

Strategies to achieve effective nitrogen activation

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Abstract

Ammonia serves as a crucial chemical raw material and hydrogen energy carrier. Aqueous electrocatalytic nitrogen reduction reaction (NRR), powered by renewable energy, has attracted tremendous interest during the past few years. Although some achievements have been revealed in aqueous NRR, significant challenges have also been identified. The activity and selectivity are fundamentally limited by nitrogen activation and competitive hydrogen evolution. This review focuses on the hurdles of nitrogen activation and delves into complementary strategies, including materials design and system optimization (reactor, electrolyte, and mediator). Then, it introduces advanced interdisciplinary technologies that have recently emerged for nitrogen activation using high-energy physics such as plasma and triboelectrification. With a better understanding of the corresponding reaction mechanisms in the coming years, these technologies have the potential to be extended in further applications. This review provides further insight into the reaction mechanisms of selectivity and stability of different reaction systems. We then recommend a rigorous and detailed protocol for investigating NRR performance and also highlight several potential research directions in this exciting field, coupling with advanced interdisciplinary applications, in situ/operando characterizations, and theoretical calculations.

KEYWORDS

activation via mediators, catalyst optimization, electrochemical nitrogen fixation, high-energy activation of nitrogen, nitrogen

1 | INTRODUCTION

1.1 | Electrochemical nitrogen reduction

Ammonia (NH₃) plays a crucial role as a fundamental chemical raw material related to the national economy and

people's livelihood, with widespread utilization in various fields, including fertilizers, environmental protection, military, and refrigeration.^{1,2} Meanwhile, NH₃ with high volumetric energy density (13.6 MJ L⁻¹) has significant advantages as an efficient hydrogen storage medium. Specifically, 1.0 L of liquid NH₃ equals 4.9 L of high-pressure hydrogen (35.0 MPa) or 1200 L of standard

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temperature and pressure hydrogen.³ Herein, NH_3 is poised to address the challenges of hydrogen energy development. Despite having a development history of over a 100 years, the Haber–Bosch process is still the traditional and efficient method for producing NH_3 . The Haber–Bosch process is currently highly inefficient, consuming nearly 3% of the world's annual energy.^{4,5} To achieve the desired yield of NH_3 synthesis, the $\text{N}\equiv\text{N}$ bond activation difficult to achieve requires operating at high pressure and temperatures, which increases capital costs and decreases equilibrium conversion. These negative impacts have motivated researchers to explore alternative approaches for small molecular activation and fixation.^{6–11}

With the rapid development of renewable energy technology, such as photovoltaics, wind power, and hydro-power, the electrochemical synthesis of NH_3 has emerged as an excellent “zero carbon” circular economy route.^{12–19} According to thermodynamics, the electrochemical nitrogen reduction reaction (NRR) into NH_3 is about 20% more energy-efficient than the Haber–Bosch process. The advantages of low-cost, long-distance storage and transportation across regions based on electrochemically synthesized NH_3 are combined with the prosperous downstream hydrogen industry.^{20–22} Unlike the huge dependence on the natural gas feedstock of the Haber–Bosch process, the electrochemical process can avoid using fossil fuels as hydrogen and energy sources by using water molecules as hydrogen sources and combining them with renewable energy technologies. Currently, the most effective strategy for synthesizing “green NH_3 ” is to replace steam reforming units by coupling electrocatalytic water splitting and

traditional Haber–Bosch reactors (Figure 1).^{23–25} This approach has been preliminarily verified on a large scale globally. Exploring and developing the coupling technology of renewable energy electrolysis to synthesize NH_3 can achieve the absorption and peak shaving of renewable energy electricity while achieving enormous advantages in modularity, scalability, and on-demand small-scale production. Such small synthetic NH_3 facilities utilizing renewable energy can achieve decentralized production of NH_3 and significantly reduce the cost of NH_3 demand in remote areas.

In general, electrocatalytic NRR mechanisms mainly include association and dissociation mechanisms (Figure 2).^{26–31} The dissociation mechanism involves the direct cleavage of $\text{N}\equiv\text{N}$ bonds before adsorption, allowing the two adsorbed nitrogen atoms to independently participate in NH_3 synthesis. In contrast, in the association mechanism, N_2 binds to the surface sites of the catalyst, and the bonding between the two nitrogen atoms is not disrupted during the hydrogenation process (forming an N_2H_x intermediate). In this terminal coordination reaction, two hydrogenation processes exist: the distal, alternating (monoadsorbed mode) pathway and the enzymatic (dual-adsorbed mode) pathway. In the monoadsorbed mode, the end-on adsorbed nitrogen atoms undergo sequential hydrogenation to form NH_3 molecules. For side-on coordinated adsorption pathways, resembling enzymatic pathways, heterogeneous electrocatalysts encounter challenges in achieving bidentate coordination of dinitrogen groups. The design of dual-coordinate electrocatalysts based on mild enzymatic pathway holds great promise. Finally,

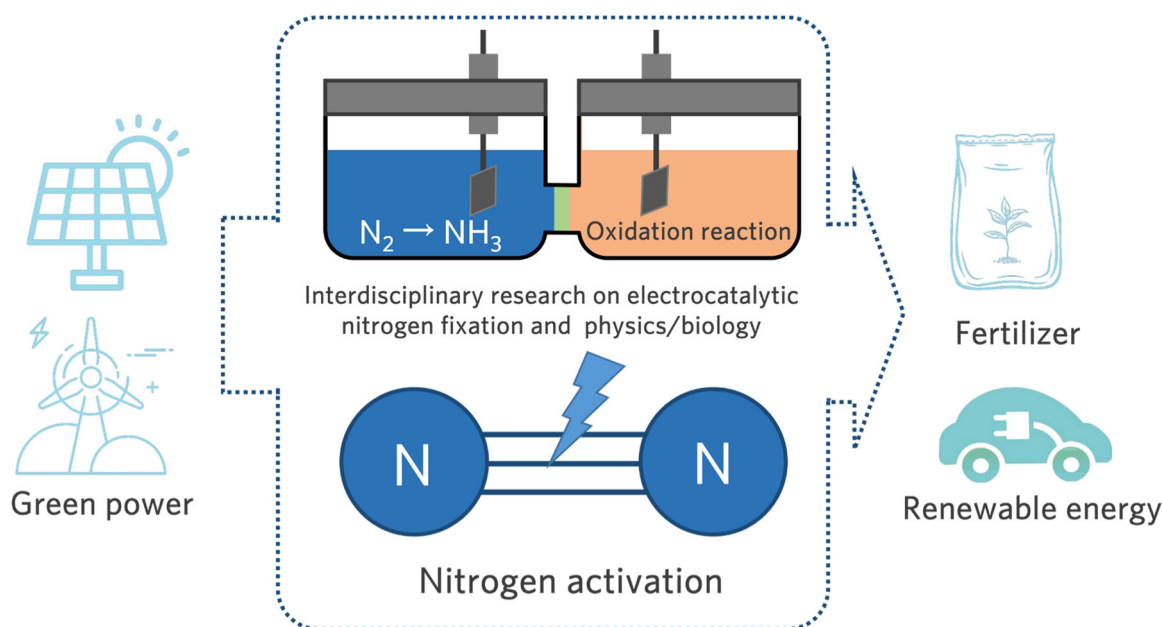


FIGURE 1 Scheme of electrochemical nitrogen reduction for “green ammonia” synthesis.

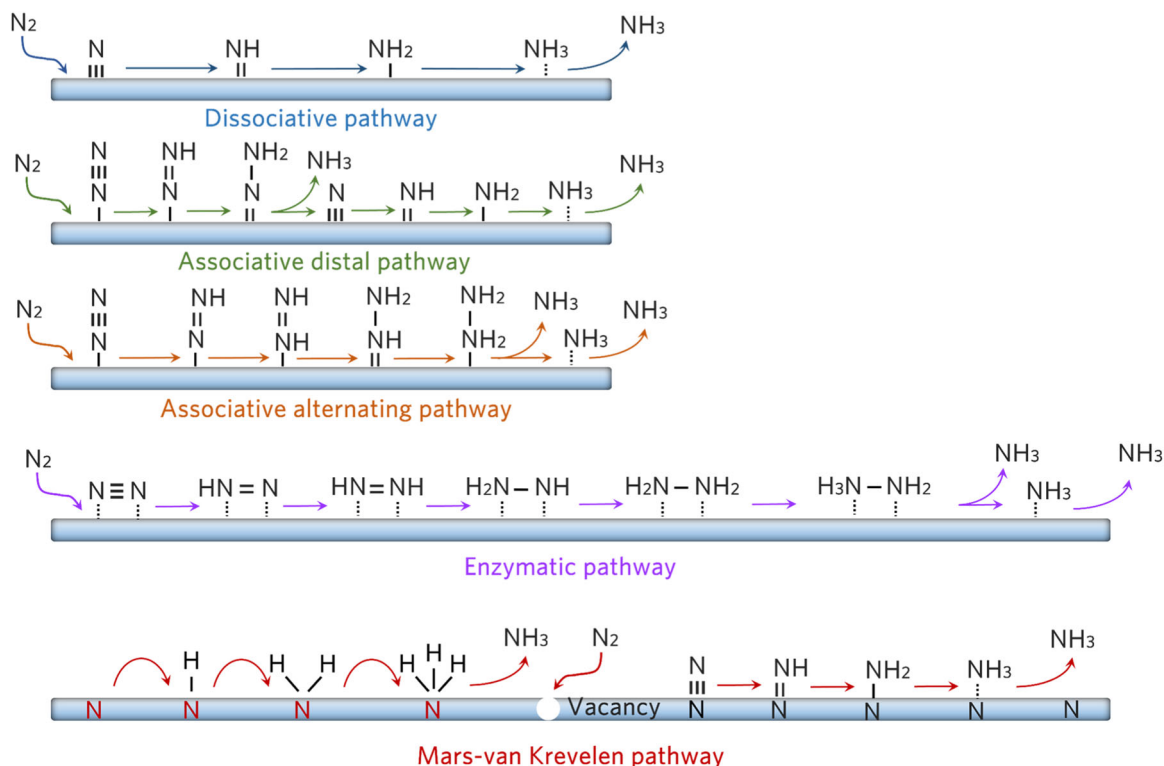
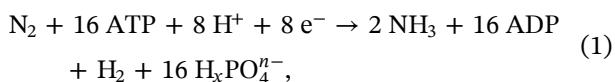


FIGURE 2 Generic mechanisms for electrochemical nitrogen reduction on heterogeneous catalysts.

the reaction pathways on transition metal nitrides predominantly adhere to the Mars–van Krevelen mechanism.^{32,33} The initial NH_3 molecule arises from the reduction of lattice nitrogen atoms within transition metal nitrides, subsequently replenishing lattice nitrogen through fusion with gaseous nitrogen molecules. The resulting nitrogen vacancies serve as a continuous avenue for nitrogen adsorption and subsequent reactions. Regardless of the above mechanisms, the lone pair electrons, strong $\text{N}\equiv\text{N}$ bond, and high ionization energy (15.58 eV) of N_2 inhibit the subsequent hydrogenation reaction. For electrochemical NRR, the activation of nitrogen is the greatest challenge.

1.2 | Bottleneck of nitrogen activation

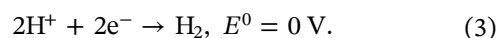
To date, the main challenge of NH_3 synthesis is the activation of nitrogen molecules which have an extremely strong $\text{N}\equiv\text{N}$ bond with large bonding energy (945 kJ mol^{-1}). In nature, iron–molybdenum enzymes (nitrogenase) can achieve nitrogen activation through iron–sulfur clusters with terminal molybdenum atoms:

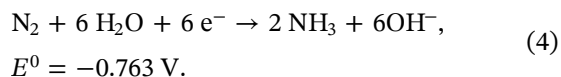


where ATP and ADP represent adenosine triphosphate and adenosine diphosphate, respectively (Equation 1).^{34–36}

The mechanism of nitrogen activation is believed to be the coordination of N_2 molecules with the terminal metal center of FeMo nitrogenase. However, there is still controversy over whether the subsequent hydrogenation process is carried out through the distal or association pathways.^{37–40} It is worth noting that the energy consumption for the entire reaction of NH_3 synthesis is 244 kJ mol^{-1} of NH_3 . The enzyme–based aqueous NH_3 synthesis at room temperature and ambient pressure has high energy efficiency, which prompted people to simulate chemical materials with similar structures in subsequent research to achieve efficient nitrogen activation, thereby achieving large–scale NH_3 synthesis.^{41–43}

As such, mild electrochemical NH_3 synthesis has become an important technology for simulating biological NH_3 synthesis, replacing the Haber–Bosch process.^{44–46} It is attractive that the electrochemical system directly achieves nitrogen and proton activation through nitrogen and water.





The above chemical equations show that the equilibrium potentials of hydrogen evolution reaction (HER) and NRR are similar in alkaline and acidic electrolytes (Equations 2–5).^{47–49} In the NRR process, the primary competitive side reaction is HER. Most H_2O or hydrogen protons in the electrochemical system tend to be reduced into H_2 rather than NH_3 , leading to serious selectivity issues. Meanwhile, the improvement of NRR selectivity is also limited by another challenge: achieving efficient nitrogen activation. For electrode materials, the regulation of active ingredients, crystal structure, and surface that strongly bind with N–H intermediates and H^* all contribute to suppressing HER and improving NRR efficiency.^{50–53} Meanwhile, as an indispensable reaction medium, electrolytes with considerable N_2 solubility and limited proton transfer ability can effectively enhance N_2 adsorption and activation.^{54–57}

This review discusses the critical research efforts on nitrogen activation, including electrocatalyst design, reaction system optimization, and nitrogen preactivation (Figure 3). A basic understanding of the roles of material

structure (electrocatalysts) and local catalytic environment (introduction of Li or enzyme mediators) in nitrogen adsorption and activation will ultimately lead to the design and development of better electrochemical NH_3 synthesis systems. Moreover, N_2 can be converted into easily reducible nitrogen oxides by high-energy physics particles. This innovative nitrogen pre-activation approach can significantly improve the efficiency of NH_3 synthesis. Therefore, this review provides potential and effective insights for N_2 activation in electrochemical heterogeneous NH_3 synthesis.

2 | THE OPTIMIZATION OF THE REACTION SYSTEM

Motivated by the rapid development of sustainable electricity and the advantages of electrochemical synthesis, environmental electrochemical NRR has attracted growing interest. So far, some effective strategies for promoting NRR catalytic performance have also been introduced to improve reaction systems, such as doping, defects, interface engineering of electrocatalysts, electrolyte optimization, and novel electrolytic cell designing.^{58–66} Meanwhile, various nanomaterials have been designed as the potential NRR electrocatalysts (Figure 4), including metal alloys, single atoms, transition metal

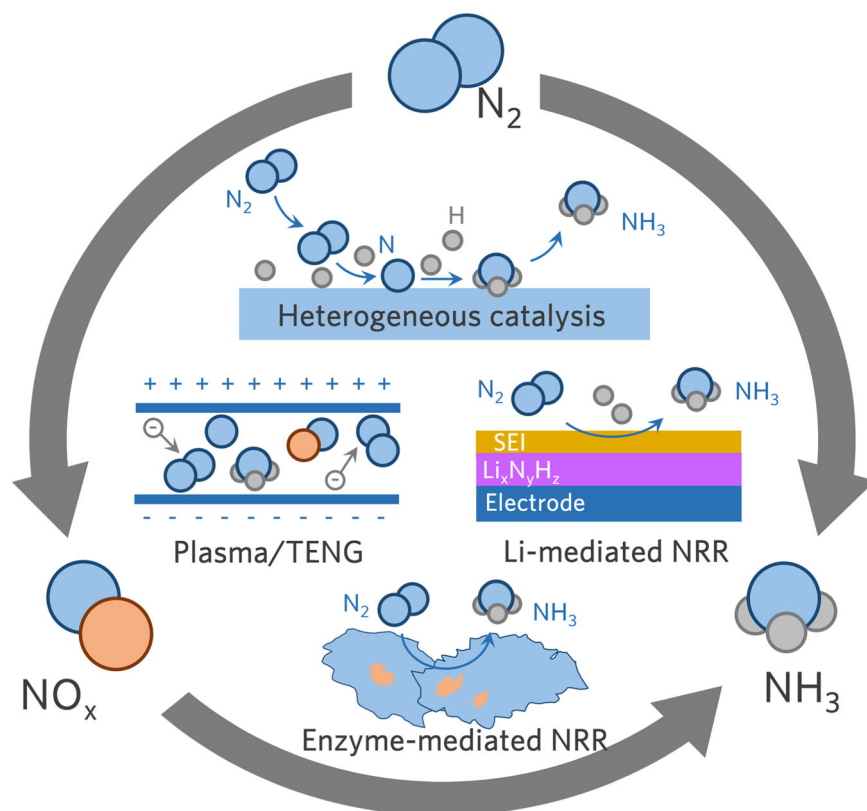


FIGURE 3 Scheme of nitrogen activation for NH_3 synthesis.

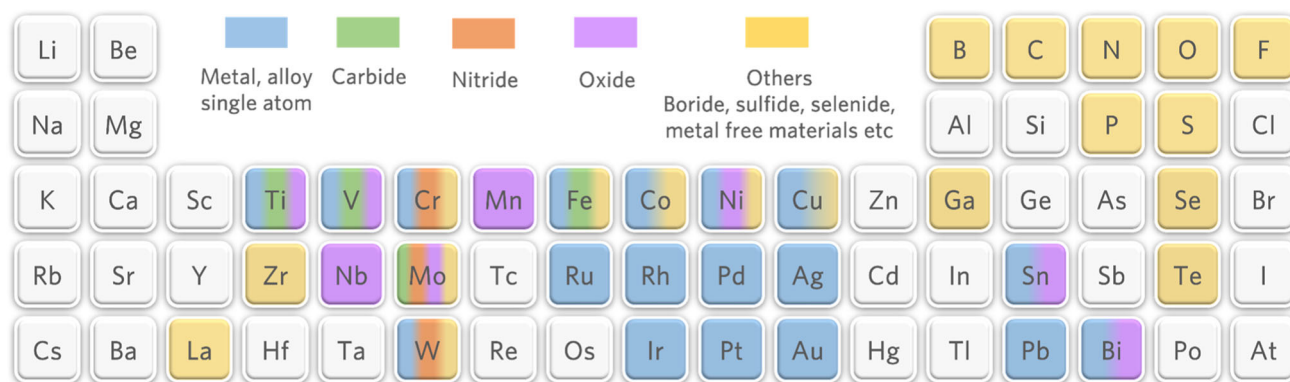


FIGURE 4 Performance map of the reported NRR electrocatalysts. Updated until July 12, 2023.

boride/carbides/nitride/oxide/sulfides, metal-free materials, and hybrids.^{67–76} Although significant progress has been made in the short term, this research field is undoubtedly still facing various problems, which are challenged by the intrinsic limitations of reactions.^{77,78} First, the overlap between the NRR work potential window and HER results in HER side reactions often dominating the hydrogenation process. The low solubility of N_2 in the water further limits the NRR performance. Second, although numerous NRR works have been conducted, the NH_3 yield of an aqueous NRR system is still relatively low (μmol level), which is highly susceptible to the influence of NH_3 and NO_x in the laboratory environment. The long-standing consensus is that rigorous validation experiments are needed to determine the nitrogen source in the NH_3 product. The materials, electrolytes, and gases currently used in the NRR field may affect the quantitative NH_3 yield. Therefore, $^{15}N_2$ isotope experiments are an essential part of NRR experiments.^{79,80} From a catalytic perspective, the cyclic synthesis of NH_3 via aqueous NRR should be performed more than 10 times, and there should be a linear relationship between the reaction time and the number of cycles. Moreover, easily overlooked key experimental parameters, such as gas flow rate, electrolyte volume, and sampling methods, still require thorough investigations of the impact on NRR activity and selectivity.

Although the aqueous NRR system still faces many challenges, its advantages of mild and environmentally friendly NH_3 synthesis make us more willing to consider it an insurmountable difficulty. To balance efficiency and accuracy, we recommend a rigorous protocol for daily NRR experiments (Figure 5).

1) Conducting NRR experiments requires a clear and detailed description of the experimental protocols and details, such as the purity of chemical reagents and source gases, the exclusion of nitrogen sources during

material synthesis, electrolytic cell design and electrochemical measurements, control experiments, cyclic tests, and various NH_3 detecting methods.

- 2) Excluding external nitrogen sources from materials, gases, and the reaction system is necessary to eliminate false positive results. Additionally, more accurate and rigorous results for NRR can be obtained through stable yield–time linear relationships.
- 3) Defining the calculation methods for NH_3 yield and Faraday efficiency (FE) is crucial. It is recommended to provide raw data on current density, ultraviolet–visible absorption spectra or NMR spectra, NH_3 yield, and FE for the control experiments at different atmospheres and other control conditions.

2.1 | Metal-based catalyst

Electrochemical NRR mainly involves three steps: nitrogen adsorption, cleavage, and hydrogenation. The sluggish kinetics of nitrogen activation has always been an important barrier limiting subsequent reactions. The d -orbital electrons of the transition-metal-based materials can achieve π backdonation effects, thereby alleviating the kinetic problems of $N\equiv N$ bond activation.^{29,81–84} Meanwhile, the excellent proton activation ability of noble metals and several transition metal-based materials can provide sufficient proton sources for subsequent nitrogen hydrogenation steps.^{85–88} This provides an extensive basis for material selection for the following material design.

As the leader of various catalysts, noble metals have good conductivity, polycrystalline surfaces with rich active sites, and the ability to combine with different reaction intermediates.^{89–92} They also exhibit excellent catalytic potential in electrochemical NRR. Bao et al.⁹³ synthesized tetrahedral Au nanorods via a seeded growth approach. This as-synthesized Au catalyst achieved the maximum NH_3

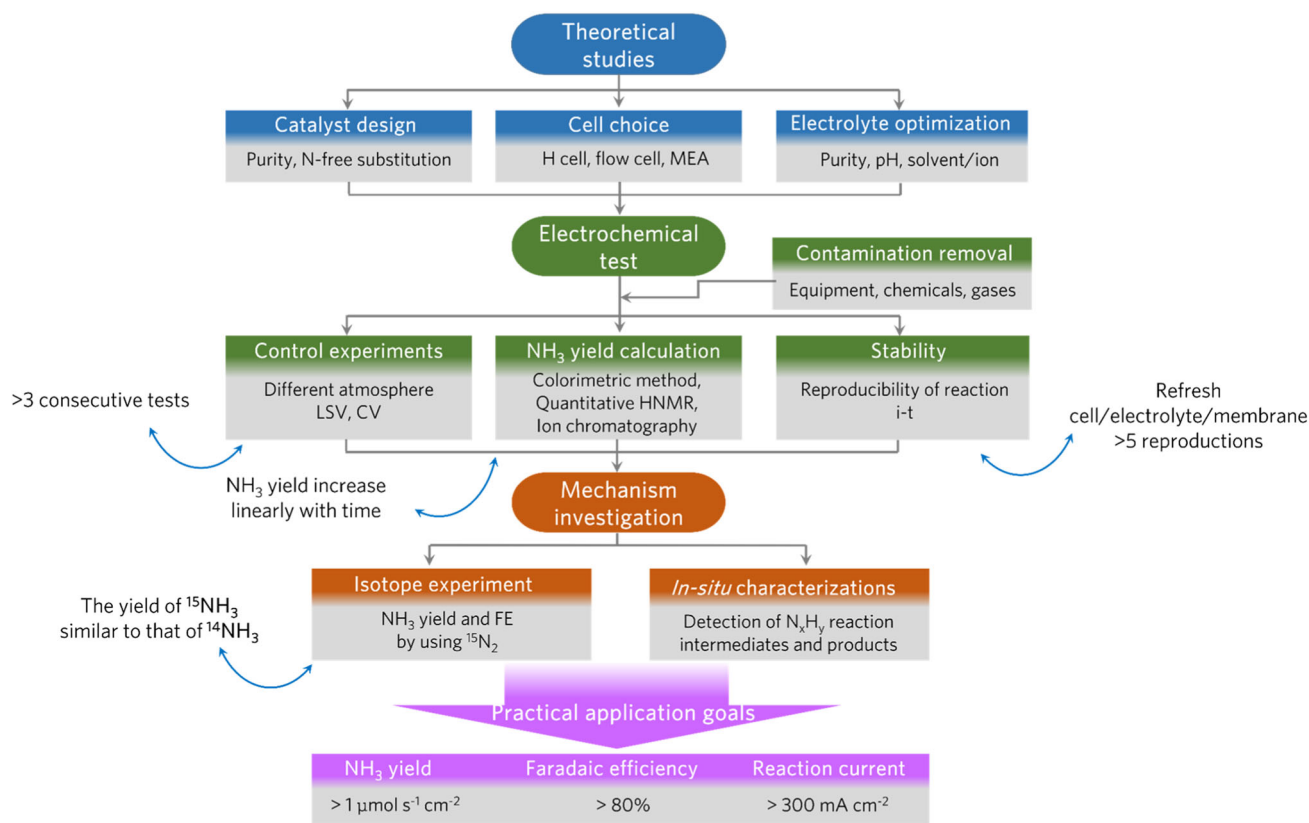


FIGURE 5 Recommended experimental protocol to rigorously conduct NRR research.

yield of $1.648 \text{ mg h}^{-1} \text{ cm}^{-2}$ with FE of 4.02% and by-product hydrazine yield of $0.102 \text{ mg h}^{-1} \text{ cm}^{-2}$. Although the above reaction efficiency and selectivity need to be improved, starting with this classic work of Au, various noble metals are gradually stepping onto the electrocatalytic NRR. Considering the ability to break through the reaction barrier and rich surface-active sites on ruthenium, rhodium, and other noble metals, various strategies, including single atom designing, alloying, morphological controlling, and surface/interface engineering, can be introduced to enhance the NRR performance of metal-based materials.^{94–99}

The ideal NRR electrocatalyst requires excellent N₂ activation ability and suitable proton transfer ability. For transition metal-based hybrid materials, the metal *d* states and *s* states of main group elements induce *sp* hybridized states on the surface.^{100–102} The excess occupied orbitals of transition metal induce the backdonation of electrons to the π -antibonding orbitals of N₂, thereby achieving N₂ cleavage. Meanwhile, based on the Lewis acid–base theory, nitrogen molecules with lone pair electrons belong to Lewis bases, while noble metals are Lewis acids.^{103,104} Introducing noble metal sites on transition metal hybrids can theoretically achieve efficient and highly selective N₂ adsorption and cleavage. Computational study suggests that transition metal carbides (the *d*², *d*³, and *d*⁴ series) are promising for nitrogen

capture and reduction. Chemisorbed nitrogen on transition metal carbides can elongate/weaken the N≡N triple bond, thus promoting its catalytic conversion into NH₃. Bin et al.¹⁰⁵ proposed an efficient laser-tuning strategy for constructing a series of noble-metal Lewis acid sites on the molybdenum carbide (Figure 6A). They imparted the Lewis acid character of noble metal on adjacent molybdenum sites with empty orbitals, yielding an outstanding NRR system by mimicking π backdonation. The laser-tuned noble metal sites achieved effective N₂ cleavage, lower thermodynamic energy barrier, and optimized N_xH_y migration pathway. The as-synthesized Rh-Mo₂C achieves an excellent NH₃ yield rate of $26.3 \mu\text{g h}^{-1} \text{ cm}^{-2}$ and FE of 15.4% in the neutral electrolytes. This general laser-tuning strategy guides the interface/surface engineering of active materials for promoting π backdonation.

Numerous metal materials exhibit specific NRR capabilities, but nitrogen activation and competitive hydrogen evolution are still the bottlenecks that limit the further improvement of NRR. Taking transition metal oxides (TMOs) as examples, they are considered potential NRR materials owing to the inappropriate hydrogen adsorption energy.^{109–111} Although TMOs can regulate subsequent hydrogenation steps, their electron-rich surface limits nitrogen adsorption in the first step.

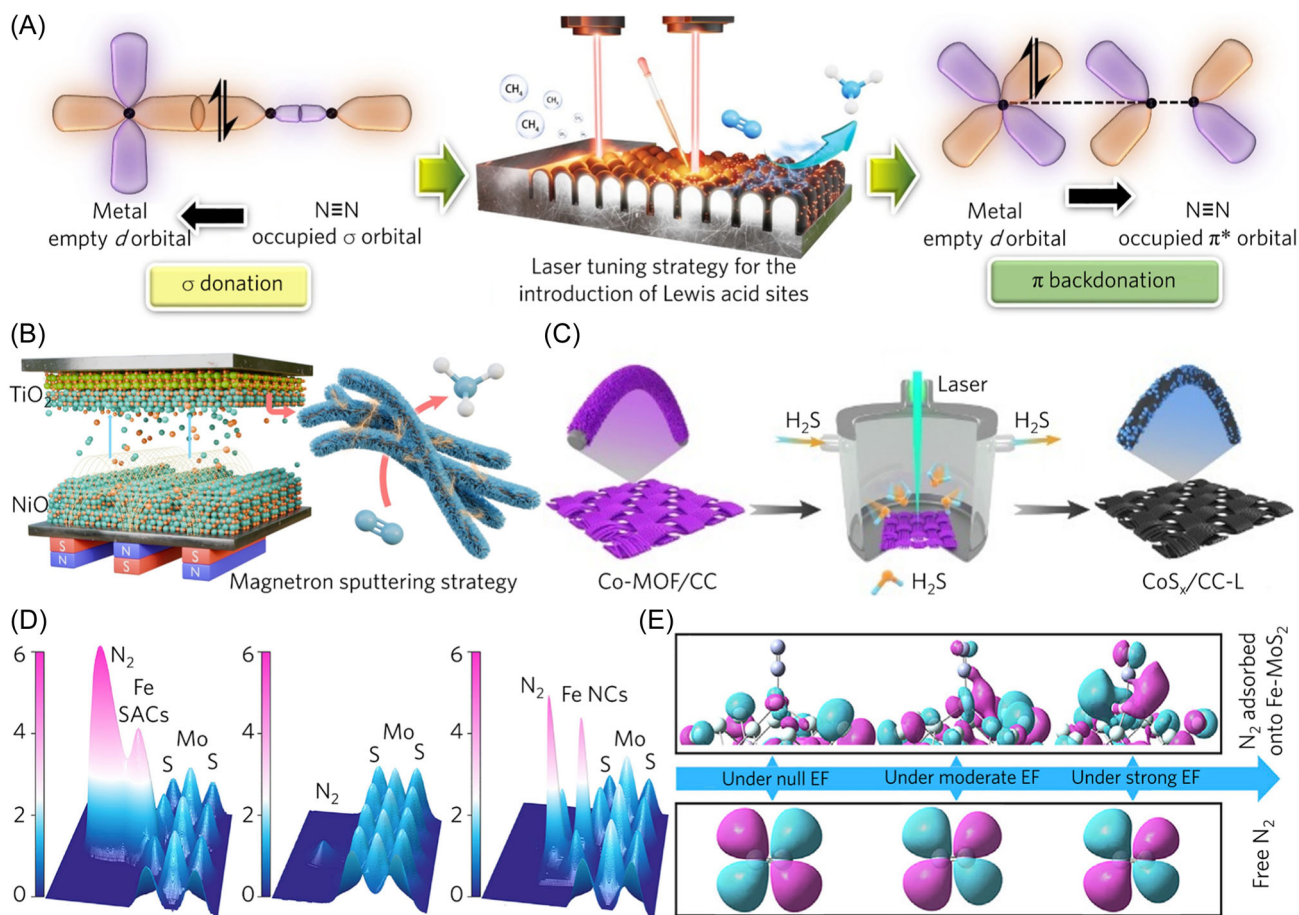


FIGURE 6 (A) Illustration of the laser-tuned concept for mimicking π backdonation. Reproduced with permission: Copyright 2023, Elsevier.¹⁰⁵ (B) Illustration of magnetron sputtering tuned active sites on transition-metal oxides. Reproduced with permission: Copyright 2022, the Royal Society of Chemistry.¹⁰⁶ (C) Illustration of laser-constructed S vacancy on CoS_x NRR electrocatalyst. Reproduced with permission: Copyright 2023, the Royal Society of Chemistry.¹⁰⁷ (D) Three-dimensional topographic potential distribution images of N₂ adsorbed onto different samples. (E) Variation trends observed in the configurations of LUMO of free N₂ and of N₂ adsorbed onto Fe-MoS₂. Reproduced with permission: Copyright 2022, Elsevier.¹⁰⁸

Chang et al.¹¹² utilized the advantages of excellent conductivity and strong chemical stability characteristics of transition metal nitrides to construct an oxynitride layer structure on the surface of TMOs. The oxynitride layer possesses additional metal valence states, which are conducive to the N₂ absorption and activation with the lone-pair electrons. The as-synthesized TMOs with oxynitride layer exhibit enhanced neutral NRR activity with a yield of 6.78 $\mu\text{g h}^{-1} \text{cm}^{-2}$ and FE of 5.6%. This chemical method to efficiently control the electronic structure of materials still needs further improvement. Meanwhile, introducing nitrides obscures the nitrogen traceability of NH₃ synthesis, and the corresponding NRR mechanisms are too complex to achieve clear investigation.^{113,114} Herein, Zhao et al.^{106,107} used high-energy physics methods such as magnetron sputtering and laser to accurately control the surface vacancy of

TMOs and sulfides, thus improving the NRR activity. The introduction of magnetron sputtering synchronously realizes the regulation of the metal valence state and oxygen vacancy (Figure 6B).¹⁰⁶ The unique electronic structure with occupied and vacant orbitals at the metal atoms significantly promotes π backdonation. After magnetron sputtering of NiO, the NRR performance of pure TiO₂ substrate has significantly improved to 10.75 $\mu\text{g h}^{-1} \text{cm}^{-2}$, which is seven times that of pure TiO₂. Similarly, metal sulfides have also been regarded as potential electrocatalysts due to the “accept and back-donate” interaction of metals with nitrogen. Defect and interface engineering are efficient strategies for promoting the intrinsic and extrinsic catalytic activity of metal sulfides. Zhao et al.¹⁰⁷ achieved promoted NRR activity on CoS_x with a yield of 12.2 $\mu\text{g h}^{-1} \text{cm}^{-2}$ by via laser to tune the sulfur vacancies on the material surface

(Figure 6C). The above works have confirmed the feasibility of controlling the π backdonation sites by physical approaches, which show great potential in modifying transition metal materials.

Single-atom catalysts are widely investigated owing to their ability to achieve efficient atomic utilization and excellent ability.^{115–120} The type of central metal species, electron configuration, and surrounding coordination environment affect their geometric and electronic structure, so these parameters control allows to tune the reaction pathways of electrochemical NRR.^{121–124} Ma et al.¹²⁵ designed a synergistic strategy in the synthesis of Mo single-atom electrocatalyst coupling with Mo₂C nanoparticles anchored on carbon nanotube. The as-synthesized material exhibited excellent acidic NRR performance with an NH₃ yield of 16.1 $\mu\text{g h}^{-1} \text{cm}^{-2}$ and FE of 7.1%. To further improve the utilization rate of single atoms, Li et al.¹⁰⁸ combined single-atom catalysts with two-dimensional materials to excite extreme electric fields and achieve nitrogen repolarization. The hetero-junction interfaces are conducive to the formation of high curvature interfacial protrusion shapes so as to fully utilize each interface atom to achieve maximum stimulation of extreme electric fields (Figure 6D). The introduction of Fe single-atom greatly increases the extreme electric field of monolayer molybdenum disulfide. The enhanced electric field polarizes N₂ to trigger interface polarization, which significantly promotes electron injection back into N₂ (Figure 6E), thereby achieving efficient NRR with the NH₃ yield of 36.1 $\text{mg h}^{-1} \text{g}^{-1}$ and FE of 31.6%. The coupling strategy of curvature-rich surface and single atom-triggered interface polarization can effectively achieve N₂ activation. This strong polarization design concept lays the foundation for future innovation in electrochemical NH₃ synthesis.

The investigations on two-dimensional transition metal carbides (MXene) in the field of electrochemical NRR are rapidly proceeding.^{126,127} Theoretically, pristine MXene possesses excellent nitrogen gas adsorption capability. Among various material models, the nitrogen hydrogenation step on Mo₂TiC₂ demonstrates thermodynamic feasibility.¹²⁸ Simultaneously, the high hydrogen evolution free energy limits the hydrogen evolution side reaction at Mo active sites, potentially leading to enhanced FE. However, in experiments, pure MXene did not exhibit the expected outstanding NH₃ yield and FE as predicted by theory.^{129,130} MXene differs from the theoretical pure carbide model due to the limitations in nitrogen adsorption and activation. Therefore, researchers have explored a series of surface modification and construction methods for MXene hybrids to overcome the energy barriers in the reaction rate determination step

(nitrogen activation or nitrogen hydrogenation).^{131–135}

The fine-tuning of the micro/nanostructure and electronic configuration through inorganic and polymer modification or heteroelement doping collectively creates a favorable environment for nitrogen adsorption. Additionally, MXene functions as a platform for hosting active sites, including single atoms, atomic clusters, and heterogeneous junctions. Guided by the earlier optimization strategies, highly unsaturated metal single-atom sites dispersed on MXene exhibit excellent activity. The strong interaction between the single atom and MXene can effectively anchor the single atoms and prevent aggregation. Peng et al.¹³⁶ have innovatively designed single-atomic ruthenium-modified Mo₂CT_x MXene nanosheets as an efficient electrocatalyst for nitrogen fixation at ambient conditions. Single-atomic Ru anchored on MXene nanosheets plays a pivotal role as essential electron backdonation centers for N₂ activation, which can not only promote nitrogen adsorption and activation behavior of the catalyst but also reduce the thermodynamic energy barrier of the initial hydrogenation step.

To sum up, noble metal-based materials typically exhibit excellent catalytic activity, while high cost and limited resources hinder the practical applications. The NRR catalytic performance of TMOs has been widely studied and confirmed, but their stability is relatively poor under negative potential conditions. Other transition metal-based materials, including sulfides, carbides, and phosphides, may be worth more explorations. Although theoretical studies have demonstrated the potential of transition metal nitrides as NRR catalysts based on the Mars-van Krevelen mechanism, the experimental research on nitride catalysts is still limited, mainly due to N vacancy poisoning and catalyst decomposition during the reaction process. It is necessary to construct more efficient and stable nitrides in suitable reaction systems to achieve excellent NRR performance. As a promising NRR catalyst, single-atom catalysts require further research to broaden the range of dispersed metal atoms from noble metals to transition metals. Moreover, metal-organic framework (MOF) or MOF-derived materials with highly porous structure and multiple catalytic active sites are considered to have promising prospects in the electrochemical conversion of nitrogen to NH₃.

2.2 | Metal-free catalysts

Transition metal-based NRR catalysts have achieved tremendous efforts in the past few years. However, further enhancement of their activity still needs to be improved by the following points: (1) The intrinsic

nitrogen adsorption capacity on the metal surface is poor, which hinders the subsequent hydrogenation process and affects the NH_3 yield. (2) Although the *d*-orbital electrons of metals can be controlled through different physical and chemical methods, the metal–nitrogen bonding is weak. The *d*-orbital electrons tend to form metal–hydrogen bonds, thus leading to strong competitive side reactions and affecting FE. (3) The intrinsic low-porosity structural characteristics of metal materials are also not conducive to nitrogen fixation. Metal-free materials formed by strong covalent bonds have many unique physicochemical characteristics, including high surface area, controllable porosity, and excellent conductivity.^{137–140} Metal-free materials with the above advantages provide abundant anchor sites for nitrogen and intermediates. Moreover, the energy band gap, spin density, and charge density of the materials can be adjusted through doping and structural engineering, which further regulate the nitrogen adsorption and activation steps in the NRR process.^{141–143} Hence, metal-free materials with the optimized structure are ideal for designing high-performance and low-cost NRR electrocatalysts.

Graphitic carbon has been extensively investigated to suppress HER. However, the limited nitrogen adsorption ability is still a significant hurdle to further applications. The positive charge density of carbon can be affected by the adjacent heteroatoms with strong electronic affinity, which is conducive to nitrogen adsorption.^{21,144–147} The intrinsic activity of metal-free catalysts originated from the heteroatoms (such as boron, nitrogen, and oxygen).^{148–150} Take boron as an example, the electronegativity of boron (2.04) is much smaller than that of carbon (2.55). Herein, the positive charge on the boron atom can be induced by the significantly polarized B–C σ bonds (Figure 7A).¹⁴¹ The reverse opposite electronegativity creates Lewis acid sites with empty orbital for adsorption of the weak Lewis base N_2 and subsequent N_xH_y intermediates (Figure 7B). Chang et al.¹⁵¹ fully utilized boron Lewis acid and boron/nitrogen Lewis acid/base pairs to design a series of boron/nitride-rich carbon (BCN) materials (Figure 7C). Comparing boron-enriched BCN (B-BCN) with nitrogen-enriched BCN (N-BCN), the density functional theory of the reaction pathway revealed that the energies of all steps of B-BCN are relatively lower than those of N-BCN, which further proves the NRR reaction facilitated by the boron Lewis acid site (Figure 7D). Based on the above theory, the author subsequently successfully prepared BCN materials with different boron and nitrogen contents, and the main structure of the materials was similar without any changes. This also makes it easier to discuss the active sources of materials at the atomic level. The prepared

BCN materials are nanomesh morphology with clear lattice fringes of the BCN(002) facet (Figure 7E). The as-synthesized B-BCN exhibits enhanced NRR activity with the NH_3 yield of $8.39 \mu\text{g h}^{-1} \text{cm}^{-2}$, three times that of N-BCN (Figure 7F). The concept of element doping or constructing multicomponent metal-free materials provides far-reaching guidance for the development of metal-free NRR materials in the future.

The particular morphology of structure and distinct electronic and chemical surface properties usually confer improved NRR activity and selectivity compared to bulk materials.^{154,155} In this sense, the reactivity of metal-free nanomaterials can be rationally tuned by constructing hierarchical porosity and defect engineering. Generally speaking, modifying the fundamental parameters (size, shape, surface composition, or loading on the support) further affects the enrichment of reaction intermediates on active sites and the electrolyte diffusion dynamics. Ma et al.¹⁵² synthesized a series of carbon-doped boron nitride (C-BN) with different microstructures at different calcination temperatures. The decomposition of raw urea released gases, inducing numerous large bubbles to form a porous structure. The as-synthesized C-BN possesses a large average-size of aperture (Figure 7G). Strong interaction between C atoms and B or N atoms leads to short bond distances of C–N/C–B. That induced the *s/p* electrons of the carbon atom, contributing to the valence band maximum. As a result, the optimized C-BN materials show an excellent NH_3 yield of $44.59 \mu\text{g h}^{-1} \text{cm}^{-2}$ and FE of 13.27% (Figure 7H). Zhang et al.¹⁵³ further regulated the structure of catalysts both at the micro level and at the nano level. The nitrogen-rich carbon with a high concentration of terminal nitrile groups and pyrazine nitrogen has been employed as an NRR catalyst. The as-obtained material shows a plate-like microscale structure with abundant small and aggregated nanoparticles inside (Figure 7I). Finally, an enhancement of NH_3 yield has been achieved at $5.68 \mu\text{g h}^{-1} \text{mg}^{-1}$ with an FE of 11.4% (Figure 7J).

To date, various works attempt to control the chemical nano/microstructures of carbon-based materials to design metal-free catalysts for potential electrochemical NRR. Considering complex catalyst active sites and complicated purposeful optimization of carbon-based materials, metal-free materials carrying high-concentration active centers with strong intrinsic activity are also developed. Based on the “like dissolves like” principle, Zhang et al.¹⁵⁶ designed and prepared few-layer black phosphorus nanosheets (BP) for electrochemical NRR. The zigzag and diff-zigzag edges of BP materials are the real N_2 adsorption/activation sites. A high acidic NH_3 yield of $31.37 \mu\text{g h}^{-1} \text{mg}^{-1}$ with FE of 5.07% is achieved. These works provide the feasibility of using noncarbon metal-free materials as nitrogen-fixing

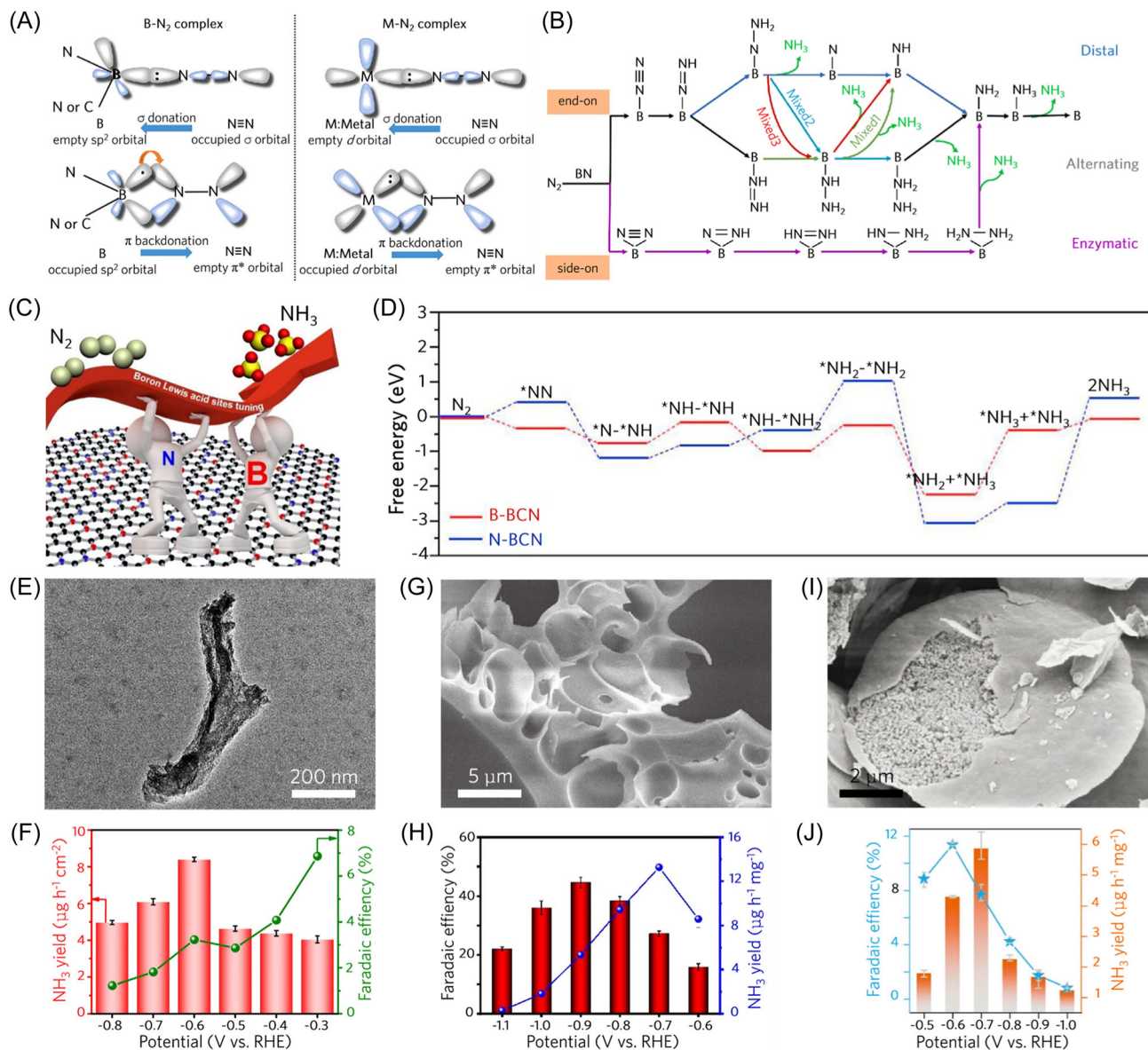


FIGURE 7 (A) Simplified schematics of N_2 bonding. (B) Schematic depiction of NRR mechanisms at the edge B atom sites. Reproduced with permission: Copyright 2021, Elsevier.¹⁴¹ (C) Scheme of boron-enhanced NRR performance of boron carbonitride (BCN). (D) Free energy profile for the NRR process on B-BCN and N-BCN. Reproduced with permission: Copyright 2022, Elsevier.¹⁵¹ (E) Transmission electron microscopy image and (F) NRR activity of B-BCN. Reproduced with permission: Copyright 2021 Elsevier.¹⁴¹ (G) Scanning electron microscopy (SEM) image and (H) NRR activity of carbon-doped boron nitride. (I) SEM image and (J) NRR activity of metal-free C_2N . Reproduced with permission: Copyright 2022, Elsevier.¹⁵² and Reproduced with permission: Copyright 2022, Wiley-VCH.¹⁵³

catalysts (such as black phosphorus and boron nitride), which can give access to the accurate investigation of the NRR mechanism.

2.3 | Electrolyte and cell optimization

Electrolytes participate in NRR by interacting with catalysts, reactants, intermediates, and products. Common aqueous electrolytes mainly contain inorganic salts, alkali metal cations, sulfate, and halogen ions. A deep

mechanistic understanding of the electrolyte effect helps to improve NRR activity and selectivity through efficient electrolyte design. Up to date, most NRRs are performed in the aqueous phase, such as acidic solutions (sulfuric acid, hydrochloric acid, and perchloric acid), neutral solutions (sodium sulfate and phosphate buffer solution), and alkaline solutions (potassium hydroxide). Although abundant works reported the effects of electrolyte ions and pH on NRR activity and selectivity, the specific mechanism of the electrolyte effects still needs to be clarified and unified.^{157–160} It is theoretically foreseeable

that the catalyst exhibits high NRR performance in acidic solutions. The abundant protons not only enhance HER but also provide sufficient proton sources for NRR. However, in actual experiments, the NRR performance can be affected by differences in cell structure, inherent characteristics of catalysts, impurity effects in electrolytes, and local pH gradients induced by reactions. Therefore, the optimization of electrolyte selection is crucial in the future development of NRR.

The optimization of electrolytes provides an opportunity to improve the selectivity of electrocatalytic NRR. In addition to traditional liquid electrolytes, lithium-mediated (such as LiClO_4 in ethanol or tetrahydrofuran [THF]) and water/alcohol mixture (water/2-propanol) electrolytes promote N_2 solubility and are also gradually being developed.^{80,161} The specific analysis of lithium-mediated NRR (Li-NRR) will be described in detail in subsequent chapters. Considering the limited solubility of nitrogen in aqueous solutions, ionic liquids can serve as an excellent homogeneous electrolyte, effectively improving nitrogen solubility and highly inhibiting the progress of HER.^{162,163} Zhou et al.¹⁶² introduced hydrophobic and high nitrogen-solubility ionic liquids electrolyte ($[\text{C}_4\text{mpyr}][\text{eFAP}]$ and $[\text{P}_{6,6,6,14}][\text{eFAP}]$) to achieve a high NRR FE of 60%. Meanwhile, Licht et al.¹⁶⁴ conducted NH_3 synthesis by air and vapor in a molten hydroxide (0.5 $\text{NaOH}/0.5$ KOH) electrolyte. NH_3 is produced with high Coulombic efficiency (35%) at 1.2 V and 200°C. Although FE is highly desired, the complexity of high-temperature molten salt systems requires improvement and optimization to adapt to further applications.

Unlike liquid electrolytes, electrolytic NRR cells with solid electrolytes have the potential to overcome the typical low conversion rate during the NRR process.^{165–167} Due to the high conductivity of polymers in the low-temperature range, Nafion polymer electrolytes (solid H^+ conductors) have good application prospects in low-temperature NH_3 synthesis. Sheets et al.¹⁵⁹ introduced Nafion polymer as the electrolyte for NH_3 synthesis from wet H_2 and dry N_2 . Nafion achieves high current efficiency as an electrolyte on the membrane. However, the water retention rate decreases

with the increase in temperature, thus blocking proton conductivity on the Nafion membrane and leading to decreased NRR activity. Lan et al.¹⁶⁸ tried to utilize $\text{H}^+/\text{Li}^+/\text{NH}_4^+$ mixed conducting Nafion membrane to resolve the issue. The treated conductive membrane increases the chemical compatibility between the acidic Nafion membrane and NH_3 . The reaction system achieved the highest NH_3 yield and FE by increasing the temperature to 80°C. However, due to the blocking effect of Li^+ on transferred protons, Li^+ ions reduce the NH_3 formation, resulting in a relatively low current at higher applied voltages. Weakly alkaline NH_3 can react with acidic membranes, which has a negative impact on yield. Therefore, it is possible to introduce alkaline electrolytes into the reaction system to enhance ion conductivity.

The solid oxide NRR systems have different working principles, which involve a proton conductor with the deposition of anode/cathode on both sides. H_2 flows on the anode to convert to H^+ . As-produced protons are transported to the cathode and react with N_2 for NH_3 synthesis. Herein, high-temperature H^+ conductors, such as SrCeO_3 and CsH_2PO_4 , show different H^+ conductivity, which can be an alternative to traditional solid-state electrolytes.^{169,170} To summarize, the stability of liquid organic electrolytes needs to be further improved. And the poor conductivity and high energy consumption of solid-state electrolyte systems directly lead to a low NH_3 conversion. In the future, liquid or solid electrolytes need to be selected, designed, and optimized according to the specific structure of the electrolytic cell.

Traditional H-type electrocatalytic cell still needs further improvement (Figure 8). The most common approach is to regulate basic operating parameters to optimize performance, such as reaction temperature, gas flow rate, and stirring rate. However, this optimization effect is extremely limited. Future works can focus on exploring the optimization of membranes and electrolytes. To improve the membrane of the H-type cell, it is possible to regulate the ion conductivity, NH_3 adsorption/leaching, interface blocking effect, and so forth. The

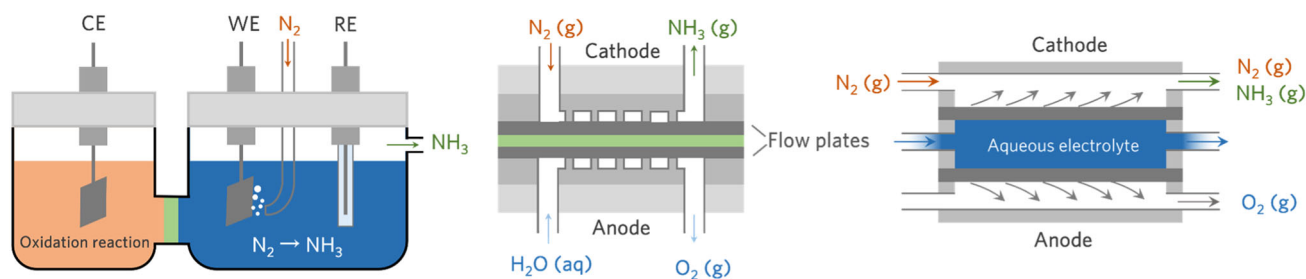


FIGURE 8 The design scheme of electrochemical cells for NRR.

site blockade of various electrolyte cations can regulate proton-coupled electron transfer and NH_3 selectivity. Optimizing electrolytes with high N_2 solubility and diffusion coefficients, such as ionic liquids or organic electrolytes, can promote dissolution while weakening the occurrence of side reactions.

Although the H-type cells have made some achievements so far, this technology still needs to reach the appropriate industrial level regarding NH_3 production, FE, current density, and stability.^{171–173} The flow cells have shown high efficiency in fuel cells (oxygen reduction) and carbon dioxide reduction.^{174–176} In theory, flow cells can generate high current density and FE by improving the N_2 concentration at the electrode interface, alleviating mass transfer limitations, and further increasing the N_2 retention time (Figure 8). However, contrary to expectations, the performance of flow cells for NRR has yet to show a breakthrough effect so far. Therefore, the thermodynamics, kinetics, and fluid dynamics mechanisms of NRR in flow cells need to be thoroughly investigated. Meanwhile, the structure of flow cells also needs further systematic optimization, such as gas diffusion layer, electrolyte, electrolyte buffer layer, ion exchange membrane, and flow field.

3 | NITROGEN ACTIVATION VIA MEDIATORS

Currently, it is still a huge challenge to break the extremely strong $\text{N}\equiv\text{N}$ bond and directly reduce N_2 into NH_3 by providing electrons and protons at a sufficiently high chemical potential without generating H_2 . As mentioned earlier, the optimization of electrolytes is one of the approaches to improve nitrogen activation efficiency. A possible way to avoid HER is to separate N_2 activation and subsequent protonation into NH_3 . As one of the most widely studied mediators, lithium serves as a bridge for the above two steps.^{177,178} Moreover, transition metal or metal-free complexes and enzymes are also utilized as mediators for N_2 conversion under mild conditions.^{179,180}

3.1 | Lithium-mediated nitrogen reduction

Li-NRR is a potential candidate as a future NH_3 synthesis technology. Strictly speaking, Li-NRR belongs to the technologies for electrochemical NH_3 synthesis rather than electrocatalysis. Although Li-NRR is one of the most feasible pathways, the reaction mechanism of Li-NRR in nonaqueous systems is still unclear. Li-NRR generally refers to the reduction of Li^+ into metal Li on the

working electrode, which reacts with N_2 to generate lithium nitride (Li_3N) (Figure 9A).^{178,183} Li_3N is protonation with proton sources (such as alcohols) to achieve NH_3 synthesis. There are four explanations for the specific reaction mechanism as follows:

- 1) Thermochemical nitrogen fixation and protonation will consume the electrodeposited lithium, thus producing NH_3 and lithium ethoxide.
- 2) Metal lithium, Li_3N , and lithium hydride are utilized as electrocatalysts, and nitrogen is adsorbed, protonated, and reduced on the surface to form NH_3 .
- 3) The relative transfer rates of lithium ions, nitrogen, and protons in a solid electrolyte interface (SEI) determine selectivity, meaning that an unbalanced diffusion rate will lead to excessive metal lithium or Li_3N or severe HERs.
- 4) The properties and concentration of proton donors determine the transfer properties of SEI.

The coupled kinetic transport model has been designed to investigate the rate influence mechanisms of Li-NRR.¹⁸¹ The FE of NH_3 synthesis is directly proportional to the N_2 pressure, indicating that the reaction is mainly related to the concentration of N_2 in the electrolyte. Therefore, increasing the partial pressure of N_2 can improve the performance of Li-NRR. Moreover, the optimal EtOH (proton carrier) concentration is ultimately determined to be 0.1 M by exploring the relationship between EtOH concentration and NH_3 yield.¹⁸⁴ The FE of NH_3 decreases under further increased EtOH concentration. At higher EtOH concentrations, the reaction between metal Li and EtOH becomes more intense, leading to a decrease in Li-NRR selectivity.

Furthermore, the role of SEI of lithium metal and its surface passivation layer in the Li-NRR process is still controversial. First, is the process driven by thermochemistry or electrocatalysis? That is, will lithium metal be consumed during the process? Second, since the Fermi energy level of lithium metal is higher than the lowest unoccupied molecular orbital (LUMO) of the existing electrolyte, it is highly susceptible to reduction. It is also necessary to confirm whether SEI is involved in the reaction. To further investigate the Li-NRR mechanism, Steinberg et al.¹⁸⁵ analyzed the entire Li-NRR process using cryoelectron microscopy. The results of cryoelectron microscopy indicate that the proton donor ethanol destroys the SEI structure by attacking the amorphous organic components in the SEI (Figure 9B).¹⁸¹ The destruction of amorphous SEI by ethanol may take various forms. The hydrogen generated by the reaction between ethanol and lithium metal can

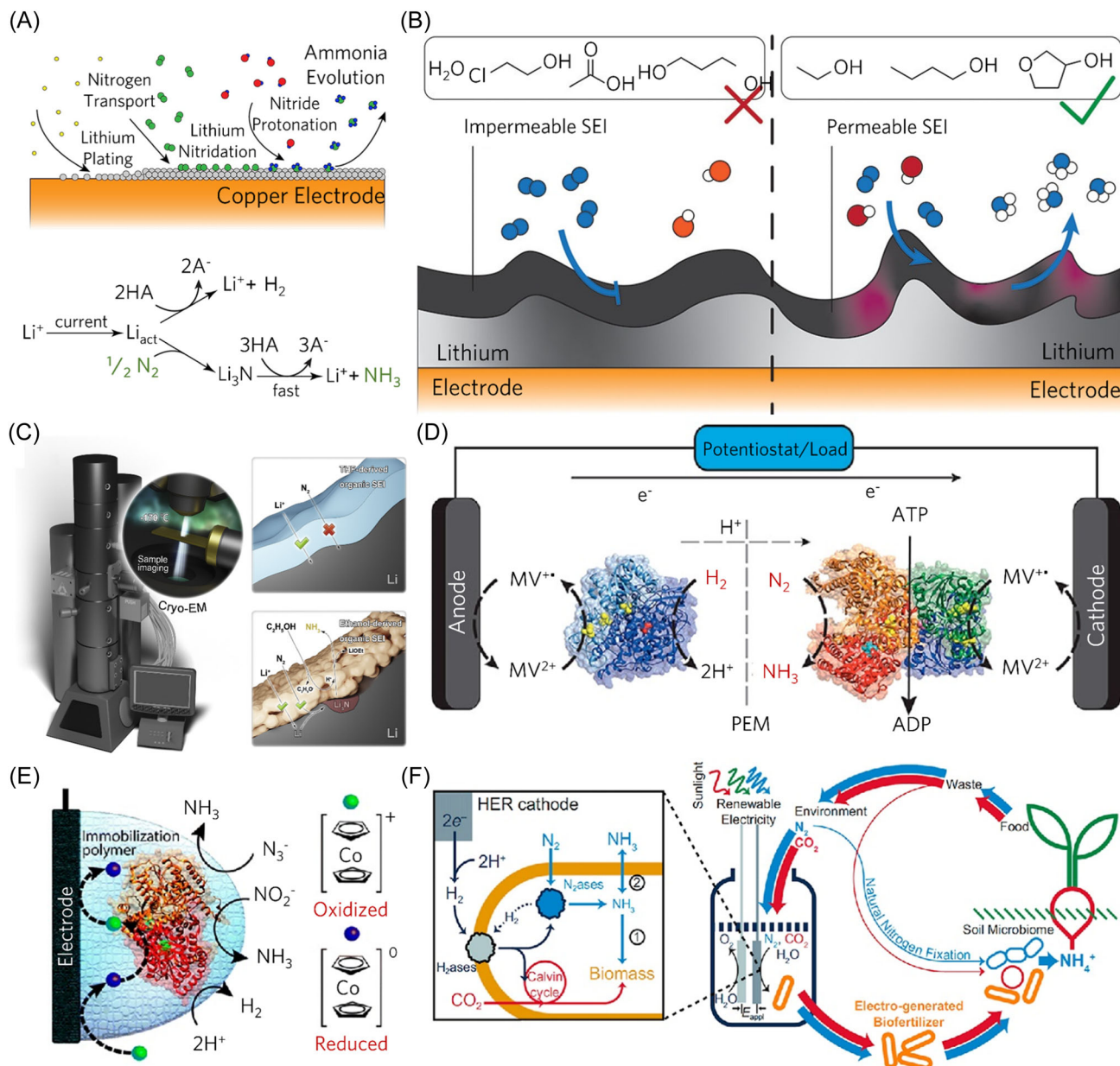


FIGURE 9 (A) Scheme of Li-NRR process. Reproduced with permission: Copyright 2019, Elsevier.¹⁷⁸ (B) Proposed SEI-based mechanism of Li-NRR in the presence of a proton donor. Reproduced with permission: Copyright 2022, American Chemical Society.¹⁸¹ (C) Imaging the reaction interface of lithium-mediated nitrogen fixation via cryoelectron microscopy. Reproduced with permission: Copyright 2023, Elsevier.¹⁸² (D) Scheme of the enzymatic fuel cell. (E) Bioelectrocatalytic NRR using the MoFe protein. (F) Single bioelectrochemical reactor for N_2 and CO_2 reduction into solid biomass. Reproduced with permission: Copyright 2020, American Chemical Society.¹⁴

disrupt the mechanical stability of SEI. Meanwhile, the reaction between ethanol and lithium metal may produce advantageous SEI components with poor passivation and strong nitrogen permeability. The cryoelectron microscopy results indicate that the proton donor ethanol is the main driving force of Li-NRR (Figure 9C).¹⁸² Without the introduction of proton donors, the decomposition products of fluoroborate ions and THF form passive SEI, while nitrogen and electrolyte cannot penetrate and pass through SEI. Meanwhile, lithium ions can diffuse in this

SEI, leading to the continuous formation of lithium dendrites, which is not conducive to the subsequent reaction.¹⁸⁴ With the introduction of ethanol, amorphous SEI will mainly consist of ethanol decomposition products. Nitrogen and electrolyte can penetrate this interface, continuously consuming the deposited lithium metal to form NH_3 . For the Li-NRR system, it is necessary to introduce some proton donors to construct SEI with poor passivation to synthesize NH_3 effectively. However, if there is an excessive reaction between metal

lithium and proton donors, hydrogen gas will be generated, leading to the irreversible loss of metal lithium.

It is still challenging to improve the Li-NRR activity and stability in the future. Currently, the strategies developed to improve the Li-NRR performance mainly include the potential cycling strategy, adding auxiliary oxygen, increasing electrode surface area, introducing gas diffusion electrodes, and optimizing electrolyte or ionic liquids as proton shuttle agents.^{186–189} Li et al.¹⁹⁰ conducted in-depth research on the reaction mechanism and reported that adding a small amount of oxygen to the reaction atmosphere significantly improves the FE and stability of the Li-NRR process. This counterintuitive result focuses on the effectiveness of controlling the competition of H^+ , N_2 , and Li^+ ions on the catalyst surface. This model indicates that oxygen can slow down the diffusion of Li^+ through the SEI layer while maintaining the optimal relationship between surface available H^+ and N_2 . Meanwhile, Fu et al.¹⁹¹ designed a Li-NRR and hydrogen oxidation coupled continuous flow electrolytic cell equipped with a $5\text{ cm} \times 5\text{ cm}$ gas diffusion electrode. A three-chamber continuous flow cell was constructed. The gas diffusion electrode based on stainless steel cloth is located between the gas flow field and the electrolyte chamber, and the gas reactants can be directly fed to one side of the stainless steel cloth electrode, while the electrolyte is fed on the other side. This reaction system exhibits excellent catalytic activity and stability. Based on current exploration, in the subsequent design and improvement of Li-NRR, it is necessary to choose appropriate lithium salts and solvent combinations and introduce high-stability proton donors to achieve SEI activation while avoiding the loss of metallic lithium and improving reaction safety and production efficiency.

3.2 | Complex-compound-mediated nitrogen reduction

To better understand the reaction mechanism and develop catalysts for NH_3 synthesis under mild conditions, tremendous efforts have been made in N_2 activation with transition metal complexes, and several catalytic systems for nitrogen fixation have also been developed.¹⁹² The detailed NRR mechanisms on the transition metal complex system closely related to nitrogenase are still unclear. Insightful mechanistic works are urgently needed to investigate the critical bond-breaking/making steps. Only one molecular electrocatalyst (tri (phosphine) borane iron system) has been reported to reliably proved the reaction mechanism, but

it needs a lower temperature (-35°C) to slow down the background HER and high reduction potential.¹⁹³ Huang et al.¹⁹⁴ first separated and characterized the neutral hydrazide complex intermediate ($[V]=NNH_2$) in the vanadium metal complexes catalyzed NRR system. Dinitrogen compounds and NH_3 were obtained by the reduction of protonation by vanadium amino complexes ($[V]-NH_2$). The distal pathway was possibly involved in the N_2 conversion into NH_3 in this system. Vanadium complexes with aryloxy auxiliary ligands serve as a unique system to stabilize active nitrogen-containing species (N_xH_y) and promote the catalytic conversion of N_2 into NH_3 .

Meanwhile, Garrido-Barros et al.¹⁹⁵ introduced a tandem approach to optimize the selectivity of electrocatalytic NRR. The HER is prevented by using a proton-coupled electron transfer mediator, tethered Brønsted base modified cobaltocenium (abbreviated as **Co**). The tandem system consists of bis(diphenylphosphinoethane) tungsten system (abbreviated as **W**) and THF solvent, 0.2 M [tetra-*N*-butylammonium][BF_4] electrolyte, and TsOH acid. In the presence of **Co**, this system achieves a high FE of 18% and excellent stability for 11 h reaction at -1.35 V . This catalyst successfully achieved the binding of $M-N_2$ and the enhanced NH_3 synthesis via different $M-N_xH_y$ intermediates. Meanwhile, the proton-coupled electron transfer step connects the electrode and TsOH acid to facilitate the formation of $N-H$ bonds at an optimized potential of -1.2 V versus ferrocenium/ferrocene and construct the closed loop of the N_2 reduction cycle. Furthermore, the investigation of different metal complexes (**W**, **Mo**, **Os**, and **Fe**) as mediators also confirmed the universality of the tandem approach.

3.3 | Enzyme-mediated nitrogen reduction

Nitrogenase is a metal enzyme closely related to the fields of agriculture, environment, and energy. Nitrogenase is widely known for its role in catalyzing the conversion of atmospheric N_2 into bioavailable NH_3 . The catalysis of traditional molybdenum nitrogenase utilizes the reductase component to transfer electrons to the catalytic component for substrate reduction.^{196–198} The reductase component (ferritin) contains ATP-binding sites and subunit bridging (Fe_4S_4) clusters within each subunit. Molybdenum iron protein, known as a catalytic component, is a type of $\alpha_2\beta_2$ -isotetramer, which contains a P-cluster ($[Fe_8S_7]$) at each α/β -subunit interface and an M-cluster (R-homocitrate $MoFe_7S_9C$) at each α -subunit. During the substrate conversion process, the two components of molybdenum nitrogenase form functional

complexes, allowing ATP-dependent electrons to transfer from the (Fe_4S_4) cluster of Fe protein through the P cluster to the M cluster.¹⁹⁹ Once MoFe proteins accumulate enough electrons, substrate reduction occurs. There has been widespread interest in the direct transfer of electrons to MoFe proteins.²⁰⁰ The alternative in vitro reducing agents effectively reduce MoFe proteins and support substrate reduction. However, this approach is usually limited by reducing substrates other than N_2 at meager rates. Up to now, various enzymes (such as bilirubin oxidase, carbon monoxide dehydrogenase, hydrogenase, and glucose oxidase) have been successfully immobilized on the electrode surface (Figure 9D).¹⁴ On the electrode surface, the heterogeneous electron transfer of enzymes supports the reduction or oxidation of enzyme substrates, respectively. Electron transfer occurs directly or through the utilization of electronic mediators. In situ observation of electron transfer to/from enzymes can evaluate enzyme-mediated mechanisms and kinetics. Furthermore, the ability to produce important chemicals via bioelectrochemical processes can avoid the need for harsh reaction conditions or expensive catalysts.

Milton et al.²⁰¹ reported the immobilization of nitrogenase β -98^{Tyr-His} MoFe protein on an electrode surface. An electron mediator, cobaltocene, was introduced to promote in situ electrochemical observation of azide/nitrite reduction to NH_3 (Figure 9E). Structural analog cobaltocene (bis(cyclopentadienyl)cobalt(III)) efficiently reduces MoFe protein at the electrode surface. In situ observation of enzyme-mediated reduction catalytic reactions provides an alternative method for exploring the kinetics, substrate interactions, inhibitory effects, and electron transfer pathways of MoFe proteins.²⁰² The observed bioelectrocatalysis has been obtained without Fe protein in MoFe protein, which negates the mechanistic rate-limiting steps related to the Fe protein cycle. Herein, this method will be conducive to investigating the mechanism details of nitrogenase and provide a technical basis for the establishment of bioelectrocatalytic technology for NH_3 synthesis at mild conditions. By regulating the concentration of local electron mediators, MoFe protein immobilized on suitable redox polymer species will increase electron flux and achieve efficient NRR.²⁰¹ In addition to the protein immobilization strategy, exploring the role of ATP in vivo will promote NRR on the surface of bioelectrodes. Based on the previous work, Liu et al.²⁰³ proposed an upgraded N_2 and CO_2 reduction reactor to solid biomass, which couples electrocatalytic water splitting with H_2 oxidizing bacteria, *Xanthobacter autotrophicus* (Figure 9F). The HER is carried out using a biocompatible catalyst of cobalt phosphorus alloy, and oxygen evolution is

achieved using oxidized cobalt phosphate. Under microaerobic conditions, *X. autotrophicus* utilizes hydrogen gas to immobilize N_2 and convert it into biomass. Moreover, when biomass formation is inhibited, NH_3 can diffuse into an extracellular culture medium, thereby achieving NH_3 synthesis.

To summarize, considering that HER occupies the dominant position on most electrode surfaces, decoupling nitrogen activation from the protonation process is a potential strategy to solve the poor selectivity of the current NH_3 synthesis system. This strategy has been successfully implemented through lithium-mediated, complex-mediated, and enzyme-mediated approaches. Although the introduction of mediators has significantly improved the FE, the NH_3 synthesis using mediators still needs to be improved to address issues of high reduction potential and high energy costs. Moreover, the risk of lithium production and the poor stability of complex/enzymes further limit the large-scale application of mediated NH_3 synthesis. Even though the mediated NH_3 synthesis technology is still in the early stages, it has shown certain development potential. It is possible to ultimately achieve efficient and stable mediated NH_3 synthesis via the targeted technology optimization and mechanism exploration.

- 1) In the Li-NRR system, the electrodeposition of Li^+ requires a high potential. Is it possible for lithium alloys (Li-Na/K/Cs/Mg/Ca) to achieve effective activation of nitrogen while reducing the deposition potential of Li^+ ?
- 2) The electrolyte used in the Li-NRR system is volatile THF, which directly affects the stability of the system. Phosphonate cation species have high chemical, thermal, and electrochemical stability, which is a potential alternative to promote Li-NRR stability. Moreover, many liquid electrolytes used in the field of lithium batteries and lithium-sulfur batteries (carbonate, cyclic carbonate, g-pantolactone, and sulfolane) may also be alternative solvents in Li-NRR systems.
- 3) The poor stability of the Li-NRR system is induced by the weak stability of the protonation reagent in the reaction of $\text{Li}_3\text{N} + 3\text{H}^+ \rightarrow 3\text{Li}^+ + \text{NH}_3$. Similar challenges exist in enzyme/complex-mediated systems. Therefore, the key point is a more stable protonation reagent, which can prevent overoxidation/reduction at the anode/cathode.
- 4) Based on the hydrophobic and anhydrous environment of nitrogenase catalytic active sites, cell additives are used to further adjust the SEI and enhance the Li-NRR activity of electrodes. A stable and mainly inorganic SEI can improve kinetic stability even in

aqueous cells. Introducing aqueous electrolytes into the Li-NRR reaction system is a challenging but potentially feasible strategy.

4 | HIGH-ENERGY ACTIVATION OF NITROGEN

As mentioned above, electrocatalytic NH_3 synthesis has significant advantages, such as mild reaction conditions, compatibility with renewable energy systems, controllable scale suitable for offsite production, and no use of hydrogen raw materials. However, the high nonreactivity of N_2 and low solubility in water make it difficult to implement electrochemical NRR directly. The current NRR system is still significantly hindered by low NH_3 generation rate and FE. Although the introduction of lithium-mediated systems significantly improves the reaction rate and current density, the significant overpotential of Li-NRR at a minimum of 3 V endows this process with inherent energy intention. The severe requirements for ultradry and oxygen-free organic solvents, high pressure and low stability, and increased requirements for pure hydrogen and metallic lithium raw materials are significant drawbacks of this approach. Unlike nitrogen, nitrate is highly soluble in solution, making it easier for NO_x to overcome the difficulty of nitrogen intermediates conversion and thus easier to reduce and synthesize NH_3 .^{204–207} Therefore, coupling electrochemistry with high-energy physics to activate nitrogen can achieve high-efficiency NH_3 synthesis while avoiding the problem of traditional homogeneous NRR systems.

4.1 | Plasma activation

Inspired by the lightning-driven nitrogen activation process in nature and the industrial process of thermal plasma nitrogen fixation, the nonthermal plasma induced by spark, glow, and dielectric barrier discharge has recently attracted wide attention and has been applied to the N_2 activation.^{208,209} Currently, nonthermal plasma composed of a series of substances with different energy levels has been utilized for various applications of rapid synthesis and surface modification of materials.^{210–212} High-energy electrons with much higher temperature than the surrounding gas are generated in the nonthermal plasma. Therefore, nonthermal plasma can weaken or even split stable N_2 into more reactive NO_x species at low temperatures.²¹³ Meanwhile, the generation of NO_x by nonthermal plasma has a lower energy consumption with a theoretical energy limit of

$5.56 \times 10^{-2} \text{ kW h/mol}_{\text{NO}_x}$, which is 2.5 times lower than that of the Haber–Bosch process ($0.4 \text{ kW h/mol}_{\text{NH}_3}$). For subsequent electrochemical reactions, the standard potential of NO_x reduction into NH_3 is more positive than that of NRR, which means that electrochemical nitrate reduction reaction (NIRR) is thermodynamically easier to perform compared to the NRR process.^{214–216} Moreover, the standard reduction potential gap between NIRR and HER is much greater than that between NRR and HER, which indicates that NIRR can be theoretically carried out in a broader range of reduction potential than NRR without interfering with the side HER reaction. Therefore, coupling nonthermal plasma with electrochemical NH_3 synthesis can significantly increase NH_3 yield. Sun et al.²¹³ have designed a plasma integrated within an H-cell electrochemical system. This NH_3 synthesis system consists of two steps: (1) nonthermal plasma activation of nitrogen gas in the air to produce NO_x with reduced specific energy consumption and (2) electrochemical conversion of the resulting NO_x into NH_3 with enhanced yield. To further investigate the characteristics of scalable plasma bubble column reactors and how they improve energy efficiency, several different design configurations were developed. The breakdown voltage was reduced owing to the generation of plasma within bubbles at lower energy inputs. The authors subsequently explored the mechanisms and pathways of NO_x generation induced by two different plasma discharge states in the reactor. The glow discharge mainly contributes to N_2 and O_2 activation with the formation of excited N^* , vibrational state N_2 , O^* , and O_3 species, as well as a small amount of NO_x . The strong $\text{N}\equiv\text{N}$ bond (9.8 eV) can be broken via vibrational excitation, and the activated nitrogen species react with the activated oxygen species to form NO_x . In the spark discharge state, higher energy levels contribute to NO_x formation, and the NO production rate is proportional to the vibration temperature of N_2 . Meanwhile, the interaction between plasma and liquid is conducive to OH radical generation, which in turn promotes the transport of reactive NO_x into the solution. Subsequently, a significant increase in NH_3 yield was achieved at the milligram level.

Integrating plasma-induced N_2 activation and electrocatalytic NO_x^- reduction has already exhibited great promise for renewable NH_3 synthesis (Figure 10A).^{219,220} Ren et al.²¹⁷ achieved efficient NH_3 synthesis by an innovative spark discharge plasma cascade electrochemical NIRR integrated system. Based on optimizing the plasma process, the plasma activation effects on N_2/O_2 and the NO_x formation process were systematically explored (Figure 10B). The spark discharge parameters (spark discharge distance and O_2 volume content in the feed gas) directly affect the composition of gas products

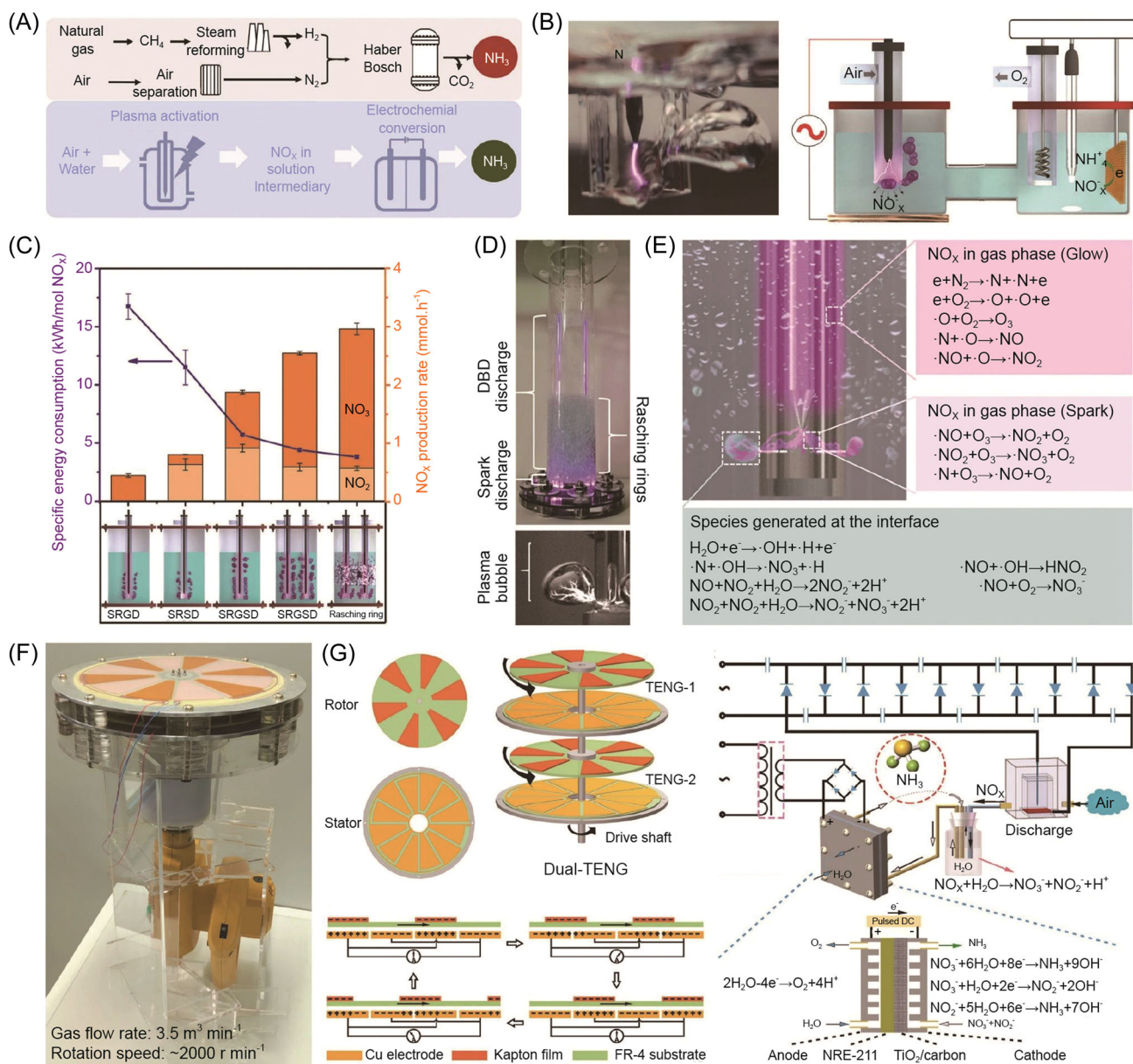


FIGURE 10 (A) Scheme of the plasma-induced NH₃ synthesis system. Digital photo of spark discharge setup with the (B) discharge times and (C) distances. (D) Concentration of NO_x at different plasma-discharge distances. (E) NH₃ partial current density and (F) NH₃ yield rate and FE with the increase of spark discharge time. Reproduced with permission: Copyright 2022, American Chemical Society.²¹⁷ (G) Schematic diagram of NO_x absorption/reduction system with TENG and corresponding working principle. (H) Schematic diagram and photograph of the self-powered radial-engine shaped TENG system. Reproduced with permission: Copyright 2022, American Chemical Society.²¹⁸

(Figure 10C). As the spark discharge distance increases, the total NO_x⁻ shows a trend of volcanic eruption. The residence time of reactants in the emission zone will increase with the extent of spark distance, ultimately increasing NO_x concentration (Figure 10D,E). The further increased spark distance will consume more energy for an electrical breakdown of reactants, thus inducing the decrease in NO_x concentration (Figure 10F). In the subsequent NIRR process, in situ electrochemical attenuated total reflection Fourier-transform infrared

spectroscopy verified the continuous protonation process of NO_x⁻ and nitrogen intermediates NH_x. In situ Raman spectroscopy revealed the in situ reconstruction of high valent copper to Cu⁰ species on Cu nanoparticles during the NIRR process. Based on the above reaction mechanism and technology optimization, the integrated system ultimately achieved a high NH₃ yield of 40 nmol s⁻¹ cm⁻² and FE of 90%, surpassing the traditional NRR process and Li-mediated NRR process. However, up to this date, the micro impact mechanisms of plasma on the N₂/O₂

activation process and the NO_x formation process are still unclear. The further development of this integration system for NH_3 electrosynthesis requires an in-depth exploration of plasma process enhancement and in situ characterizations.

4.2 | Triboelectric activation

Triboelectric nanogenerator (TENG), which originated from Maxwell's displacement current, is a novel technology for energy collection with great practical value. A series of TENGs was utilized to convert various forms of mechanical energy into electrical energy for further energy conversion applications.^{221,222} The strong electric field established by TENG can easily realize chemical $\text{N}\equiv\text{N}$ bond cleavage. Han et al.²²³ constructed a novel TENG, which can directly utilize air as the nitrogen source for electrocatalytic NH_3 synthesis (Figure 10G). TENG-generated high pressure induced air discharge for further N_2/O_2 ionization and NO_x formation. Water flushing with NO_x gas flows directly forms electrolytes containing NO_3^- and NO_2^- for further NRR. Driven by another working TENG, an electrochemical cell using TiO_2 as a catalyst undergoes electrocatalytic NRR to synthesize NH_3 . Considering the strong ultraviolet absorption interference, the authors introduced a dual-chamber cell with a fuel cell structure. Two peristaltic pumps were applied to recycle pure water and nitrate solution to the anode and cathode regions. After the reaction, the NH_3 production yield in the cathode reached $27.5 \mu\text{g h}^{-1}$.

Han et al.²¹⁸ further constructed a self-powered system with TENG by coupling a dual-chamber electrochemical cell and the aforementioned discharge device (Figure 10H). The blower, as an exhaust gas source, combined with dual TENG and commercial turbochargers to drive the system to synthesize NH_3 . After voltage reduction and rectification, TENG outputs approximately 3.1 V and 8.9 mA voltage and current for the dual chamber electrocatalytic cell, respectively. After 10 h of reaction, the self-powered system successfully synthesized NH_3 . By measuring the volume of the solution involved in the cathodic reaction, it was found that the NH_3 yield of this self-powered system reached $2.4 \mu\text{g h}^{-1}$ without any energy input. The above works prove that it is feasible to reuse the residual kinetic energy of factory exhaust gas to drive the NH_3 synthesis system with the coupling of turbochargers. Compared with traditional NH_3 synthesis strategies, this system demonstrates enormous potential in NH_3 synthesis with the advantages of self-power supply, low cost, easy manufacture, environmental protection, scalability, and easy installation.

5 | SUMMARY AND OUTLOOK

Environmental electrochemical NRR for green NH_3 synthesis is considered a potential alternative to the Haber–Bosch process. Tremendous efforts have been proceeded to explore electrocatalysts, electrolytes, and cell configurations for the promotion of NH_3 synthesis selectivity, efficiency, and stability. However, the NRR performance is still limited by issues such as low nitrogen solubility, difficult nitrogen activation, strong hydrogen evolution side reactions, and susceptibility to NH_3 pollution in the system. The complexity of the six electron/proton reduction involved in the reaction is extreme, with challenges in mechanism analysis. Thus, to improve the nitrogen activation ability and the feasibility of NRR experiments, this review summarizes a series of strategies, including the design of different materials, the optimization of electrolyte and electrochemical cell systems, and advanced interdisciplinary applications. Based on the in-depth analysis of the representative works, we propose some novel insights and feasible research directions for achieving effective nitrogen activation and completing subsequent hydrogenation reactions with high selectivity and stability.

5.1 | For effective NRR electrocatalysts

Regulation of surface reactions is crucial for enhancing affinity toward N-materials and improving NRR reaction kinetics. Most currently developed NRR electrocatalysts are still in their bulk or microstructure forms. The introduction of strategies to control surface reactions is highly desirable, such as defect engineering, heteroatom doping, interface/surface engineering, and ion regulation (Figure 11). The development of nanostructured electrocatalysts or self-supported independent electrodes is conducive to the accessibility of beneficial active sites and mass transfer. Designing nanostructured electrocatalysts, such as ultrathin two-dimensional nanosheets and single-atom catalysts, is highly desirable for significantly improving the density of the NH_3 synthesis active site. Meanwhile, the crystal structure and exposed facets significantly affect the adsorption behavior of reactants in NRR. The optimal samples can be determined by preparing and screening electrocatalysts with different surface structures. Based on the volcano mapping, selecting appropriate bimetallic, multimetallic, or high-entropy alloys to change the binding configuration of reaction intermediates is recommended. Modifying the *d*-block transition metals with *p*-block elements can break the linear scaling relationship between the energy of $^*\text{N}_2\text{H}$ and $^*\text{NH}_2$. For instance, the introduction of

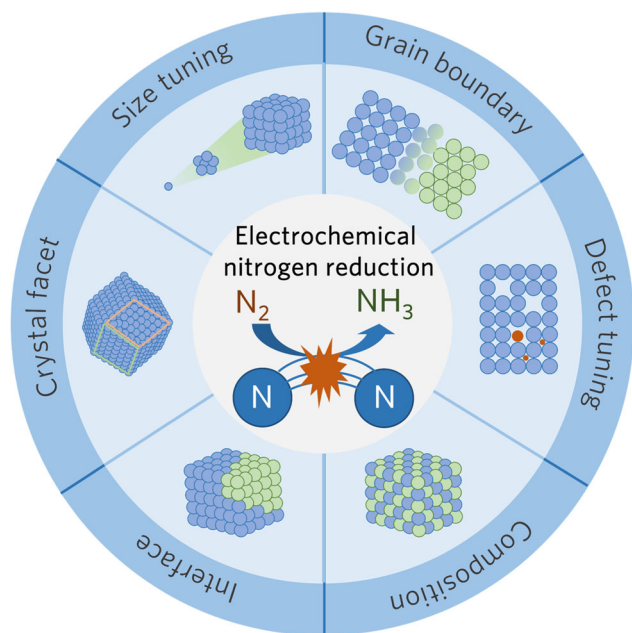


FIGURE 11 Scheme of various strategies for designing aqueous NRR electrocatalysts.

Lewis acidic B element into the system can facilitate the π -backdonation effect, achieving efficient N_2 activation and adsorption and optimizing subsequent hydrogenation reactions. Moreover, semiconductor electrocatalysts (TiO_2 , Fe_2O_3 , MoS_2 , etc.) have also shown specific potential for limiting the availability of electrons, thereby suppressing HER and consequently enhancing NRR selectivity and stability.

5.2 | For optimized reaction systems

Nonaqueous Li-NRR and complex/enzyme-mediated NRR face many challenges, such as high cell voltage, high ohmic resistance, evaporation of organic solvents, proton transport limitations, the safety of lithium metals, and stability of mediated catalytic systems (Figure 12). To achieve high FE and high stability in flow cells at industrial current densities, there are still many optimization points for mediated catalytic systems in the future. The local microenvironment and mass transfer conditions need to be optimized by regulating the Helmholtz buffer layer on the electrode surface with a tuned electrode–electrolyte–gas three-phase interface. The key to further improving the stability of the reaction system is to introduce electrolytes with high chemical, thermal, and electrochemical stability and stable protonation reagents (to prevent excessive oxidation/reduction of anode/cathode). In

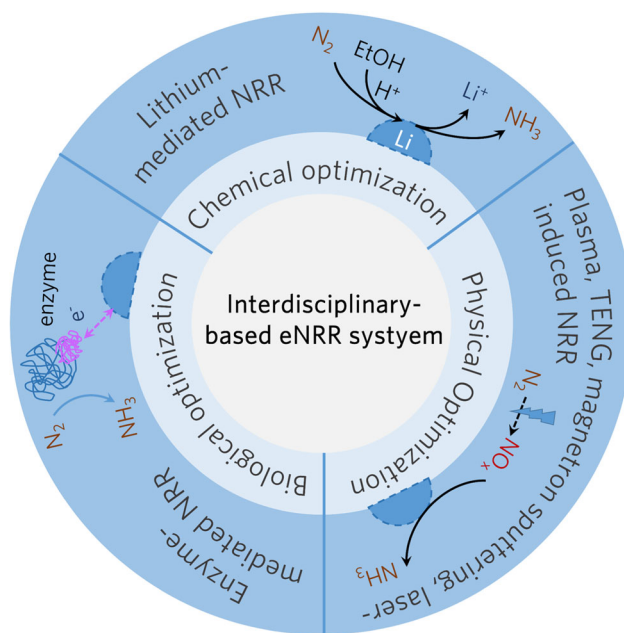


FIGURE 12 Scheme of advanced interdisciplinary strategies for NRR system optimization.

addition, researchers have made progress in understanding the strategies for controlling NRR selectivity in plasma and TENG-mediated processes, but the specific reaction mechanisms still need further exploration. High-energy physics activation of nitrogen (plasma, TENG, magnetron sputtering, or even laser) coupled with electrocatalytic NH_3 synthesis is an important research direction for future development.

5.3 | For mechanism investigation

NRR possesses complex reaction pathways, and the catalyst structure may change during the reaction process. The application of in situ/operando characterization techniques in NRR is highly desirable to establish a precise structure–performance relationship by exploring the interactions between nitrogen, N_xH_y intermediates, catalytic active sites, and solvent and cation effects. Despite the impressive progress made in in-situ/operando characterizations, there still remain several challenges in this field. Due to the limited catalytic information provided by any single in situ/operando technique, it is necessary to perform multiple tests on the same reactor to simultaneously detect changes in the catalyst structure and the intermediate evolution. Furthermore, the signal intensities of N_xH_y intermediates require improvement owing to the low coverage. Another major challenge of in situ/operando experiments is the optimal design of specific electrolytic cells coupling multiple in situ/operando

techniques and NRR systems with mediators at high temperatures or pressures. Obtaining effective information is more convincing for exploring aqueous NRR or Li-/complex/enzyme-mediated NRR mechanisms. Theoretical research on adsorption-free energy, microscopic kinetic models, volcanic mapping, and *d*-band centers can be applied to predict the catalytic behavior of electrocatalysts and obtain a fundamental understanding of catalytic mechanisms. Currently, many theoretical studies have been carried out to reveal the novel NRR systems and the corresponding catalytic mechanisms (such as changes in the electronic structure of the catalyst, association or dissociation mechanism, reaction process, and corresponding intermediate/direct products). In the future, the close integration of theoretical calculations and in situ/operando experiments is a practical approach to exploring reaction thermodynamics/kinetics and pathways.

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CONFLICT OF INTEREST STATEMENT

The authors declare that there are no conflicts of interests.

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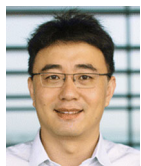
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