

ACCEPTED VERSION

Laiquan Li, Cheng Tang, Dazhi Yao, Yao Zheng, Shi-Zhang Qiao
Electrochemical nitrogen reduction: identification and elimination of contamination in electrolyte
ACS Energy Letters, 2019; 4(9):2111-2116

This document is the Accepted Manuscript version of a Published Work that appeared in final form in Energy and Fuels, copyright © 2017 American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <http://dx.doi.org/10.1021/acsenergylett.9b01573>

PERMISSIONS

<http://pubs.acs.org/page/4authors/jpa/index.html>

The new agreement specifically addresses what authors can do with different versions of their manuscript – e.g. use in theses and collections, teaching and training, conference presentations, sharing with colleagues, and posting on websites and repositories. The terms under which these uses can occur are clearly identified to prevent misunderstandings that could jeopardize final publication of a manuscript (**Section II, Permitted Uses by Authors**).

[Easy Reference User Guide](#)

7. Posting Accepted and Published Works on Websites and Repositories: A digital file of the Accepted Work and/or the Published Work may be made publicly available on websites or repositories (e.g. the Author's personal website, preprint servers, university networks or primary employer's institutional websites, third party institutional or subject-based repositories, and conference websites that feature presentations by the Author(s) based on the Accepted and/or the Published Work) under the following conditions:

- It is mandated by the Author(s)' funding agency, primary employer, or, in the case of Author(s) employed in academia, university administration.
- If the mandated public availability of the Accepted Manuscript is sooner than 12 months after online publication of the Published Work, a waiver from the relevant institutional policy should be sought. If a waiver cannot be obtained, the Author(s) may sponsor the immediate availability of the final Published Work through participation in the ACS AuthorChoice program—for information about this program see <http://pubs.acs.org/page/policy/authorchoice/index.html>.
- If the mandated public availability of the Accepted Manuscript is not sooner than 12 months after online publication of the Published Work, the Accepted Manuscript may be posted to the mandated website or repository. The following notice should be included at the time of posting, or the posting amended as appropriate:
"This document is the Accepted Manuscript version of a Published Work that appeared in final form in [JournalTitle], copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see [insert ACS Articles on Request author-directed link to Published Work, see <http://pubs.acs.org/page/policy/articlesonrequest/index.html>]."
- The posting must be for non-commercial purposes and not violate the ACS' "Ethical Guidelines to Publication of Chemical Research" (see <http://pubs.acs.org/ethics>).
- Regardless of any mandated public availability date of a digital file of the final Published Work, Author(s) may make this file available only via the ACS AuthorChoice Program. For more information, see <http://pubs.acs.org/page/policy/authorchoice/index.html>.

26 November 2020

<http://hdl.handle.net/2440/121687>

Electrochemical Nitrogen Reduction: Identification and Elimination of Contamination in Electrolyte

Large scale ammonia production is always one of the most critical issues in regard to human survival and sustainable development.¹⁻⁵ Nowadays, ammonia is industrially manufactured by the century-old Haber-Bosch process, which produces more than 170 million tons of ammonia every year.⁶ Despite its wide application, it is a massively energy-consuming process that uses fossil fuels as the hydrogen source and accounts for ~1% of annual global greenhouse gas emission.⁷ The electrochemical ammonia synthesis via nitrogen reduction reaction (NRR) driven by renewable energy under mild conditions is a highly attractive alternative and has received intensive attention and exploration over the past few years.^{1, 8-11} However, electrochemical N₂ fixation is still plagued with poor ammonia yield and faradaic efficiency due to the extremely low solubility of N₂ in aqueous electrolytes, the competing hydrogen evolution as well as the sluggish kinetics.¹²⁻
¹³ The amount of produced ammonia is usually as low as nanomole level so that it is challenging to accurately measure and unequivocally attribute it to electrochemical N₂ fixation, especially with the interference of various contamination.

Recently, discussion has arisen among researchers in this field regarding the need to improve on how ammonia detection and control tests are conducted.¹⁴⁻²² To ensure the detected ammonia is produced from dinitrogen rather than other extraneous contamination, the key task is to identify and exclude all the contamination sources as specific and thorough as possible. Several groups have recently investigated various contamination sources present in laboratory environments.^{11, 15-}

¹⁶ We also proposed a set of rigorous experimental protocols to study electrochemical NRR with

a thorough discussion of various experimental parameters.¹⁷ The contamination sources can be classified into two groups: *out-system* and *intra-system*. The *out-system* contamination mainly includes ammonia or NO_x present in the air, human breath and rubber gloves. As a closed system is mandatory for NRR tests,¹⁶⁻¹⁷ such *out-system* contamination can be rationally excluded with careful and rigorous operation and may not cause substantial influence. However, the *intra-system* contamination, such as nitrogen-containing compounds in the feeding gas, electrocatalysts and membrane, is more indeterminate and even cannot be probed independently, thus usually resulting in a significant impact on the ammonia yield and even unreliable results. Without sufficient and rigorous control experiments, it would be unreliable to evaluate the NRR activity of electrocatalysts. Although many papers have been reported to identify and exclude various contamination, no any work claims that the electrolyte solution may also be a considerable source of contamination.

Herein, we found that trace amount of nitrate and nitrite exist in some lithium salts, for example, Li₂SO₄ and LiClO₄, which are usually used in the preparation of electrolyte. Significant ammonia production with excellent reproducibility and accumulative effect was observed using a bare substrate (Ti foil, carbon paper, or copper foam) without loading any catalyst both in N₂ and Ar saturated Li₂SO₄ solution. The detected ammonia was demonstrated to be electrochemically reduced from the trace amount of nitrate and nitrite in Li₂SO₄ rather than N₂ as schematically shown in **Figure 1**. Simple and versatile spectrophotometric methods were employed to quantitatively determine such contamination and an effective approach by high-temperature annealing was then proposed to eliminate nitrate and nitrite. This Viewpoint highlights several critical issues in regard to the identification and elimination of contamination in the electrolyte and will contribute to more accurate and reliable NRR research.

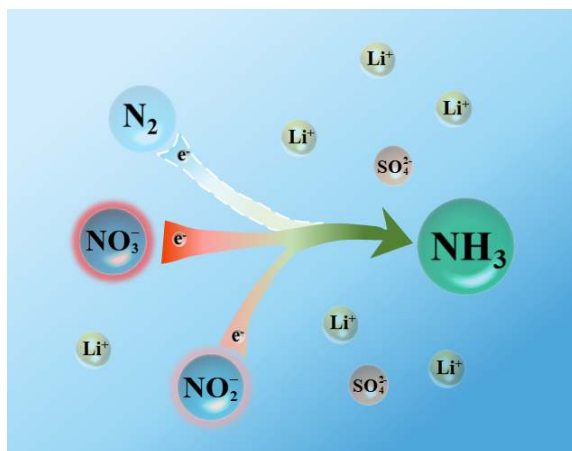


Figure 1. Schematic illustration showing the electrochemical conversion of various nitrogen-containing species in the Li₂SO₄ electrolyte. The nitrate and nitrite contamination in the electrolyte can be electrochemically reduced to ammonia, resulting in false positive N₂ reduction performance.

“Perfect” data for NRR without electrocatalysts. Due to the extremely low ammonia yield and influence of extraneous contamination in laboratory, NRR study always suffers from fluctuation and variability when the ammonia production is measured. As a result, it is usually very challenging to achieve ammonia yields with desirable reproducibility or accumulative effect, especially in aqueous solutions. Whereas, we observed excellent reproducibility and accumulative effect only using a bare Ti foil in 0.5 M Li₂SO₄ electrolyte (Sigma-Aldrich, L6375, ≥ 98.5%). Initially, we conducted the NRR experiment by applying a fixed negative current density on a Ti foil (1 cm × 1 cm) in N₂ atmosphere. For each current density, we repeated the NRR test 3 times with fresh Li₂SO₄ electrolyte and omitted the first cycle to exclude any possible pre-absorbed ammonia contamination on the Ti foil. The produced ammonia is quantitatively determined by indophenol blue method, in which the absorbance value at wavelength of 655 nm for the indophenol blue indicator stained electrolyte is proportional to the ammonia concentration.²³ As shown in **Figure 2a**, the ammonia yields achieved for the second and the third cycles are almost

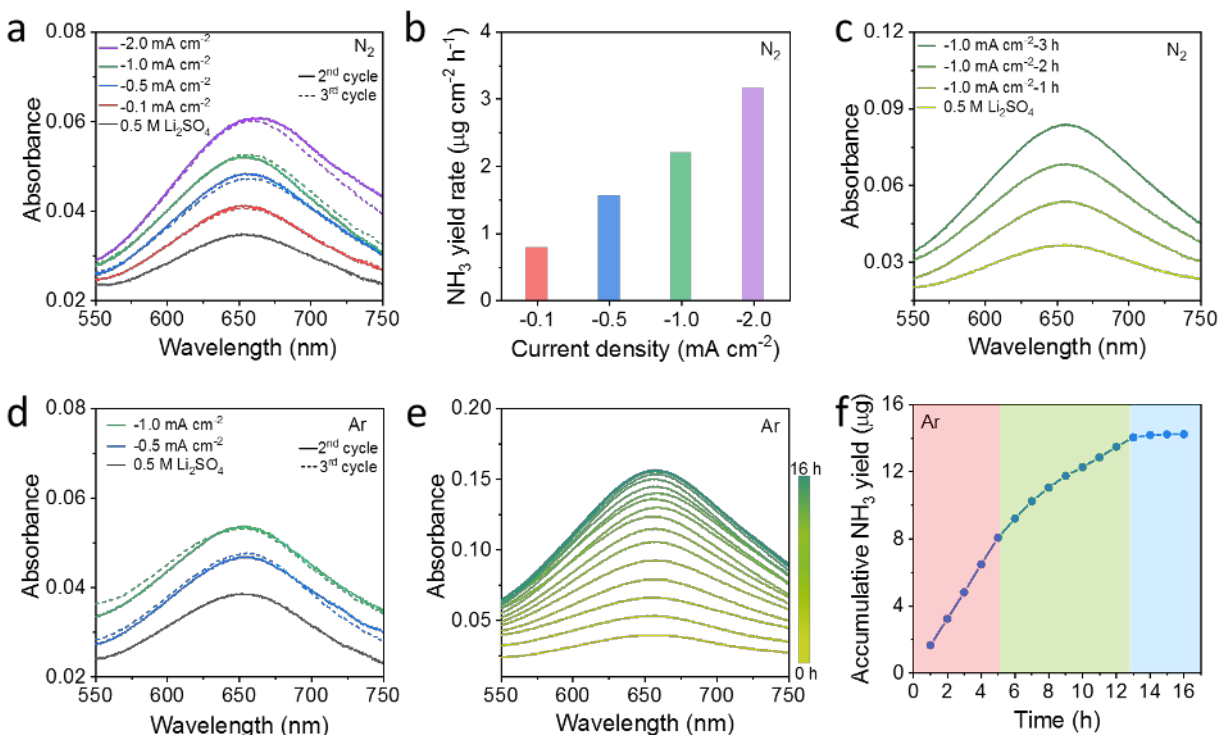


Figure 2. False positive NRR performance observed in both N_2 and Ar atmosphere using a bare Ti foil without loading any catalyst in 0.5 M Li_2SO_4 solution. (a) UV-vis spectra for the indophenol blue indicator stained electrolytes after electrolysis at -0.1 , -0.5 , -1.0 and -2.0 $mA\ cm^{-2}$ in N_2 for 1 h and (b) the corresponding ammonia yield rates at each current density. (c) UV-vis spectra for the indophenol blue indicator stained electrolytes after electrolysis at -1.0 $mA\ cm^{-2}$ in N_2 for 1, 2 and 3 h. (d) UV-vis spectra for the indophenol blue indicator stained electrolytes after electrolysis at -0.5 and -1.0 $mA\ cm^{-2}$ in Ar for 1 h. (e) UV-vis spectra for the indophenol blue indicator stained electrolytes after electrolysis at -1.0 $mA\ cm^{-2}$ in Ar for 1–16 h and (f) the corresponding accumulative ammonia yield. In (a) and (d), the solid lines exhibit the results for the 2nd cycle and the dash lines show the results for the 3rd cycle. In (a), (c), (d) and (e), the lowest line shows the result for the fresh electrolyte before electrolysis.

the same on each applied current density, demonstrating excellent reproducibility. A considerable ammonia yield rate as high as $3.16\ \mu g\ cm^{-2}\ h^{-1}$ is obtained at the current density of $-2.0\ mA\ cm^{-2}$ (Ammonia calibration curve refers to Figure S1), which is comparable to and even higher than many reported electrocatalysts.¹⁶⁻¹⁷ It is noteworthy to mention that the ammonia yield rate

increases with the applied current density (**Figure 2b**), indicating that the detected ammonia is electrochemically produced. Besides the excellent reproducibility, good accumulative effect is also observed when different electrolysis periods are applied even though not any catalyst is used. The concentration of the ammonia in the electrolyte increases linearly in 3 h continuous electrolysis process (**Figure 2c** and S2). Such good reproducibility and accumulative effect are very favorable indications of electrochemical NRR activity. However, we finally realized that the ammonia was produced from contamination as similar ammonia yield can also be observed in Ar atmosphere (**Figure 2d**), with as good reproducibility as observed in N₂ atmosphere. During the long-term electrolysis in Ar atmosphere, the good accumulative effect can also be observed within the initial 5 h, after which the ammonia increment decreases gradually and comes to a standstill after 13 h (**Figure 2e and f**). In addition, ammonia production can also be achieved using a bare carbon paper and copper foam in the same Li₂SO₄ electrolyte in Ar atmosphere without using any catalyst (Figure S3). However, no ammonia yield can be observed using Ti foil in either 0.5 M Na₂SO₄ or K₂SO₄ electrolyte and in either N₂ or Ar atmosphere (Figure S4). Thus the above results lead us to conclude that the detected ammonia is electrochemically synthesized but not derived from electrocatalyst, electrode substrate, or inlet gas, which is most likely ascribed to the influence of electrolyte-dependent contamination.

Identification of nitrate and nitrite in the electrolyte. Most of the extraneous ammonia contamination usually causes accidental positive results that are easy to be independently identified and rationally excluded by rigorous controls.^{14-15, 17-18} However, NO_x in the feeding gas or electrolyte can be electrochemically reduced to NH₃ and result in continuous production of ammonia.^{11, 16} With the knowledge that the feeding gases (N₂ and Ar) are of ultrahigh purity (99.999%), we focused our attention on the Li₂SO₄ electrolyte. It is thus assumed that the detected

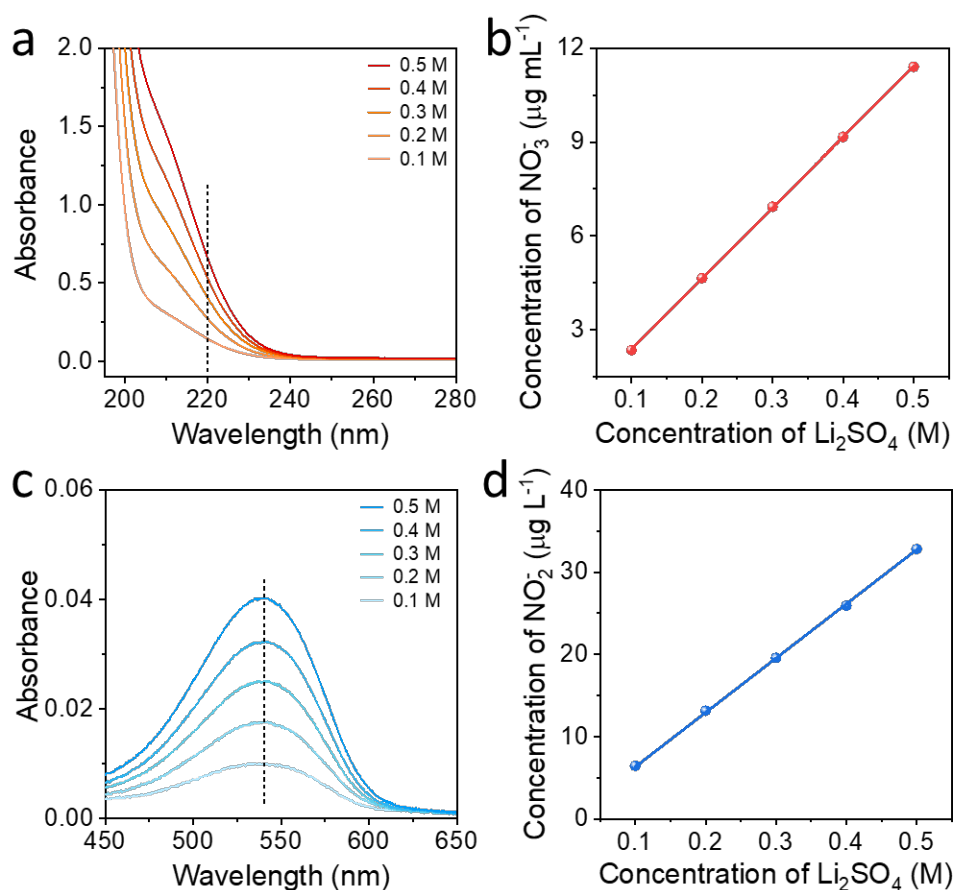


Figure 3. Quantitative detection of nitrate and nitrite in Li_2SO_4 solution. (a and c) UV-vis spectra for nitrate and nitrite determination. (b and d) Concentrations of detected nitrate and nitrite in different concentrations of Li_2SO_4 solutions.

ammonia originates from the trace amount of the nitrogen-containing impurity in Li_2SO_4 such as nitrate or nitrite. Therefore, we examined the presence of NO_3^- and NO_2^- in Li_2SO_4 solution using spectrophotometric methods. Nitrate shows typical absorption to ultraviolet light at the wavelength of 220 nm,²⁴⁻²⁵ in which the absorbance value is in proportion to its concentration (Figure S5). As shown in **Figure 3a and b**, the presence of NO_3^- in Li_2SO_4 electrolyte is identified as the absorbance value at 220 nm increases linearly with the concentration of Li_2SO_4 . The concentration of NO_3^- in 0.5 M Li_2SO_4 is measured to be as high as $11.19 \mu\text{g mL}^{-1}$ (**Figure 3b**). If electrocatalysts with high activity towards nitrate reduction to ammonia were used in such nitrous electrolyte, false

positive results and overestimation of the NRR activity would likely be delivered (Figure S3). The detection of NO_2^- is based on the Griess-Ilosvay reaction, in which nitrite reacts with two aromatic amines in sequence, producing pink azo dye that can be spectrophotometrically assayed by visible light at 540 nm (Figure S6).²⁴⁻²⁵ The presence of NO_2^- in Li_2SO_4 electrolyte is thus confirmed by the linear increase of the absorbance value at 540 nm with increasing Li_2SO_4 concentration (**Figure 3c and 3d**). The concentration of NO_2^- in 0.5 M Li_2SO_4 is determined to be $32.8 \mu\text{g L}^{-1}$, which is $\sim 0.3\%$ of the concentration of NO_3^- . Spectrophotometric tests also show that almost no NO_3^- exists in either 0.5 M Na_2SO_4 or K_2SO_4 solution (Figure S7), and only a very tiny amount of NO_2^- can be detected in K_2SO_4 . Given the high ammonia yield in 0.5 M Li_2SO_4 while undetectable ones in 0.5 M Na_2SO_4 and K_2SO_4 , we thus suppose the produced ammonia stems from the electrochemical reduction of NO_x^- , especially NO_3^- in the Li_2SO_4 electrolyte, rather than N_2 .

Elimination of NO_x^- from Li_2SO_4 . It is known that metal sulfates usually possess much higher thermal stability than metal nitrates and nitrites. For example, Li_2SO_4 has a boiling point of 1377°C , much higher than that of LiNO_3 (600°C) and LiNO_2 (350°C).²⁶ To eliminate the nitrate or nitrite from Li_2SO_4 and to further verify the origin of the detected ammonia, we then annealed Li_2SO_4 in Ar atmosphere at 800°C for 4 h. The XRD pattern of the as-annealed Li_2SO_4 can be well assigned to monoclinic Li_2SO_4 (JCPDS No.: 20-0640) (Figure S8). We further tested the concentration of nitrate and nitrite in the annealed Li_2SO_4 using spectrophotometric methods. As shown in **Figure 4a and 4b**, both the absorbance values at 220 nm for NO_3^- and 540 nm for NO_2^- significantly decrease after annealing at high temperature. Furthermore, the concentration of NO_3^- and NO_2^- does not change with the concentration of Li_2SO_4 after high-temperature annealing (Figure S9 and S10), indicating the successful elimination of nitrate and nitrite in Li_2SO_4 . The above results indicate that high-temperature treatment is highly effective for eliminating the nitrate

and nitrite while keeping Li_2SO_4 unchanged. We further conducted electrolysis at a constant current density of -1.0 mA cm^{-2} in 0.5 M as-annealed Li_2SO_4 using Ti foil under otherwise identical conditions. No ammonia can be detected in either Ar or N_2 atmosphere (**Figure 4c and 4d**). Notably, the Nafion membrane is not the ammonia source as it has not been replaced during all tests, including electrolysis in the pristine Li_2SO_4 , as-annealed Li_2SO_4 , Na_2SO_4 and K_2SO_4 electrolytes. The above results on the one hand demonstrate the Ti foil is inactive for NRR, and on the other hand reveal that the feeding gas is NO_x free. Therefore, we conclude that the detected ammonia is produced from the reduction of nitrate and nitrite in the pristine Li_2SO_4 .

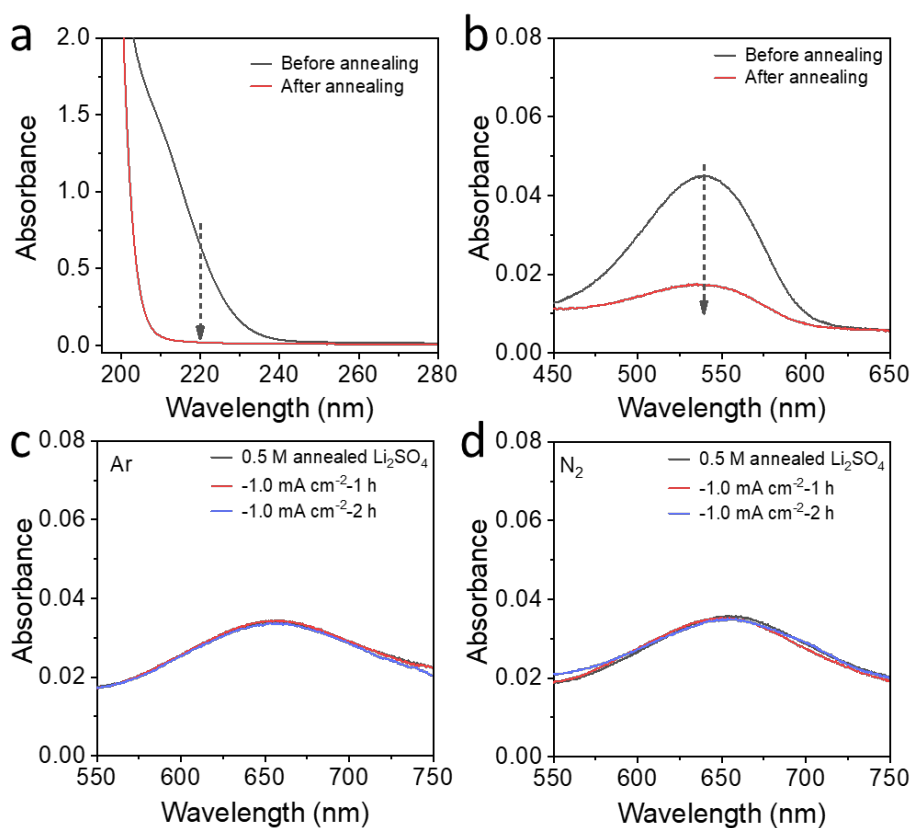


Figure 4. Elimination of nitrate and nitrite by high-temperature treatment. (a and b) UV-vis spectra for the determination of nitrate and nitrite in 0.5 M Li_2SO_4 before (grey lines) and after (red lines) annealing treatment. (c and d) UV-vis spectra for the 0.5 M annealed Li_2SO_4 electrolytes before (grey lines) and after (other lines) electrolysis with bare Ti foil at -1.0 mA cm^{-2} for 1 and 2 h in Ar and N_2 .

Identification of NO_x⁻ contamination in various lithium salts. As Li₂SO₄ is a commonly used electrolyte in NRR, especially for the investigation of electrolyte effect on NRR performance, the trace amount of NO_x⁻ contamination may cause substantial interference for determining the activity of electrocatalysts and lead to unreliable conclusions. To probe the universality of this issue, we measured the NO_x⁻ concentration in several Li₂SO₄ products with various brands and product codes (**Table 1**). The concentration of nitrate and nitrite is revealed to vary significantly among different Li₂SO₄ products (**Figure 5a and 5b, Table 1, Figure S11**). Most importantly, the ammonia yields achieved after electrolysis with bare Ti foil at -1.0 mA cm⁻² in Ar for 1 h in different Li₂SO₄ electrolytes are positively correlated with the concentration of nitrate instead of nitrite (**Figure 5b, Figure S11**), confirming that the false positive results are dominantly derived from the NO₃⁻ contamination. We realize that not all Li₂SO₄ chemicals contain nitrate or nitrite contamination, since no obvious NO₃⁻ is detected in the fresh electrolyte and no ammonia yield is achieved after electrolysis using some untreated Li₂SO₄ products (Sigma-Aldrich, 203653; Aladdin, L130839) (**Figure 5b**). The nitrate and nitrite in Li₂SO₄ most probably originate from lithium carbonate, which is the upstream product for most of commercial lithium salts.²⁷ In fact, the lithium carbonate chemical (Sigma-Aldrich, 431559), even though with a high purity of 99.99%, is labeled with a NO₃⁻ content of 5 mg kg⁻¹. Generally, the lithium carbonate is industrially produced from either spodumene or continental brines.²⁷⁻²⁸ The spodumene route starts with a heating process at 1100°C to change α-spodumene to β-spodumene,²⁸ which could eliminate nitrate or nitrite for the downstream products. However, the production of lithium carbonate from brines, which contain trace amount of nitrate and nitrite,²⁹ is generally realized by a series of evaporation, adsorption, solvent extraction and membrane processes.^{28, 30} As nitrate and nitrite are highly dissoluble in aqueous solutions, it is usually difficult to totally remove them in the industrial

processes. As a result, all the lithium sulfate monohydrates are labeled with a certain amount of nitrate (**Table 1**). Besides, other lithium salts which are produced from lithium carbonate may also contain a trace amount of NO_x^- contamination, such as LiClO_4 , another commonly used electrolyte in NRR. As shown in **Figure 5c**, nitrate is detected in 0.5 M LiClO_4 solutions with assay of both 95.0% (Sigma-Aldrich, 205281) and 99.99% (Sigma-Aldrich, 431567). The nitrate-derived false positive ammonia yield is thus achieved for both cases and is more significant in the 95.0% LiClO_4 electrolyte due to its much higher content of NO_3^- contamination (**Figure 5c and 5d**).

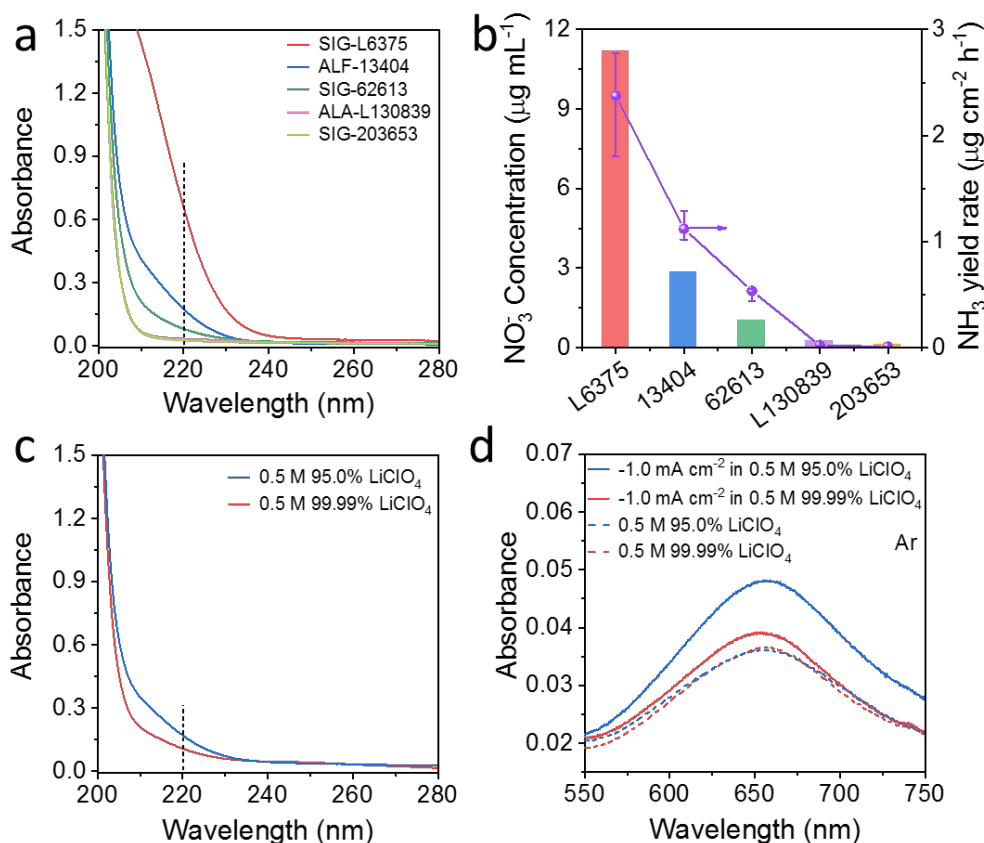


Figure 5. Identification of nitrate contamination in various lithium salts. (a) UV-vis spectra for determining nitrate and (b) the relationship between the concentration of nitrate and the ammonia yield rate after electrolysis with bare Ti foil at -1.0 mA cm^{-2} in Ar for 1 h in 0.5 M Li_2SO_4 solutions with different brands and product codes (SIG: Sigma-Aldrich, ALF: Alfa Aesar, ALA: Aladdin). (c) UV-vis spectra for determining nitrate in different LiClO_4 solutions. (d) UV-

vis spectra for indophenol blue indicator stained electrolytes before (dashed lines) and after (solid lines) electrolysis with bare Ti foil at -1.0 mA cm^{-2} in Ar for 1 h in different LiClO_4 solutions.

Table 1. The labeled NO_3^- content in various lithium salts and detected NO_3^- concentration in their 0.5 M solution.

Chemical	Brand	Product code	Assay	Labeled NO_3^- content ^a	$[\text{NO}_3^-]$ in 0.5 M solution ($\mu\text{g mL}^{-1}$) ^b
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	Sigma-Aldrich	398152	$\geq 99.0\%$	$\leq 0.001\%$	/
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	Sigma-Aldrich	62612	$\geq 99.0\%$	$\leq 10 \text{ mg kg}^{-1}$	/
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	Sigma-Aldrich	62609	$\geq 99.0\%$	$\leq 10 \text{ mg kg}^{-1}$	/
Li_2SO_4	Sigma-Aldrich	203653	$\geq 99.99\%$	N.A.	Not detected
Li_2SO_4	Sigma-Aldrich	L6375	$\geq 98.5\%$	N.A.	11.19
Li_2SO_4	Sigma-Aldrich	62613	$\geq 98.0\%$	N.A.	1.02
Li_2SO_4	Alfa Aesar	13404	$\geq 99.7\%$	N.A.	2.82
Li_2SO_4	Aladdin	L130839	$\geq 98.5\%$	N.A.	Not detected
LiClO_4	Sigma-Aldrich	431567	$\geq 99.99\%$	N.A.	1.39
LiClO_4	Sigma-Aldrich	205281	$\geq 95.0\%$	N.A.	2.38
Li_2CO_3	Sigma-Aldrich	431559	$\geq 99.99\%$	$\leq 5 \text{ mg kg}^{-1}$	/
Li_2CO_3	Sigma-Aldrich	62470	$\geq 99.0\%$	$\leq 5 \text{ mg kg}^{-1}$	/

Note: *a*, the content is read from the labels on the bottles of the chemicals; *b*, the concentration of NO_3^- in 0.5 M solution of lithium salts is determined by the spectrophotometric method; N.A. means no information about nitrate is labeled on the product specification.

In summary, we systematically identified, quantified and eliminated the trace amount of nitrate and nitrite contamination in some commercial lithium salts towards more reliable electrocatalytic NRR study. Even though those impurities exist in ppm or lower level, they could cause significant false positive results with deceptive reproducibility and accumulative effect, which may misguide

researchers. We experimentally demonstrated that the possible nitrate and nitrite contamination in the electrolyte can be efficaciously prejudged by simple spectrophotometric methods, and can be effectively removed by high-temperature treatment. Although demonstrating false positive results for NRR, our study highlights several critical issues to which attention needs to be paid in order to develop both reliable electrocatalysts and electrolytes. First, we highlight that extra attention must be paid to the electrolyte in electrocatalytic NRR study, and the prejudgment of NO_x^- in electrolyte is strongly recommended prior to NRR tests. Second, the electrolyte has been highly expected to play important roles on enhancing the NRR selectivity and activity by optimizing the solvent, concentration, pH value, cation, etc.³¹⁻³⁵ However, the present results raise the demand on further investigation and even re-evaluation of the electrolyte effects on NRR performance, especially the reported improvement ascribed to Li^+ ions. Last but not least, we claim that understanding all of the negative results is just as important as identifying positive results, especially at the current stage of NRR research. We appeal and encourage to directly confront those “negative” results and thoroughly uncover the nature of potential interferences in this promising research area, which is believed to promote the healthy development and reliable breakthrough in the electrochemical NRR field.

Laiquan Li

Cheng Tang

Dazhi Yao

Yao Zheng

Shi-Zhang Qiao*

Center for Materials in Energy and Catalysis, School of Chemical Engineering and Advanced Materials, The University of Adelaide, Adelaide, SA 5005, Australia

ASSOCIATED CONTENT

Supporting Information. Experiment details, material characterization, determination of ammonia, nitrate and nitrite and supplementary figures.

AUTHOR INFORMATION

Corresponding Author

*E-mail: s.qiao@adelaide.edu.au.

ORCID

Laiquan Li: 0000-0002-3301-9029

Cheng Tang: 0000-0002-5167-1192

Dazhi Yao: 0000-0002-8019-0160

Yao Zheng: 0000-0002-2411-8041

Shi-Zhang Qiao: 0000-0002-4568-8422

Author Contributions

L.Q. Li and C. Tang contributed equally to this work.

Notes

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS.

The authors declare no competing financial interests.

ACKNOWLEDGMENT

The work is financially supported by the Australian Research Council (ARC) through the Discovery and Linkage Project programs (FL170100154, DP160104866, LP160100927).

REFERENCES

- (1) Chen, J. G.; Crooks, R. M.; Seefeldt, L. C.; Bren, K. L.; Bullock, R. M.; Darensbourg, M. Y.; Holland, P. L.; Hoffman, B.; Janik, M. J.; Jones, A. K.; Kanatzidis, M. G.; King, P.; Lancaster, K. M.; Lymar, S. V.; Pfromm, P.; Schneider, W. F.; Schrock, R. R. Beyond Fossil Fuel-driven Nitrogen Transformations. *Science* **2018**, *360* (6391), eaar6611.
- (2) Nørskov, J.; Chen, J.; Miranda, R.; Fitzsimmons, T.; Stack, R. Sustainable Ammonia Synthesis –Exploring the Scientific Challenges Associated with Discovering Alternative, Sustainable Processes for Ammonia Production. *US DOE Office of Science* **2016**, <https://doi.org/10.2172/1283146>.
- (3) Smil, V. Detonator of the Population Explosion. *Nature* **1999**, *400* (6743), 415-415.
- (4) Guo, J. P.; Chen, P. Catalyst: NH₃ as an Energy Carrier. *Chem* **2017**, *3* (5), 709-712.
- (5) Fryzuk, M. D. Ammonia Transformed. *Nature* **2004**, *427*, 498-499.
- (6) Soloveichik, G. Electrochemical Synthesis of Ammonia as a Potential Alternative to the Haber-Bosch Process. *Nat. Catal.* **2019**, *2* (5), 377-380.
- (7) Ye, L.; Nayak-Luke, R.; Banares-Alcantara, R.; Tsang, E. Reaction: "Green" Ammonia Production. *Chem* **2017**, *3* (5), 712-714.
- (8) Shipman, M. A.; Symes, M. D. Recent Progress towards the Electrosynthesis of Ammonia from Sustainable Resources. *Catal. Today* **2017**, *286*, 57-68.
- (9) Guo, C.; Ran, J.; Vasileff, A.; Qiao, S.-Z. Rational Design of Electrocatalysts and Photo(electro) Catalysts for Nitrogen Reduction to Ammonia (NH₃) under Ambient Conditions. *Energy Environ. Sci.* **2018**, *11*, 45-56.
- (10) Foster, S. L.; Bakovic, S. I. P.; Duda, R. D.; Maheshwari, S.; Milton, R. D.; Minteer, S. D.; Janik, M. J.; Renner, J. N.; Greenlee, L. F. Catalysts for Nitrogen Reduction to Ammonia. *Nat. Catal.* **2018**, *1* (7), 490-500.
- (11) Chen, G.-F.; Ren, S.; Zhang, L.; Cheng, H.; Luo, Y.; Zhu, K.; Ding, L.-X.; Wang, H. Advances in Electrocatalytic N₂ Reduction—Strategies to Tackle the Selectivity Challenge. *Small Methods* **2019**, *3* (6), 1800337.

- (12) Montoya, J. H.; Tsai, C.; Vojvodic, A.; Nørskov, J. K. The Challenge of Electrochemical Ammonia Synthesis: A New Perspective on the Role of Nitrogen Scaling Relations. *ChemSusChem* **2015**, *8* (13), 2180-2186.
- (13) Bratsch, S. G. Standard Electrode Potentials and Temperature Coefficients in Water at 298.15 K. *J. Phys. Chem. Ref. Data* **1989**, *18* (1), 1-21.
- (14) MacLaughlin, C. Role for Standardization in Electrocatalytic Ammonia Synthesis: A Conversation with Leo Liu, Lauren Greenlee, and Douglas MacFarlane. *ACS Energy Lett.* **2019**, *4* (6), 1432-1436.
- (15) Suryanto, B. H. R.; Du, H.-L.; Wang, D.; Chen, J.; Simonov, A. N.; MacFarlane, D. R. Challenges and Prospects in the Catalysis of Electroreduction of Nitrogen to Ammonia. *Nat. Catal.* **2019**, *2* (4), 290-296.
- (16) Andersen, S. Z.; Čolić, V.; Yang, S.; Schwalbe, J. A.; Nielander, A. C.; McEnaney, J. M.; Enemark-Rasmussen, K.; Baker, J. G.; Singh, A. R.; Rohr, B. A.; Statt, M. J.; Blair, S. J.; Mezzavilla, S.; Kibsgaard, J.; Vesborg, P. C. K.; Cargnello, M.; Bent, S. F.; Jaramillo, T. F.; Stephens, I. E. L.; Nørskov, J. K.; Chorkendorff, I. A Rigorous Electrochemical Ammonia Synthesis Protocol with Quantitative Isotope Measurements. *Nature* **2019**, *570* (7762), 504-508.
- (17) Tang, C.; Qiao, S.-Z. How to Explore Ambient Electrocatalytic Nitrogen Reduction Reliably and Insightfully. *Chem. Soc. Rev.* **2019**, *48* (12), 3166-3180.
- (18) Greenlee, L. F.; Renner, J. N.; Foster, S. L. The Use of Controls for Consistent and Accurate Measurements of Electrocatalytic Ammonia Synthesis from Dinitrogen. *ACS Catal.* **2018**, *8* (9), 7820-7827.
- (19) Minteer, S. D.; Christopher, P.; Linic, S. Recent Developments in Nitrogen Reduction Catalysts: A Virtual Issue. *ACS Energy Lett.* **2019**, *4* (1), 163-166.
- (20) Hu, B.; Hu, M.; Seefeldt, L.; Liu, T. L. Electrochemical Dinitrogen Reduction to Ammonia by Mo₂N: Catalysis or Decomposition? *ACS Energy Lett.* **2019**, *4* (5), 1053-1054.
- (21) Zhao, Y. X.; Shi, R.; Bian, X. A. N.; Zhou, C.; Zhao, Y. F.; Zhang, S.; Wu, F.; Waterhouse, G. I. N.; Wu, L. Z.; Tung, C. H.; Zhang, T. R. Ammonia Detection Methods in Photocatalytic and

Electrocatalytic Experiments: How to Improve the Reliability of NH₃ Production Rates? *Adv. Sci.* **2019**, *6* (8), 1802109.

(22) Tang, C.; Qiao, S.-Z. True or False in Electrochemical Nitrogen Reduction. *Joule* **2019**, *3* (7), 1573-1575.

(23) Li, L.; Tang, C.; Xia, B.; Jin, H.; Zheng, Y.; Qiao, S.-Z. Two-Dimensional Mosaic Bismuth Nanosheets for Highly Selective Ambient Electrocatalytic Nitrogen Reduction. *ACS Catal.* **2019**, *9* (4), 2902-2908.

(24) Carvalho, A. P.; Meireles, L. A.; Malcata, F. X. Rapid Spectrophotometric Determination of Nitrates and Nitrites in Marine Aqueous Culture Media. *Analisis* **1998**, *26* (9), 347-351.

(25) Polatides, C.; Kyriacou, G. Electrochemical Reduction of Nitrate Ion on Various Cathodes- Reaction Kinetics on Bronze Cathode. *J. Appl. Electrochem.* **2005**, *35* (5), 421-427.

(26) Stern, K. H. High Temperature Properties and Decomposition of Inorganic Salts Part 3, Nitrates and Nitrites. *J. Phys. Chem. Ref. Data* **1972**, *1* (3), 747-772.

(27) Lithium and Lithium Compounds. In *Ullmann's Encyclopedia of Industrial Chemistry*, pp 1-38.

(28) Peiro, L. T.; Mendez, G. V.; Ayres, R. U. Lithium: Sources, Production, Uses, and Recovery Outlook. *Jom* **2013**, *65* (8), 986-996.

(29) Analysis of Anions in Geological Brines Using Ion Chromatography. Sandia National Laboratories. Albuquerque, N.M., **1985**.

(30) Kumar, A.; Fukuda, H.; Hatton, T. A.; Lienhard, J. H. Lithium Recovery from Oil and Gas Produced Water: A Need for a Growing Energy Industry. *ACS Energy Lett.* **2019**, *4* (6), 1471-1474.

(31) Wang, J.; Yu, L.; Hu, L.; Chen, G.; Xin, H.; Feng, X. Ambient Ammonia Synthesis via Palladium-catalyzed Electrohydrogenation of Dinitrogen at Low Overpotential. *Nat. Commun.* **2018**, *9* (1), 1795.

(32) Mukherjee, S.; Cullen, D. A.; Karakalos, S.; Liu, K.; Zhang, H.; Zhao, S.; Xu, H.; More, K. L.; Wang, G.; Wu, G. Metal-organic Framework-derived Nitrogen-doped Highly Disordered

Carbon for Electrochemical Ammonia Synthesis using N₂ and H₂O in Alkaline Electrolytes. *Nano Energy* **2018**, *48*, 217-226.

(33) Song, Y.; Johnson, D.; Peng, R.; Hensley, D. K.; Bonnesen, P. V.; Liang, L.; Huang, J.; Yang, F.; Zhang, F.; Qiao, R.; Baddorf, A. P.; Tschaplinski, T. J.; Engle, N. L.; Hatzell, M. C.; Wu, Z.; Cullen, D. A.; Meyer, H. M.; Sumpter, B. G.; Rondinone, A. J. A Physical Catalyst for the Electrolysis of Nitrogen to Ammonia. *Sci. Adv.* **2018**, *4* (4), e1700336.

(34) Chen, G. F.; Cao, X.; Wu, S.; Zeng, X.; Ding, L. X.; Zhu, M.; Wang, H. Ammonia Electrosynthesis with High Selectivity under Ambient Conditions via a Li⁺ Incorporation Strategy. *J. Am. Chem. Soc.* **2017**, *139* (29), 9771-9774.

(35) Zhou, F.; Azofra, L. M.; Ali, M.; Kar, M.; Simonov, A. N.; McDonnell-Worth, C.; Sun, C.; Zhang, X.; MacFarlane, D. R. Electro-synthesis of Ammonia from Nitrogen at Ambient Temperature and Pressure in Ionic Liquids. *Energy Environ. Sci.* **2017**, *10*, 2516-2520.