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A Versatile Method for Ammonia Detection in a Range of Relevant Electrolytes via Direct Nuclear Magnetic Resonance Techniques

Adam C. Nielander,[†] Joshua M. McEnaney,[†] Jay A. Schwalbe,[†] Jon G. Baker,[†] Sarah J. Blair,[†] Lei Wang,[†] Jeffrey G. Pelton,[‡] Suzanne Z. Andersen,[§] Kasper Enemark-Rasmussen,[∇] Viktor Čolić,[§] Sungeun Yang,[§] Stacey F. Bent,[†] Matteo Cargnello,[†] Jakob Kibsgaard,[§] Peter C. K. Vesborg,[§] Ib Chorkendorff,[§] and Thomas F. Jaramillo*[,†]

[†]Department of Chemical Engineering, Stanford University 443 Via Ortega, Stanford, California 94305, United States

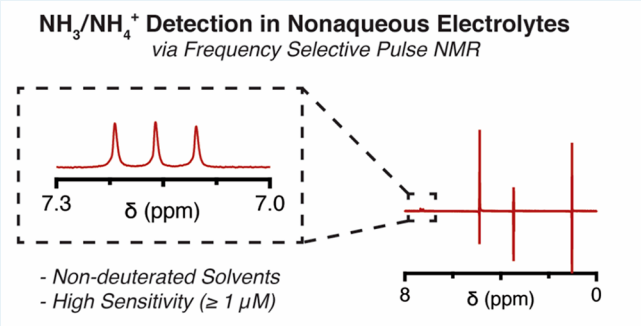
[‡]QB3 Institute, University of California, Berkeley, California 94720, United States

[§]Department of Physics, Technical University of Denmark, Building 311, Fysikvej, DK-2800 Kgs. Lyngby, Denmark

[∇]Department of Chemistry, Technical University of Denmark, Building 207, DK-2800 Kgs. Lyngby, Denmark

Supporting Information

ABSTRACT: Electrocatalytic N_2 reduction to ammonia has recently attracted a great deal of interest as a possible renewable energy-driven alternative to the Haber−Bosch process. However, the detection of NH_3 after attempting electrocatalytic reduction of N_2 can be hampered by low NH_3 yields, ambient NH_3 contamination, and the need for multistep chemical separation of NH_3 from the electrolyte. Herein, we report a frequency-selective pulse nuclear magnetic resonance (NMR) method and quantify the efficacy of this method to measure the concentration of NH_3 (present in the assay as NH_4^+) in an electrolyte after electrocatalysis. This NMR method was demonstrated to be effective in a variety of nondeuterated, nonaqueous and aqueous electrolytes, and did not require the separation of NH_3 from the electrolyte. NH_3 sensitivity down to 1 μM was readily achieved with isotopic and chemical specificity. Compatible electrolytes and solvents included ethanol, tetrahydrofuran, dimethyl sulfoxide, acetonitrile, propylene carbonate, diethyl either, hexanes, and water. The efficacy of the commonly employed Berthelot method was also quantified and compared to the NMR method in a range of nonaqueous and aqueous electrolytes, including ethanol, THF, propylene carbonate, and water.



KEYWORDS: *nitrogen reduction, ammonia detection, NMR, electrocatalysis, nonaqueous electrochemistry*

INTRODUCTION

Electrocatalytic reduction of molecular nitrogen to ammonia at ambient temperature and pressure offers an intriguing route to sustainable ammonia production. Utilizing electromotive force to overcome the kinetic barriers associated with N_2 to NH_3 transformation in lieu of the high temperatures and pressures required for the thermal activation of N_2 via the Haber−Bosch process could enable the coupling of renewable electricity sources (e.g., wind, solar) to ammonia production, as well as the decentralization and on-demand production ammonia.[1−3]

Electrocatalytic N_2 reduction in aqueous electrolytes has been explored, but low catalytic activities and low Faradaic efficiencies toward ammonia, with concurrently high production rates toward undesired hydrogen evolution, have hampered development in this area.[4−6] Furthermore, the low NH_3 concentrations and mass yields that are often observed under aqueous N_2 reduction conditions, in concert with a range of pernicious NH_3 contaminants that can be found under ambient electrochemical conditions, may lead to the reporting of spurious results. There is a need in the N_2 electrocatalysis field for method development toward the unambiguous assignment of NH_3 observed in an electrolyte as having been electrochemically generated and not the result of contamination.[3,7−11]

The use of nonaqueous electrolytes with precisely controlled proton activities has been suggested as a strategy for the improvement in selectivity toward ammonia, relative to hydrogen production during electrochemical N_2 reduction, and recent experimental reports support this hypothesis.[12,13] However, the strategy of impeding the hydrogen evolution reaction may not necessarily improve the activity of N_2 electrocatalysts, leaving the challenge of distinguishing electrochemically synthesized NH_3 from NH_3 contamination unresolved for low activity catalysts. Employing nonaqueous

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electrolytes also adds the confounding factor that many of the methods for ammonia quantification, including the classic Berthelot colorimetric method, are either unoptimized for or incompatible with nonaqueous electrolytes.[14,15] This issue could potentially be overcome by using vacuum transfer or liquid−liquid extraction of ammonia to aqueous solution, but these methods require further manipulation of the electrolyte, as well as consideration of other incompatibilities (e.g., low vapor pressure solvents are incompatible with vacuum transfer; water miscible solvents are incompatible with extraction and may also transfer supporting electrolyte salts).[16,17] Methods capable of the direct detection of ammonia in various nonaqueous and aqueous electrolytes with high sensitivity, with ready discrimination against contaminant NH_3, and without the need for NH_3 transfer or advanced chemical manipulation, would be valuable to the field of N_2 electrocatalysis.

In this study, we developed and optimized a frequency-selective nuclear magnetic resonance (NMR) method for the direct interrogation of nondeuterated electrolyte solutions for the presence of ammonia after N_2 reduction electrocatalysis without requiring significant electrolyte manipulation. The use of NMR, which has been widely employed in the CO_2 electrocatalysis community for the detection of various carbon-based products, was an attractive strategy for ammonia detection for several reasons, including its inherent ability to discriminate between nitrogen isotopes.[18−21] The NMR method for the detection of electrocatalytically generated NH_3 in various electrolyte-based analytes was developed by evaluating NMR pulse sequences, nondeuterated solvent compatibility, supporting electrolyte compatibility, required proton concentration, and locking solvent compatibility in order to optimize the sensitivity, specificity, and stability of NH_3 detection. We further compare this NMR method to the Berthelot colorimetric method in a representative set of electrolytes in order to understand the advantages of the NMR method, with respect to NH_3 detection after electrocatalytic N_2 reduction.

■ RESULTS AND DISCUSSION

In order to accurately and efficiently quantify ammonia concentration in nondeuterated nonaqueous and aqueous electrolytes via NMR, both the NMR pulse sequence and the analyte solution conditions need to be carefully controlled. We explored a range of analyte conditions including acid concentration, locking solvent, and calibration standard, as well as a series of NMR pulse sequences, in order to identify the most effective NMR detection method. We draw a nomenclatural distinction here between the electrolyte and analyte, where the electrolyte is a hypothetical electrolytic solution of interest in a given electrochemical experiment and the analyte is the electrolyte once it has been prepared for NMR analysis. Importantly, while the analyte may have stringent chemical requirements (e.g., acid concentration), the electrolyte is not beholden to these same requirements as the preparation of the electrolyte for analysis can be accomplished after electrochemical testing. Table 1 provides a summary of these optimized analyte conditions for ammonia detection in various electrolytes and a representative list of compatible solvents for this detection method.

The primary challenge to the detection of ammonia in nondeuterated electrolytes via NMR is the minimizing of the ^1H signals from the solvent. While the use of deuterated electrolytes could alleviate this issue, the cost of these solvents and limitations on the available solvent species make this strategy problematic. We found a straightforward and versatile means to minimize proton solvent signals while obtaining a strong NH_4^+ signal through the use of a frequency-selective pulse sequence (see Figure S2 in the SI) consisting of a pulsed gradient spin echo (PGSE) pulse sequence that utilizes a selective, shaped 180° pulse to target the NH_4^+ signal.[22]

Table 1. Optimized Conditions and Compatible Solvents for Ammonia Detection in Nondeuterated Aqueous and Nonaqueous Electrolytes via NMR Assay[a]

	analyte/assay conditions
acid	H_2SO_4 (aq) [0.1 M]
locking solvent	DMSO-d_6 [0.5 M]
calibration standard	ERETIC2,[b] chloroform, 1,3,5-trimethoxybenzene
demonstrated solvent compatibility[c]	ethanol, THF, DMSO, propylene carbonate, acetonitrile, diethyl ether, hexanes, water
pulse sequence	frequency-selective pulsed gradient spin echo

[a]Reported concentrations of H_2SO_4 (0.1 M) and DMSO-d_6 (0.5 M) are for final analyte conditions. Chemical calibration standard concentrations were between 33−100 μM. See SI for an extended description of the pulse sequence. [b]ERETIC2 refers to a synthetically generated NMR signal used as a calibration standard using the previously reported PULCON method. [c]The following solvents were those tested herein. Other solvents may also be compatible with this technique.

The use of frequency selective pulses provided a number of challenges. Frequency-selective pulses are relatively long, low-power pulses, which allow them to target specific spectral frequency ranges relative to a standard "hard" pulse. These selective pulses often suffer from two issues: (1) loss of phase information away from the pulse center frequency and (2) imperfect frequency selection away from the pulse center frequency, allowing signals far from the selected region to appear in a spectrum.[23] Imperfect frequency selection can be solved through the use of the appropriate shaped pulse.[24] Avoiding loss of phase information can be achieved through the use of a pulsed gradient spin echo sequence (PGSE). PGSE experiments are well-known and have been employed to a number of ends, including measuring molecular diffusion coefficients and in the selective removal of specific frequency regions from NMR spectra.[25,26] In this instance, the phase information otherwise lost due to the use of a selective 180° pulse is recovered through the generation of a spin echo via the use of two identical gradient pulses surrounding a 180° pulse. The frequency selective methods we employed herein, which we use to observe only the targeted spectral region of ∼7.5−6.5 ppm, are in contrast to many common solvent suppression methods such as WATERGATE, excitation sculpting, continuous wave presaturation, and others. These suppression methods may use both selective and nonselective pulses, but instead of observing only the spectral region of interest, they target specific spectral regions to eliminate only the unwanted solvent signal from the resultant spectrum.[27] While these solvent suppression methods are effective in water, it can become complex to employ such methods in solvents with multiple ^1H signals (see the Supporting Information (SI)).

Briefly, the pulse sequence used here (henceforth referred to as "frequency-selective PGSE") is composed of a hard 90° pulse, which serves to effectively excite all of the ^1H signals in the analyte, and a combination of two gradient pulses surrounding the selective, Gaussian-shaped 180° pulse, serving

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to "scramble" all of the ^{1}H signals via the gradient pulses except those excited by the selective 180° pulse (see the SI for experimental details). Figure 1 displays a comparison of an

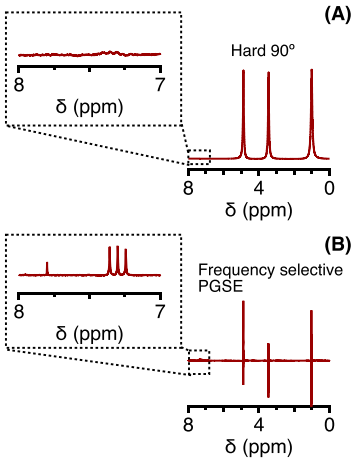

Figure 1. ^{1}H NMR spectrum of a 100 μM NH_4Cl/0.1 M LiOTf electrolyte in nondeuterated ethanol acquired using (A) a standard hard 90° pulse and (B) a frequency-selective PGSE pulse sequence. Each spectrum consists of an accumulation of 64 scans for a total experiment time of ∼2 min. In each, the three signals from ethanol are observed. The 1:1:1 triplet at 7.17 ppm in panel (B) is assigned to NH_4^+. The wobbling baseline observed in panel (A) did not display a coupling constant consistent with the $J_{^{14}N-^1H}$ value of 52 Hz observed in panel (B).

NMR spectrum of an electrolyte consisting of 100 μM NH_4Cl and 0.1 M LiOTf (where OTf = triflate anion) in ethanol obtained using a standard 90° hard pulse with an NMR spectrum of an identical solution to which the frequency-selective PGSE pulse sequence was applied. Using that pulse sequence, the 1:1:1 triplet at 7.17 ppm in Figure 1b is readily assigned to NH_4^+, based on the unique splitting pattern associated with the spin 1 ^{14}N nucleus and the symmetrical ^{1}H environment, whereas the signals are not visible with a simple hard 90° pulse sequence. A range of other pulse sequences was explored, including a simple selective 90° pulse, jump and return sequences, and single-channel spin saturation techniques (see Figure S3 in the SI). These methods suffered variously from reduced sensitivity to NH_4^+, loss of phase information, inefficient silencing of multiple solvent signals, and loss of signal due to proton exchange, and were therefore excluded from further use. The standard double pulse field gradient spin echo pulse sequence was also found to be effective but added complexity without improving experimental sensitivity; thus, the gradient spin echo technique noted in Table 1 was found to be optimal.[25] In addition, in a recent study, we employed a 1D NOESY solvent suppression technique, which required additional experimental complexity due to the need to employ additional channels and shaped pulses to suppress multiple solvent signals. While this technique displayed reduced signal-to-noise ratios, compared to the frequency-selective PGSE method, it did have the advantage of allowing for possible observation of degradation products and impurities away from the NH_4^+ chemical shift (see the SI).[7]

A calibration curve using the method described in Table 1 was generated for the quantification of NH_4^+ in ethanol as an illustrative example of the method accuracy and sensitivity over a relevant NH_4^+ concentration range (Figure 2). The

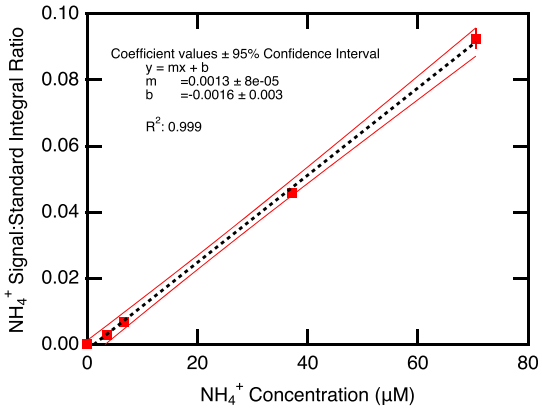

Figure 2. Calibration curve generated via NMR for the determination of NH_4^+ concentration in ethanol. Measurements of the NH_4^+ signal:standard integral ratio were taken in triplicate at concentrations of 70, 37, 7, 4, and 0 μM. The dotted black line represents the fitted curve and the red lines indicate the 95% confidence band for the generated fit curve. Error bars around each point represent the standard deviation for each triplicate measurement. The standard was generated synthetically using the ERETIC2/PULCON method. Note that the slope of the calibration line depends on the concentration of the chosen NH_4^+ standard.

confidence bands plotted with respect to the regression line in Figure 2 indicate with 95% confidence that the measured NH_4^+ concentration curve is to be no farther than ∼3% from the true value. The sensitivity of the method was also found to be remarkable, with the ability to detect NH_4^+ at 1 μM in ethanol within <1 h (see Figure S4 in the SI). While sensitivity was enhanced through the use of high-field, cryoprobe-equipped NMR instruments, such an advanced instrument is not essential for the technique. We were able to resolve NH_4^+ resonances at similarly low concentrations (≤10 μM) using a 600 MHz instrument equipped with a conventional room-temperature probe (see Figure S5 in the SI). Analysis of the analyte below 1 μM was not performed as analyte solutions to which no NH_3 had been actively added were also measured to have ∼1 μM NH_4^+ present, which we attributed to ambient contamination sources. This serves as a conventional lower bound for NH_3 detection methods applied to electrocatalysis. Another feature of the method presented herein is the use of the ERETIC2/PULCON method, which was used to generate synthetic standard resonances.[28−30] This avoids the need to identify chemically compatible calibration standards on an electrolyte-specific basis, providing further versatility to the method. The NH_4^+ signal was stable over weeks under ambient laboratory temperature and illumination conditions, further supporting the robustness of the method.

The frequency-selective PGSE NMR method was found to be generally applicable across a range of electrolytes. The method was successfully applied to a range of solvents, including ethanol (EtOH), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), diethyl ether (Et_2O), propylene carbonate (PC), hexanes, and water without significant modification to the technique (see Figure 3 and Figure S6 in the SI). We additionally developed a calibration curve using

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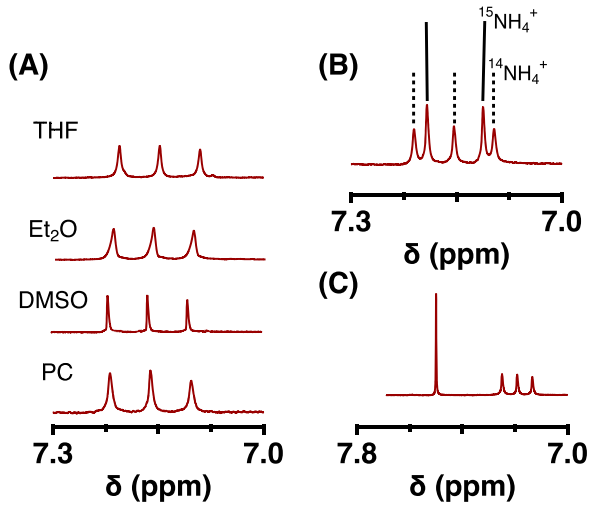

Figure 3. ^{1}H NMR spectra of NH_4^+ under various conditions: (A) NMR spectra of 100 μM NH_4^+ in THF, Et_2O, DMSO, and PC; (B) NMR spectrum of a 50 μM:50 μM mixture of $^{14}NH_4^+$:$^{15}NH_4^+$ in EtOH. J^{14}_{N-1H} = 51 Hz, J^{15}_{N-1H} = 72 Hz; and (C) NMR spectrum of 0.2 M $LiClO_4$/THF electrolyte after electrochemical N_2 reduction using a previously reported method.[31] NH_4^+ (triplet, 7.15 ppm) is present and chloroform (singlet, 7.5 ppm) was included as a standard reference.

this method for NH_4^+ concentration in H_2O and found that the resulting fit line was very similar to that observed in ethanol (Figure S7 in the SI). As expected, ^{15}N and ^{14}N were readily discriminated, on the basis of their nuclear spin (^{15}N: $s = {}^1/_2$ and ^{14}N $s = 1$) and were observed as a 1:1 doublet and a 1:1:1 triplet, respectively (Figure 3b). This fact, in concert with the ready ability to relate NMR signal integrations to NH_4^+ concentrations, makes this technique compatible with quantitative $^{15}N_2$ labeling studies that are crucial to discerning the contribution of contaminants to electrocatalytic ammonia yields. In order to demonstrate the practical utility of this NMR technique, an electrochemical N_2 reduction method previously reported was executed and the resultant ammonia detected directly from the electrolyte via NMR.[31] Using this N_2 reduction method, an ammonium concentration of greater than 100 μM was observed (Figure 3c).

These solvents were selected to represent a broad spectrum of electrolytes commonly used in other areas of electrochemistry as well as solvents commonly used in the reduction of N_2 to NH_3 catalyzed by homogeneous molecular species.[16,32−35] The superior miscibility characteristics of ethanol were employed where needed to favor the homogeneous mixing of the relevant species (e.g., homogenizing small volumes of 0.5 M $H_2SO_{4,aq}$ and NH_4Cl with hexanes). The addition of the electrolyte salt LiOTf to each solvent (until saturation or up to a maximum of 0.5 M) resulted only in minor changes to the 90° pulse time, and no major changes in the signal/noise ratios were observed. Minor differences in the NH_4^+ peak intensities may be due to the nonuniform excitation profile and illustrate the importance of using a consistent position for the shaped pulse (see Figure S8 in the SI). We also investigated the effect of the presence of a paramagnetic ion, Cu^{2+}, in an aqueous electrolyte on the quality of the NH_4^+ signal. No discernible change in signal quality between an aqueous 100 μM NH_4^+ solution with and without a 1 mM $CuSO_4$ was observed (see Figure S9 in the SI). Other paramagnetic species may have a more significant effect on the NH_4^+ signal, and care should be taken to ensure that the presence of a paramagnetic is not limiting the ability to observe NH_4^+ in the analyte via NMR. Fortunately, we observed that a common chelating agent (EDTA) did not interfere with NMR detection (see the SI).

The NH_4^+ signal was not observed in the absence of additional acid, but rapidly became apparent as the H_2SO_4 concentration increased beyond 100 μM (see Figure S10 in the SI), which is consistent with an increase in the concentration of NH_4^+ in the analyte, as well as a decrease in the rate of proton exchange between NH_4^+ and the solvent. This is in contrast to NH_3, which does not have a readily discernible ^{1}H NMR signal in EtOH, consistent with quadrupolar coupling of the ^{14}N nucleus in a nonsymmetric proton environment and rapid proton exchange. NH_3 has been observed in highly nonpolar solvents, such as benzene, and may also serve as a valuable reference signal under unique nonpolar electrochemical conditions.[36] A minimal amount of deuterated solvent was added as required to facilitate frequency locking during the detection; DMSO-d_6 served this purpose well, but other deuterated solvents with nonexchangeable protons, such as acetonitrile-d_3, were also found to be effective. It is important to select a deuterated solvent without readily exchangeable ^{2}H to avoid the formation of NH_4^+ isotopologues, which can degrade the signal quality (see Figure S11 in the SI).

Recently, multiple reports have stressed the importance of proper control experiments when investigating N_2 reduction electrocatalysts.[2,3,7,9,10] Electrolytes can become inadvertently contaminated with ammonia, or with species that are easily converted to ammonia (e.g., NO_x, NO_3^-, NO_2^-), which could lead to the erroneous reporting of N_2 electroreduction catalysts. There are various strategies that can rigorously confirm the N_2 reduction activity of a catalyst when performed appropriately, but demonstrating the formation of $^{15}NH_3$ from $^{15}N_2$ is, from our perspective, the most convincing characterization method. As noted above, the NMR assay described herein is particularly well-suited to analyzing these isotopically labeled experiments. Not only is the difference between $^{15}NH_4^+$ and $^{14}NH_4^+$ stark in NMR spectra, but the quantitative nature of the assay is crucial in analyzing the resultant data. Because $^{15}N_2$ often contains $^{15}NO_x$ and $^{15}NH_3$ impurities, it can be a challenge to be certain that the presence of a $^{15}NH_4^+$ in an NMR spectrum is unequivocal evidence that $^{15}N_2$ was electrochemically reduced. If rigorous purification of the $^{15}N_2$ is not performed, the apparent labeled ammonia may be from exogenous sources.[7,37] The $^{15}NH_4^+$ signal is most effective as an indicator of successful N_2 reduction if it can be quantitatively demonstrated via NMR signal integration that the concentration of $^{14}NH_4^+$ and $^{15}NH_4^+$ are the same after performing electroreduction under purified $^{14}N_2$ or $^{15}N_2$ feeds, respectively.

While NMR is a highly valuable technique for the detection of electrocatalytically generated NH_3, the ability to execute colorimetric NH_3 detection in nonaqueous electrolytes with a standard ultraviolet−visible (UV-vis) spectrometer would make colorimetric detection a valuable complementary technique. Therefore, we endeavored to understand whether a modified Berthelot method would be robust under nonaqueous electrolyte conditions. The Berthelot method is a well-studied, analytical colorimetric test that has been employed extensively in N_2 electrocatalysis research, predominantly but not exclusively in aqueous systems.[38] It is

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dependent on an organic transformation for the detection of ammonia in aqueous solutions through the formation of a strongly absorbing blue organic product when NH_3 is present in the analyte.[14,15,39,40] As such, we developed modified Berthelot conditions and analyzed the effect of nonaqueous solvent and high-salt concentrations (≥0.1M) on the extinction coefficient, reaction rate, color stability, salt dependence, and illumination dependence of the Berthelot reaction in four common electrochemical solvents (THF, propylene carbonate, ethanol, and water; see the SI for experimental details and results). We found that while ammonia is directly detectable in any of the four electrolytes using the Berthelot method, careful control of the reaction conditions is required if using it as an analytical technique in nonaqueous electrolytes. Effectively all of the analytical parameters varied with changes in the reaction conditions, and we observed particularly significant reductions in the measured apparent extinction coefficient, and therefore sensitivity, in THF and propylene carbonate electrolytes, as well as significant variability in the measured ammonia concentration, with respect to the calculated calibration curve. These observations suggest a limited amenability of the Berthelot method to quantitative measurement of NH_3 after N_2 electrocatalysis in nonaqueous electrolyte (See Table S1 and Figures S12 and S13 in the SI) and imply that calibration curves derived from the exact electrochemical conditions under which the relevant N_2 electrocatalysis conditions must be generated prior to using the Berthelot method in a quantitative way.

While the direct detection of ammonia in nondeuterated, electrolytic solutions is possible by both ^{1}H NMR and colorimetric detection without the need for separation of ammonia from an electrolyte, the frequency-selective PGSE NMR method has several advantages, with respect to NH_3 detection. The chemical specificity is exquisite, as the presence of the 1:1:1 triplet is unambiguously specific to NH_4^+. The isotope specificity inherent to the NMR technique is particularly valuable, as noted above, insofar as it is compatible with isotope labeling studies that are necessary to delineate electrochemically synthesized ammonia from contaminant ammonia.[7] Conversely, the Berthelot colorimetric detection is only mildly chemically specific as any species with absorption in the region of λ = 660 nm may be detected as NH_3, and is not expected to be isotopically specific at all. Many positive and negative interferences for the Berthelot reaction, as well as an alternative colorimetric technique (Nessler's method), have been reported in the literature.[41,42] However, the ease of performing colorimetric methods with readily obtained equipment suggests that it may be a valuable tool for preliminary interrogation of an electrolyte after N_2 reduction electrocatalysis.

In summary, an NMR method for the detection of micromolar concentrations of ammonia in a range of electrolytes using a frequency-selective pulse sequence was elaborated. It was demonstrated to be a general strategy for the fast, accurate quantification of ammonia down to 1 μM in nonaqueous and aqueous electrolytes while requiring minimal sample preparation and demonstrating a high level of analyte stability over time. The frequency-selective PGSE technique employed herein should be generally useful whenever a compound of interest has an NMR resonance peak that does not overlap with the relevant solvent peaks. The careful, effective use of these methods, with an emphasis on *quantitative* NMR detection when ambiguities regarding the source or identity of NH_3, should be invaluable in confirming the presence of electrocatalytically synthesized NH_3 in a fast, simple, and unambiguous way.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b00358.

Detailed experimental methods; comparison of NMR frequency-selective vs suppression pulse sequences; characterization of frequency selective PGSE method compatibility with various solvents, NMR field strengths, acid concentrations, selective pulse frequencies, and locking solvents; characterization of comparable colorimetric methods for NH_3 detection (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jaramillo@stanford.edu.

ORCID

Adam C. Nielander: 0000-0002-3639-2427
Joshua M. McEnaney: 0000-0003-3697-2533
Jon G. Baker: 0000-0002-8903-7306
Sarah J. Blair: 0000-0001-6680-0199
Lei Wang: 0000-0002-1931-7767
Stacey F. Bent: 0000-0002-1084-5336
Jakob Kibsgaard: 0000-0002-9219-816X
Peter C. K. Vesborg: 0000-0002-3761-4212
Ib Chorkendorff: 0000-0003-2738-0325
Thomas F. Jaramillo: 0000-0001-9900-0622

Notes

The authors declare no competing financial interest.

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