The Use of Controls for Consistent and Accurate Measurements of Electrocatalytic Ammonia Synthesis from Dinitrogen

Lauren F. Greenlee,[1*] Julie N. Renner,[2] Shelby L. Foster[1]

[1]University of Arkansas, Ralph E. Martin Department of Chemical Engineering, 3202 Bell Engineering Center, Fayetteville, AR 72701

[2]Case Western Reserve University, Department of Chemical and Biomolecular Engineering, Cleveland, OH 44106

*Corresponding Author: greenlee@uark.edu; Ph: 610-507-6390

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Introduction

With this Viewpoint, the authors aim to discuss sources of ambient ammonia, the status of the field of low-temperature electrochemical ammonia synthesis with regard to controls for ambient ammonia, and opportunities for the field to improve on how ammonia measurements and control experiments are performed.

The Haber-Bosch process for ammonia production enabled an exponential population explosion through the 20th century by supporting ammonia-based fertilization. Today, federal agencies, researchers, and industry alike see a need for a step change in the technology that is available for ammonia production. A next-generation process will successfully achieve a key trifecta: energy efficiency, scalability/modularity, and CO_2-free emissions. Low-temperature electrocatalytically-driven reduction of nitrogen (N_2) and water to ammonia has the potential to meet this trifecta. While explored by a handful of researchers prior to several years ago, low-temperature electrocatalytic ammonia synthesis has experienced renewed interest since 2015 (**Figure 1**), with a primary drive toward a fundamental performance metric: improvement in the Faradaic efficiency of the electrocatalyst at the cathode. The intense focus on improvement of Faradaic efficiency results from extreme inefficiency in most reported electrocatalyst materials for the N_2 reduction reaction (NRR); the majority of low-temperature electrocatalysts have Faradaic efficiencies of less than 1%, with the hydrogen evolution reaction (HER) as the dominant reaction.

There are strong energy efficiency and device design arguments for operating at temperatures less than 100 °C, including the ability to use well-established polymer electrolyte membrane electrode assembly (MEA) technology developed in the fuel cell and water electrolyzer fields. These devices are expected to be scalable, energy efficient, and easily assimilable with renewable energy generation, thus creating a carbon-free route to NRR. Since the publication of Licht et al.,[1] the field of low-temperature NRR in aqueous and/or solid polymer electrolyte systems has seen contributions from experimental research groups aiming to demonstrate significant (> 5 – 10x) improvements on the state-of-the-art in Faradaic efficiency.

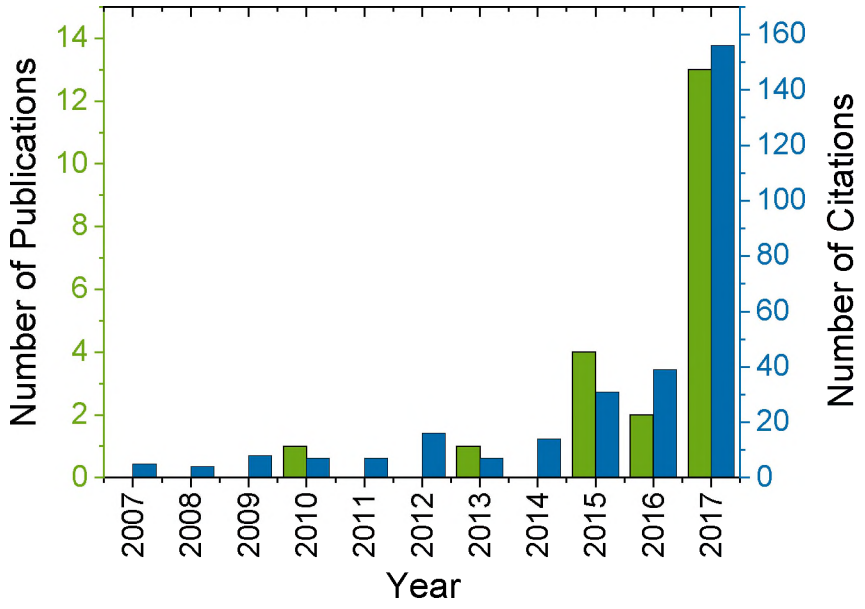

Figure 1. Publications which fall under the term "electrochemical+ammonia+synthesis" in a Web of Science search and the total number of citations for all of the articles in the search per year for the past 10 years.

Over the past several years, published literature on electrocatalysts for low-temperature NRR has indeed focused on reporting increases in Faradaic efficiencies, where Faradaic efficiency (FE) is calculated by comparing the measured ammonia produced against the theoretical ammonia production possible based on measurement of current and the 6-electron transfer reaction for 1 mol of N_2. The clear and inherent challenge in determining efficiency is the accurate and reliable measurement of the ammonia produced during electrocatalysis.

Sources of Ambient Ammonia

Why is the measurement of electrochemically synthesized aqueous ammonia difficult?

The ammonia molecule has a key set of properties that result in its ubiquity in all aqueous solutions and on many surfaces. Ammonia is a small, polar molecule with an aqueous solubility of 482 g/L at 24 °C.[2] This solubility data is valid for either form of ammonia (ammonium, NH_4^+ or ammonia, NH_3), where the form of the aqueous species will be dependent on, and controlled by, the pH of the aqueous solution. Ammonia has a pKa of 9.25 at 25 °C, and follows the equilibrium relationship shown in Equation 1.[3] As a result, $NH_{3,(aq)}$ will be the primary species above this pKa (by ~ pH 10.25), and $NH_4^+{}_{(aq)}$ will be the primary species below this pKa (by ~ pH 8.25).[4] Due to its polarity, high aqueous solubility, and its basic character (i.e., it accepts protons from water, Equation 1), ammonia not only easily dissolves into water, but easily adsorbs to a wide range of surfaces, including common laboratory materials (e.g., tubing) and surfaces.[5] In fact, gaseous ammonia has been shown to have a short atmospheric lifetime of 12 hours to 5 days, due to its rapid deposition on surfaces.[6] Further, aerosolized ammonium has a longer ambient lifetime of 5 to 10 days, which enables longer range regional transport of ammonia in the atmosphere.[6] Thus, ambient gas phase ammonia will always provide a background level of ammonia in aqueous experimental samples, whether from gas phase dissolution or from solid surface desorption.

$$NH_{3,(aq)} + H_2O_{(l)} \leftrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \quad (1)$$

Where does ambient ammonia come from?

The sources of ambient ammonia can be traced to its primary industrial use today: fertilization and agricultural activities. Ammonia is the primary pollutant emitted from animal production facilities,[5] and ammonia also volatilizes from field-applied ammonia fertilizer chemicals.[5, 7] A study in 2000[6] compared local ammonia emissions in North Carolina (NC) between the years of 1982 and 1997 to recorded ammonium concentrations in rain precipitation over the same time period. The study focused on the proposed idea that increasing nitrogen nutrient loading observed in rivers and estuaries was primarily coming from increasingly intense animal production operations. In 1995, estimated NC emissions from animal production operations (i.e., swine, cattle, and poultry) ranged from 24,952 to 68,540 tons of ammonia N per year, while fertilizer application resulted in 8,270 tons N/year and other point sources resulted in 1,665 tons N/year.[6] From 1982 to 1997, the study identified a statistically significant 4 year cycle and an overall increasing trend in ammonium concentrations in precipitation from 150 μg/L to more than 350 μg/L. Notably, emissions from animal production had a marked increase from 1990 to 1997, and data analysis suggested that ammonium concentrations in precipitation started to increase significantly around the 1989-1990 time period. Results from this study suggest that there is a direct correlation between ambient ammonia emissions and concentrations of ammonia in precipitation, thus demonstrating the importance of understanding that ambient ammonia sources will result in ammonia in water samples.

A more recent study by Butler et al. in 2016[7] reported on data obtained from 18 passive atmospheric ammonia samplers of the National Atmospheric Deposition Program (NADP) Ammonia Monitoring Network (AMoN) that are located across the United States and operated bi-

weekly from 2008 to 2015. The study found that on average, the ambient gaseous ammonia concentration increased 7% per year. During the same time period, reported ammonia concentrations in precipitation data increased 5% per year. Butler et al.[7] report precipitation concentrations for the Midwest region of 196 – 379 μg/L in 2008 (range is the result of seasonal variability) and of 260 – 504 μg/L in 2014. If we compare the data reported from 1982 to 1997 in Walker et al.[6] to the data recorded from 2008 to 2015 in Butler et al.,[7] it is clear that across the U.S., there has been regional and seasonal variability, as well as an overall increasing trend, in ammonia concentration for both gaseous ambient and aqueous environmental samples. From these two exemplar studies, we can only conclude that ambient ammonia concentrations will at least be at 2015 levels and are likely to increase as national food demand tracks with population increase in future years. As such, to approach low-temperature electrochemical ammonia synthesis with experimental thoroughness, we should expect to always observe, measure, and potentially mitigate background ammonia concentrations in any aqueous samples in the laboratory. Further, we can expect that the background ammonia concentration will likely be variable over time. These conditions necessitate rigorous controls performed for each experimental catalyst, each time the catalyst is tested, with multiple repeats to ensure statistical significance.

Status of the Field

How does ambient ammonia affect the field of low-temperature electrocatalytic synthesis of ammonia?

The authors of this Viewpoint write from experience, as in 2015 we reported initial results on a suite of iron-nickel monometallic and bimetallic nanoparticle catalysts for electrochemical ammonia synthesis from N_2.[8] In this initial work, we reported FE values of 2 – 3.5 % for our best-performing catalysts in a membrane electrode assembly (MEA) test rig, with ammonia production

rates ranging from $1.33 \times 10^{-12} - 3.80 \times 10^{-12}$ mol.cm^{-2}.s^{-1}. We did not run argon (Ar) controls, and the flow rates we obtained were within the same order of magnitude as the background ammonia measurements we now perform. In subsequent experiments, our research team started running Ar controls against N_2 tests, and we obtained FE values of much less than 1%. As we have continued in this field, we have developed an approach to our experiments that includes background, non-electrochemical, and electrochemical controls; these control measurements are performed for each catalyst, for multiple repeats, at each condition. As an example, we show in **Figure 2** datasets from our own catalyst testing data, where duplicate electrodes were prepared, and the electrodes were put through a series of steps that included Ar- or N_2-bubbled electrolyte (1 M NaOH) with no electrochemistry and then Ar- or N_2-bubbled electrolyte under applied potential. Each electrochemical cell was connected in-line to an acid trap (0.02 M H_2SO_4), and each acid trap was sampled for ambient ammonia before any experiments. The measurements shown in **Figure 2** include subtracted ambient concentrations. In **Figure 2a**, when the Ar electrochemistry control is included, the measured FE was 0.09 %, but if this Ar control is excluded, the FE increases to 0.12 %. Even more dramatic is the result of **Figure 2b**, where Ar controls show that no ammonia was produced, but without these controls, one might assume that the catalyst produced ammonia. The extent to which Ar control measurements impact FE calculations will vary based on many factors, including, but not limited to, ambient ammonia concentration/contamination, setup, experimental conditions, human experimental variance, and catalyst preparation.

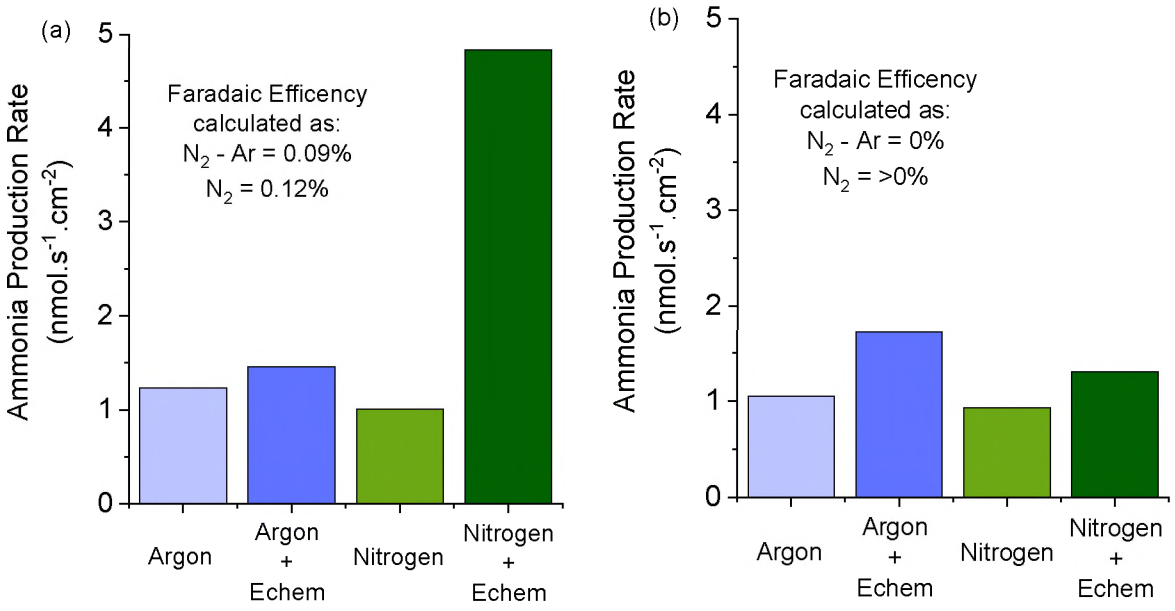

Figure 2. Example datasets used to demonstrate calculation of Faradaic efficiency with and without background Ar measurements. (a) and (b) represent two different bimetallic compositions of an iron-nickel nanoparticle catalyst tested in the authors' experimental research. Experimental testing conditions were: 50 °C cell temperature, 1 M NaOH electrolyte, E = -1.19 V vs. Ag/AgCl (-0.24 V vs. RHE), 65.7 μg/cm^2 catalyst mass loading, 1 hour chronoamperometry experiment.

In this Viewpoint, our goal is to present and discuss the status of the low-temperature NRR field in terms of how control experiments are currently reported, what controls appear to be typical within the majority of studies, and where there are gaps in either reporting or experimentation with regard to controls. This article will consider low-temperature (< 100 °C) NRR primarily, except for a few references. There is also a need for controls in research on high-temperature and non-electrocatalysis[9] approaches (e.g., LiH mediated NH_3 synthesis), but low-temperature technologies are more impacted when an incomplete approach to controls is used. Ammonia production rates

are lower at low temperatures, and as a result, ambient ammonia will make up a larger percentage of the ammonia measured. Fundamental research at the laboratory scale further amplifies this problem because electrode surface areas are small, and ammonia concentrations and flow rates can approach ambient background measurements. We aim to highlight key efforts of the authors to conduct appropriate controls but also to point out opportunities for broad improvement. We also aim to illustrate the need for detailed reporting of all experimental methods and approaches. As the field grows, we want to establish a high level of understanding that enables newcomers to the field and experts alike to conduct successful, reliable, and repeatable experiments, with the ability to confidently compare results among published literature. Our discussion focuses on a set of papers published within the past two years,[10-17] where authors have reported the use of some form of controls and FE values ranging from less than 1% to almost 14% (**Figure 3**), along with flow rates that vary over 3 orders of magnitude. The potential progress in increased FE in recent years is compelling and should further motivate the field toward the use of rigorous controls.

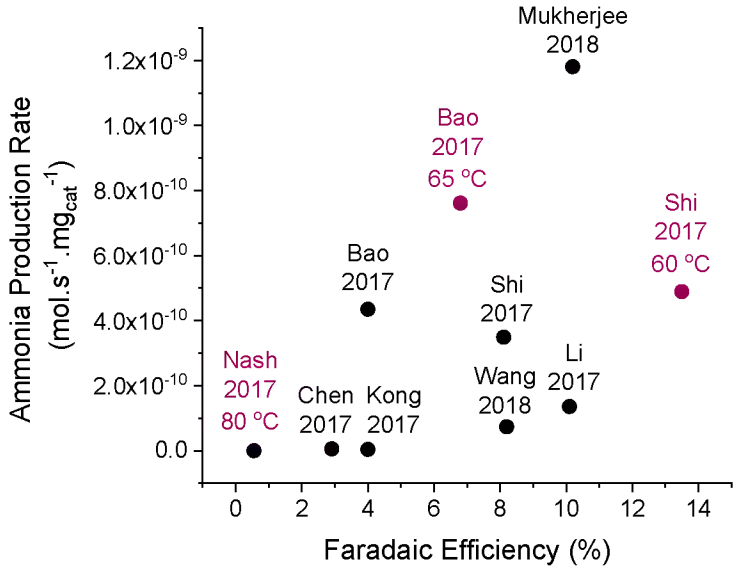

Figure 3. State of the Art:[10-17] Reported flow rates and Faradaic efficiencies from studies that have performed Ar controls. The majority of studies that perform Ar control experiments have an implicitly assumed background subtraction in calculations of ammonia flow rate and Faradaic efficiency, or the studies report no detection of ammonia background contamination. Black symbols denote data obtained at 25 °C.

Controls in Literature: Recent Efforts

What can we learn by a thorough read of current literature?

Here, we review the set of recent publications from the past several years that have conducted at least some level of control experiments. We aim to highlight the level of experimental rigor and quality of these papers as well as to point out opportunities for future improvement, where we, as a research field, can learn from these publications as well as build from this body of work to continue to strive for excellence in the electrochemical NRR field. All of the studies reviewed in this Viewpoint performed, at a minimum, background measurements of ammonia concentration in either the electrolyte or the acid trap solution used in experiments. Most studies use a spectrophotometric method, where ammonia is reacted with a set of chemicals in aqueous solution, then forms a compound with visible light absorbance, and is measured against a standard curve. Most studies report the standard curve data for at least one set of standards and one set of ammonia measurements (i.e., control experiment and N_2 electrochemical experiments). Among these studies, we find several trends which prompt the following suggestions for the future: (1) The details of control experiments should be prominently, thoroughly, and clearly reported, and the execution should be as thorough as rest of the experiments (i.e., conducted with repeats at all

experimental conditions); (2) A secondary validation of the results should be performed when possible, such as isotope-labeled nitrogen (i.e., $^{15}N_2$), and when validation is performed, efforts should be made to make the results quantitative; (3) The sensitivity of the detection method should be discussed or reported, and the detection method should be optimized to the experimental conditions (i.e., pH), which can affect detection sensitivity.

To fully understand what a team of authors has done, one must typically read in detail the supplementary information (SI) file that accompanies the main published manuscript. The reporting of the full details of how the experiments were performed, including the control experiments, is critical to the field of low-temperature NRR as we work to advance catalyst materials with higher ammonia production rates and Faradaic efficiencies. One must consider both as an author and as a reviewer of submitted manuscripts that the SI must be reviewed as critically as the primary manuscript. Currently, there is a range of clarity and detail in how authors report the experimental approach.

Control and Verification Experiments Presented as Results

The work by Stuart Licht and co-authors[1] in 2014 is seminal for heterogeneous NRR not only because the team demonstrated NRR Faradaic efficiencies of up to 35% (at 200 °C in a molten hydroxide electrolyte and in the presence of N_2 and steam) with a nanoparticulate Fe_2O_3 catalyst, but because the authors ran a set of control experiments that showed ammonia production under Ar. Further, the results with Ar were not placed in the SI but were presented as part of the key research results in Figure 3[1] of the authors' *Science* publication.[1] While such high efficiencies have yet to be achieved at low temperature (< 100 °C), the control experiments in Ar importantly show a contribution to the measured NRR electrolysis efficiency. The authors' approach to reporting both the experiments with N_2 and the experiments with Ar is also exemplary in that it

guarantees that a reader will see and understand the use of control experiments, as well as communicates a message to the reader and the scientific community at large that control experiments are important. Since this publication, no other publication has published control experiments with this approach; if controls are part of the study, the details of ammonia measurements and any results for ammonia detection in the control experiments are reported in the SI file. We note that several studies[12, 15] do report the difference in measured current density, typically as one cyclic voltammogram, each, in the presence of N_2 and Ar and the target catalyst material. Licht et al.[1] did not perform ^{15}N isotope experiments.

Zhu et al.,[18] while a study focused on photochemical rather than electrochemical N_2 reduction, has a thorough experimental design approach and is discussed here in terms of the control experiments used. The authors report in the main article (Figure 3[18]) a complete set of Ar control experiments for each time step that was also evaluated in the presence of N_2. A dark control is also reported in Figure 4[18] in comparison to a set of experiments on the influence of laser excitation wavelength. In Figure 5,[18] the authors report a set of isotope-labeled ^{15}N experiments with infrared spectroscopy as the detection method, which qualitatively support their other N_2 reduction experiments and ammonia production results. The reporting of control and verification experiments within the main set of figures of the published article enables the reader to directly compare ammonia flow rates and communicates to the readership the importance of measuring ammonia within an appropriate set of control experiments.

Prior to the Licht et al.[1] and Zhu et al.[18] studies, Yandulov and Schrock[19] present quantitative ^1H NMR results for $^{14}NH_4^+$ versus $^{15}NH_4^+$ experiments, where the quantitative yield of NH_4^+ was determined (i.e., 8.06 equivalents versus 8.18 equivalents, respectively, for $^{14}NH_4^+$ versus $^{15}NH_4^+$) to confirm spectrophotometric evidence of N_2 reduction to NH_3 by a molybdenum complex. The

authors report the ^{1}H NMR results in Figure 2[19] of the main article, with details in SI. This approach to reporting of experimental validation is currently lacking in the low-temperature heterogenous NRR field but is arguably necessary to elevate the overall level of accuracy and accountability as the field grows. It is important for the success of every research group and for the field as a whole that our experimental approach to controls be transparent and repeatable, as has been illustrated by the works of Licht et al., Zhu et al., and Yandulov and Schrock.[1, 18-19]

Low-Temperature NRR: State-of-the-Art in Half Cell Experiments

Half cell experiments focus on the use of a liquid electrolyte that is bubbled or sparged with gas. The majority of experiments are performed as 3-electrode setups, where the cathodic NRR occurs at the working electrode, the counter electrode supports the oxygen evolution reaction, and a reference electrode is used to isolate and control the applied potential of the working electrode. A range of electrolytes has been tested, including acidic (e.g., 0.1 M HCl),[15] neutral (e.g., 0.1 M phosphate buffer),[16] alkaline (e.g., 0.1 M NaOH, 0.1 KOH),[10, 17] or non-aqueous (e.g., ethanol in tetrahydrofuran)[20] solutions. The testing time for each experiment also varies from study to study.

Authors tend to either sample directly from the electrolyte solution[13, 15-17] or from an in-line acid trap[10, 21] to obtain aliquots for aqueous ammonia measurement. The choice of where to sample may, in part, be driven by the type of electrolyte used and the pH; in more alkaline solutions, it may be assumed that aqueous NH_3 will be off-gassed during electrochemical synthesis as N_2 gas is continuously bubbled through the electrolyte solution. However, given the high solubility of ammonia in aqueous solutions, it is also possible that even at high pH, some of the ammonia in the system will remain in the electrolyte. The majority of authors are publishing the standard curve used for spectrophotometric detection of aqueous ammonia, but many studies only report one standard curve. The sensitivity of the spectrophotometric method(s) and the lowest measured

ammonia concentration vary across studies. The indophenol blue spectrophotometric method is perhaps the most common method, and reported lower limits of ammonia concentration measurement range from 0.12 μM[17] to 22 μM.[15]

Electrochemical testing typically includes cyclic voltammetry (CV) and chronoamperometry (CA), where CV experiments are used to characterize the electrochemical behavior across a relevant potential range, while CA experiments are used to calculate FE values and evaluate the short-term stability of the catalyst. The majority of studies report at least one set of CV data in the presence of Ar and N_2,[15] but often no more than one set of CV data is shown, and the data reported is one forward and one reverse scan for each gas. A set of CA data taken at specific applied potential values is often reported, and these data are reported to be used to calculate FE. Many of the papers reviewed include the equations used for calculating experimental (exp) and theoretical (theo) ammonia production, as well as FE, as follows:

$$r_{NH_3,exp} = \frac{[NH_3] * V}{t * A} \quad (2)$$

$$r_{NH_3,theo} = \frac{I}{F * \frac{3\ mol\ e^-}{mol\ NH_3}} \quad (3)$$

$$Faradaic\ Efficiency = \frac{r_{NH_3,exp}}{r_{NH_3,theo}} \times 100\% \quad (4)$$

Where r is ammonia production rate (mol.s^{-1}.cm^{-2}), [NH_3] is the experimentally-measured ammonia concentration (mol/L), t is time (sec), V is volume (L), A is electrode surface area (cm^2), I is current density (A/cm^2), and F is the Faraday constant (96,485 C/mol e$^-$). None of the studies explicitly state that Ar control experiments and/or ambient ammonia measurements are subtracted from measured ammonia during N_2 electrochemical experiments to determine FE values (either in the reported equations or in the discussion text). Most studies do not report more than one set of

control experiments with Ar, and most only include an electrochemical Ar control. Some studies include a non-electrochemical N_2 control.[10]

Lee et al.[20] report a full set of N_2 and Ar experiments under applied potential (Figure S6[20]), where ammonia flow rates, values for FE, and turnover frequency are reported. While the authors did not explicitly subtract the Ar control experiments from the N_2 experiments, the reader is able to do this calculation easily from the data presented in Figure S6.[20] The authors also make a significant effort to include estimated ammonia contaminant contributions to their measurements in both the N_2 gas flow and as dissolved in tetrahydrofuran (THF) (pages 11 and 12 of the SI[20]).

With extensive control experiments and evaluation of exogenous nitrogen contamination, Zhou et al.[21] is one of the most thorough publications in the NRR literature to date. In Zhou et al.,[21] the authors discuss at length their efforts to conduct control experiments as a main section of the article on page 2518. The control experiments and approach included: purification of the ionic liquids until no ammonia was detectable (limit of detection (LOD) of 1 nmol/mL), "blank" experiments under identical conditions but with no applied voltage, and electrochemical experiments under Ar gas. Under Ar or in the absence of applied voltage, the authors detected a background of ~4 nmol ammonia in their experimental setup, while electrochemical experiments with N_2 resulted in 10 – 50 nmol of ammonia. The authors also tested the stability of the ionic liquids under the relevant applied potential range and confirmed that the only source of H_2 was from the tested Pt electrode. Further, none of the ionic liquids used contained nitrogen groups so that the only source of nitrogen was the N_2 gas supplied to the electrochemical setup. For an additional confirmation that the ammonia produced from N_2 electrochemical experiments originates from the N_2 gas, the authors also performed a quantitative isotope labeled ^{15}N study, where ^{1}H NMR was used for detection and $^{15}NH_4Cl$ was used to make a standard curve. The isotope study resulted in 15 nmol $^{15}NH_4^+$

and 5.5 nmol $^{14}NH_4^+$ measured, as compared to a parallel indophenol blue spectrophotometric test, which resulted in 19 nmol NH_4^+ measured. The 5.5 nmol $^{14}NH_4^+$ measured is in line with the background measurements reported (i.e., ~4 nmol ammonia). The authors acknowledge and provide citations for evidence in prior studies that ambient ammonia contamination can be the source of measured ammonia at the lab scale where ammonia production rates are quite low, as in photochemical ammonia synthesis or low-temperature ammonia synthesis. The control experiments of Zhou et al.[21] show that the background of ambient ammonia ranges from 8 % to 40 % of the ammonia produced from electroreduction of N_2 gas, and if not accounted for, could significantly skew reported flow rates and FE values.

State-of-the-Art: MEA Experiments

MEA experiments have been explored by some research groups as an approach that is more similar to a potential commercial ammonia electrolyzer process and perhaps better in terms of limiting the amount of water that is accessible at the catalyst surface (and thereby minimizing water reduction to hydrogen through HER). However, an MEA setup is also inherently more complicated with electrode engineering, cell components, and membrane separators as potential sources of ammonia contamination or unoptimized operation, both of which can confound results. Kong et al.[12] conducted a study in both N_2-bubbled aqueous electrolyte and in a humidified N_2 MEA setup. For MEA experiments, the authors supplied humidified gaseous N_2 to the cathode and an aqueous alkaline electrolyte to anode of the MEA. For MEA experiments, the produced gaseous ammonia was captured by an in line aqueous acid trap (0.01 M H_2SO_4), and an Ar control under voltage was performed to confirm ammonia production. In both half cell and MEA experiments, the authors pre-treated the γ-Fe_2O_3 catalyst-electrode material at 350 ^oC in the presence of air; the potential adsorption or desorption of N_2 onto the catalyst surface from this pretreatment could be considered

in future studies. Further, the data presented in Figure S6[12] suggest that ammonia produced was absorbed by the membrane in the MEA setup.[12]

Nash et al.[14] studied a suite of noble metal catalysts for NRR in both acidic and alkaline MEA tests, where produced ammonia was collected by an in line acid trap connected to the MEA setup. Catalysts were also evaluated through cyclic voltammetry in acid and alkaline aqueous electrolyte. The authors importantly state in the publication abstract that degradation of the alkaline exchange membrane and leaching of the quaternary ammonium ion erroneously contributed to ammonia measurements. The authors also use a "break in" procedure for the cathode of the MEA, where H_2 was fed to the cathode side for 1 hr before N_2 was fed for NRR. During NRR, the cathode was fed humidified N_2 and the anode was fed humidified H_2. Acid traps were used for both the cathode and anode sides of the MEA, and in the acidic case (which used a Nafion polymer electrolyte membrane), the membrane was soaked in sulfuric acid post-NRR to evaluate the ammonia content of the membrane. In the results of Nash et al.,[14] the authors provide a discussion of sources of variability in results, including different quantification methods, repeatability from one assembled MEA to another, and the use of membranes that have been pre-exchanged with ammonium (where the ammonium ion may be evolved on the cathode side). Absent from this work is the use of Ar control experiments, although the authors spend considerable time in the article discussing H_2 control experiments to determine contributions of membrane and ionomer degradation to ammonia measurements. The use of H_2 control experiments may be a suitable replacement for Ar controls in the MEA setup as long as non-electrochemical control experiments are performed to determine any non-electrochemical contribution to ammonia synthesis. It may also be useful to compare H_2 and Ar control experiments to confirm both approaches are valid.

Reporting of NRR "Selectivity"

Important to the field of NRR is the meaning of the word "selectivity". Kong et al.[12] and Lee et al.[20] discuss selectivity of the electrocatalyst for the NRR reaction in terms of NH_3 formation versus H_2 formation through HER, which is essentially the description of Faradaic efficiency. Other publications, such as those of Shi et al.[15] discuss selectivity in terms of NH_3 versus hydrazine (N_2H_2) formation. Shi et al. focus on NH_3 versus N_2H_2 because prior work on gold-based catalysts showed significant N_2H_2 production, which is undesirable in the context of ammonia synthesis. Neither version of "selectivity" is necessarily incorrect; the key is to define the specific use of the word within the context and discussion of results. Lee et al.[20] uses a simple approach to calculate NRR selectivity (over HER) by taking the difference between the current measured under N_2 and the current measured under Ar and dividing by the current under N_2. The assumption that the authors make is that all of the additional current goes, or should go, toward NRR. Kong et al.,[12] however, do not make the assumption that the increase in the measured current under N_2 versus Ar goes to NRR and include a discussion of maximum possible ammonia production (based on the $\Delta I_{N2\text{-}Ar}$ as measured during CVs) versus measured ammonia production. Few of the papers reviewed directly measure H_2 production to confirm their selectivity statements.

In Lee et al.[20] the cartoons of Figure 1a[20] and 3e[20] suggest that the authors are testing ZIF rejection of H_2O molecules as the primary mechanism for the enhanced selectivity and FE. While the approach of by Lee et al.[20] is unique and interesting, the conclusions made should be approached with caution for those working in aqueous electrolytes because their work was performed in a non-aqueous electrolyte ($LiCF_3SO_3$ (0.2 M) in a solvent mixture containing ~1% ethanol in dry THF) with ethanol as the proton donator during NRR. Future studies based on this work would benefit from testing controlled addition of water to the system to compare results with fully water flooded systems.

An Approach to Experimental Controls

While not the only way to rigorously conduct NRR experiments, we recommend performing a set of non-electrochemical and electrochemical experiments in both Ar and N_2 for each catalyst tested and for each time the catalyst is tested. We also recommend performing repeat measurements for each catalyst type/composition and verifying that ammonia measurements are repeatable and reliable day-to-day and electrode prep-to-electrode prep. Aliquots should be taken from any prepared solution (i.e., electrolyte or acid trap) that is used during testing, and blanks should be tested from any water sources used. These background samples should also be repeated regularly over time to understand the ambient ammonia contamination and variability in the ammonia background of one's laboratory. All control experiments (non-electrochemical and electrochemical) should be performed for the same amount of time as the N_2 electrochemical experiment. A diagram of this general approach is shown in **Figure 4**.

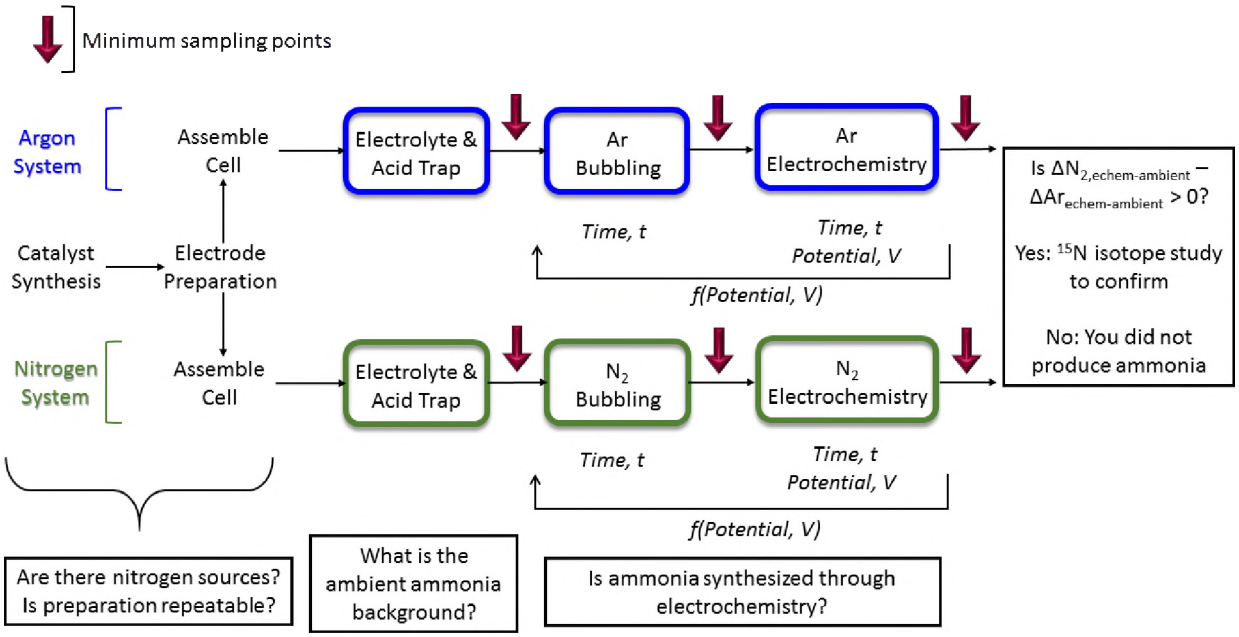

Figure 4. Flow diagram of steps in an experiment.

Once control experiments have been performed, one must select a method for ammonia quantification; it is generally accepted that spectrophotometric methods will be used in day-to-day experiments, and isotope studies should be used for verification of results due to the expense of $^{15}N\ N_2$. There are several different options for spectrophotometric methods, including indophenol blue, Nessler's reagent, and commercial kits that use either chemical or enzymatic reactions to form a color change in solution. These methods can have sensitivity to pH, time, and reagent chemical concentrations. Nessler's reagent does not distinguish between ammonia and hydrazine and generally has a higher LOD than the indophenol blue method. For example, Bao et al.[10] used an ammonia assay kit from BioVision (which is a chemical assay based on the indophenol blue method), with a manufacturer LOD of 10 μM, and Nessler's reagent, with a reported LOD of approximately 28 μM (0.5 mg/L). The indophenol blue method is perhaps the most common amongst recent studies, where authors are using a specific recipe of chemicals to produce blue-green solutions. However, the indophenol blue method can have a range of sensitivity and LOD, dependent on pH,[22] phenol concentration,[22] chemical additives,[23] and other sample preparation steps.[24] It is thus important to understand the chemistry of these colorimetric assays and perform experiments to optimize the selected assay for one's sample conditions (e.g., pH of electrolyte) and to ensure that the assay enables measurement of ambient ammonia background.

Ammonia test kits exist, such as the BioVision assay (mentioned above), the QuantiFluo Ammonia Assay kit (BioAssay Systems, uses o-phthalaldehyde and forms a fluorescent product), and the Amplite™ Colorimetric Ammonia Quantitation Kit *Blue Color* kit (AAT Bioquest, based on an enzyme-coupled reaction of ammonia in the assay and results in a blue color that can be measured spectrophotometrically). The stated LOD for the o-phthalaldehyde approach is 12 μM (216 μg/L

NH_4^+) and for the enzyme test kit is 1 μM (18 μg/L NH_4^+). While this type of enzyme-based approach can provide improved sensitivity over chemical reagent spectrophotometric methods, such as the indophenol blue or Nessler's reagent approaches, the method does have sensitivity to pH. Basic (high pH) samples disrupt the function of the enzyme, and lower pH samples must be used; a best practice is to confirm the pH of the samples and perform a standard curve in the same electrolyte background and pH as the experimental samples.

Once a promising NRR catalyst is identified with Ar control testing, quantitative isotopic ^{15}N experiments should be performed. The amount of $^{15}NH_4^+$ measured through isotope experiments should match the amount of ammonia measured by the selected spectrophotometric method. ^{15}N confirmation of N_2 reduction does not preclude a complete and repeated set of Ar controls. A set of Ar control experiments in a parallel, or in the same, setup allows measurement of the background NH_3 in the test system, while ^{15}N measurements confirm that N_2 is in fact being reduced to NH_3, and ^{15}N measurements confirm the source of N_2.

Ammonia production rates should subsequently be calculated following Equation 5, where the ammonia measured in an Ar electrochemical control experiment is subtracted from the ammonia measured in a N_2 electrochemical experiment, and both of those measurements include background and non-electrochemical ammonia subtractions.

$$r_{NH_3,exp} = \frac{[NH_{3,N2} - NH_{3,Ar}] * V}{t * A} \quad (5)$$

Even with isotope experiments, one must consider contamination of all commercial gases, including ^{15}N and ^{14}N N_2 and Ar. Dabundo et al.[25] recently reported on the contamination of commercial ^{15}N with ammonia, nitrate/nitrite, and nitrous oxide. Zhou et al.[21] provide detailed descriptions as to how the authors sampled and evaluated the ammonia and nitrogen oxide (NO_x)

species in their N_2 and Ar gases and the potential for these species to contribute to measured ammonia. These contamination studies demonstrate that even with isotope confirmation of ammonia synthesis, a full set of N_2 and Ar controls with and without electrochemistry should ideally be run (for both ^{15}N and ^{14}N).

Other Considerations: Catalyst Stability, Experimental Setup, & Other Sources of Nitrogen During Experiments

Catalyst preparation can be a source of nitrogen, and while not all nitrogen sources will be converted to ammonia, the presence of the nitrogen species highlights the need for rigorous controls. For example, Lee et al.[20] have several potential sources of nitrogen other than gaseous N_2, including residual polyvinylpyrrolidone (PVP) stabilizer and the imidazole of the metal organic framework (MOF) (zeolitic imidazolate framework-71) used in the catalyst design. Li et al.[13] synthesized a multi-component catalyst where a source of nitrogen in the synthesis procedure as the cerium precursor was cerium nitrate. The authors report a detailed x-ray photoelectron spectroscopy (XPS) analysis of their samples with no survey spectra or nitrogen binding energy regions reported, so we have no direct evidence that the catalyst was nitrogen-free as-synthesized. Chen et al.[11] studied a Fe_2O_3-carbon nanotube (CNT) catalyst, where the synthesis approaches of both the CNTs and the Fe_2O_3 components included nitrogen sources (nitric acid and iron precursor ferric nitrate). The authors report XPS results for iron species characterization but do not report survey spectra or nitrogen binding energy scans to demonstrate the lack of nitrogen species on the as-synthesized catalyst. A good example of control experiments performed to identify other sources of nitrogen/ammonia in an experimental setup is found in the work by Bao et al.[10] which includes examples of control experiments with N_2 and no applied potential, with uncoated carbon

paper electrodes, with Nafion deposited on carbon, and in the presence of cetyl trimethylammonium bromide (CTAB).

In addition to catalyst preparation and composition, the experimental setup itself may contribute to variation in ambient ammonia background. The electrode support, ionomers, polymers, and any other materials may have adsorbed ammonia, and gas flow rates should be controlled as flow rate can cause variation in ambient/control measurements. We recommend having a dedicated experimental setup for Ar and N_2 experiments with dedicated flow lines, cells, and all other components. All cells should be cleaned with sulfuric acid (as opposed to nitric acid).

Conclusions and Recommendations

Our review of literature illustrates that while researchers are performing control experiments, more rigorous execution and reporting of the controls in the future will enable accurate comparisons and support a robust and explicit experimental approach across the field. As a result, future breakthroughs in catalyst performance and increases in FE will be more rapidly accepted and developed and eventually lead to a robust renewable electrochemical ammonia process.

In summary, we make the following recommendations. In publications, the NRR community should specify not only what controls were run but whether controls were run for each experiment, calculated averages and standard deviations for all measurements, and whether the ammonia measurements in control experiments were subtracted from measured ammonia to calculate ammonia flow rate and FE. Authors should specify how selectivity is defined and calculated. Publications should include a more extensive reporting of results from control experiments either in tabulated or graphical form to demonstrate how controls were implemented and used to evaluate

catalyst performance. A discussion of controls in publications is absolutely necessary – details in this case are needed to establish the expectations of the field, to establish a standard of experimental controls to be used across the field, and to enable comparison and repeatability as catalysts are developed. This discussion should include all experimental approaches, standard curves, detection limits, and complementary techniques used for measurement of ammonia in solution. Ideally, the NRR field should report both negative and positive results in terms of electrocatalyst performance, such that the community as a whole can better understand promising directions in terms of catalyst design. Finally, we recommend that as a field, we begin to make our full data sets publicly available in a data repository (e.g., Ag Data Commons) upon publication in a peer-reviewed journal. While this recommendation may seem unreasonable and daunting, other fields (e.g., genomics) have seen tremendous progress and scientific gains for the whole research community because of, and not in spite of, making data publicly available for others to analyze.

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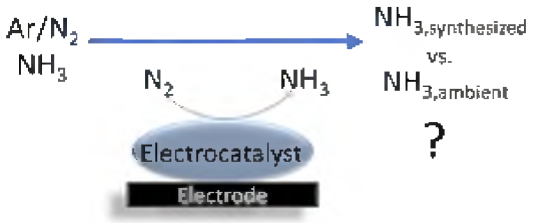
TOC Graphic


Ar/N2
NH3
NH3,synthesized
vs.
NH3,ambient
?
N2
NH3
Electrocatalyst
Electrode