Robust catalyst assessment for the electrocatalytic nitrate reduction reaction

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Abstract

The electrochemical nitrate reduction reaction (NO₃RR) shows great promise for the distributed conversion of waste nitrate to ammonia. We highlight complexities of the reaction mechanism and possible waste feedstocks, and advocate best practices for robust measurement of catalyst activity, selectivity, and Faradaic efficiency in this burgeoning field. While fundamental studies of the reaction mechanism and environment are still needed, rigorous performance assessment in well-defined conditions will best enable catalyst design. Progress will be most dynamic and responsive with shared community standards that enable comparison between groups while reflecting the complexity of possible feedstocks.

Introduction

Fertilizer use, fossil-fuel combustion, and industrial processes have increased nitrate concentrations in many wastewaters and watersheds to levels that threaten environmental and human health^{1,2}. This disruption to the nitrogen cycle primarily originates from energy intensive production of ammonia by the Haber-Bosch process, which concomitantly emits more CO₂ as a byproduct than any other chemical production process³⁻⁷. Interest in closing this portion of the

nitrogen cycle motivates the nitrate electroreduction reaction (NO₃RR), using water and electrons as reducing agents to produce ammonia/ammonium (NH₃/NH₄⁺, depending on the pH), with O₂ produced as a byproduct at the anode. Although reducing N⁵⁺ in nitrate (NO₃⁻) requires more electrons than reducing N⁰ in the dinitrogen reduction reaction (N₂RR), NO₃RR circumvents the stability of the N=N bond, substantially lowering the energetic input⁸. Together with the ability to investigate high concentrations of reactant NO₃⁻ (in comparison to dissolved N₂), the investigation of NO₃RR targeting NH₃/NH₄⁺ has seen rapid growth over relatively short timescales⁹.

The NO₃RR is a complex reaction network, with a diverse range of pH-dependent reaction pathways and products that range from dissolved molecules to ions to gasses¹⁰⁻¹². Drawing parallels to CO₂ electroreduction (CO₂RR), this results in specific concerns regarding mass transport and product detection. The NO₃RR often proceeds at electrochemical potentials where the hydrogen evolution reaction (HER) from water is also possible, resulting in a competition between reactions for protons in solution (H⁺) and on the surface (H^{*}).^{13,14}

This comment shares the rationale behind practices in NO₃RR that enable the assessment of catalyst performance in ways that facilitate comparison. This is rooted in a brief summary of the important mechanistic aspects that necessitate specific practices for NO₃RR and explain the limitations in comparing material performance. We highlight the diversity of possible feedstocks, their inherent complexities, and suggest common platforms for testing. This testing requires specific needs in reactor configuration and product analysis. We conclude with a critical assessment of what is required for accurate comparison of catalyst performance.

Implications of the reaction mechanism on product distribution

On many catalysts and in many experimental conditions, NO₃RR proceeds at appreciable rates below 0 V vs the reversible hydrogen electrode (RHE), where HER can also thermodynamically occur. At these electrochemical potentials adsorbed NO_3^- is first reduced to nitrite, NO_2^- . This NO_2^- intermediate can desorb from some catalyst surfaces, and depending on electrochemical potential, also reduce¹⁵. Subsequent reduction to NO is generally understood to proceed via two primary pathways¹⁶: one where NO desorbs or one where NO stays bound and/or dissociates. We focus on the latter, which yields hydroxylamine, NH₂OH, or NH₃/NH₄⁺ depending on pH. Against this backdrop, important metrics frequently discussed are the NO₃RR Faradaic efficiency (FE):

$$FE = \frac{q_{NO3RR}}{q_{total}}$$
(1)

where q_{NO3RR} is the charge passed in generating detected products for NO₃RR (e.g. 8 e^- per NH₃/NH₄⁺) and q_{total} is the total charge passed, including other concurrent processes like HER, double layer charging, and corrosion. Product specific FEs are also discussed, considering NH₃ for example:

$$FE_{NH3} = \frac{q_{NH3}}{q_{total}}$$
(2)

Where q_{NH3} is the charge passed in generating NH₃. Selectivity, S, can be defined for a given product relative to the N-atom, considering NH₃ for example:

$$S_{NH3} = \frac{N_{NH3}}{N_{NO3RR}}$$
(3)

Where N_{NH3} is the number of moles of NH₃ produced, and N_{NO3RR} the number of moles of NO₃⁻ reduced. Electron selectivity can also be defined, here referred to as S^e , again considering NH₃:

$$S_{NH3}^{e} = \frac{q_{NH3}}{q_{NO3RR}} \tag{4}$$

Both definitions have utility in describing electrocatalyst performance, and it is important to specify which is presented.

Because the NO₃RR reaction proceeds under conditions where NO_3^- competes with H⁺ for surface sites, comparison across different solution concentrations or applied potentials can

manifest in large differences in surface coverages (θ , Fig. 1a)¹⁷. These different site distributions can subsequently impact reaction rates, evident from the potential-dependent NO₃⁻ reaction rate order, and microkinetic modeling suggests possible implications in NO3RR mechanism as well¹⁷. For these reasons, catalyst performance should only be compared at the same applied potential (on the reversible hydrogen electrode, RHE, scale) and same concentration of NO₃⁻ in solution.



Fig. 1 a Calculated electrochemical-potential-dependent NO_3^- and H coverage (θ) from a competitive adsorption model in ref ¹⁷. **b** Speciation of NO₃RR products at a series of electrons passed per initial NO₃⁻ ion observed in ref ¹⁸. **c** Schematic illustrating that large local pH gradients can arise in circumneutral media with limited buffering. **d** Calculated reduction potential with fractional NO₃⁻ conversion (assuming 100% selectivity to the noted product).

Measurements of product distribution in batch systems illustrate that on some catalysts (e.g. Cu), NO_2^- is an intermediate that can dissolve into solution and presumably re-reduce on the surface¹⁹, yielding an eventual product of NH₃/NH₄⁺ (Fig. 1b)¹⁸. This has important implications on the condition at which products are measured and compared, as products and FE will depend on the amount of NO_3^- reduced, or converted (tied to the amount of charge passed and convoluted with the frequently used measure of time passed). Explicit measurement of the electrochemical potential at which NO_2^- can be reduced is also informative in understanding the NO₃RR mechanism and product distribution¹⁹. Although isotopic labeling is generally unnecessary to distinguish that NH₃/NH₄⁺ originates from NO_3^- given high yields, it can be informative in identifying possible contributions from dissolved intermediates, like NO_2^- ²⁰.

At the electrochemical potentials of relevance to NO₃RR, most metals are below their potential of zero charge (pzc) and thus have negative surface charge²¹⁻²³. Electrostatically this acts against the adsorption of the nitrate anion²⁴. The nature of cations in solution therefore impacts the NO₃RR performance. The involvement of 9 H⁺ for NH₃ production also gives pH-dependence to the reversible potential and resultant overpotential, highlighting the importance of measuring and/or controlling the local pH. Historical studies of cation and anion effects are convoluted with pH changes from unbuffered neutral electrolytes, differences in proton donor strengths of hydrated cations compared to water, and local electric fields^{25,26}. Though systematic investigations are lacking, NO₃RR ion effects can likely impact not only rate but also FE and selectivity, similar to CO₂RR.

Complexities of NO₃RR feedstocks

Given that NO₃RR is inherently sensitive to electrolyte composition, it would be desirable to identify/establish a standard reaction environment for catalyst testing. However, the applications of interest for NO₃RR span a wide range of reaction environments, and one catalyst may not represent the best performer in every scenario. We here introduce three model systems for representative catalyst assessment and comparison and note particular complexities inherent to them for further investigation (Table 1).

Motivating	NO3 ⁻ salt component	pH fixing electrolyte	Additional
application			complexities
Low-level nuclear	1.0 M NaNO ₃	1.0 M NaOH	+0.3 M NaNO ₂
waste ^a			+0.1 M Na ₂ SO ₄
			+0.01 M NaCl
			+0.002 M Na ₂ CrO ₄
Industrial waste	1.0 M NaNO ₃	1.0 M H ₂ SO ₄	Organics
water ^b			Less acidic
Ground/surface	0.002 M NaNO ₃ *	0.1 M Na _x H _{3-x} PO ₄	50x less buffering
water ^c		buffer at pH 7	Na ₂ CO ₃

 Table 1 | Model electrolyte systems for NO₃RR

^aApproximately a 2x dilution of the composition of the decontaminated salt-solution from the Savannah riversite²⁷

^b5-10x more concentrated than e.g. ammunitions factories²⁸

^cApproximately the concentration where human health concerns arise²⁹, \sim 2x the EPA limit of NO₃⁻ *The concentrated waste stream from ion exchange regeneration is also of interest, e.g. 0.1 M NaNO₃, with appreciable content of NaCl *Low-level nuclear waste.* The highest NO_3^- concentrations are typically attributed to low-level nuclear waste, in many cases exceeding 1 M.²⁷ These waste streams are also high pH, often exceeding 14. Typical streams also include appreciable amounts of NO_2^- , with potential implications on reaction mechanism and product distribution. Other complexities include the presence of sulfate (SO₄²⁻) and chloride (Cl⁻) anions, which may compete for surface sites and reduce NO₃RR rates²⁶. In addition, streams may include heavy metal ions, such as from Cr and Pb, that could plate out on the electrocatalyst at the reducing potentials of NO₃RR.

Industrial wastewater. Industries including ammunitions factories²⁸, steel manufacturing³⁰, and food processing³¹ all produce waste streams that contain appreciable quantities of NO_3^- waste. The stream composition is highly dependent on the industry and specific plant. For example, streams could potentially contain NH_4^+ at levels comparable to NO_3^- , have other dominant cations such as K⁺, large amounts of organics, and pH levels as high as 6. We suggest a model system on the high end of $[NO_3^-]$ and low end of pH for simplicity and to better enable comparison across systems.

Ground and surface waters. Agricultural runoff from fertilizer application and animal waste results in NO_3^- concentrations above levels safe for human consumption²⁹, but two to three orders of magnitude lower than that in industrial and nuclear waste water. These water streams are circumneutral and often have a similar amount of PO_4^{3-} and NO_3^- , which can compete for surface sites and provide some level of buffering. Ground water can also contain similar amounts of CO_3^{2-} with additional buffering capacity at a higher pK_a. Although buffering in natural systems is low, we suggest a higher concentration of buffer than found in natural systems to better establish the local pH for fundamental studies and catalyst comparison. The concentrated waste stream from

the regeneration of ion exchange columns (commonly employed at water treatment plants) is also of interest, with higher NO_3^- concentration and additional salt content.

These three model systems illustrate the wide range of NO₃RR reactant concentrations (NO₃⁻ and H⁺ equivalents) in potential feedstocks. Beyond these bulk descriptions, the consumption of 9/10 H⁺ to produce NH₃/NH₄⁺ can locally increase the pH,³² particularly in circumneutral media with limited buffering (Fig. 1c)³³. Local pH increases are also tied to less cathodic potentials on the RHE scale (and therefore lower driving forces for NO₃RR). While we suggest a 0.1 M phosphate buffer to help maintain the local pH, its ability to do so is tied to the rate of reaction and limited by mass transfer³⁴. For example, calculations with 0.1 M buffer pairs with a pK_a of 7 can sustain only 10 mA/cm² at a rotation rate of 1600 rpm in rotating disk electrode (RDE) experiments while maintaining a difference in surface and bulk pH equal or less than 0.2³⁵. The local pH can be measured using a rotating ring disk electrode³⁶, which may enable more representative understanding of the pH-dependent driving force. Variation in local pH towards more alkalinity may alter rate, FE, and selectivity uniquely compared to bulk alkaline conditions due to presence of a pH gradient.

Performing NO₃RR measurements

With important metrics in the field including FE and selectivity, direct identification and quantification of products is necessary. This requires separating the anode and cathode via a membrane that allows for ion transport but prevents NO₃RR products from re-oxidizing at the anode. Crossover of products to the anolyte compartment is possible even using such membranes³⁷, however, and should be explicitly measured. In some scenarios like RDE measurements focusing on reaction rates for samples with known product distribution, a cell single volume cell may be

used if counter electrode reactions do not impact the cathode performance. The electrochemical potential at the counter electrode should be explicitly measured to ensure the reactions taking place do not influence catalytic performance in either reactor geometry (as could e.g. oxidative dissolution at the counter). We note that oxygen, either from ambient or produced at a counter electrode, reduces more readily than NO_3^- and should be removed from the solution by sparging with an inert gas. We suggest doing so with Ar, rather than N₂, to enable possible N₂ detection. Care should also be taken to ensure ions from the reference electrode, such as Cl⁻, are isolated such as via a secondary frit to prevent surface poisoning³⁸.

Product quantification requires a combination of analytical chemistry tools³⁹. Ionic species such as NO_2^- and remaining NO_3^- can be quantified by ion or liquid chromatography (IC and LC, respectively) although spectrophotometric methods also exist⁴⁰. NH₃/NH₄⁺ is typically quantified by spectrophotometric methods, with NMR required in cases employing isotope labeling⁴¹. For some conditions and catalysts, quantification of these two products is sufficient to close the nitrogen balance and determine NO₃RR FE. In alkaline conditions hydroxylamine may be formed, quantifiable by fluorescent⁴² and spectrophotometric methods⁴³ and liquid chromatography-mass spectrometry (LC-MS). Gaseous products including a range of NO_x products and N₂ are also possible, quantifiable by MS (although distinct speciation can be challenging). Gaseous NH₃ (formed above ~9.3) is highly soluble under the conditions suggested here for measurement, but care should be taken if the catholyte is not gas tight and under constant sparging with inert gas, which could lead to displacement. We refer the reader to other works for a more detailed discussion of the complexities associated with possible solution processes and pH-dependent decomposition processes that may occur^{39,44}.

Although NO_3^- is highly soluble in comparison to gaseous N₂, it's transport to the catalyst surface, as well as that of proton sources, can appreciably impact measured rates and product distribution³². The regime under which kinetic effects dominate will be a balance between catalyst surface area (dispersion), reaction rate of NO₃RR, rate of competing HER (also consuming protons), convection, and diffusion. Researchers should consider the impact of mass transport by e.g. comparing performance at different stir or flow rates. In cases where mass transport effects might not be avoided – e.g. considering low NO_3^- concentrations at high overpotentials – care should be taken to fully report sufficient information (including the exposed catalyst surface area and catholyte volume) for reproducibility and catalyst comparison.

Assessment of NO₃RR catalysts also requires a rigorous understanding of the applied electrochemical potential to fix the overpotential, or reaction driving force. In considering the reversible potentials, E, for NO₃RR to NO₃⁻ and NH₃, it is apparent that Nernstian shifts result for consideration of high conversions:

$$E_{\mathrm{NO}_{3}^{-}/\mathrm{NO}_{2}^{-}} = 0.85 - \frac{RT}{2F} \ln \frac{a_{NO_{2}^{-}}a_{H_{2}O}}{a_{NO_{3}^{-}}(a_{H^{+}})^{2}}$$
(5)

$$E_{\text{NO}_3^-/NH_3} = 0.82 - \frac{RT}{8F} \ln \frac{a_{NH_3} (a_{H_2O})^3}{a_{NO_3^-} (a_{H^+})^9}$$
(6)

Where a_i is the activity of species <u>i</u> and R, T, F are the conventional variables. As shown in Fig. 1d, the reversible potential for $E_{NO_3^-/NO_2^-}$, shifts by over 50 mV upon reaching a fractional conversion (the amount of NO₃⁻ consumed divided by the initial amount) of 0.5, but 4x less for $E_{NO_3^-/NH_3}$. Given the exponential relationship between rate and overpotential from the Butler-Volmer equation, measurement at constant voltage would then result in appreciably lower driving

force at high conversion (with additional implications from changing coverages in a competitive adsorption reaction landscape). As such, measurements in batch cells with the goal of assessing catalyst FE, selectivity, and kinetics should be limited to low NO_3^- conversions. Conversion should be reported explicitly, however the most transparent and controllable parameter in electrochemical measurements is the number of electrons passed (e.g. $0.1 e^-/NO_3^-$). We suggest passing not more than $0.1 e^-/NO_3^-$, which corresponds to 5% conversion in the case of 100% FE to NO_2^- and 1.25% conversion for 100% FE to NH₃. However, in cases where FE is low, particularly in conjuncture with low NO_3^- concentrations in ground/surface water, a higher number of electrons may be required to have sufficient concentration for reliable quantification via the chosen analytical methods.

As also evident from Eqs **5-6**, the pH dependence of the NO₃RR requires that this understanding is coupled to knowledge of the (local) pH to quantify or fix the driving force. The potential should also be corrected for ohmic drop in the electrolyte via electrochemical impedance spectroscopy (EIS).

Comparing catalyst rates

As discussed earlier, catalyst performance⁴⁵—including reaction rate—should be performed at low conversion in systems with known (facile) mass transport, at well-defined electrochemical potential and driving force. We offered suggestions for the composition of model electrolytes and controlled variables (e^- passed/NO₃⁻), as well as required information (catalyst surface area, electrolyte volume) in cases where mass transport effects cannot be mitigated. Ideally catalyst rates are normalized to the number of active sites. For systems like single metal atoms in a carbon matrix²⁰, the active site identity is reasonably well-known and controllable via metal precursor loading. For other systems such as metal nanoparticles, films, and alloys, assumptions and approximations must be made in choosing an appropriate strategy to normalize rate. The exposed surface area is typically used, in the absence of more detailed understanding of the system (e.g. that defect sites or a specific element is most active). Quantifying this area is challenging, and approaches can be system specific. For example, the surface area of Pt and Pd nanoparticles can be assessed via the underpotential deposited hydrogen (H_{upd}) charge⁴⁶. The stripping of deposited metals, such as Cu or Pb can also be used to estimate surface area in some cases (though care should be taken to avoid contamination resulting from this)^{47,48}. Measurement of the electrochemical surface area (ECSA), while often employed⁴⁹, is limited by a factor of ~7 uncertainty⁵⁰. However, its measurement is typically reproducible in comparison across research groups, and others recommend a specific capacitance of 0.035 mF cm⁻² in 1 M H₂SO₄ and 0.040 mF cm⁻² in 1 M NaOH for comparison across metallic systems^{49,51}.

Conclusion

NO₃RR targeting NH₃/NH₄⁺ production is a dynamic area of research, where the performance of electrocatalysts in a wide range of conditions is of interest. We offer suggestions for model systems of study, parameters to report and control, and approaches to take into account to better enable comparison across studies and ultimately drive understanding of this complex reaction network. We note, however, that many unanswered questions regarding the mechanisms of NO₃RR, complexities of the active site, and role of the electrical double layer still necessitate fundamental studies that investigate beyond these suggestions. These studies may include unique electrolyte compositions and mass transfer limitations or consider higher

conversions to assess application of electrocatalysts to real-world systems. Together with rigorous assessment of catalyst performance in well-defined conditions, the field is poised for rapid progress in our ability to transform waste NO_3^- into value-added NH_3/NH_4^+ in distributed electrochemical systems, employing renewable electricity to help close the nitrogen cycle.

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