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Review Article

Theoretical advances in understanding the active site microenvironment toward the electrocatalytic nitrogen reduction reaction in aqueous media

Tongwei Wu^{1,2}, Marko M. Melander³ and Karoliina Honkala³**Abstract**

The electrocatalytic nitrogen reduction reaction (eNRR) in aqueous media has received substantial attention because it enables the direct conversion of N₂ to NH₃ under benign conditions. There are, however, many factors limiting the overall eNRR efficiency, including the competing hydrogen evolution reaction (HER) and sluggish reaction kinetics due to a strong N≡N bond. These challenges call for more systematic theoretical insight into the eNRR reaction mechanism to guide the rational optimization of experimental designs. In this review, we present the latest computational advances in eNRR in an aqueous medium, including the key aspects of both catalyst design and proton accessibility. Specifically, we discuss the importance of constant potential and explicit solvent simulations, the role of the electrochemical interface, and the impact of the active center microenvironment on eNRR activity and selectivity. Finally, the current challenges and the future prospects for eNRR are addressed.

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Keywords

Electrocatalysis, Ambient NH₃ synthesis, Microenvironment, Theoretical calculations.

Introduction

Ammonia (NH₃) is one of the most fundamental raw materials in modern industry and agricultural production [1–6]. Additionally, it is regarded as an excellent hydrogen carrier due to its small carbon footprint and ease of storage and transportation [3]. The industrial Haber–Bosch process is a mature technology to synthesize NH₃, but it requires high temperatures and pressures. Such harsh conditions consume 2–3% of the world's energy supply annually and require hydrogen as a proton feedstock [6]. Traditionally, hydrogen is produced via steam reforming, which emits large amounts of carbon dioxide [6–8]. Therefore, it is particularly important to develop methods to produce ammonia under mild conditions without utilizing fossil hydrogen as a proton source [8,9].

The electrocatalytic N₂ reduction reaction (eNRR) has recently gained increasing attention because it can achieve NH₃ production under mild conditions utilizing renewable electricity and water as a hydrogen source [10–18]. Currently, eNRR efficiency in aqueous media is below what is needed at the industrial scale or associated with naturally occurring nitrogenase enzymes [18,21–23]. The Li-mediated process in organic solvents has been experimentally verified and extensively reviewed recently [19,20]. We focus on how the aqueous eNRR activity and selectivity could be improved through advanced electrode design principles. This is motivated by a recent review [25] highlighting the fact that despite many false-positive eNRR catalysts and general disbelief in the viability of aqueous eNRR, advanced electrode design approaches deserve further investigation before conclusively dismissing aqueous eNRR [14,24,25].

At the atomic level, efficient eNRR requires a catalyst to bind a N₂ molecule and carry out the multiple proton-coupled electron transfer (PCET) steps to form NH₃ [18]. A natural nitrogenase enzyme can catalyze a key step of the nitrogen cycle, converting atmospheric nitrogen into bioavailable NH₃ through a FeMo cofactor under mild conditions [21,22]. This cofactor possesses

associative pathway, including multiple reaction species, is widely accepted as a possible mechanism under mild reaction conditions [30]. The role of the binding environment of key reaction intermediates on catalyst surfaces has been extensively studied at the atomic level. For instance, Nørskov *et al.* have calculated the binding energies for all the reaction intermediates along the associative eNRR pathway including NH_x and N_2H_x ($x = 0, 1, 2$) molecules on the variety of metal surfaces [33,34]. They found that the binding energies of NH_x and N_2H_x scale well with N binding energy ($E_{\text{ad}[\text{N}^*]}$), which can be used as a descriptor, see Figure 1b and 1c. This linear scaling between reaction intermediates precludes the tuning of binding energies independently from each other, which is represented in the form of volcano plot [33–35]. Importantly, it is noted that the linear scaling relationships of $^*\text{N}_2\text{H}$ and $^*\text{NH}_2$ fundamentally limit eNRR activity on solid metal surfaces due to strong binding on the catalytically active sites [34]. Furthermore, the comparison of hydrogen evolution reaction (HER) and eNRR limiting potentials as a function of $E_{\text{ad}[\text{N}^*]}$ descriptor shows that the HER limiting potential is less negative than that for eNRR, as shown in Figure 1d and e. This is consistent with the fact that low eNRR activity and selectivity generally originate from the severely competing HER process [18] and implies that the $E_{\text{ad}[\text{N}^*]}$ descriptor is an appropriate descriptor for monitoring eNRR activity, but it is certainly not the only one. Indeed, other adsorption energies, such as $^*\text{NH}$ and N_2H^* , have also been used as the activity descriptors [36–39].

In addition, conventional energetic descriptors, also multiple electronic descriptors, have been proposed, including the polarization response of an active site, an electric dipole of the adsorbed N_2 , and the number of d orbital electrons and empty orbitals [40–43]. For instance, it has been demonstrated that the dipole moment of the adsorbed N_2 molecule can also be used as an effective theoretical indicator for the catalytic performance of active sites for eNRR, as shown in Figure 2a and b. Based on the dipole indicator, several single transition metal (TM) atoms were screened via density functional theory (DFT) calculations in two-dimensional phthalocyanine (2D Pc) organic frameworks, and 2D Mo-Pc was proposed as a promising SAC for eNRR with extremely low onset potential of -0.25 V [44]. The origin of such high catalytic activity was associated with the large dipole moment introduced into the $\text{N}\equiv\text{N}$ bond via strong Mo–N interactions, thus promoting the activation of the $\text{N}\equiv\text{N}$ triple bond through the occupation of π^* antibonding orbitals [44]. N_2 activation can take place either by donating electrons from N_2 to the empty orbitals of an active site or by accepting electrons from the partially occupied orbitals of an active site to the antibonding orbitals of N_2 [45,46]. Recently, sandwich structures with a single TM atom between hexagonal boron nitride (h-BN) and

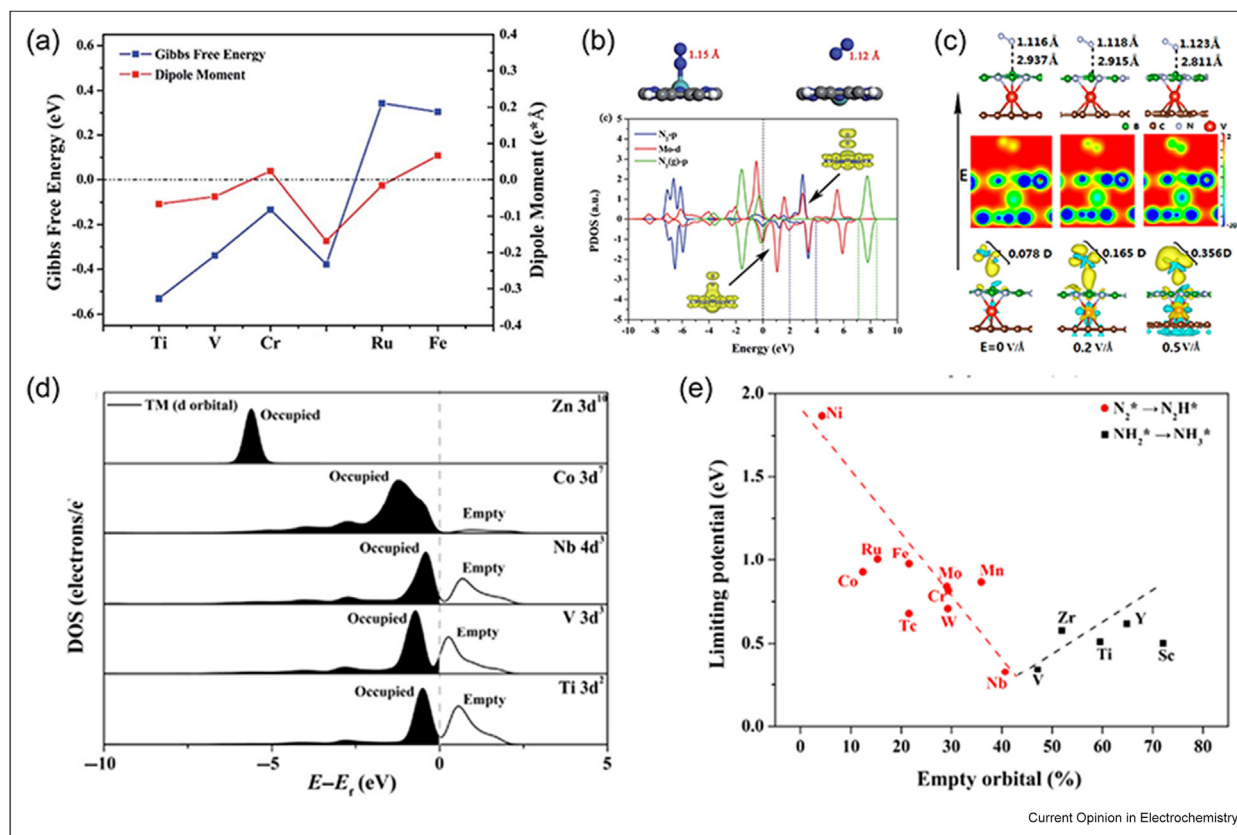
graphene sheets (namely, BN/TM/G) were designed for eNRR through DFT calculations [47], which suggested that TM SACs can donate charge to h-BN and then create an optimized polarization field on the surface, as shown in Figure 2c. This interfacial polarization field enables electron donation from the TM atom to a neighboring B atom, which then acts as the active site to catalyze eNRR (Figure 2c) [47]. Accounting for charge transfer at the reaction center to activate N_2 , the relationship between the intrinsic electronic properties and catalytic activity was established through a high-throughput DFT screening of 23 TM-SACs. The identified electronic descriptor of empty d orbitals explains the low overpotential and good eNRR activity, as shown in Figure 2d and e [48]. This analysis suggests that catalytic activity correlates with the local microenvironment of active centers and that eNRR can be enhanced by adjusting the orbital occupation at the active site.

While major efforts have been undertaken to improve the eNRR catalysts, the rational design of active and efficient electrocatalysts is still far from satisfactory. Three reasons can be identified for this. Firstly, the poor activity and high eNRR overpotentials originate from the scaling relations (volcano relationships) between adsorption energies of nitrogen-containing intermediates (NH_x and N_2H_x) on catalyst surfaces and prevent electrocatalysts to approach the region of optimal eNRR activity. To achieve high eNRR activity at low overpotentials, the simultaneous competitive HER process should be avoided [8,18]. Secondly, the kinetics of the first PCET step to form N_2H^* limits activity [18]. Thirdly, computational models often exclude components defining the properties of electrochemical interfaces, such as pH, electrolyte, solvent, and electrode potential effects, leading to electrostatic and other non-covalent interactions, and dynamic processes [49,50]. Hence, to move forward, we need to simultaneously establish strategies to break eNRR scaling relationships, limit HER, accelerate the PCET kinetics, and control the electrochemical interface. This calls for the use of advanced computational techniques and tighter integration with experiments [50].

New strategies for eNRR: the electrode potential, solvent, and electrolyte effects

Besides structural modifications, the explicit inclusion of the electrode potential via grand-canonical ensemble (GCE) DFT [51] may enable breaking the scaling relations. Unlike canonical DFT with the computational hydrogen electrode (CHE) model, GCE-DFT can be used to model thermodynamics, kinetics, and charge transfer as a function of the electrode potential [52–55]. Recent GCE-DFT calculations lead to different scaling relations than canonical DFT calculations because non-PCET steps also depend on the

Figure 2



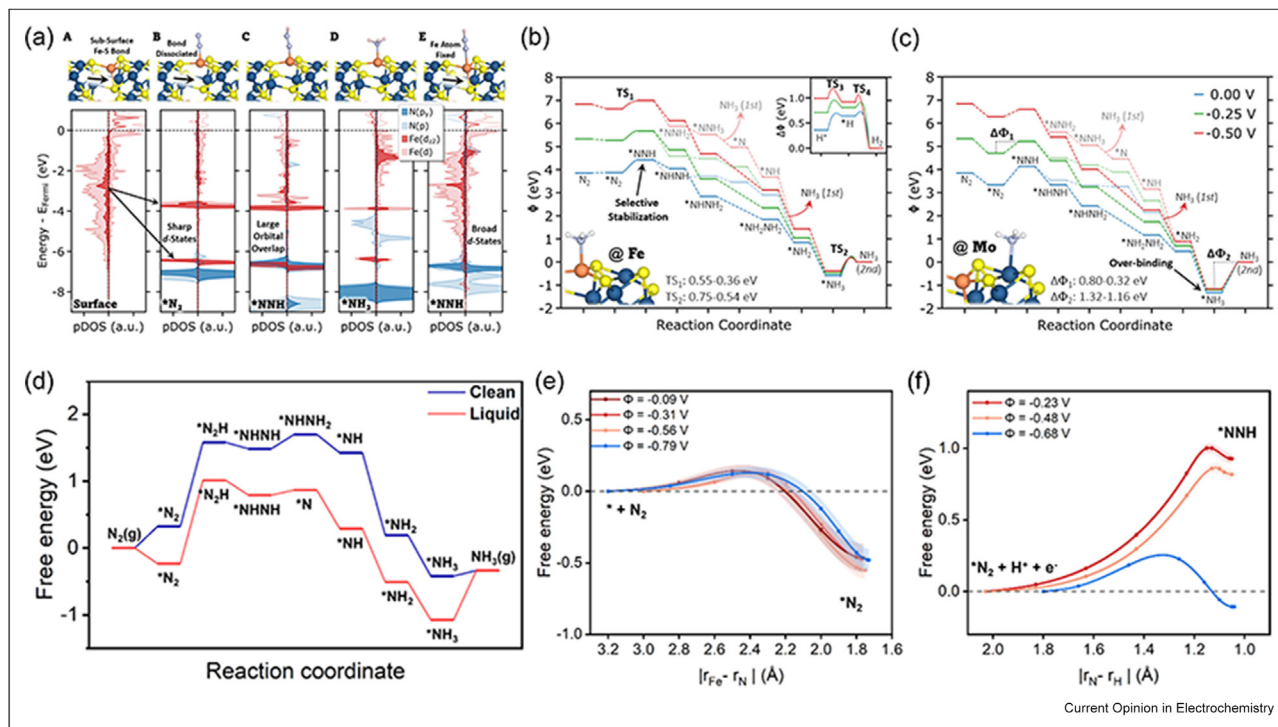
(a) Variation of Gibbs free energies and dipole moments of the N_2 molecule adsorbed on 2D TM-Pc with different transition metals [44]. (b) The optimized N_2 adsorption configurations on the 2D Mo-Pc, and the project density of states (PDOS) for the N-2p and Mo-4d states in the end-on adsorption geometry together with the 2p states of an isolated N_2 molecule [44]. Reproduced from Ref. [44] with permission from the Royal Society of Chemistry. (c) Geometrical structures (top panel), electrostatic potential along the plane across the N_2 and B sites (middle panel), and electron density differences (bottom panel) of N_2 adsorbed on BN/V/G [47]. Reproduced from Ref. [47] with permission from the American Chemical Society. (d) The PDOS plot is projected onto the d orbital of different metal atoms [48]. (e) The relationship between the percentage of empty d orbital and limiting potential [48]. Reproduced from Ref. [48] with permission from Springer Nature.

electrode potential [56]. In another study, GCE-DFT calculations [57] ascribed the experimentally verified [58] activity of the Chevrel phase $Fe_2Mo_6S_8$ surface, containing a similar Fe–S–Mo coordination environment as a nitrogenase enzyme’s FeMo-cofactor, to the simultaneous N_2 adsorption and dissociation of a sub-surface Fe–S bond that leads to the formation of free atom-like d-states, see Figure 3a. These d-states selectively stabilize the $*NNH$ intermediate relative to $*N_2$ or $*NH_3$ because they significantly overlap with the p-states of $*NNH$ but minimally with the p-states of $*N_2$ or $*NH_3$, see Figure 3a. The computational study shows the need to explicitly include the electrode potential but also demonstrates that the dynamic nature of proposed eNRR active site resembles the one suggested for the nitrogenase FeMo-cofactor where two Fe–S bonds break to produce the active Fe site. The Fe–S subsurface bond remains broken until $*NH_3$ desorbs, and when a proton adsorbs at Fe active site to enable HER, the broken Fe–S bonds will return to their initial state.

The dynamic restructuring of the atomic environment around the Fe active site allows breaking the scaling relations as the catalyst selectively stabilizes the nitrogen intermediates to decrease ΔG of the first hydrogenation step, while binding $*NH_3$ weakly to release NH_3 gas, see Figure 3b and c.

In general, considering the explicit electrode potential and solvent effects is crucial for modeling eNRR. On a single Fe atom catalyst embedded in N-doped graphene ($Fe-N_4$), eNRR depends sensitively on both the electrode potential and solvent [59]. The comparison between gaseous and aqueous systems shows that the water environment can facilitate the adsorption and activation of N_2 on the Fe site due to stronger N_2 adsorption and electron injection to the empty π^* orbital, respectively, as shown Figure 3d [59]. Furthermore, the electrode potential modifies kinetics for the hydrogenation step as the distal N of $*N_2$ gains more electrons and makes it more capable of accepting

Figure 3



(a) Atomic structure and PDOS plots for the bare $\text{Fe}_2\text{Mo}_6\text{S}_8$ surface, the $\text{Fe}_2\text{Mo}_6\text{S}_8$ surface with $^*\text{N}_2$, $^*\text{NNH}$ and $^*\text{NH}_3$, and $^*\text{NNH}$ [57]. The associative alternating (opaque) and associative distal (transparent) eNRR pathways at Fe (b) and Mo (c) surface sites in H_2O solvent at different electrode potentials [57]. Reproduced from Ref. [57] with permission from the American Chemical Society. (d) Free energy profile of the preferred reaction pathway in clean (no solvation) and liquid (explicit solvation) systems on a FeN_4 catalyst [59]. Calculated free energy profiles for N_2 adsorption (e) and the first N_2 protonation step (f) at different electrode potentials [59]. Reproduced from Ref. [59] with permission from the American Chemical Society.

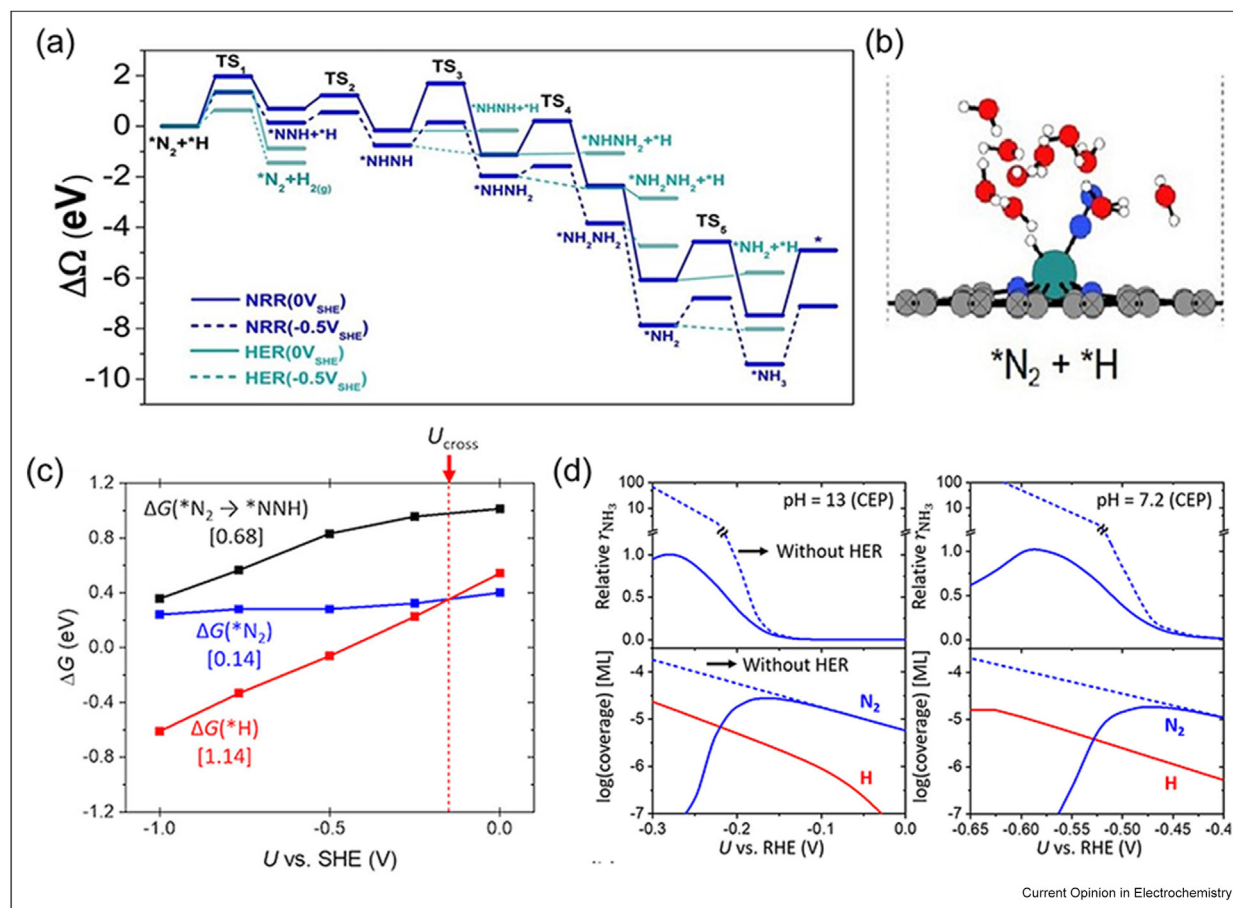
protons at negative electrode potential without a significant impact on N_2 adsorption, see Figure 3e and f. Finally, the estimated electrode potential for eNRR agrees well with the experimental results supporting the necessity to consider electrode potential and explicit solvation effects in calculations.

We have also recently addressed the eNRR on a graphene-embedded Ru-N_4 model, using GCE-DFT to study the reaction mechanism, thermodynamics, and kinetics as an explicit function of the electrode potential [60]. Our results show that the eNRR/HER competition cannot be understood without using GCE-DFT to address the potential dependency of the reaction. The charge transfer from an initial state to a final state for Volmer and N_2 hydrogenation reactions at the Ru-N_4 exhibits unusual nonlinear behavior, in contrast with metallic Au and Pt systems making the activation energy more sensitive to the electrode potential than the reaction energy. The study further highlights the importance of the coadsorption of key reaction intermediates (N_2^* and H^*), and the pivotal role of the non-innocent ligands may play in eNRR selectivity, as shown in Figure 4a and b. This allowed us to disentangle different factors that

contribute to eNRR activity on Ru-N_4 , but unfortunately, HER is more favorable than the first $^*\text{N}_2$ protonation step hampering the catalytic activity of the Ru-N_4 catalyst in experiments [60,61]. In similar vein, eNRR on a Fe-N_4 electrocatalyst was studied by combining GCE-DFT calculations and the microkinetic analysis to identify the potential-dependent crossover between the H- and N_2 -binding affinities. At low potentials, $^*\text{N}_2$ is favored over $^*\text{H}$, but at more negative potentials, the trend is reversed as shown in Figure 4c and d [62]. This observation is consistent with experiments displaying the activity drop for eNRR as a function of potential. The crossover from $^*\text{N}_2$ to $^*\text{H}$ is due to the larger charge transfer in the formation of H^* compared to N_2^* , which shows that potential-dependent charge transfer affects the relative affinity of surface intermediate, thus crucially impacting NRR activity.

While the above examples demonstrate that GCE-DFT and explicit solvent models are needed to simulate eNRR, experiments have shown that eNRR is also very sensitive to electrolyte, hydrophobicity, and pH effects [18,63–68]. For instance, a hydrophobic electrochemical interface constructed using fluorinated solvents limits

Figure 4



(a) The grand free energies of the competing eNRR (blue) and HER (green) pathways [51]. (b) The coadsorption model of *N_2 and *H including electrode potential U and explicit H_2O solvent [60]. Reproduced from Ref. [60] with permission from the American Chemical Society. (c) Change of ΔG ($^*N_2 \rightarrow ^*NNH$), $\Delta G(^*N_2)$, and $\Delta G(^*H)$ by the electrode potential (U), where the red vertical dashed line represents the crossover potential U at $\Delta G(^*H) = \Delta G(^*N_2)$ [62]. (d) NH_3 production rates and coverages obtained with the GCE-DFT-based microkinetic analysis [52]. Reproduced from Ref. [62] with permission from Nature.

the supply of protons, which, in turn, leads to a higher N_2 coverage on the catalytic sites, improved N_2 solubility compared to water, and consequently enhanced the Faradaic efficiency toward NH_3 [67]. More generally, microkinetic [12] and transport [68] studies have established some efficient ways for modulating the N_2 and H^+ mass transport in the electric double layer to facilitate eNRR. A practical way to achieve this is through modulating catalyst pore sizes as larger pores are suggested to enhance N_2 mass transport and improve the Faradaic efficiency toward NH_3 [29]. Another strategy to control mass transfer is to use proton-filtering covalent organic frameworks (COFs) to enhance N_2 flux to a catalyst [69]. Molecular dynamics simulations have showed that electrostatic interfaces between the COF charge centers and H^+ suppress HER while dispersion interactions between COF and N_2 concentrate nitrogen at the active catalyst sites [69].

While the importance of controlling the electrochemical interface microenvironment to improve eNRR activity and selectivity has been widely recognized [18,28], computational models are still in their infancy. Atomic and bottom-up multiscale models to understand, for example, cation effects, solvent dynamics and reorganization, and mass transfer in eNRR are scarce. These factors have, however, been investigated for other electrocatalytic reactions, such as CO_2RR and ORR, which can serve as inspiration for eNRR modeling [53,70–73]. Yet, as it stands, atomistic understanding of the electrochemical interface during eNRR is highly limited and should be considered as the next frontier in the theoretical treatments of electrocatalytic ammonia production. Overall, these considerations indicate that aqueous eNRR may still be a viable approach to produce ammonia, but novel catalytic design concepts are needed.

Concluding remarks

In summary, the electrocatalytic N₂ reduction reaction accounts for a promising strategy for ammonia synthesis. However, the competing HER process, nitrogen scaling relations, and slow kinetics fundamentally limit the activity and selectivity of eNRR electrocatalysts far below the requirements of industrially viable electrocatalytic NH₃ synthesis. To improve the robustness of computational studies toward designing improved aqueous eNRR catalysts, future models should consider the following aspects:

- (1) Computational studies typically model eNRR catalysts and mechanisms at a solid–vacuum interface, using conventional constant charge approaches, while real electrochemical reactions correspond to constant potential conditions and feature mobile electrolyte solutions. This calls for a wider adoption of constant potential methods and development of ways to treat the electrolyte efficiently.
- (2) While assuming mostly a static active site, real catalytic active centers are dynamic and respond to changes in a reaction environment and conditions. These dynamic effects also control the proton availability. Thus, the dynamic catalytic mechanisms for eNRR calculations must be carefully considered.
- (3) Aside from the solid catalysts, electrochemical interfaces possess a wealth of physicochemical interactions for eNRR, which significantly affect catalytic activity and proton availability. Thus, simulating only catalysts and binding sites is insufficient, and we need to pay more attention on investigating how the entire electrochemical interface impacts eNRR

Author contributions

T.W. wrote the first version of the manuscript. M.M.M. and K.H. revised the work.

Declaration of competing interest

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Data availability

This is review based on published works.

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