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Perspective

The pitfalls in electrocatalytic nitrogen reduction for ammonia synthesis

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ABSTRACT

Ammonia synthesis by electrocatalytic nitrogen reduction reaction (EC-NRR) has gained momentum in recent years fueled by its potential to operate at ambient conditions, unlike the highly energy-intensive yet long-standing Haber-Bosch process. However, the large disparity of the yields and Faradic efficiencies reported for EC-NRR raises serious concerns about the reliability of the experimental results. In this perspective, we elaborate on the potential sources of error when assessing EC-NRR and update the testing protocols to circumvent them, and more importantly, we pose a general call for consensus on ammonia production analysis and reporting to lay the solid foundations that this burgeoning field requires to thrive.

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1. Introduction

Ammonia is a bulk commodity chemical that currently supports the large and ever-growing fertilizer industry, and its production is foreseen to even grow further in the upcoming years if ammonia consolidates as an energy carrier and hydrogen source [1]. Currently, ammonia production relies on the Haber-Bosch process, one of the most energy-intensive and CO_2 emitting industrial processes, which consumes 1–2% of the global energy and half of global hydrogen production (~30 Mt year^{-1}), and contributes 1% of global carbon dioxide emissions (~4200 MT year^{-1}) annually [2]. To meet the UN sustainable development goals, novel routes that electrify the ammonia synthesis are stepping up to challenge this century-old process. One of them is the electrocatalytic nitrogen reduction reaction (EC-NRR), whereby ammonia is produced at ambient conditions from abundant feedstocks like nitrogen and water in a process merely powered by electricity, which could be sourced from renewables (solar, wind, etc.). The attractiveness of this strategy lies on the potential not only to decarbonize the ammonia synthesis but also to disrupt the industrial model itself, enabling a decentralized production that circumvents large infrastructure investments [3]. In the last few years, the field of electrocatalysis has witnessed a burst of publications and citations related to the EC-NRR (Fig. 1). This is mainly motivated by the global demand in green ammonia synthesis. In addition, the false-positive results in the early development of EC-NRR field lead to the illusion that it is easy to occur and almost any material has good performance. Therefore, more and more researchers devote themselves to this field and causes a "gold rush" in this field, which led to a surge of EC-NRR publications, increasing by ~ 3 times in 2019 compared with 2018 (and ~ 7 times in 2018 compared with 2017).

Admittedly, focusing international research in a specific subject propels development, but rapid growths often lack a compelling framework of protocols required to standardize measurements and align or compare results. In this sense, the "gold rush" in the EC-NRR has led to many unintentional yet unnoticed errors in the assessment of the ammonia production that could propagate erroneous practices among researchers. In fact, the very low current-to-ammonia conversion efficiencies as well as the very modest yields (nanomole scale) of the EC-NRR provide the perfect breeding ground for errors in the assessment of ammonia production.

To date, many materials have been reported to excel at performing the EC-NRR at ambient conditions [4–6], but the diversity of methodologies used in the literature to assess the ammonia production and even the lack of precise details on the experimental conditions makes it difficult for other groups to reproduce the results and further progress in that particular branch of research and shed some doubts on the reliability of the conclusions. For instance, noble metals such as Rh and Ru have been widely studied

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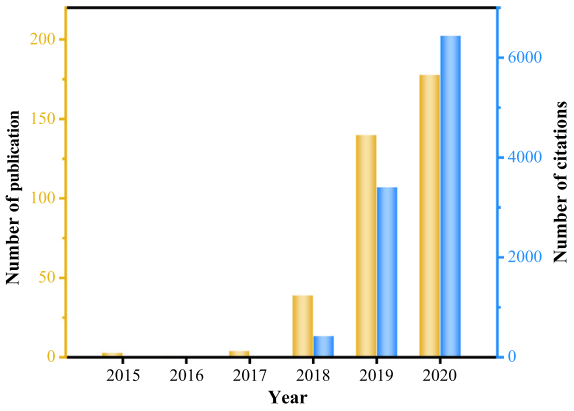


Fig. 1. Number of publications (yellow bar) and citations (blue bar) related to the field of EC-NRR from 2015 up to December 23, 2020, which were obtained by searching keywords electrochemical EC-NRR, ammonia and nitrogen reduction in Web of Science.

for EC-NRR since they are predicted to be located at the top of the volcano plot of this reaction, and accordingly several reports have displayed promising activities for ammonia production [7–9]. However, recent and more rigorous studies following strict protocols to assess the nitrogen conversion have revealed that those noble metals, namely Ru, Rh, Re and Au, among others, do not exhibit apparent catalytic activity towards the EC-NRR likely because of the serious competition of the hydrogen evolution reaction (HER) [10,11]. Aside from precious metals, bismuth bulk powder has been also highlighted as a potential candidate for EC-NRR [12], but recent studies demonstrated to be unable to reproduce the encouraging results reported previously nor even detect EC-NRR catalytic activity [13]. Overall, these negative and adverse results cast doubt on the whole body of work of metal catalysts for EC-NRR.

The occurrence of these false positive results is not unexpected, and it arguably responds to the lack of international consensus on the testing protocols, i.e. a set of standard practices to ensure the correct assessment of the EC-NRR. With this idea in mind, here we point out the unforeseen in many cases sources of error when evaluating EC-NRR at ambient conditions (Fig. 2), and provide an updated testing protocol to prevent them. We are convinced that the thoughtful practices reported in this work will benefit both early and experienced researchers that intend to dive in this exciting field while providing an unambiguous set of standardized methods that guarantee the reliability of reported data.

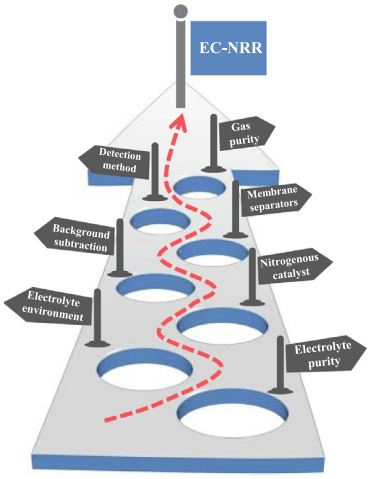


Fig. 2. Schematic of potential sources of error in EC-NRR test.

2. Possible sources of error

2.1. Nitrogenous catalyst

Nitrogen-containing electrocatalysts such as metal nitrides have been profusely screened both theoretically and experimentally for EC-NRR, given the possibility to operate via the Mars-van Krevelen (MvK) mechanism [14]. Unlike the conventional associative-dissociative mechanism wherein N_2 adsorbs on the catalytic surface, suffers various redox transformations and eventually desorbs as ammonia, the MvK proceeds with the reduction of the lattice N into NH_3 followed by the adsorption of a N_2 molecule from the medium to fill the resulting N vacancy and regenerate the catalyst. In stark contrast with literature reports that claim the exceptional resistance of nitrides, model materials such as MoN, NbN and VN have been reported to decompose during the EC-NRR [14,15]. They were demonstrated to generate ammonia but slowly deactivated under operation hinting at changes at the interface, likely related to the irreversible loss of surface N atoms, i.e., the active sites. Therefore, when dealing with nitrogen-containing electrocatalysts, it is fundamental to test the chemical and electrochemical stability of the material as the first step. Of course, in some cases the nitrides may also be stable during EC-NRR. For instance, 2D W_2N_3 with nitrogen vacancies has proven to be very robust by multiple characterization techniques [16]. In addition, we note that materials that supposedly do not contain nitrogen in the structure could indeed retain nitrogen traces from the synthesis, when either solvents or surfactants containing nitrogen are employed. These nitrogen species may contain ammonia or other reducible nitrogenous species, leading to erroneous conclusions. One strategy that could be implemented to remove the potential contaminants within the material is a rigorous pre-washing method, which is to wash the catalyst material several times before EC-NRR until the wash supernatant does not show nitrogen-containing impurities [2,17]. In addition, pre-reduction treatment is an effective strategy to remove the potential contaminants within the material. Specifically, in our previous work, it was found that the presence of NO_x contaminants in the Pd NSs catalyst could lead to false positive results in the EC-NRR process [18]. In fact, without the pre-reduction treatment, the catalyst showed apparent catalytic activity for ammoina production, which originated from the reduction of NO_x impurities. Interestingly, including a pre-reduction treatment, i.e. submitting the catalyst at –0.1 V vs RHE for 2 h under Ar, resulted in a catalyst with almost no activity for ammoina production, which indicates that the NO_x was removed during the pre-reduction process.

2.2. Electrolyte environment

The stability of electrochemical environment during EC-NRR test has great influence on the accuracy of testing method. The use of unbuffered neutral salts, such as Na_2SO_4, as supporting electrolyte is commonplace among the studies of EC-NRR since it can reduce the competition of HER, and it is also used in the calibration curve of NH_3. However, changes in the pH of the solution upon test can drastically affect the evaluation of the EC-NRR conversion efficiency. For the catalyst with obvious HER rate in the EC-NRR process, scanning at potentials below 0 V vs RHE leads to a noticeable HER contribution. Long-term experiments at this condition will consume a significant portion of H^+ in the solution, which will result in the increase of electrolyte pH. However, this phenomenon is often ignored. Thus, for calibrating the standard curve,

neutral electrolytes containing different amounts of ammonia are still used. As spectrophotometric detection method is sensitive to the pH, this will result in inaccuracy in determining the amount of ammonia. For the alkaline and acidic electrolytes, it will not cause obvious detection error as the electrolyte can maintain the pH in this condition. For non-aqueous electrolytes, the spectrophotometric detection method should be modified according the reaction condition. For example, after the EC-NRR test, the non-aqueous electrolyte can be added with HCl, then the solvent can be evaporated to leave ammonia in the form of the NH_4Cl salt, which is dissolved with water and then detected by spectrophotometric method as aqueous case [10]. In addition to the influence on detection method, the change of electrolyte pH will result in the miscalculation of the electrode potential, increasing the unrepeatability of the results. To avoid the adverse effects that come with the changes of the electrolyte environment under operation, it is advised to replace neutral salts by buffer systems to maintain the stability of electrolyte environment.

2.3. Electrolyte purity

Lithium salts have been widely used as electrolytes for EC-NRR. Some reports attribute the high EC-NRR selectivity and activity to Li^+ ions in the electrolyte [12]. However, the preparation of lithium carbonate, the upstream product of most commercial lithium salts, produces NO_3^- and NO_2^-, which will remain in the lithium salts and can be reduced to produce ammonia, leading to potential errors [19]. Therefore, when using Li salt as electrolyte, researchers should be cautious, and the purity of purchased electrolyte reagents should be tested first to avoid the possibility that unnoticed nitrogen species in the starting solution resulted in enhanced or false-positive EC-NRR performance. Besides the electrolyte itself, the purity of all chemical reagents used during the EC-NRR must be carefully checked to track the potential sources of nitrogen.

2.4. Gas purity

The main source of nitrogen during the EC-NRR is the N_2 gas supplied, more specifically, $^{14}N_2$ and $^{15}N_2$, therefore it is crucial to employ high-purity gas devoid of any other nitrogen species that could impact the results. In fact, some studies have found traces of ammonia, nitrite/nitrate or nitrous oxide in N_2 gas stocks [20]. Likewise, ensuring the purity of argon or other inert gases such as Helium used in the control experiment is also important since it will be used to determine the background ammonia content in the absence of N_2. Eventually, the EC-NRR will be evaluated by subtracting the background to the signal obtained in the presence of N_2, and thus, the inaccuracy in either the background collection or the actual EC-NRR could affect drastically the assessment.

2.5. Membrane separators

At present, most of the EC-NRR experiments are carried out in an H-cell with a Nafion membrane as the separator. However, Nafion membranes are not completely inert, and they can absorb and release ammonia during the EC-NRR test causing significant errors in the readings of ammonia production, as previously highlighted by several reports and our group's previous work [10,18,21]. Celgard 3401 and 3501 have shown less ammonia absorption compared with Nafion and other membranes, and therefore, are currently the preferred choices [10,18].

2.6. Detection method

Spectrophotometric/colorimetric assays and ion chromatography (IC) spectroscopy are amongst the most common methods for detecting the NH_3 produced in the EC-NRR, but each method features different detection limit and threshold. Ion chromatography has high efficiency, high sensitivity (a few ppb), high selectivity (inorganic and organic cations) and good stability. However, IC equipment is expensive, and the chromatography column is vulnerable to common Li^+ and Na^+ containing electrolytes [2,22]. The detection ranges of Nessler method and the Indophenol blue (IB) method are 0.02–5 ppm and 0.02–1.25 ppm (1.17×10^{-6} –2.94×10^{-4} mol/L and 1.17×10^{-6} –7.35×10^{-5} mol/L), respectively [23]. However, the IB method is known to be less accurate at higher concentration (>2.94×10^{-5} mol/L) and in acidic media [24]. Likewise, ammonia yields could be overestimated when using the Nessler method in the presence of metal ions such as Ru^{3+}, Ce^{3+} or Fe^{2+}, or when applying the IB protocol in the presence of methanol or formaldehyde. In addition, recent reports show that nuclear magnetic resonance (NMR) method is effective for ammonia detection in a variety of nondeuterated, nonaqueous and aqueous electrolytes [25,26]. The most important advantage of NMR is the direct and highly selective nature of the analysis for both $^{14}NH_4^+$ and $^{15}NH_4^+$, which is in contrast to indirect spectrophotometric detection after derivatization and ion chromatographic analysis. Therefore, choosing carefully the detection method is of paramount importance to perform an accurate measurement.

2.7. Background subtraction

Control experiments performed at open circuit potential and under Ar provide qualitative, but relevant information about the purity of the electrolyte and gas, the presence of reactive nitrogen species in the electrocatalyst, the test cell or even the equipment utilized for the assessment of ammonia, among others. However, many reports omit the presentation of these control experiments, and if presented, they are generally insufficient. For example, when it comes to analyze the production of ammonia at a certain applied potential, several studies utilized control tests that evaluate the background production of ammonia at potentials different from the ones explored for the EC-NRR. This might lead to errors on the assessment of the ammonia production. Likewise, some reports display control experiments where the background concentration of ammonia is statistically significant, and thus, it cannot be neglected, but it was not specified in the reports whether the background ammonia was being accounted for or not in the EC-NRR results. Obviously, these practices lead to errors on the assessment of the ammonia production. Therefore, it is recommended to show the background-corrected EC-NRR data for the sake of the discussion in the reports, but if it is not possible, we encourage researchers to present the control experiments under different test conditions (e.g. applied potentials) to convincingly provide information on the participation of the background signal to the experimental measurements of EC-NRR.

2.8. Reporting the experimental details

Being scrupulous at describing the methods, the setup of the experiments and details related to the operations performed during the analysis is crucial to not only guarantee the reproducibility but also to build a critical mass of researchers that share and work together at further polishing some instrumental protocols. Here, we encourage researchers in the field of EC-NRR to include all relevant information regarding the experiments that are performed, even though it could appear to be conventional or that have no impact on the resulting performance, namely, rate of N_2 or Ar bub-

bling, temperature of the system, electrochemical cell type or tubing materials, etc. In addition, it is recommended that the raw data or absolute values of UV–vis absorption spectra, NMR spectra, current density, NH_3 yield, and faradaic efficiency for all experiments (N_2, Ar, blank, and other controls) to be showed in the supplementary information of the manuscript [2], as exemplified by Yao et al. [27]. Admittedly, the EC-NRR is in its early stage of development and details that today are overlooked could be of great importance to ensure the reproducibility of the results. Overall, we must encourage detail reporting and require a thorough description of the experimental details prior acceptance for publication to establish the solid grounds required for this field to thrive.

2.9. Selectivity and faradaic efficiency

We have noticed that the concepts of selectivity and faradaic efficiency are not clear at present, which could be misleading when analyzing and comparing the results in the literature. In general, selectivity is the percentage or ratio of desired product generated (e.g. NH_3) to the total nitrogen reduction products (e.g. NH_3, N_2H_4.) in the reaction, which excludes the side-reaction of HER that produces H_2 [28]. The faradaic efficiency is the current efficiency, that is, the percentage or ratio of the current employed in the targeted transformation (i.e. NH_3 production) to the total current, which includes the current for H_2 formation through HER [29,30]. The equations for calculating the Faradaic efficiency and NH_3 selectivity are listed as Eq. (1) and (2) below. Even so, we suggest the scientists in the field to clearly state which parameter they use to assess the performance of the electrocatalyst, and to describe in detail how they calculate this value to avoid confusion.

$$\text{Faradaic efficiency} = (3 \times F \times c_{NH3} \times V)/(14 \times Q) \quad (1)$$

$$\begin{aligned} NH_3\text{selectivity} &= c_{NH3}/(2 \times \Delta c_{N2}) \times 100\% \\ &= c_{NH3}/(c_{NH3} + 2 \times c_{N2H4}) \times 100\% \end{aligned} \quad (2)$$

Where F is the Faraday constant, c_{NH3} is the measured NH_3 concentration, V is the volume of the electrolyte and Q is the total charge passing the electrode. $\triangle c_{N2}$ represents the concentration of nitrogen that has been electrochemically reduced and c_{N2H4} is the measured N_2H_4 concentration.

3. Updated protocol for performing EC-NRR

As more and more pitfalls in EC-NRR are constantly revealed, reaching a consensus on the testing protocol is a priority to ensure the reproducibility of the research. Indeed, the international research community has made efforts to establish international standards for testing the EC-NRR which are constantly updated and optimized [10,31]. Based on previous literature and our own experience in the field [10,18], we have designed a flow chart to guide scientists on how to proceed when performing the EC-NRR while circumventing commonplace sources of error (Fig. 3). Note that methods to eliminate nitrogen-containing impurities were also included, since this is a key step to assure the correct assessment of ammonia synthesis.

Before the rigorous test, we can prescreen the catalyst for EC-NRR quickly at one suitable potential. If no ammonia is detected, it might be not necessary to continue testing. If ammonia is detected, we should carry out rigorous tests according to the following protocol (Fig. 3). Unlike previous protocol, we recommend to prioritize the conditioning (elimination of contaminants) of all the components involved in the EC-NRR test, namely, performing all the control experiments and completing all the treatments to remove the potential contaminant or species that could interfere with the EC-NRR evaluation before starting the tests of the EC-NRR. Such as confirming Ar and N_2 gas purity, conducting control experiments without applied potential or under Ar condition. If "control experiment without applied potential" shows that ammonia is detected, it indicates that the system has pollution, for example, the ammonia impurity may come from nitrogen gas, the catalyst or catalyst decomposition, or from electrolysis cell, electrode or membrane, etc. If "control experiment under Ar" shows that ammonia is detected. In addition to the above-mentioned possible ammonia pollution in electrolytic cell, electrode, catalyst, electrolyte, diaphragm, etc., NO_x pollution may also exist in these places. Therefore, these two control experiments can help assess the purity of the system. After that, targeted experiments will be necessary to quantify the impurities in electrolyte, membrane, catalyst or container. In addition, we incorporated some steps specifically designed to remove NO_x species in the electrolyte and electrocatalyst. These steps involved, for instance, boiling all the tools, the electrochemical cell, counter electrode, etc. in ultrapure water (18.2 MΩ•cm) and dried to remove potential contaminants, checking the purity of the gases used in the experiment, such as N_2 and Ar, via ion chromatography and gas chromatography technique, and of the electrolyte, electrocatalyst and testing cell. The impurities found in the membrane, electrocatalyst or electrolyte could be addressed by finding a more appropriate membrane, pre-reducing the catalyst or calcining the electrolyte salts, etc [18,19]. Once these steps are completed the strict EC-NRR test could be conducted.

Regarding the stage wherein the EC-NRR is tested, if the detected levels of ammonia are significantly higher than those observed in the control (in the absence of N_2), and the ammonia production increases steadily over time, it can be preliminary concluded that the electrocatalysts indeed performs the EC-NRR. Subsequently, the use of isotopically labeled $^{15}N_2$ to confirm the formation of $^{15}NH_3$ via direct N_2 fixation is very important and the most convincing experiment for the accurate detection of ammonia, which enables reliable quantification of the ammonia from EC-NRR [10]. Therefore, quantitative EC-^{15}NRR testing should be conducted. If the amount of detected $^{14}NH_4^+$ and $^{15}NH_4^+$ is consistent, it can be established that the electrocatalyst is active towards the EC-NRR. It should be noted that ^{15}N-containing impurities in $^{15}N_2$ must be removed before the EC-^{15}NRR test. Otherwise, the conclusions gathered from the isotope experiment will not be valid. We suggest that EC-^{15}NRR should be conducted at least at a single-potential, such as at the optimal potential. Of course, if high activity catalyst is found and the ammonia production is much higher than the current level, such as orders of magnitude higher, which will not be obviously interfered by contaminants, the ^{15}N isotope experiments might be omitted. Finally, to ensure reproducibility and facilitate comparison with the state-of-the-art and future literature in the field, we recommend to repeat the EC-NRR tests and report the statistical results, as well as include measurements of stability (hours range), the geometric area and mass normalized yield rate, faradaic efficiency for NH_3 production and selectivity.

4. Finding encouraging "Needles in the EC-NRR haystack

After screening the body of work on EC-NRR at ambient conditions, we find that very few reports follow a rigorous testing protocol that guarantees the reliability of the results. By no means we claim that other results are wrong or fraudulent, but certainly lack of consistent data that unambiguously support their claims. In this section we will highlight a couple of studies that are good examples of good practices when assessing the EC-NRR, including exhaustive analyses of the results in solid and encouraging findings. Firstly, the report of Zhou et al. on the use of Fe-based cata-

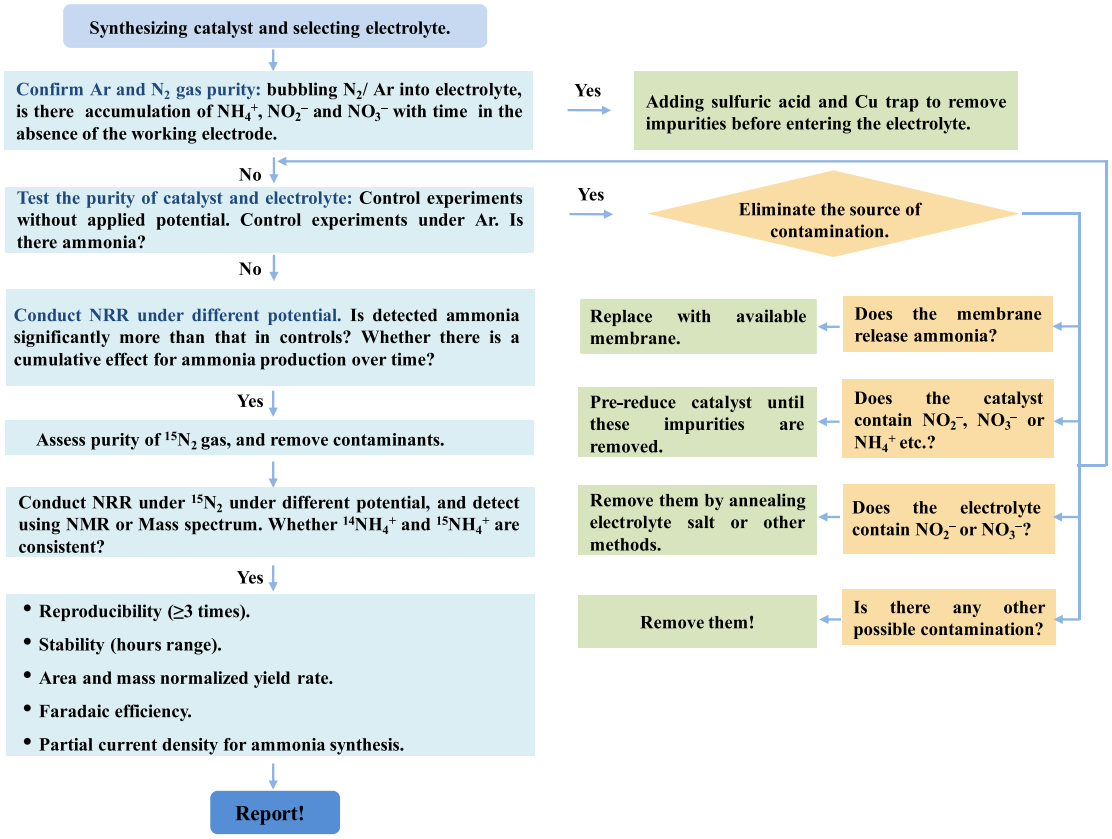


Fig. 3. Flow chart for determining the EC-NRR activity of a catalyst.

lysts in ionic liquids (ILs) to achieve a selectivity for ammonia of up to 60% [32]. In this work, authors carried out satisfactory control experiments, the main item being quantified $^{15}N_2$ experiments, and more importantly, the possible N-species impurities in $^{15}N_2$ were purified before the experiment, which is what most works lack. The attractiveness of the ILs lies on the fact that they are non-aqueous electrolytes highly tunable that can exhibit a very low water content and high nitrogen solubility. These features promote the EC-NRR while inhibit the competitive HER. In addition, the larger electrochemical window of ILs, compared to aqueous electrolytes, affords to study the EC-NRR at higher potentials, and hence, to achieve higher NH_3 production rates [33]. Despite the encouraging results, there is still room for significant improvement. The low conductivity and high viscosity compared to conventional electrolytes currently limit the performance, but ongoing research on ILs engineering aims at patching this issue. Second, the work on lithium-mediated EC-NRR which has reached a top faradaic efficiency of 18.5% with a production rate of around 8 nmol cm^{-2} s^{-1} [34]. This work stands out among others because it has carried out strict control experiments and a quantitative $^{15}N_2$ experiment, they checked the purity of $^{15}N_2$ before the experiment. Ongoing works directed to better understand the reaction mechanism, to optimize the nitridation of lithium and to replace the conventional ethanol by other proton donors that improve the protonation are being pursued to further enhance the performance of this EC-NRR route.

Although these strategies are different from the mainstream EC-NRR in aqueous electrolytes, they have great potential in terms of experimental integrity and preliminary results on NH_3 production. Theoretically, N_2 can be activated on the surface of any conductive material at an enough negative potential. However, in the aqueous electrolyte, HER is favored due to their kinetic advantage and much higher concentration in solution. Note that the solubility of N_2 in aqueous solvent is very low, less than 0.7 mM at a N_2 pressure of 1 bar, which imposes severe mass transport limitations during the reaction and limits the partial current of the EC-NRR [35]. However, admittedly ammonia synthesis in aqueous electrolyte is the most appealing approach in terms of sustainability and waste production, and hence, greater efforts should be directed to increase the concentration of N_2 at the proximity of the electrodes and reduce the mass transport problems. Recently, non-aqueous gas diffusion electrodes for rapid ammonia synthesis have been demonstrated to overcome the low solubility of N_2 gas [36]. The research of the aqueous gas diffusion electrodes for efficient ammonia synthesis is also worth studying.

5. Conclusion and prospect

In summary, EC-NRR is unlike other mainstream electrocatalytic reactions such as water or CO_2 reduction, requiring an exquisite care to evaluate the degree of conversion. The ubiquitous presence of nitrogen species in the testing cell and the yet low conversion yields turns the assessment of the ammonia synthesis into a daunting task. Today, the rapid burgeoning of new materials for the EC-NRR and the increasing number of groups diving into this field are leading to a rapid growth in the publications. Unfortunately, the lack of a set of guidelines to characterize this very sensitive systems is leading to a situation where a large number of the reported results are unreliable, very difficult to reproduce or in some cases misleading [10,11,13–15]. With the aim to address this issue, here, we point out some potential pitfalls in EC-NRR and

update the standard protocols to circumvent common sources of error when performing, analyzing and reporting the EC-NRR. We also would like to take the opportunity to encourage researchers and scientists to not only follow the protocols proposed, but take them as a starting point to design in-house standard procedures for the use of techniques, catalyst preparation, etc. and also good practices for the researchers working in the experiment.

Although there are many difficulties in the study of ammonia synthesis by EC-NRR, its significance and prospects are beyond doubt. Here, we propose three research directions in this field to simultaneously be tackled in the near future. Firstly, it is necessary to re-visit and explore the electrocatalytic activity towards the EC-NRR of old and new materials. Although many have been studied, the lack of reliable and standardized protocols for the characterization renders most of the materials' performance as a big question mark. Therefore, exploring the performance of various materials using the strict testing process can help us to have a preliminary understanding of the EC-NRR, which is conducive to the selection of catalyst materials in the follow-up work. Admittedly, the rational design of electrocatalysts and catalytic systems is the cornerstone for enhancing the yield and efficiency of EC-NRR. Here, we can take advantage from the lessons learnt in similar catalytic reactions feed by gaseous species such as CO_2RR, ORR and so on, wherein not only the catalyst formulation assisted by theoretical calculations, but also novel cells' designs have boosted the performance. From the perspective of the electrolyte, developing alternative proton sources to the aqueous solution may dramatically improve the faradaic efficiency while preventing competing HER. Secondly, the mechanism for many EC-NRR electrocatalyst is still unknown due to the significant influence of HER which poses serious technical challenges to isolate the contribution of the EC-NRR. Many studies lack the required painstaking experimental or theoretical exploration of the mechanism, whereas other works base their conclusions in a series of assumptions that are far from the operative conditions. This is unfavorable for clarifying the EC-NRR mechanism and improving the performance of EC-NRR. In future studies, researchers should study the EC-NRR mechanism by combining theoretical calculation with in situ characterization, such as surface enhanced infrared absorption spectroscopy (SEIRAS) and Raman technique, etc. Likewise, it is worth noting that these in-situ techniques are of great importance not only because they will allow to identify the active sites, but because they will be capable of monitoring changes in the reactive interface under operation (e.g. reconstruction), which could affect the reactivity [27,37]. Thirdly, aside from the dark electrocatalysis, enabling new schemes that could be directly powered by sunlight to trigger the EC-NRR are worth exploring. For instance, the study of photoelectrochemical (PEC) devices for EC-NRR could not only benefit from recent advances in the sister topic of PEC water splitting but also from those in the field of electrocatalysts for EC-NRR. More importantly, the exploration of semiconductor materials for direct solar to ammonia production from N_2 could reveal new catalytic pathways to be exported in the form of electrocatalysts, which could in turn broaden our understanding of the complex EC-NRR.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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