Engineering of electrocatalyst/electrolyte interface for ambient ammonia synthesis

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Abstract
Ammonia is not only an important platform chemical for industrial and agricultural use but is also a novel energy-carrying molecule. The electrochemical reduction method for ambient ammonia synthesis is emerging as a promising strategy for the replacement of the current Haber–Bosch ammonia synthesis method, which consumes a large amount of energy and natural gas (hydrogen resource) while releasing substantial greenhouse gases (eg, carbon dioxide). The challenges in electrochemical ammonia synthesis, also known as nitrogen reduction reaction, primarily include the cleavage of extremely stable N≡N bonds and the competitive hydrogen evolution reaction in routine aqueous media, which significantly leads to a low production rate and Faradaic efficiency. The rational design and engineering of the electrocatalyst/electrolyte interface are crucial to address these challenges. Herein, recent achievements for catalyst/electrolyte interface engineering are reviewed to provide insights into enhancing the production rate and Faradaic efficiency. Perspectives on future research and development of the electrochemical ammonia synthesis from theory to practice will be provided.

KEYWORDS
ammonia synthesis, Faradaic efficiency, interfacial effects, nitrogen reduction reaction, production rate

1 INTRODUCTION

Ammonia is an important raw material in the chemical industry and agriculture. Meanwhile, ammonia also acts as an important carbon-free energy carrier because of its high hydrogen content of 17.6%. Due to its wide applications, the annual global demand for the production of ammonia is about 200 million tons, which is expected to increase in the near future due to the booming population as well as the search for new energy conversion and storage strategies.

Essentially, ammonia is produced by reducing nitrogen in the presence of hydrogen, that is, nitrogen reduction reaction (NRR, \( \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \)). In thermodynamics, the NRR is considered as an exothermal and spontaneous reaction. However, the extremely stable N≡N bonds in nitrogen...
lead to sluggish kinetics.\(^5\) To efficiently activate and break the N≡N bond, an extremely large external energy (>600 kJ/mol NH\(_3\))\(^6\) is needed. Therefore, the widely used Haber–Bosch approach requires high temperature and high pressure—reaching 300–550°C and 200–350 atm in the reactors to practically produce ammonia. This ammonia synthesis consumes large quantities of H\(_2\) and approximately 1–2% of the world’s annual fossil energy, leading to about 300 metric tons of CO\(_2\) emission.\(^4,7\)

Similar to the electrochemical strategies for the synthesis of value-added chemicals,\(^8\) the electrocatalytic NRR used for the production of ammonia is an emerging and promising alternative for the replacement of the conventional Haber–Bosch ammonia synthesis. The advantages of the electrocatalytic methods include but are not limited to: (i) the mild working conditions—electrocatalytic NRR can be operated at ambient or near-ambient temperature and pressure; (ii) direct extraction of required hydrogen element from electrolyte—no additional hydrogen resources are needed; and (iii) more importantly, an easily controlled production process—the electrocatalytic reactions highly depend on interfacial parameters in the electrochemical double layers including catalyst surfaces, electrolyte, and applied potential, etc. So far, the electrochemical ammonia synthesis or NRR study has become one of the most fast-growing fields. However, this method still faces some challenges, namely, the low production/yield rate and low selectivity, which can usually be addressed through catalyst-surface-electrolyte interface engineering.\(^9\) For example, the interfacial effects of both the catalyst, including active site composition and configuration, and the electrolyte, including pH value and the cations, have been intensively investigated to improve the production rate of ammonia and Faradaic efficiency (FE) of NRR. Inspired by recent advances, we therefore present herein a crucial progress report for the improvement of the production rate and FE of electrochemical ammonia synthesis which will be discussed in terms of interfacial effects for the catalyst and the electrolyte. Our insights into future research and development to minimize the gaps between the theoretical and practical NRR will be provided.

2 | REACTION PATHWAY AND CATALYST/ELECTROLYTE INTERFACE FOR NRR

2.1 | NRR mechanisms

The net NRR follows equations below:

In acidic media

\[
\text{N}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 2\text{NH}_3
\]

(1)

In basic media

\[
\text{N}_2 + 6\text{H}_2\text{O} + 6\text{e}^- \rightarrow 2\text{NH}_3 + 6\text{OH}^-
\]

(2)

Although abundant reaction mechanisms have been proposed, it should be noted that the detailed NRR pathways are complicated and they are not yet fully understood. The NRR probably follows either a dissociative or associative pathway.\(^10\) The dissociative pathway can be described using the Equations (3–6) (referring to Figure 1):

\[
\text{N}_2^* \rightarrow 2\text{N}^*
\]

(3)

\[
\text{N}^* + \text{H}^+ + \text{e}^- \rightarrow \text{NH}^*
\]

(4)

\[
\text{NH}^* + \text{H}^+ + \text{e}^- \rightarrow \text{NH}_2^*
\]

(5)

\[
\text{NH}_2^* + \text{H}^+ + \text{e}^- \rightarrow \text{NH}_3^*
\]

(6)

Such a pathway follows the initial cleavage of the N≡N bonds, thus, requiring large external energy, which is not likely to be the favorable pathway. In contrast to the dissociative pathway having a huge energy barrier, the associative pathway gradually breaks the N≡N bond step-by-step, which is plausibly the favorable pathway. The associative
pathway steps can vary according to the adsorption configurations of the nitrogen molecules on the catalyst surface. When the nitrogen molecules adsorb through the “end-on” configuration, the pathways can be associative alternating pathway (Equations 7–12) and associative distal pathway (Equations 13–18) (Figure 1).

**Associative alternating pathway**

\[ \text{N}_2^* + \text{H}^+ + e^- \rightarrow \text{NNH}^* \]  
(7)

\[ \text{NNH}^* + \text{H}^+ + e^- \rightarrow \text{NNNH}^* \]  
(8)

\[ \text{NNNH}^* + \text{H}^+ + e^- \rightarrow \text{NNNH}_2^* \]  
(9)

\[ \text{NNNH}_2^* + \text{H}^+ + e^- \rightarrow \text{NH}_2\text{NH}_2^* \]  
(10)

\[ \text{NH}_2\text{NH}_2^* + \text{H}^+ + e^- \rightarrow \text{NH}_2^* + \text{NH}_3 \]  
(11)

\[ \text{NH}_2^* + \text{H}^+ + e^- \rightarrow \text{NH}_3^* \]  
(12)

**Associative distal pathway**

\[ \text{N}_2^* + \text{H}^+ + e^- \rightarrow \text{NNH}^* \]  
(13)

\[ \text{NNH}^* + \text{H}^+ + e^- \rightarrow \text{NNNH}_2^* \]  
(14)

\[ \text{NNNH}_2^* + \text{H}^+ + e^- \rightarrow \text{N}^* + \text{NH}_3 \]  
(15)

\[ \text{N}^* + \text{H}^+ + e^- \rightarrow \text{NH}^* \]  
(16)

\[ \text{NH}^* + \text{H}^+ + e^- \rightarrow \text{NH}_2^* \]  
(17)

\[ \text{NH}_2^* + \text{H}^+ + e^- \rightarrow \text{NH}_3^* \]  
(18)

An associative enzymatic pathway was proposed when the nitrogen molecules adsorb via the “side-on” configuration (Figure 1), based on the theoretical calculations where two nitrogen atoms in one molecule are simultaneously adsorbed on an active site, a pathway believed favorable for NRR on a single Mo/BN model.11 With the technology and techniques developed so far, the distinction of these configurations is extremely difficult on the real-world NRR catalyst surfaces. Therefore, more efforts for the advancement of experimental technologies and theoretical calculations are encouraged in the future.

In addition to the cathodic NRR, the coupled anodic reaction, that is, oxygen evolution reaction (OER), which always takes place during the electrochemical ammonia synthesis, should also be considered in the electrolyzer reactor. The net OER equations in acidic (Equation 19) and alkaline (Equation 20) media are given as follows:

In acidic media

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \]  
(19)

In basic media

\[ 4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \]  
(20)

The OER always suffers from sluggish kinetics, leading to a huge overpotential at the anodes.12-14 On the other hand, the NRR also requires a large overpotential to overcome the activation energy barrier. These challenges lead to significant energy waste, that is, low energy efficiency, indicating that the investigations of electrochemical ammonia synthesis in reactors should also include the OER anode in addition to the NRR cathode. Although the anodic OER is not in the scope of this article, we would like to point out that the advanced OER catalysts with low overpotential need to be developed.15,16 An alternating route includes the replacement of the OER by other anodic reactions that produce value-added chemicals.8

By combining cathodic NRR and anodic OER (Equations 1 and 19, 2 and 20), the overall reaction equation can be obtained for the electrolyzers to synthesize ammonia:

\[ 2\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{O}_2 + 4\text{NH}_3 \]  
(21)

As shown in Equation (21), the hydrogen element required for ammonia synthesis can be directly extracted from the water in the electrolyte. However, the hydrogen evolution reaction (HER) usually takes place following Equations (22) and (23) at the potential range where NRR takes place.

In acidic media

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \]  
(22)

In basic media

\[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \]  
(23)

Therefore, the competitive HER leads to low FE for ammonia synthesis, that is, a large amount of the supplied
electrons are used for HER, rather than NRR. The competitive HER is the one reaction that must be considered when investigating NRR.

Based on the above discussion on reactions, including NRR as well as the competitive HER, the key parameters that the researchers should focus on during electrochemical NRR investigations can be concluded. On one hand, the NRR kinetics is sluggish due to the stability of the $\text{N}_\equiv\text{N}$ bonds and therefore, the yield or production rate, which represents the amount of ammonia produced in a specific period over a specific amount of catalyst, emerges as a key parameter. On the other hand, given that the HER is highly competitive at the catalyst/electrolyte interfaces, a part of the electrons are consumed to generate hydrogen, leading to low FE of NRR. In this report, we mainly discuss the interfacial effects on the NRR production rate and FE. Accordingly, Table 1 summarizes recently reported production rates and FEs in the literature regarding NRR under ambient or near-ambient conditions.

2.2 | Catalyst/electrolyte interface

The heterogeneous electrocatalytic process is significantly influenced by the interface properties between the catalyst and the electrolyte, that is, the electrochemical double layer. In fundamental electrochemistry, the conventional hydrogen- and oxygen-related reactions in aqueous media have been more investigated. The interface between catalyst surface and local electrolyte phase determines the mechanisms and kinetics of electrochemical reactions. Particularly, the inner Helmholtz plane (IHP) plays a crucial role in the electrocatalytic process of the specifically absorbed species where the kinetics is strongly determined by the nature of the electrode, that is, the catalyst surface. On the other hand, the outer Helmholtz plane (OHP) is the locus of the nonspecifically adsorbed, hydrated species (Figure 2).95 For NRR, the specifically absorbed hydrogen and nitrogen species might be in IHP simultaneously as HER is a competitive reaction. Some hydrated metal cations in OHP might also influence the kinetics and selectivity of NRR. There is still a lack of specific investigations on the electrochemical double layers toward NRR. Due to the similarity between NRR and hydrogen-/oxygen-related reactions, the interfacial effects are expected to play important roles in determining the production rate of ammonia and/or hydrogen (relevant to the FE) under electrocatalytic conditions.

The catalyst surfaces and the local electrolyte are important for the construction of the electrochemical double layer. In the following sections, we will focus on the catalyst surface-related (e.g., active site composition and configuration) and electrolyte-related effects (e.g., pH value and cation), which significantly determine the production rate of ammonia and FE for NRR.

3 | EFFECTS OF ELECTROCATALYST/ELECTROLYTE INTERFACE ON THE PRODUCTION RATE OF AMMONIA

3.1 | Catalyst surfaces

3.1.1 | Metal-free active sites

The pristine carbon material is inert for electrocatalysis—the defects and/or surface dopant can break the well-defined C-C bonds, modify the local electronic structure and trigger adsorption of reactant species, that is, nitrogen molecule for NRR.96 As a rising-star material, the N-doped carbon has been emerging as a promising metal-free catalyst towards many different electrocatalytic reactions including oxygen reduction reaction,97 carbon dioxide reduction reaction,98 as well as the NRR.99,100 There are different N-dopant configurations in the N-doped carbon materials97 and their effect on NRR production rate was recently investigated.

The ZIF-8 was employed as the nitrogen and carbon precursor (Figure 3A), which derived a highly disordered N-doped carbon (Figure 3B).17 The N dopant configurations are found dependent on the pyrolysis temperatures. To be specific, the pyridinic and pyrrolic N are formed below 900°C and the pyrrolic N disappears at the temperature over 1000°C. However, only pyridinic and graphic
| Catalyst                                | Production rate (µg/mg cat/h) | Faradaic efficiency (%) | Working conditions | Electrolyte | Ref. |
|-----------------------------------------|-------------------------------|-------------------------|--------------------|-------------|------|
| **Metal-free catalysts**                |                               |                         |                    |             |      |
| N-doped nanoporous carbon               | 72.25\(^a\)                  | 10.2                    | −0.3               | 0.1 M KOH   | [17] |
| Black phosphorus nanosheets             | 31.37\(^b\) (−0.7 V)         | 5.07 (−0.6 V)           | −0.7 to −0.6       | 0.01 M HCl  | [18] |
| B\(_2\)C nanosheets                    | 26.57                         | 15.95                   | −0.75              | 0.1 M HCl   | [19] |
| S-doped graphene                        | 27.3\(^b\) (−0.6 V)          | 11.5 (−0.5 V)           | −0.6 to −0.5       | 0.1 M HCl   | [20] |
| N-doped porous carbon                   | 23.8\(^a\)                   | 1.42                    | −0.9               | 0.05 M H\(_2\)SO\(_4\) | [21] |
| O-doped hollow carbon microribbons      | 22.3\(^a\)                   | 9.98                    | −0.4               | 0.005 M H\(_2\)SO\(_4\) | [22] |
| Black phosphorus nanosheets             | 31.37\(^b\) (−0.7 V)         | 5.07 (−0.6 V)           | −0.7 to −0.6       | 0.01 M HCl   | [18] |
| S-doped carbon nanosphere               | 19.07                         | 7.47                    | −0.7               | 0.1 M Na\(_2\)SO\(_4\) | [24] |
| Defect-rich fluorographene nanosheet     | 9.3                           | 4.2                     | −0.7               | 0.1 M Na\(_2\)SO\(_4\) | [25] |
| Polymeric carbon nitride                | 8.09                          | 11.59                   | −0.2               | 0.1 M HCl   | [26] |
| N-doped porous carbon                   | 15.7                          | 1.45                    | −0.2               | 0.1 M KOH   | [27] |
| B-N pairs enriched defective carbon nanosheets | 7.75                         | 13.79                   | −0.3               | 0.1 M HCl   | [28] |
| N,P codoped porous carbon               | 0.97                          | 4.2                     | −0.2               | 0.1 M HCl   | [29] |
| N-doped carbon nanospheres              | 97.18\(^b\)                  | 11.56                   | −1.19              | 0.25 M LiClO\(_4\) | [30] |
| Defective nitrogen-free carbon cloth    | 15.85\(^a\)                  | 6.92                    | −0.3               | 0.1 M Na\(_2\)SO\(_4\) + 0.02 M H\(_2\)SO\(_4\) | [31] |
| Pristine N-doped porous graphitic carbon membrane | 0.8\(^b\) (−0.3 V)          | 5.2 (−0.2 V)            | −0.3~−0.2          | 0.1 M HCl   | [32] |
| **Noble metal-based catalysts**         |                               |                         |                    |             |      |
| Ru SAs/N-C                              | 120.9                         | 29.6                    | −0.2               | 0.05 M H\(_2\)SO\(_4\) | [33] |
| PdRu tripods                            | 37.23                         | 1.85                    | −0.2               | 0.1 M KOH   | [34] |
| PdRu nanorod                            | 34.2                          | 2.4                     | −0.2               | 0.1 M HCl   | [35] |
| Au flowers                              | 25.57                         | 6.05                    | −0.2               | 0.1 M HCl   | [36] |
| Au clusters/TiO\(_2\)                   | 21.4                          | 8.11                    | −0.2               | 0.1 M HCl   | [37] |
| PdCuIr                                  | 13.43                         | 5.29                    | −0.3               | 0.1 M Na\(_2\)SO\(_4\) | [38] |
| Ultrathin Rh nanosheet nanoassemblies    | 23.88                         | 0.217                   | −0.2               | 0.1 M KOH   | [39] |
| Au SAs/N-doped porous and highly oxidizing carbon | 3.87\(^a\)               | 12.3                    | −0.2               | 0.1 M HCl   | [40] |
| Amorphization Au/Co\(_3\)O\(_2\)-RGO   | 8.3                           | 10.1                    | −0.2               | 0.1 M HCl   | [41] |
| Pd\(_{0.5}\)Cu\(_{0.5}\)/rGO           | 2.8\(^b\) (−0.2 V)           | 4.5 (−0 V)              | −0.2 to 0          | 0.1 M KOH   | [42] |
| Ru/MoS\(_2\)                            | 5.57\(^a\)                   | 12.2                    | −0.15              | 0.01 M HCl  | [43] |
| Au SAs/C\(_3\)N\(_4\)                   | 1305\(^a\)                   | 11.1                    | −0.1               | 0.005 M H\(_2\)SO\(_4\) | [44] |
| Pd/C                                    | 4.5\(^b\)                    | 8.2                     | +0.1               | 0.1 M PBS (pH = 7.2) | [45] |
| Au NPs/pristine N-doped porous graphitic carbon membrane | 3600\(^b\)\(^c\) (−0.2 V) | 22 (−0.1 V)            | −0.2 to −0.1       | 0.1 M HCl   | [32] |
| Ru NPs/Carbon Papers                    | 55\(^b\)\(^c\) (−0.1 V)      | 5.4 (+0.01V)            | −0.1 to 0.01       | 0.01 M HCl  | [46] |
| RuPt/C                                  | 18.36\(^b\)\(^c\)           | 13.2                    | 0.123              | 1.0 M KOH   | [47] |
| Porous Au film/Ni foam                  | 9.42\(^a\)                   | 13.36                   | −0.2               | 0.1 M Na\(_2\)SO\(_4\) | [48] |
| Hollow Au nanocages                     | 4.22\(^b\)\(^c\) (−0.5 V)   | 35.9 (−0.4V)            | −0.5 to −0.4       | 0.5 M LiClO\(_4\) | [49] |
| Au hollow gold nanocages                | 3.9\(^b\)\(^c\) (−0.5 V)    | 30.2 (−0.4V)            | −0.5 to −0.4       | 0.5 M LiClO\(_4\) | [50] |
| Ag nanosheet                            | 2.83\(^b\)\(^c\)            | 4.8                     | −0.6               | 0.1 M HCl   | [51] |

(Continues)
### TABLE 1 (Continued)

| Catalyst                        | Production rate (µg/mg_cat/h) | Faradaic efficiency (%) | Working conditions | Electrolyte | Ref.   |
|---------------------------------|-------------------------------|--------------------------|--------------------|-------------|--------|
| **Tetrahexahedral Au nanorod**  | 1.648 (5)                     |                          | −0.2              | 0.1 M KOH   | [52]   |
| **Non-noble metal-based catalysts** |                               |                          |                    |             |        |
| Bi nanocrystals                 | 3400 (a)                      | 66                       | −0.6 V            | Acidic K₂SO₄ (pH 3.5; 1.0 M K⁺) | [53]   |
| Mo,C nanorod                    | 95.1                          | 8.13                     | −0.3              | 0.1 M HCl   | [54]   |
| Nb₂O₅ nanoparticles             | 11.6 (−0.65 V)                | 32 (−0.6 V)              | −0.65 to −0.6     | 0.05 M H₂SO₄ | [55]   |
| Nb₂O₅ nanofiber                 | 43.6                          | 9.26                     | −0.55             | 0.1 M HCl   | [56]   |
| Mo₂N nanorod                    | 78.4                          | 4.5                      | −0.3              | 0.1 M HCl   | [57]   |
| Fe₃S₄                           | 75.4                          | 6.45                     | −0.4              | 0.1 M HCl   | [58]   |
| Fe-N/C/CNTs                     | 34.83                         | 9.28                     | −0.2              | 0.1 M KOH   | [59]   |
| Fe SAs/N-C                      | 7.48                          | 56.55                    | 0                 | 0.1 M KOH   | [60]   |
| Mo/N-C                          | 34                            | 14.6                     | −0.3              | 0.1 M KOH   | [61]   |
| TiO₂/Ti₃C₂Tx MXene              | 32.17 (−0.55V)               | 16.07 (−0.45V)           | −0.55 to −0.45    | 0.1 M HCl   | [62]   |
| MoO₃ nanosheets                 | 29.43 (−0.5V)                | 1.9 (−0.3V)              | −0.5 to −0.3      | 0.1 M HCl   | [63]   |
| Cr₂O₃ nanofiber                 | 28.13                         | 8.56                     | −0.75             | 0.1 M HCl   | [64]   |
| Bi₅V₆O₁₉/CeO₂                   | 23.21                         | 10.16                    | −0.2              | 0.1 M HCl   | [65]   |
| MoO₂                            | 12.2                          | 8.2                      | −0.15             | 0.1 M HCl   | [66]   |
| Ti₃C₂Tx (T = F, OH) MXene       | 20.4                          | 9.3                      | −0.4              | 0.1 M HCl   | [67]   |
| Fe₂O₃/TiO₂                      | 16.5 (5)                      | 0.31                     | −0.577            | 1.0 M KOH   | [68]   |
| Co hollow nanocage              | 10.78 (−0.4V)                | 7.36 (0 V)               | −0.4 to 0         | 1.0 M KOH   | [69]   |
| MoS₂                            | 43.4                          | 9.81                     | −0.2              | 0.1 M Li₂SO₄ | [70]   |
| MoS₂-rGO                        | 24.82                         | 4.58                     | −0.45             | 0.1 M LiClO₄ | [71]   |
| β-FeOOH nanorods                | 23.32 (−0.75V)               | 6.7 (−0.7)               | −0.75 to −0.7     | 0.5 M LiClO₄ | [72]   |
| TiO₂-rGO                        | 15.13                         | 3.3                      | −0.9              | 0.1 M Na₂SO₄ | [73]   |
| CoO quantum dots on rGO         | 21.5                          | 8.3                      | −0.6              | 0.1 M Na₂SO₄ | [74]   |
| M₄O₈@rGO                       | 17.4                          | 3.52                     | −0.85             | 0.1 M Na₂SO₄ | [75]   |
| Mo₃O₄ Nanocube                  | 29.28                         | 8.34                     | −0.4              | 0.1 M Na₂SO₄ | [76]   |
| M₃O₄ Nanocube                   | 25.3                          | 6.78                     | −0.9              | 0.1 M Na₂SO₄ | [77]   |
| Bi nanosheet                    | 13.23                         | 10.46                    | −0.8              | 0.1 M Na₂SO₄ | [78]   |
| Fe₂O₃ nanorods                  | 15.9                          | 0.94                     | −0.8              | 0.1 M Na₂SO₄ | [79]   |
| Mn₃O₄ Nanocube                  | 11.6                          | 3                       | −0.8              | 0.1 M Na₂SO₄ | [80]   |
| Cu-CeO₂-3.9                     | 8.1 (a)                       | 19.1                     | −0.45             | 0.1 M Na₂SO₄ | [81]   |
| Spinel Fe₂O₃ on Ti mesh         | 4.6 (a)                       | 2.6                      | −0.4              | 0.1 M Na₂SO₄ | [82]   |
| Fe₂O₃/CNT                       | 22 (a,c)                      | 0.035                    | −2 (vs. Ag/AgCl)  | 0.5 M LiClO₄ | [83]   |
| V₃O₈ Nanowire on carbon cloth    | 15.18 (a,c)                   | 3.58                     | −0.3              | 0.1 M HCl   | [84]   |
| MoN nanosheets/Carbon cloth     | 18.42 (a,c)                   | 1.15                     | −0.3              | 0.1 M HCl   | [85]   |
| Sn₂O₃ on carbon cloth           | 9.0 (b,c)                     | 2.17                     | −0.8 to −0.7      | 0.1 M Na₂SO₄ | [86]   |
| VN nanosheet on Ti mesh         | 5.14 (a)                      | 2.25                     | −0.5              | 0.1 M HCl   | [87]   |
| TiO₂ nanosheets on Ti plate     | 5.6 (b,c)                     | 3.34                     | −0.7 to −0.6      | 0.1 M Na₂SO₄ | [88]   |
| Defective TiO₂ on Ti mesh       | 7.6 (a,c)                     | 9.17                     | −0.15             | 0.1 M HCl   | [89]   |
| MoS₂                            | 4.9 (a,c)                      | 1.17                     | −0.5              | 0.1 M Na₂SO₄ | [90]   |
| Ti₃C₂T₂/stainless steel mesh    | 4.72 (a)                      | 4.62                     | −0.1              | 0.5 M Li₂SO₄ + HCl (pH = 2) | [91]   |

(Continues)
### TABLE 1 (Continued)

| Catalyst                   | Production rate $(\mu g/mg_{cat}/h)$ | Faradaic efficiency (%) | Working conditions | Electrolyte                        | Ref.  |
|----------------------------|--------------------------------------|-------------------------|--------------------|-----------------------------------|-------|
| Ti$_3$C$_2$Tx/FeOOH        | 0.53$^b,c$ $(-0.5V)$                 | 5.78$(-0.2V)$           | −0.5 to −0.2       | 0.5 M Li$_2$SO$_4$ + HCl (pH = 2) | [91]  |
| (110)-oriented Mo nanofilm | 1.89$^a,b,c$ $(-0.49V)$              | 0.72$(-0.29V)$          | −0.49 to −0.29     | 0.01 M H$_2$SO$_4$                | [92]  |
| α-Fe@Fe$_3$O$_4$           | 1.44$^c$                            | 32                      | −0.65 (vs. NHE)    | Aprotic fluorinated solvent–ionic liquid mixture | [93]  |

Fe$_3$O$_4$                 | 0.19$^c$                            | 8.29                    | −0.3               | 0.1 M PBS (pH = 7.2)              | [94]  |

$^a$The data in the table are recalculated based on the information provided in references, to normalize the units.

$^b$The highest production rate and FE are obtained at different potentials.

$^c$The production rate data in the table are reported in the unit of “µg/cm$^2$/h”.

$^d$The production rate data in the table are reported with respect to the metal mass, rather than the catalyst mass.

N exist in the N-doped carbon sample pyrolyzed at 1100°C; both high temperature and long pyrolysis time lead to the increased ratio of graphitic N to pyridinic N. These facts suggest the series of N-doped carbon catalysts can act as adequate models for the study of the relationship between the N dopant configurations and the production rates. As demonstrated in Figure 3C, the highest production rate achieved was $3.4 \times 10^{-6}$ mol/cm$^2$/h in 0.1 M KOH at −0.3 V versus RHE under ambient pressure by the N-doped carbon catalyst pyrolyzed at 1100°C for 1 h. By normalizing with respect to the catalyst loading (0.8 mg/cm$^2$), the highest production rate in this work is equal to 72.25 µg/mg/h, which is top ranking compared with the published results (Table 1). The increased production rate is likely related to both the pyridinic and graphitic N as well as the carbon defects.

To further unravel the detailed N-dopant structure, various possible active sites were examined by DFT calculations in this work. However, only the configuration (pyridinic N$_3$) consisting of a protonated pyridinic N and an adjacent vacancy (likely derived from the removal of a pyridinic N at high temperature), as shown in Figure 3D, is thermodynamically favorable for nitrogen adsorption by the vacancy. The energy profile in Figure 3E is presented according to the configurations in Figure 3D, suggesting the promoted reactions at −0.3 V. It should be noted that the graphitic N-related sites are not responsible for the nitrogen adsorption (ie, not the active sites) by theoretical calculation, but more graphitic N is beneficial for high production rate in experiments. This may be due to the modified electronic structure of carbon and the nitrogen adsorption on pyridinic N$_3$ sites, which is still not quite clear.

In addition to N, the effects of other dopants, such as S, B, and dual-element dopants, such as B-N and N-P, on the production rate have also been discussed. However, the understanding of the configurations for the active moieties in these heteroatom-doped carbon catalysts is still not enough. Even the most investigated N-doped carbon, the nitrogen dopant structures have yet to be fully understood, for example, the function of graphitic N mentioned in Ref. [17]. The model heteroatom-doped carbon catalyst with individual dopant structure, for example, the highly oriented pyrolytic graphite with controllable nitrogen dopant, will be helpful in fully understanding the metal-free active site effects on NRR kinetics.

#### 3.1.2 Noble metal-based active sites

Metals are widely used as the active electrocatalysts in many fields due to their unique electronic structure and properties. For example, Pt is used for oxygen reduction reaction and hydrogen oxidation reaction, Ni is used for HER, Ir/Ru oxides for OER, etc. The use of metals which would act as possible active sites for NRR was investigated. According to the Sabatier Law, the active site should bind the reactant species neither too weakly nor too strongly. To be specific, the proper adsorption strength of nitrogen is preferred to achieve fast adsorption of nitrogen as N$_2$H* as well as fast protonation of NH* to NH$_2$* (on flat surfaces) or the removal of NH$_2$* into NH$_3$ (on stepped surfaces). Figure 4 presents the volcano curves where it is possible to observe that the noble metal surfaces, including Ru, Rh, and non-noble metal surfaces, including Mo, Fe, are located near the top of these curves, indicating that
these metals are promising in catalyzing NRR.\textsuperscript{103} For noble metal-based catalysts, so far, the noble Ru-,\textsuperscript{34–35,46,105,106} Rh-,\textsuperscript{39} and Au-based\textsuperscript{32,36,37} catalysts present good ammonia production rates in practice (Table 1).

Recent study suggests that the single-atom catalysts are promising due to both low noble metal usage and enhanced intrinsic NRR activity.\textsuperscript{107} As shown in Figure 5A, the Ru single atoms (Ru SAs) loaded by N-doped carbon were synthesized via the carbonized ZIF method.\textsuperscript{35} The resultant Ru SAs/N-C catalyst demonstrated well-defined single atomic features (Figure 5B and C) and uniformly dispersed Ru, C and N elements (Figure 5D). The Ru SAs/N-C catalyst demonstrated an extremely high ammonia production rate of 120.9 $\mu$g/mg/h (Figure 5E). As calculated in this work, the Gibbs free energy on Ru-N$_3$ configuration for Equation 14 ($\text{NNH}^* + \text{H}^++e^- \rightarrow \text{NNH}_2^*$) is 0.12 eV, much lower than Equation 8 ($\text{NNH}^* + \text{H}^++e^- \rightarrow \text{NHNH}^*$, 0.6 eV), which demonstrates that the primary reaction mechanism...
3.1.3 Non-noble metal-based active sites

In the view of cost efficiency, non-noble metal catalysts are an important direction for NRR application. Based on the analysis in Figure 4, the metallic Mo and Mo-based materials as non-noble metal catalysts are promising for NRR. In fact, the facets in Mo metal catalysts significantly influence the NRR kinetics, similarly to the preferential facet effects observed in Pt catalysts for oxygen reduction reaction. To be specific, the increased Mo (110) facet results in improved activity, while the increased Mo (211) facet leads to lowered NRR kinetics. Recently, the single-atom Mo-N-C catalyst demonstrated a high ammonia production rate of 34 μg/mg cat/h, suggesting the potential of Mo-based catalysts for NRR. The detailed structure of single-atom non-noble metal NRR catalysts has not been well understood although some efforts have been made on, for example, the most promising Fe-N-C catalyst.

The most studied single atom moiety is the FeN₄, which is believed to demonstrate the lowest activation energy barrier for NRR, although this subject is still controversial. In a recent report, the single-atom Fe-N-C catalyst was controlled by using the popular ZIF-8 precursor method in the presence of carbon nanotubes (Figure 6A). The resultant catalyst presents well-defined tubular morphology (Figure 6B and C), absent crystalline Fe phase (Figure 6D and E), and uniform element distribution (Figure 6F), suggesting single atomic characters. Interestingly, based on the theoretical calculation results, the FeN₃ site, rather than the conventional FeN₄ active site for ORR, is believed to deliver a lower free energy barrier (Figure 6G and H), which is consistent with other reports.

As representative Mo-based NRR catalysts, Mo₂C, Mo₂N, Mo₂S, MoO₃, and MoO₂ were investigated and are listed in Table 1. The surface engineering of these materials is an important direction for NRR application. For example, oxygen vacancy (OV) of MoO₂ was facilely tuned by changing the hydrogen concentration of atmosphere from 5 to 20% during the pyrolysis process (Figure 7A), deriving two types of MoO₂: oxygen vacancy-poor (OVs-poor) and oxygen vacancy-rich (OVs-rich) MoO₂. As shown in Figure 7B-D, the OVs-rich MoO₂ presented much higher production rate of ammonia than the OVs-poor MoO₂ (Figure 7E) indicating the significantly promoted effect of surface oxygen vacancy. On one hand, the oxygen vacancy facilitates the chemical adsorption of nitrogen and its activation as well as electron transfer. On the other hand, more importantly, the OVs-rich MoO₂ favors the hybrid associative distal/alternating pathway with the formation of NNH* from N₂* as the rate-determining step (Figure 7F). It is notable that the OVs-excess MoO₂ (treated under 20% hydrogen) suffers a different rate-determining step in the associative distal pathway, that is, the conversion from NH* to NH₂* (Figure 7G), which might be due to the extremely strong chemical adsorption for nitrogen on the OVs-excess MoO₂.

3.2 Local electrolyte environments and catalyst/electrolyte interface

3.2.1 Cations

The cations in the electrolyte are crucial for the NRR process because of the possible interaction between the cations and nitrogen that might influence the absorption and activation of nitrogen for NRR. Accordingly, the perchlorates having counterions with Li⁺, Na⁺, and K⁺ were used as the electrolyte. As shown in Figure 8A, it is clear that the Li⁺ is beneficial for enhancing the ammonia production rate in a wide potential range followed by Na⁺ and K⁺. This is due to the strong interaction between Li⁺ and nitrogen (attracting high-concentration nitrogen) and the enhanced electric field by decreasing the thickness of the double layer (the radius of Li⁺ is lower than the other.
FIGURE 5 (A) The synthetic illustration of Ru SAs/N-C catalyst; (B) the HAADF-STEM image of Ru SAs/N-C catalyst; (C) the magnified HAADF-STEM image of Ru SAs/N-C catalyst; (D) the EDS elemental mapping results of Ru SAs/N-C catalyst; (E) the ammonia production rates at different potentials using Ru SAs/N-C and referential Ru NPs/N-C catalysts; (F) the free energy profile of the NRR mechanisms on Ru1N3, Ru1N4, and Ru (101) sites. (A-F) Reproduced with permission from Geng Z, Liu Y, Kong X, et al. Copyright 2018, Wiley

Two ions. This experimental result seems true because the same trend in the neutral electrolyte can be obtained when the anion is alternating, for example, from perchlorate salt (Figure 8A) to sulfate salt (Figure 8B), although different electrocatalysts are employed in these two studies (nitrogen-doped carbon nanospikes for Ref. [30] and S-rich MoS2 nanosheets for Ref. [70]). In the latter case, the Li-S interaction on the S-edge sites in MoS2 (i.e., at the catalyst/electrolyte interface) was proposed: the Li-S interaction leads to positively charged Mo sites, which was proved to be beneficial for the nitrogen adsorption and following reduction. As shown in Figure 8C, the presence of Li-S interactions improved the electron transfer from Mo-edge site to nitrogen (gaining 0.40 e). The calculated free energy profile in Figure 8D demonstrated that the Li-S interaction leads to decreased activation energy which is required to push the first hydrogenation process of nitrogen.

It should be emphasized that the cation effects might be dependent on the employed environments. For example, in alkaline electrolyte, the KOH with potassium cation is more favorable than NaOH by using N-doped carbon as an NRR catalyst. This was attributed to the K+ ion which probably donates electrons and promotes the evolution of the second ammonia. Compared with Figure 8A, where the nitrogen-doped carbon nanospikes counterpart is used as the catalyst (Na+ is more favorable than K+), the cation effects probably dependent on the pH value, for example, alkaline versus neutral. The relationship between cation effects and the catalyst surface still needs much more work.

3.2.2 pH values

The pH value of the electrolyte is an important factor for electrocatalysis. One can see that the pH value might influence the cation effects as discussed above. Three typical electrolytes, including acidic 0.05 M H2SO4 (pH = 1.2), neutral 0.1 M phosphate buffer solution (PBS, pH = 7.2), and alkaline 0.1 M NaOH (pH = 12.9), were employed to
investigate the pH value effects through using the same Pd/C as the NRR catalyst. As shown in Figure 9, the ammonia production rate in PBS is almost two times that in H₂SO₄ and NaOH. This is primarily attributed to the suppressed HER process in PBS electrolyte. The competitive pH-dependent HER significantly affect the production rate, which has been confirmed by both Refs. [45] and [17]. Once the HER consume abundant electrons at the cathode in the electrolyzer reactors, the resulting overall current density might be high, but the ammonia production rate will be low and the FE for ammonia production will be pretty low as well. In this regard, the FE, another important parameter for NRR, will be discussed in the next section.

4 | EFFECTS OF ELECTROCATALYST/ELECTROLYTE INTERFACE ON THE FARADAIC EFFICIENCY FOR NRR

Since the targeted reaction for ammonia synthesis is NRR, we hope the supplied electrons will be completely used for NRR, rather than participate in the side reactions. Therefore, high FE is required during electrochemical ammonia synthesis process. As shown in Table 1, in practice, most cases show a similar tendency for the production rate and FE versus different applied potentials. That is, at the optimal applied potential, both the highest production rate and FE can be achieved. However, in some cases the tendencies...
are slightly different,\textsuperscript{47,83} indicating that high production rate is not equivalent to the high FE. The key to enhance FE is to suppress the competitive side reaction, that is, HER.\textsuperscript{113,114}

### 4.1 Catalyst surfaces

To compare the HER and NRR overpotentials on specific metallic catalysts, the limiting potentials of these two reactions were plotted versus the N* binding energy.\textsuperscript{115} Note that the descriptor for HER should be the binding energy of H*, which scales with the binding energy of N*, so that the N* binding energy was reasonably used as the descriptor for HER. As shown in Figure 10, the HER on all the investigated metal surfaces, that is, both (111) and (211) facets, demonstrate less negative limiting potentials than NRR. Besides, the gaps in limiting potential between HER and NRR on the (111) facets are smaller than that on the (211) facets in a specific range; even though, the investigated metals show the smallest gap larger than 0.4 V in limiting potential. This is bad news which indicates that the HER is a non-negligible competitor toward NRR and can significantly reduce the FE.

It is still difficult to screen the ideal electrocatalysts with a very low overpotential for NRR and a high overpotential for HER. Fortunately, the interface engineering strategies have proven to be promising for the suppression of the HER, such as decreasing the size of Mo\textsubscript{2}C as catalyst, that is, the Mo\textsubscript{2}C nanodots on carbon nanosheets.\textsuperscript{116} The isolated Mo\textsubscript{2}C nanodots can reduce the surficial coverage of hydrogen spillover, providing higher possibility for nitrogen adsorption. As an ultimate small catalyst size, the effects of a single atom catalyst for the competitive HER have been investigated. As shown in Figure 11A-D, four different single-atom models, M@C\textsubscript{3}, M@C\textsubscript{4}, M@N\textsubscript{3}, and M@N\textsubscript{4} were built.\textsuperscript{117} Based on the calculation results, it can be concluded that most single-atom catalysts have suppressed H adsorption compared with the corresponding metal surface (Figure 11E). This is good news providing strategies to suppress the competitive HER during electrochemical ammonia synthesis. By comparing the
NRR and HER, it is expected that the single-atom catalysts locating in the $^\ast$N$_2$ dominant region in Figure 11F are beneficial for nitrogen adsorption, which will be less hindered by H adsorption. Experimentally, the single Ru atom catalyst has demonstrated remarkably enhanced FE as near as 30%, which is superior in Table 1. These investigations indicate that the single-atom catalysts are a promising direction to increase the FE for NRR.

Since the routine aqueous electrolytes contain the reactant species for HER, the interface engineering strategy to appropriately limit the access of aqueous solution will be helpful to increase the FE for NRR. For example, the surface engineering method by coating a layer of hydrophobic ZIF-71 (Figure 12A and B) was proposed to suppress the HER on Ag-Au catalyst. Meanwhile, the conventional aqueous electrolyte was replaced by 0.2 M LiCF$_3$SO$_3$ in a solvent containing approximately 1% ethanol and dry tetrahydrofuran. As shown in Figure 12C and D, compared with the Ag-Au catalyst without ZIF coating (Figure 12D), Ag-Au@ZIF electrode presented no signal related to “water electrolysis” (Figure 12C). More importantly, the coated Ag-Au@ZIF shows significantly improved NRR selectivity (Figure 12E), which can be due to the hydrophobicity of ZIF-71 coating that prevents water molecules, and nitrogen enrichment of MOF materials enabling high nitrogen concentration near the catalyst/electrolyte interface (Figure 12F).
**Figure 10** Comparison of HER and NRR limiting-potential volcanoes. Reproduced with permission from Montoya JH, Tsai C, Vojvodic A, and Norskov JK. Copyright 2015, Wiley.

**Figure 11** Four calculation models for single-atom catalysts including (A) M@C₃, (B) M@C₄, (C) M@N₃, and (D) M@N₄ (red, brown, and blue balls represent transition metal, carbon, and nitrogen atom); (E) Difference between H adsorption free energy on the single-atom sites and the adsorption free energy on the corresponding surfaces; (F) the locations of different single-atom catalysts in *N₂ and *H dominant regions. (A-F) Reproduced with permission from Choi C, Back S, Kim N-Y, et al. Copyright 2018, American Chemical Society.
4.2 Local electrolyte environments and catalyst/electrolyte interface

To suppress the HER, two strategies are proposed: lowering the proton availability and the enhancement of nitrogen solubility at the catalyst/electrolyte interface, which have been discussed in terms of the interface engineering of catalyst surfaces. For local electrolyte, the aprotic, highly fluorinated solvents are promising in this regard. Accordingly, the unique ionic liquid (IL) salt with high solubility is required in these solvents. The salt 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate as the IL salt and 1H,1H,5H-octafluoropentyl-1,1,2,2-tetrafluoroethyl ether as the solvent were used to identify the effects of solvent-IL ratio ($X_{\text{IL}}$) on the FE employing $\alpha$-Fe@Fe$_3$O$_4$ nanorods as the NRR catalyst. As shown in Figure 13A, the different cathodic current densities can be obtained using the electrolytes with different $X_{\text{IL}}$ values. Specifically, at $X_{\text{IL}} = 0.23$, the current density is about 23 $\mu$A/cm$^2$, only higher than the $X_{\text{IL}} = 0.12$ case and lower than the other cases. Interestingly, the $X_{\text{IL}} = 0.23$ case demonstrates the highest FE of 23.8% as well as the highest production rate of ammonia as shown in Figure 13B. The NRR mechanisms were calculated as shown in Figure 13C and D, where the most endergonic steps including both the $\text{NHNH}^* \text{to NNNH}_2^*$ and $\text{NH}^* \text{to NH}_2^*$. It should be noted that a number of proton is necessary because it is the reactant for ammonia synthesis; otherwise, the production rate will be low. The mixed solvent with organic and water, for example, 2-propanol and water, is promising but the negative effects of water are still challenging. This dilemma requires breakthroughs in suppressing HER in the presence of proton-involved electrolyte.
Reference [53] presents an excellent example in achieving both high production rate and FE in an aqueous electrolyte. This work employs the Bi nanocrystals (NCs) as the NRR catalysts and K\(^+\) ion as the counterion in the electrolyte because Bi has lower free energy for the potential determining step (Figure 14A). Interestingly, the presence of K\(^+\) further decreases the free energy barrier (Figure 14B) and tunes the diffusion pathways for the favorable nitrogen and competitive proton (Figure 14C and D). In this work, the Bi NC catalyst is composed of Bi(012), (110), and (104) facets (Figure 14E). As shown in Figure 14F, the Bi NCs catalyst unprecedentedly demonstrated a FE of up to 66% in aqueous media. The presence of K\(^+\) also decreases the free energy barrier, thus, leading to extremely high production rate of ammonia.

5 SUMMARY AND PERSPECTIVES

5.1 Summary

The electrochemical ammonia synthesis is conducted based on NRR. At ambient and near-ambient conditions, the NRR suffers from sluggish kinetics, thus leading to
unsatisfactory ammonia production rate. On the other hand, the HER is competitive and is difficult to avoid during the NRR process, significantly lowering the FE. It should be noted that obtaining high production rate does not mean high FE will be achieved. The interfacial effects related to the catalyst surface and local electrolyte environment significantly determine the production rate and FE. Rational design of catalysts, including single-atom materials, preferential facets, etc., as well as the electrolyte, such as the use of appropriate cations, pH values, non-aqueous solvent, etc. has been proved to be beneficial for promoting the NRR kinetics and suppressing the HER. Great efforts have been made to push the milestones forward. Today’s production rate and FE have achieved up to over 3000 μg/mgcat/h and >50% through rational engineering of catalyst/electrolyte interface. However, it should be emphasized that the electrochemical ammonia synthesis is still in its preliminary stage, and more efforts are needed to study the fundamental mechanisms and to fill the gap between the fundamental understanding and practical ammonia production.

5.2 | Perspectives

5.2.1 | Fundamental study

**Toward reaction mechanisms**

The active sites and reaction mechanisms of NRR are still not well understood. For example, in Ref. [122], the double-atom sites were believed to be more favorable for NRR than the conventional single-atom sites. We can see that most publications regarding NRR include theoretical calculations to obtain more information about the active sites and reaction mechanisms. However, the majority of theoretical calculations are conducted under the ideal vacuum...
environment using models, that is, the effects of applied potential, free ions and hydrated ions in electrolyte, and the heterogeneity of real catalyst surface, have to be ignored. In this regard, the development of advanced tools for theoretical calculations should be gaining much more attention. Besides, the developed physical characterizations, especially the in-situ/operando technique, will be helpful in detecting the intermediates in electrochemical systems and understanding the reaction mechanism. In addition, the controllable design and synthesis methods will be powerful to fabricate well-defined model catalysts. By combining the electrochemical performance, the structure of model catalysts, the physical and chemical characters and theoretical simulation results, the active sites and reaction mechanisms will be uncovered.

Towards degradation mechanisms
There have not been much investigations focusing on the degradation mechanisms, which are important for industrial production. On one hand, the degradation of catalyst will lead to a decrease in its performance and the failure of electrolyzer reactors will be observed; and on the other hand, the degraded catalyst may result in impurities for the NRR. To fully understand the degradation mechanisms, efficient test protocols should be proposed and generally agreed in accelerating the catalyst degradation during NRR. Again, the controllable model catalyst synthesis, advanced physical characterizations and accurate theoretical calculations will be helpful in identifying the degradation mechanism.

Towards interface study
Although the optimal electrolyte and engineered catalyst/electrolyte interface have been proved promising in promoting NRR and suppressing HER, the relationships among catalyst (composition and configuration) and electrolyte (cation and pH) effects are still not well understood. For example, on the similar nitrogen-doped carbon catalysts, the Na\(^+\) cation is more favorable than K\(^+\) in neutral media; while the K\(^+\) cation is better than Na\(^+\) in alkaline media. In this case, the relationship of cation effect with pH value and catalyst surfaces has not been confirmed and investigated. The researches on this kind of topic will be helpful in rational design for the catalyst/electrolyte interface.

Towards experimental standard operating procedures
It should be particularly pointed out that the standard operating procedures (SOP) in different laboratories are different in NRR investigations. It has been claimed that the most promising catalysts for ammonia synthesis did not actually produce ammonia—some N-containing products were wrongly identified as ammonia. Besides, the metal nitride as a catalyst was challenged if it provides the nitrogen element and participates in the ammonia production; the commercial catalysts were reported involving nitrogen-containing species, which, however, were overlooked. Such problems significantly hinder the progress of NRR. Therefore, more efforts are necessary to find all the possible and uncontrollable factors that could arise during NRR investigations, as well as to determine the efficient and effective SOP. The insights into counterpart electrochemical reactions, including oxygen/hydrogen reduction/evolution reactions, as well as carbon dioxide reduction, etc., can be learned in the field of electrochemical ammonia synthesis.

5.2.2 Practical ammonia production

Towards reactors
To push the ammonia production from laboratory level to industry level is an important direction for the future. In a laboratory, the NRR is usually performed in a conventional three-electrode system and/or two-electrode system filled with aqueous solutions. However, an electrolyzer cell can suffer from low nitrogen solubility and heavy weight/big volume. Adapting from the fuel cell technology, the NRR can also be operated in the membrane electrode assembly which consists of a cathode, an anode, and an ion-exchange polymer membrane, for example, Nafion membrane. For example, the ammonia can be produced directly using air and water as reactants in the fuel cell-type device. It is noteworthy that, based on Equation 5, the electrochemical ammonia synthesis requires a large amount of water, so that the rational design of cells, especially in water management, should be considered in practical applications, for example, insertion of a hydrophobic layer on the catalyst layer. To overcome the challenges of using and managing water and production separation, the solid-state electrolyte can be a promising alternative.

To obtain higher production rate, increasing the operating temperature is promising. However, the high temperature not only improves the production rate but also lowers the FE in some cases because HER is facilitated at high temperature. Although this report is focused on ambient ammonia synthesis, we believe the high-temperature ammonia synthesis should be studied as well.

Towards coupled reactions
In a real-world reactor for ammonia synthesis, the related reactions in addition to NRR should be considered. The overall energy efficiency of the devices should be a key parameter to compete with the existing technique. As
pointed out in Section 2.1, the coupled anodic reactions, for example, OER, should be considered due to the large overpotential, which leads to the waste of a large amount of electronic energy. Besides, the coupled OER should also be taken into consideration during the integration of catalysts into the devices. For example, the optimal electrolytes for OER and NRR are probably different. When integrating them into a device, the excellent membrane/separater matching both electrolyte requirements is needed. Last but not least, suppressing the competitive HER is expected extremely important in practical ammonia synthesis. The knowledge and insights into this topic are highly recommended in the future research and developments. Novel strategies to construct advanced catalyst/electrolyte interface will be needed.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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