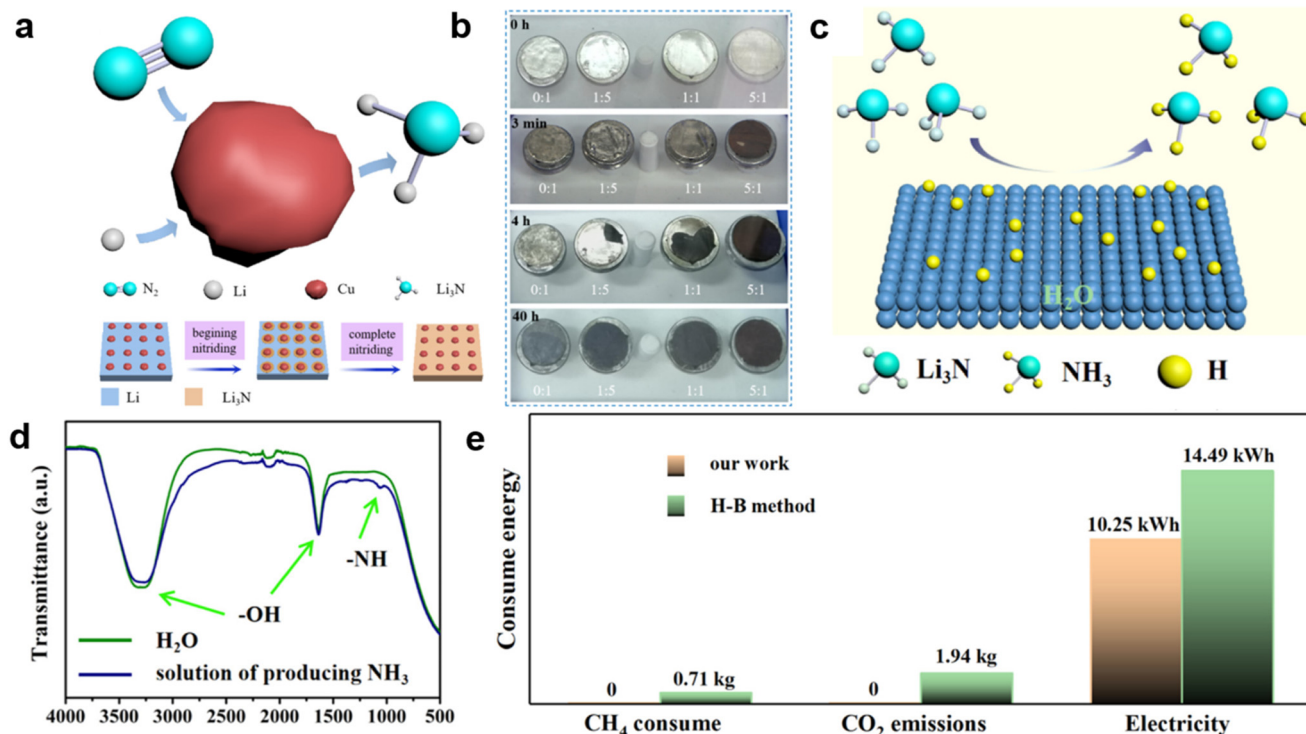
Fig. 7 (a) Illustration of Cu-catalyzed lithium nitridation (top panel) and steps for the formation of Li_3N/Cu from Li/Cu (bottom panel); (b) catalytic effect of Cu-to-Li mass ratio on the nitridation process; (c) illustration of NH_3 synthesis from the reaction of Li_3N and H_2O; (d) infrared spectra of H_2O and the electrolyte solution after reaction; (e) comparison of this work with the H–B process in terms of energy consumption for production of 1 kg of NH_3.[14]

fixation route using insulated solid electrolyte can reach close to 100%.

2.2.2.2 Molybdenum (Mo). In addition to Cu, Mo also does not alloy with Li and has been used as a cathode for Li-mediated eN_2RR.[6,61] An NH_3 FE of ~10% at a current density of 100 mA cm^{-2} was achieved on a Mo working electrode in 0.5 M $LiClO_4$ in THF with the addition of a small amount of EtOH (0 to 5 vol%).[41] Andersen *et al.*[38] reported a simple

strategy for improving the NH_3 FE by cycling the applied voltage between a Li deposition favored region and a Li dissolution facilitated regime (Fig. 8a and b). The NH_3 FE was enhanced from ~21.2% under constant Li deposition to 37% after potential cycling on a Mo electrode with 0.3 M $LiClO_4$ electrolyte in THF containing 1 vol% ethanol. Li *et al.*[59] discovered that the addition of a small amount of O_2 could greatly improve the NH_3 FE and stability of the
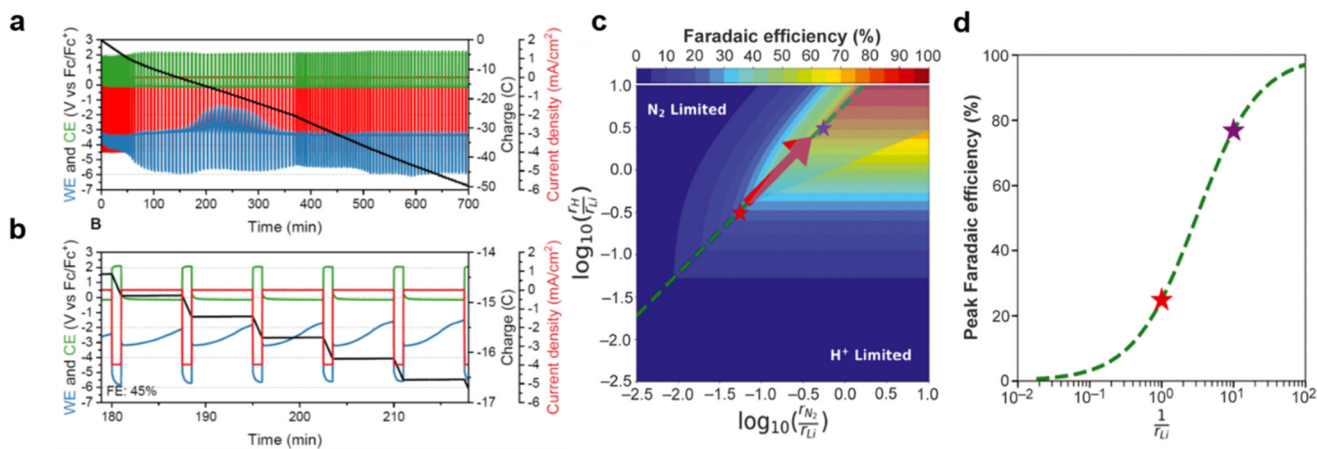
Fig. 8 (a) Cycling method between −2.0 and 0.0 mA cm^{-2} (red) for a total of 100C of charge passed (black); (b) a close-up of the cycling;[38] (c) Heatmap of the predicted FE against the ratio of N_2 to lithium (*x* axis) and proton to lithium (*y* axis) diffusion rates; (d) a one-dimensional plot of NH_3 FE cut along the optimal r_{N_2}/r_H ratio.[59]

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lithium-mediated eN_2RR. A high NH_3 FE of up to $78 \pm 1.3\%$ was obtained at 0.6 to 0.8 mole% O_2 in 20 bar of N_2 with 0.3 M $LiClO_4$ electrolyte in THF containing 1 vol% ethanol. The NH_3 FE was found to increase with the decrease of Li diffusion rate (Fig. 8c). This can be associated with the fact that Li electrodeposition competes with the N_2RR for electrons. Ideally, Li diffusion or deposition should be slow enough to consume a minimal number of electrons while still providing a full monolayer of clean and freshly plated Li to dissociate N_2. O_2-induced changes in the SEI layer can lead to delayed Li diffusion, thereby boosting the FE toward NH_3. The oxygen content also affected the rates of nitrogen and proton diffusion, r_{N_2} and r_H, due to induced modification of the SEI layer. An optimal O_2 content was proposed to follow as a trade-off between the Li^+ diffusivity limited regime and the dominant ORR (over the N_2RR) regime (Fig. 8d).

2.2.2.3 Lithium–liquid alloy-salt (Li–Sn liquid alloy & molten LiCl–KCl). Apart from the application of solid-state electrolytes, the use of liquid alloys with molten salts have recently been reported. To overcome the limitation of the scaling relation between the activation barrier and binding energy of N_2, Tang et al.[62] introduced a Li-based loop using a Li–Sn liquid alloy (having LiSn, Li_7Sn_3, Li_5Sn_2, and $Li_{13}Sn_5$ intermetallic phases) and molten LiCl–KCl salt as a catalyst for the generation of NH_3 from N_2 and H_2 gases at ambient conditions. The looping process involved a three-step reaction cascade. During the first step, the Li present in Li–Sn alloy reacted with N_2 to form Li_3N, which dissolved readily in the molten salt. In the consecutive second step, the Li_3N underwent hydrogenation to yield NH_3 and LiH. The third step involved the decomposition of LiH and regeneration of Li metal in the presence of Sn. This looping process at 450 °C exhibited an NH_3 yield rate of 0.12 μg s^{-1} during the 81 h electrocatalytic test (Fig. 9). The highest activity of this catalytic system (Li–Sn alloy and molten LiCl–KCl salt) was found to be 0.249 μmol g^{-1} h^{-1}, which was higher than that of pure Na but considerably lower than the looping process catalyzed by LiH/Li_2NH.[62]

2.2.2.4 Stainless steel cloth (SSC). The use of conventional gas diffusion electrodes (GDEs) with non-aqueous electrolytes is hampered by the absence of hydrophobic repulsion between the solvent and carbon fibre skeleton. A recent study by Lazouski et al.[22] demonstrated an approach to overcome transport limitations in THF by using SSC as a cathode and an anode GDE substrate (Fig. 10) for Li-mediated eN_2RR, giving rise to an NH_3 partial current density and FE of 8.8 ± 1.4 mA cm^{-2} and $35 \pm 6\%$, respectively. The total NH_3 FE did not markedly vary when the flow rate of N_2 across the SSC was changed; less NH_3 was observed in the gas phase at lower flow rates. However, the NH_3 formation rate decreased with electrolysis time. The reason for this degradation needs to be further explored.

2.2.3 Non-metal catalysts for eN_2RR

2.2.3.1 Li^+ incorporated poly(N-ethyl-benzene-1,2,4,5-tetracarboxylic diimide)–carbon cloth (Li^+–PEBCD/CC). Chen et al.[3] reported a dramatic increase in the efficiency and selectivity of the eN_2RR process (at ambient conditions) by employing Li^+-PEBCD/CC as the catalyst. DFT calculations as well as experimental studies verified the association of the Li^+ with the oxygen atoms that inhibit the HER. Further, it also facilitates the adsorption of N_2, and the hydrogenation reaction proceeds in a "$[O–Li^+]\cdot N_2–H_x$" manner (Fig. 11a). The highest values of FE and NH_3 yield rate of 2.85% and 2.01 μg h^{-1} cm^{-2} were achieved at −0.5 and −0.7 V, respectively (Fig. 11b and c). The durability tests suggested 82% performance retention and stable behavior of the Li^+-PEBCD/CC electrode with a slight change of FE after 6 cycles (Fig. 11d).[3]

2.2.3.2 N-doped carbon nanospikes (CNS). Song et al.[34] demonstrated the effect of N-doped CNS as a physical catalyst to promote the eN_2RR. The catalyst does not contain noble or non-precious metals, but instead the sharp nanospikes of the carbon act as the electrocatalytic surface as they concentrate the electric field at the tips and catalyze the eN_2RR process of the dissolved N_2 at the electrode. The counter ion (i.e., Li^+, Na^+, and K^+) present in the electrolyte was also observed to

Fig. 9 (a) Graphical illustration of Li-eN_2RR containing Li–Sn alloy and molten LiCl–KCl salt forming a biphasic system; (b) NH_3 yield rate against electrolysis time on Li–Sn and pure Sn.[62]
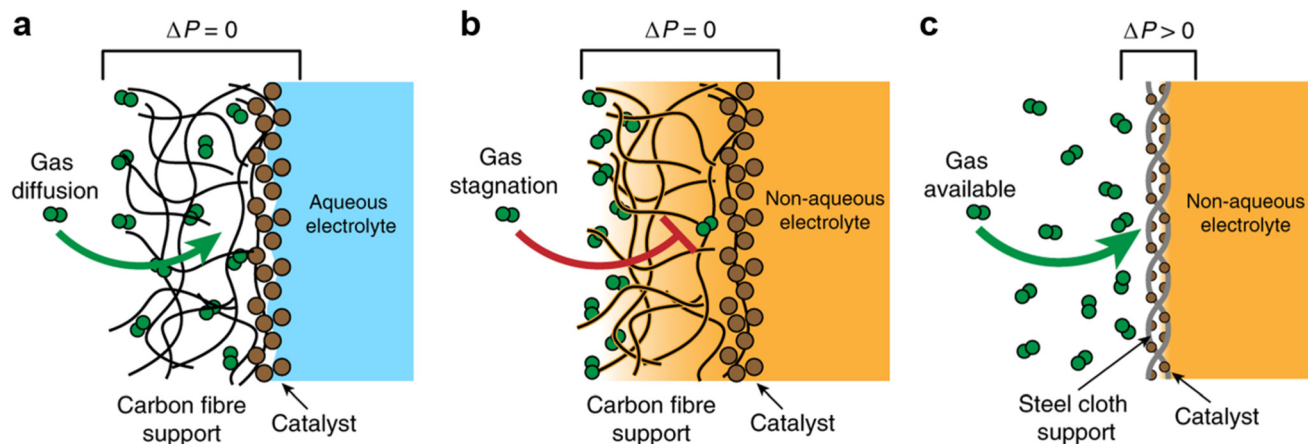
Fig. 10 (a) A hydrophobic GDE with an aqueous electrolyte; (b) a hydrophobic GDE with a non-aqueous electrolyte; (c) a catalyst-coated (SSC) GDE with a non-aqueous electrolyte.[22]

critically influence the performance of the reaction by enhancing the electric field and N_2 concentration in the Stern layer. Moreover, the CNS suppresses the HER by formation of a cation layer around the tip of the spikes, which excludes water and provides access to a high electric field to the N_2 molecules. The counter-ions enhanced the NH_3 production rate in the order of $Li^+ > Na^+ > K^+$. Using $LiClO_4$ as an electrolyte and CNS as a catalyst, an NH_3 FE, NH_3 yield rate, and energy efficiency of 11.56%, 97.18 μg h^{-1} cm^{-2}, and 5.25% were achieved, respectively.[34]

Among the reported catalysts for Li-mediated eN$_2$RR, as illustrated in Table 2, HBT Cu gives the best NH_3 yield rate,

possibly due to its porous structure with high surface area benefiting the lithium-mediated process. The Cu/Li composite exhibited a 100% NH_3 FE. However, the metal-free CNS demonstrated both high yield and FE toward NH_3 with a corresponding value of 97.18 μg h^{-1} cm^{-2} and 11.56%, respectively.

2.3 Electrolytes reported for Li-mediated N_2 reduction

In the electrochemical method, a proton donor is required to reduce the N_2 (such as LiN_3) so that NH_3 is released and Li ions are recovered. There are reasons to think that the proton
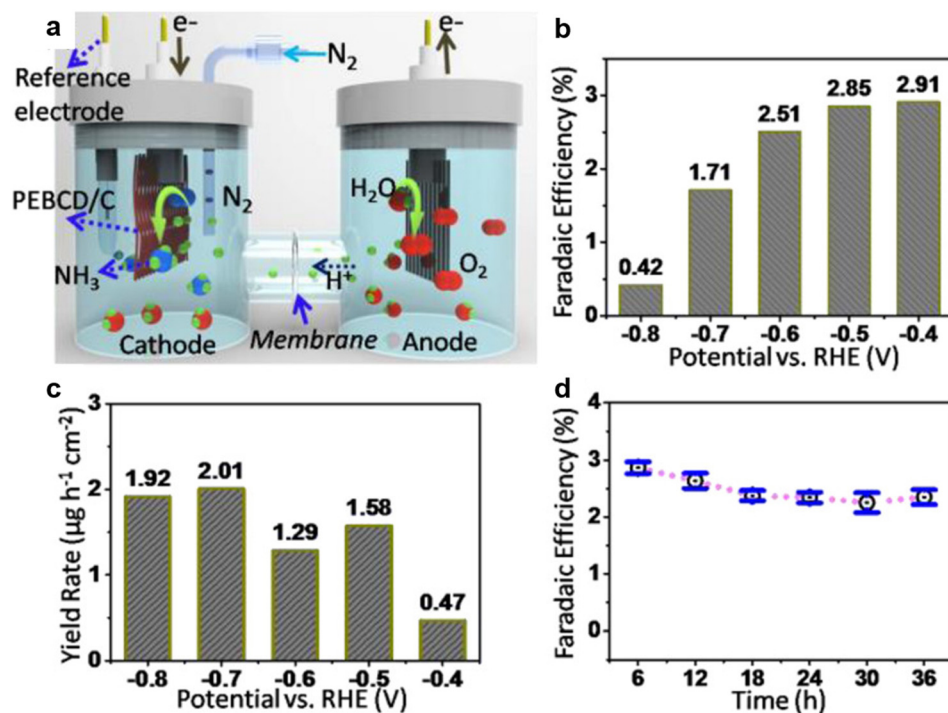
Fig. 11 (a) The graphic illustration of the configuration of the electrochemical cell for the eN$_2$RR process; (b) FEs of the Li$^+$-PEBCD/CC catalyst at different potentials during the eN$_2$RR; (c) NH_3 yield rate against applied potential during the eN$_2$RR; (d) durability test results for Li$^+$-PEBCD/CC.[3]

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Table 2 A summary of reported electrocatalysts for the Li-mediated eN$_2$RR

Sr #	Cathode catalyst	NH$_3$ FE (%)	NH$_3$ yield/NH$_3$ yield rate	Electrolyte	Ref.
Noble metal catalyst					
1	Ru NPs@C	4.2	4.46 mg	1 M LiCF$_3$SO$_3$ in TEGDME	60
		1.4	66 mg		
2	Ag wire	8.4	—	0.2 M LiClO$_4$ in THF with 1 vol% EtOH	61
3	Au/CP	34	50 μg h^{-1} cm^{-2}	0.2 M LiClO$_4$ in THF with 1% EtOH	23
Non-precious metal catalyst					
4	HBT Cu on Ni foam	13.3 ± 2	46 ± 6.8 nmol s^{-1} cm$_{geo}^{-2}$@−100 mA cm$_{geo}^{-2}$	2 M LiClO$_4$ in THF with 1 vol% of EtOH	58
5	Cu foil	18.5 ± 2.9	7.9 ± 1.6 nmol s^{-1} cm$_{geo}^{-2}$	1 M LiBF$_4$ in THF with 0.1 M EtOH	11
6	Cu/Li composite	100	—	—	14
7	Mo	~10	—	0.5 M LiClO$_4$ in THF with 1 vol% ethanol	41
8	Mo foil spot-welded with Mo wire	21.2 ± 1.6	—	0.3 M LiClO$_4$ in THF with 1 vol% ethanol	38
9	Mo foil spot-welded with Mo wire	78 ± 1.3	—	0.3 M LiClO$_4$ in THF with 1 vol% ethanol (at 0.6 to 0.8 mole% O$_2$ in 20 bar of N$_2$)	59
10	Li–Sn liquid alloy		0.249 μmol g^{-1} h^{-1}	Molten LiCl–KCl	62
11	SSC	35 ± 6	—	1 M LiBF$_4$ in THF with 0.11 M EtOH	22
Non-metal catalyst					
12	Li$^+$-PEBCD/CC	2.85	2.01 μg h^{-1} cm^{-2}	0.5 M Li$_2$SO$_4$ (aq)	3
13	CNS	11.56	97.18 μg h^{-1} cm^{-2}	0.25 M LiClO$_4$ (aq)	34

donor's function extends beyond supplying NH$_3$ with H atoms. It may also act as the catalyst for the reaction between Li metal and N$_2$ gas. The thermodynamic activity of the proton donor is significant for selective continuous N$_2$ reduction, according to a theoretical study of general eN$_2$RR.[6] In a previous assessment of proton donors, it was found that the identification of the proton donor can significantly alter the NH$_3$ yields in the Li-mediated N$_2$ reduction process.[8] The proton donor is the source of hydrogen that is necessary for NH$_3$ formation from N$_2$ in Li-eN$_2$RR.

Notably, the electrolyte plays a key role and provides an ideal environment for any electrochemical reactions to take place. However, obtaining a high yield and production rate of NH$_3$ during electrochemical synthesis is seriously hampered by the problem of N$_2$ solubility in traditional aqueous electrolytes. Thus, the most crucial problem must be resolved, namely, the dissolution of a useful concentration of N$_2$ molecules into the electrolyte so that they are accessible to the catalyst surface for their subsequent reduction.[63] Ren and co-workers have recently reviewed the N$_2$RR literature, and found that most of the work (90.7%) has been done on catalyst development and only 4.7% on electrolytes.[64] Below are some of the recently used electrolytes for Li-mediated eN$_2$RR.

2.3.1 Lithium triflate (Li(CF$_3$SO$_3$)). In an early work reported by Tsuneto et al.,[6] five different electrolytes (i.e., LiClO$_4$, LiBF$_4$, Li(CF$_3$SO$_3$), NaClO$_4$, and Bu$_4$NClO$_4$) were compared for eN$_2$RR under 50 atm nitrogen on Cu cathode. The FE of NH$_3$ synthesis was found to increase to more than 40% when lithium salts were used as electrolyte. While NaClO$_4$ and Bu$_4$NClO$_4$ only generated negligible amounts of NH$_3$. Among the three Li-based salts employed in the experiment, Li(CF$_3$SO$_3$) afforded the best FE of 59.8% for NH$_3$ formation.

2.3.2 Molten LiOH. The electrochemical process in aqueous conditions is considered to limit the efficiency of NH$_3$ formation due to the competitive and dominant HER. To circumvent the HER and attain selective nitrogen reduction, McEnaney et al.[1] in 2017 reported a novel stepwise pathway for the synthesis of NH$_3$ from N$_2$ and H$_2$O at ambient conditions (22–100 °C, atmospheric pressure) using molten LiOH as the electrolyte via an electrochemical lithium cycling process. The three-step reaction sequence involves LiOH electrolysis (6LiOH → 6Li + 3H$_2$O + 3/2O$_2$), nitridation of Li (6Li + N$_2$ → 2Li$_3$N), and hydrolysis of Li$_3$N (2Li$_3$N + 6H$_2$O → 6LiOH + 2NH$_3$) to realize the formation of NH$_3$ with a high current efficiency of 88.5%. The formation of NH$_3$ is an exothermic process that regenerates LiOH and completes the cycle. This stepwise route prevents direct N$_2$ protonation, which significantly reduces the undesirable HER and results in a high initial current efficiency of 88.5%. The fundamental features of the cycle are the straightforward dissociation of the robust N≡N bond over metallic Li and the diffusion processes that results in Li$_3$N at ambient temperature. The reaction was performed with an overnight N$_2$ flow (12 h) and resulted in complete conversion to nitride regardless of the temperature used (within the 22–100 °C), which further resulted in ~100% conversion efficiency to NH$_3$.[1]

2.3.3 Molten LiCl–KCl–Li$_3$N. Ito et al. discovered that azide ion (N^{3-}) synthesis from N$_2$ could be obtained electrochemically through a molten LiCl–KCl–Li$_3$N eutectic melt system,[65] which was then used for electrochemical NH$_3$ synthesis. The reactions that take place at the cathode (eqn (3)) and anode (eqn (4)) are as follows:

$$N_2 + 6e^- \rightarrow 2N^{3-} \quad \text{(cathode)} \quad (3)$$

$$2N^{3-} + 3H_2 \rightarrow 2NH_3 + 6e^- \quad \text{(anode)} \quad (4)$$

Fig. 12 (a) NH_3 yield and (b) NH_3 FE in the presence and absence of 0.03 M $CsClO_4$ at 220 °C over time.[8]

In the molten electrolytes, the efficiency of NH_3 synthesis was found to depend upon the partial pressure of hydrogen, and the dissolution/diffusion of hydrogen is the rate-determining step.

2.3.4 Cesium salt ($CsClO_4$). Kim et al.[8] found that during NH_3 formation the Li-plating morphology plays a significant role in controlling the NH_3 FE. The addition of $CsClO_4$ (0.03 M) in propylene carbonate (organic electrolyte) enhanced the morphology of the Li plating, which suppressed the side reactions occurring between Li metal and propylene carbonate. With the introduction of cesium salt, the FE of the Li-mediated NH_3 synthesis increased up to 82.3% (Fig. 12). The performance of the thicker Li plating, plated in a cylindrical form, meant there was less total interfacial area exposed to cause side reactions.[8]

2.3.5 LiClO₄-poly(methyl methacrylate) (PMMA) composite. To overcome the limitation of electrodeposition

of Li during the Li-mediated NH_3 synthesis at a higher temperature, Kim et al.[66] in 2019 introduced a membrane-free approach for electrodeposition of Li under ambient conditions which could be used for an enhanced nitridation reaction followed by NH_3 synthesis. The membrane-free biphasic system is based on the immiscible organic–aqueous hybrid electrolyte system. The biphasic hybrid electrolyte system consisted of aqueous $LiClO_4$ (1 M) and $LiClO_4$ in propylene carbonate incorporated with PMMA (1 M) that acted as a LISICON-based cell. The stable biphasic system at 5 mA cm^{-2} required a lower operating voltage of 5.3 V, as compared with the 6.2 V required for the LISICON-based cell. This strategy afforded an NH_3 FE of up to 57.2 with an NH_3 yield of 1.21×10^{-9} mol cm^{-2} s^{-1} (Fig. 13). This approach provides a way to design next-generation energy storage devices. By using biphasic electrolytes having high stability

Fig. 13 (a) Schematic diagram and (b) NH_3 yield and FE of the biphasic hybrid catalytic system catalyzed by $LiClO_4$ (aq) and $LiClO_4$–PMMA composite.[66]

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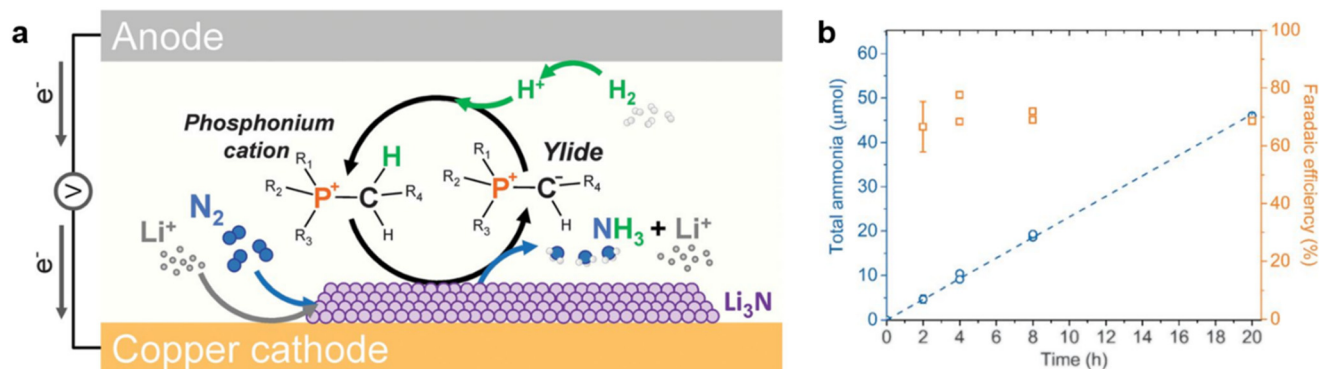*Ind. Chem. Mater.*, 2023, **1**, 563–581 | **575**

Fig. 14   (a) Schematic illustration of eN_2RR catalysis using a phosphonium salt; (b) NH_3 yield and FE as a function of time.[24]

against Li, solid electrolyte interphase formation could be alleviated.[66]

2.3.6 Phosphonium salt $[P_{6,6,6,14}]^+$. Li-mediated eN_2RR requires sacrificial proton sources to thwart the competing side reactions. Recently, Suryanto *et al.*[24] demonstrated the use of phosphonium salt as a proton shuttle. It was found that the phosphonium cation $[P_{6,6,6,14}]^+$ meets the criteria to act as a proton shuttle, and also exhibits an enhanced ionic conductivity that enables a robust synthetic route to synthesize NH_3 from N_2 (19.5 bar) and H_2 (0.5 bar) *via* a Li-mediated eN_2RR. The use of phosphonium salt allowed Suryanto *et al.* to attain a high NH_3 yield rate of 60 (nmol cm^{-2} s^{-1}) and a FE of 78% during 20 h of electrolysis, which was previously unachievable (Fig. 14).[24]

2.3.7 Imide-based lithium salt (LiNTf$_2$). A significant contribution toward the improvement of the NH_3 synthesis *via* the eN_2RR was made by Du *et al.*[67] in 2022. They demonstrated an efficient, robust, and flexible pathway for the synthesis of NH_3 that utilizes compact ionic layering at the electrode–electrode interface. An imide-based Li-salt, LiNTf$_2$, was used as an electrolyte, affording an NH_3 yield (3.9 mmol) at a high rate of 223 nmol cm^{-2} s^{-1} (average NH_3 yield rate) and 150 nmol cm^{-2} s^{-1} (stabilized NH_3 yield rate after 24 h) with a FE of 99% and a current-to-NH_3 efficiency rate of approximately 100%. The ionic assembly formed at the electrode–electrode interface hampers the decomposition of the electrolyte and improves the performance by supporting stable N_2 reduction.[67]

3 Conclusions and future remarks

This review has focused on the considerable advancements during recent years toward the development of a sustainable and green eN_2RR process. Li-mediated eN_2RR performance such as NH_3 yield, FE, current to NH_3 efficiency rate, *etc.*, is low when aqueous electrolytes are used at ambient temperature and pressure conditions due to competitive reactions. We have critically discussed the main factors such as the nature of electrolyte, the material of the electrode, and mechanisms involved in the Li-mediated eN_2RR. The mechanistic understanding derived through investigation of

the various factors that play a vital role in governing the performance parameters will help guide the search for the technological solutions for the current challenges in eN_2RR catalysis.

The main challenge for the Li-mediated eN_2RR process is to design selective electrocatalysts that can boost the activation of N_2 and hydrogenation to afford NH_3 by actively controlling the mass and charge transport during the process.[38] Non-aqueous solvents and different salts as electrolytes have been used to ameliorate the competing HER side reaction,[68] with Li-mediated N_2 reduction in non-aqueous electrolytes exhibiting a high NH_3 yield rate and FE. However, some other serious challenges such as high overpotential, unsustainable proton source from sacrificial solvent, a large ohmic resistance, and organic solvent recovery have arisen.[22,64,69–72]

To overcome the existing limitations and challenges of Li-eN_2RR systems, we propose the following strategies to improve the efficiency of the process: the overpotential for Li^+ electrodeposition could be lowered by use of either active Li or its alloys with other metals, which deserves further exploration for N_2 activation.[70,72] Besides, alternative liquid electrolytes should be investigated for use in Li-mediated eN_2RR systems, and the mechanisms of electrolyte decomposition should be explored to avoid the use of conventional low boiling organic electrolytes (*e.g.*, THF).[71,73,74] Most of the Li-mediated eN_2RR process have been investigated in a batch-type electrochemical cell (*i.e.*, a single compartment or an autoclave), which suffers from the limitation of mass transport due to the low solubility of both N_2 and H_2 in liquid electrolytes. The limitation of mass transport can be resolved by using continuous-flow electrolyzers to significantly enhance the rate of N_2 reduction by providing gaseous reactants at the catalytic surface (Fig. 15a).[41,75–77] Solid state electrolyzes can be implemented to realize the selective and efficient synthesis of NH_3 at ambient temperature and pressure. To realize electrosynthesis of NH_3 at industrial scale, gas diffusion electrodes should be used to continuously providing gaseous reactants to the catalytic active sites. Flow cells and membrane electrode assembly (MEA) electrolyzers should be
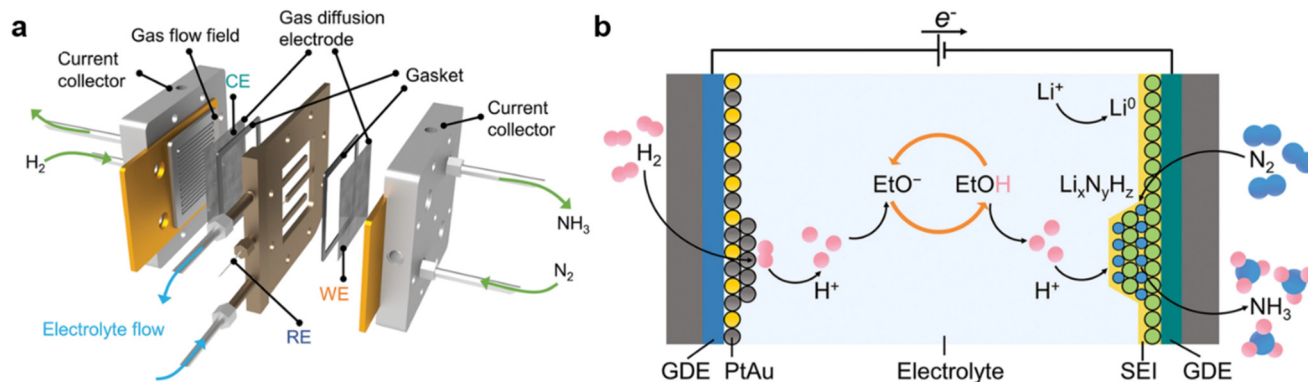
Fig. 15 (a) Expanded view of the continuous-flow electrolyzer configuration; (b) schematic process of the Li-NRR in a continuous-flow electrolyzer.[72]

designed and optimized that could significantly enhance the rate of eN_2RR.[56,76,77]

The eN_2RR process requires a proton donor which plays a crucial role in the production of NH_3 *via* N_2 reduction. A variety of proton donors have been shown to promote the reaction, and the donor's capacity to boost the reaction significantly depends on the proton donor structure and concentration. The proton donors induce changes in the solid electrolyte interphase, thereby facilitating selective diffusion of N_2 species to active sites on the electrode for reduction.[68] Hence, solid electrolyte interphases can enhance the selectivity as well as NH_3 yield by accelerating the homogenous deposition of lithium, as well as hindering the HER and uncontrolled electrolyte decomposition reactions. Lithium fluoride-based electrolytes have been found to achieve high selectivity due to the formation of a fluoride-rich SEI.[72] Note that most eN_2RR studies applied a sacrificial solvent as a proton donor, which leads to difficulty in scaling up fabrication in batch reactors. To circumvent this issue, employing a hydrogen oxidation reaction (HOR) on the anode (with the hydrogen sourced from water splitting) appears to be a promising strategy to provide a sustainable hydrogen source for NH_3 production (Fig. 15b). To this end, the design and development of active and robust HOR anode materials (such as PtAu) in organic electrolytes for replacing the archetype Pt is crucial.

More efforts are suggested to be devoted to conducting deep mechanistic investigations.[78] Along with experimental studies, theoretical calculations in combination with *in situ/operando* analysis using advanced techniques could help reveal the phase changes, reaction pathways, and insights into the composition of the SEI layer and its interaction with adsorbed surface species.[79,80] This will aid in the rational design of efficient Li-eN_2RR systems for practical applications at ambient conditions.[81–85]

Among others, standard protocols should be developed for accurate quantification of the N_2RR process. This is crucial to tackle the problem of false positives due to the presence of N_2 species from several other sources such as the solvent, electrolyte, or the catalyst itself. It should be ensured through a rigorous procedure (*i.e.*, gas purification and quantitative isotope measurements) that the only N_2 species that are

utilized to yield NH_3 *via* the eN_2RR should be the N_2 reactant itself so that the catalyst efficiency can be estimated with accuracy.[86] Due to the emerging eN_2RR, we believe that the sustainable and green synthesis of NH_3 will be extended for practical implementation in industry in the near future, which will bring a revolution in NH_3-based energy storage and conversion materials/devices.[87]

Conflicts of interest

The authors declare that they have no conflict of interest.

Acknowledgements

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