

## ACCEPTED VERSION

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**Electrochemical nitrogen reduction: identification and elimination of contamination in electrolyte**  
ACS Energy Letters, 2019; 4(9):2111-2116

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# Electrochemical Nitrogen Reduction: Identification and Elimination of Contamination in Electrolyte

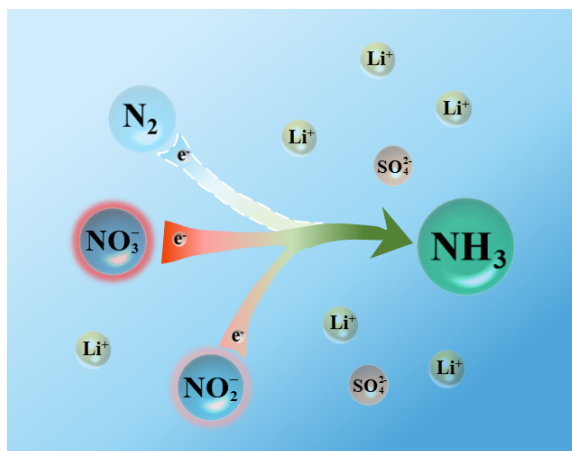
Large scale ammonia production is always one of the most critical issues in regard to human survival and sustainable development.<sup>1-5</sup> Nowadays, ammonia is industrially manufactured by the century-old Haber-Bosch process, which produces more than 170 million tons of ammonia every year.<sup>6</sup> 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.<sup>7</sup> 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.<sup>1, 8-11</sup> However, electrochemical N<sub>2</sub> fixation is still plagued with poor ammonia yield and faradaic efficiency due to the extremely low solubility of N<sub>2</sub> in aqueous electrolytes, the competing hydrogen evolution as well as the sluggish kinetics.<sup>12-</sup>  
<sup>13</sup> 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 N<sub>2</sub> 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.<sup>14-22</sup> 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.<sup>11, 15-</sup>

<sup>16</sup> We also proposed a set of rigorous experimental protocols to study electrochemical NRR with

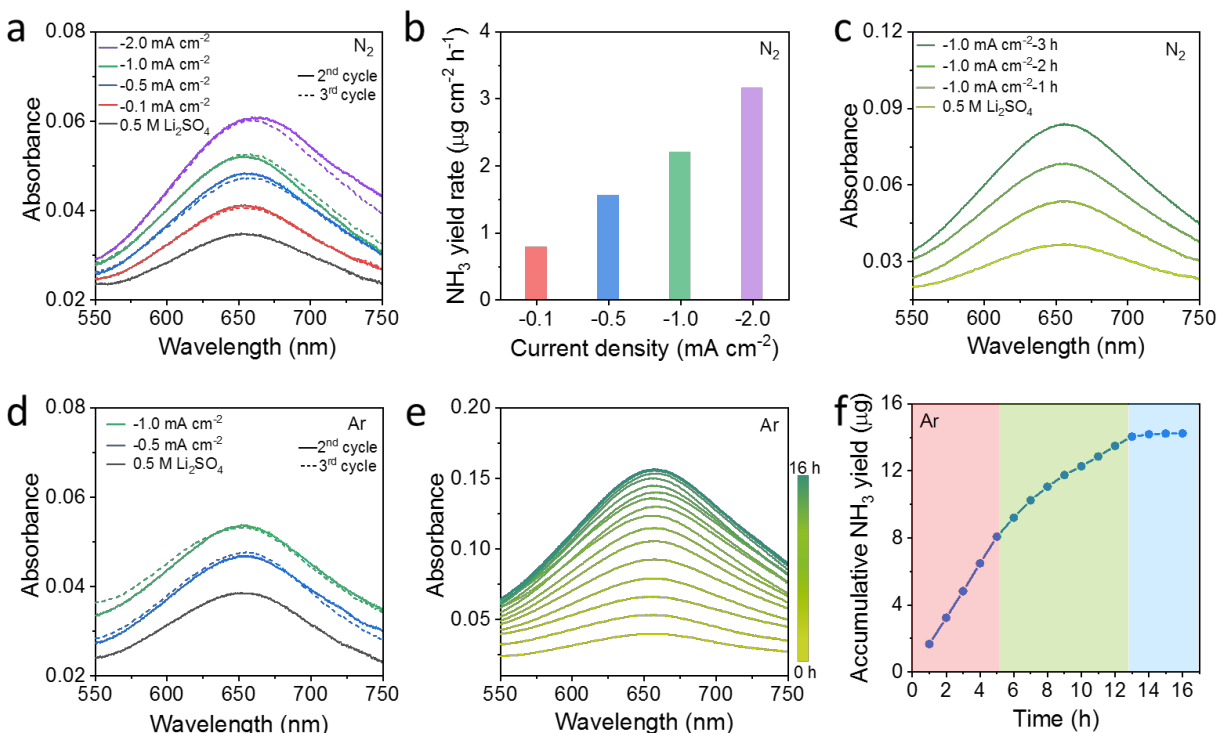
a thorough discussion of various experimental parameters.<sup>17</sup> The contamination sources can be classified into two groups: *out-system* and *intra-system*. The *out-system* contamination mainly includes ammonia or NO<sub>x</sub> present in the air, human breath and rubber gloves. As a closed system is mandatory for NRR tests,<sup>16-17</sup> 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, Li<sub>2</sub>SO<sub>4</sub> and LiClO<sub>4</sub>, 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 N<sub>2</sub> and Ar saturated Li<sub>2</sub>SO<sub>4</sub> solution. The detected ammonia was demonstrated to be electrochemically reduced from the trace amount of nitrate and nitrite in Li<sub>2</sub>SO<sub>4</sub> rather than N<sub>2</sub> 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  $\text{Li}_2\text{SO}_4$  electrolyte. The nitrate and nitrite contamination in the electrolyte can be electrochemically reduced to ammonia, resulting in false positive  $\text{N}_2$  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  $\text{Li}_2\text{SO}_4$  electrolyte (Sigma-Aldrich, L6375,  $\geq 98.5\%$ ). Initially, we conducted the NRR experiment by applying a fixed negative current density on a Ti foil (1 cm  $\times$  1 cm) in  $\text{N}_2$  atmosphere. For each current density, we repeated the NRR test 3 times with fresh  $\text{Li}_2\text{SO}_4$  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.<sup>23</sup> As shown in **Figure 2a**, the ammonia yields achieved for the second and the third cycles are almost

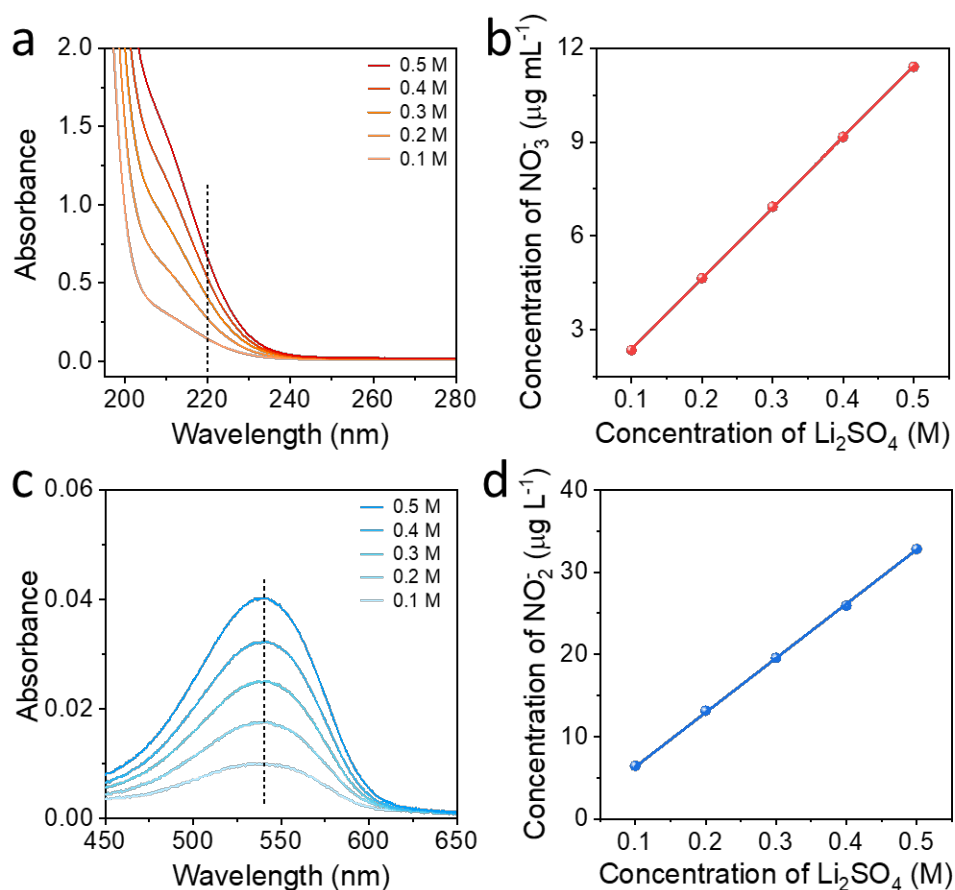


**Figure 2.** False positive NRR performance observed in both  $N_2$  and Ar atmosphere using a bare Ti foil without loading any catalyst in  $0.5\text{ M Li}_2\text{SO}_4$  solution. (a) UV-vis spectra for the indophenol blue indicator stained electrolytes after electrolysis at  $-0.1$ ,  $-0.5$ ,  $-1.0$  and  $-2.0\text{ mA cm}^{-2}$  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  $-1.0\text{ mA cm}^{-2}$  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  $-1.0\text{ mA cm}^{-2}$  in Ar for 1 h. (e) UV-vis spectra for the indophenol blue indicator stained electrolytes after electrolysis at  $-1.0\text{ mA cm}^{-2}$  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 2<sup>nd</sup> cycle and the dash lines show the results for the 3<sup>rd</sup> 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  $3.16\text{ }\mu\text{g cm}^{-2}\text{ h}^{-1}$  is obtained at the current density of  $-2.0\text{ mA cm}^{-2}$  (Ammonia calibration curve refers to Figure S1), which is comparable to and even higher than many reported electrocatalysts.<sup>16-17</sup> 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 N<sub>2</sub> 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 Li<sub>2</sub>SO<sub>4</sub> 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 Na<sub>2</sub>SO<sub>4</sub> or K<sub>2</sub>SO<sub>4</sub> electrolyte and in either N<sub>2</sub> 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.<sup>14-15, 17-18</sup> However, NO<sub>x</sub> in the feeding gas or electrolyte can be electrochemically reduced to NH<sub>3</sub> and result in continuous production of ammonia.<sup>11, 16</sup> With the knowledge that the feeding gases (N<sub>2</sub> and Ar) are of ultrahigh purity (99.999%), we focused our attention on the Li<sub>2</sub>SO<sub>4</sub> electrolyte. It is thus assumed that the detected



**Figure 3. Quantitative detection of nitrate and nitrite in  $\text{Li}_2\text{SO}_4$  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  $\text{Li}_2\text{SO}_4$  solutions.

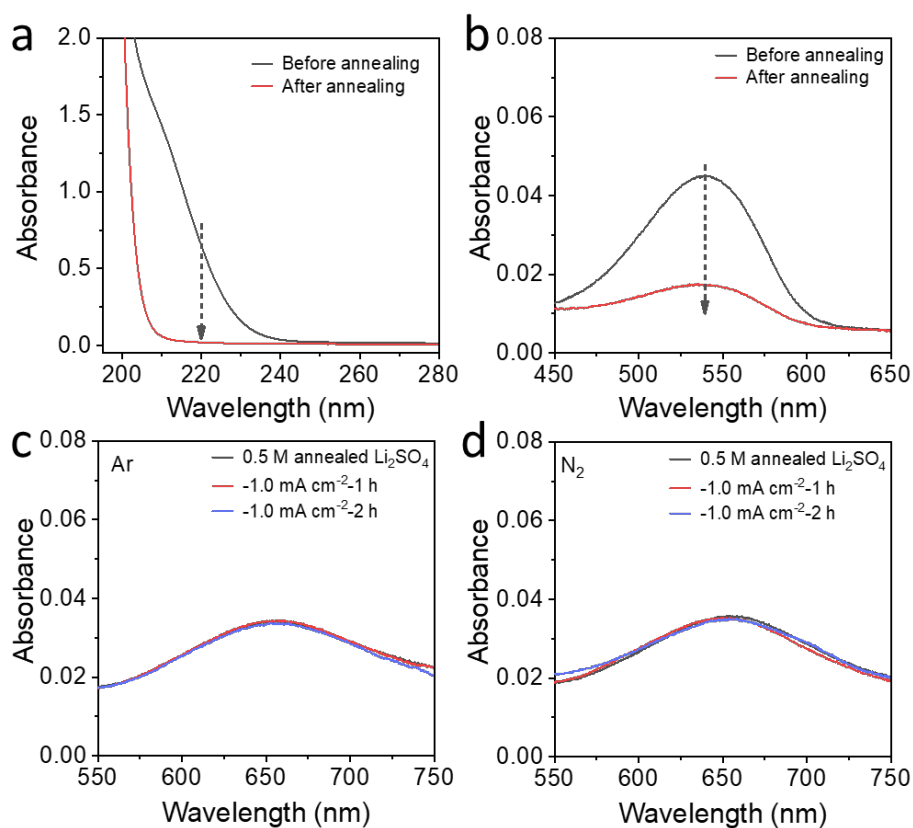
ammonia originates from the trace amount of the nitrogen-containing impurity in  $\text{Li}_2\text{SO}_4$  such as nitrate or nitrite. Therefore, we examined the presence of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in  $\text{Li}_2\text{SO}_4$  solution using spectrophotometric methods. Nitrate shows typical absorption to ultraviolet light at the wavelength of 220 nm,<sup>24-25</sup> in which the absorbance value is in proportion to its concentration (Figure S5). As shown in **Figure 3a and b**, the presence of  $\text{NO}_3^-$  in  $\text{Li}_2\text{SO}_4$  electrolyte is identified as the absorbance value at 220 nm increases linearly with the concentration of  $\text{Li}_2\text{SO}_4$ . The concentration of  $\text{NO}_3^-$  in 0.5 M  $\text{Li}_2\text{SO}_4$  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  $\text{NO}_2^-$  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).<sup>24-25</sup> The presence of  $\text{NO}_2^-$  in  $\text{Li}_2\text{SO}_4$  electrolyte is thus confirmed by the linear increase of the absorbance value at 540 nm with increasing  $\text{Li}_2\text{SO}_4$  concentration (**Figure 3c and 3d**). The concentration of  $\text{NO}_2^-$  in 0.5 M  $\text{Li}_2\text{SO}_4$  is determined to be  $32.8 \mu\text{g L}^{-1}$ , which is  $\sim 0.3\%$  of the concentration of  $\text{NO}_3^-$ . Spectrophotometric tests also show that almost no  $\text{NO}_3^-$  exists in either 0.5 M  $\text{Na}_2\text{SO}_4$  or  $\text{K}_2\text{SO}_4$  solution (Figure S7), and only a very tiny amount of  $\text{NO}_2^-$  can be detected in  $\text{K}_2\text{SO}_4$ . Given the high ammonia yield in 0.5 M  $\text{Li}_2\text{SO}_4$  while undetectable ones in 0.5 M  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ , we thus suppose the produced ammonia stems from the electrochemical reduction of  $\text{NO}_x^-$ , especially  $\text{NO}_3^-$  in the  $\text{Li}_2\text{SO}_4$  electrolyte, rather than  $\text{N}_2$ .

*Elimination of  $\text{NO}_x^-$  from  $\text{Li}_2\text{SO}_4$ .* It is known that metal sulfates usually possess much higher thermal stability than metal nitrates and nitrites. For example,  $\text{Li}_2\text{SO}_4$  has a boiling point of  $1377^\circ\text{C}$ , much higher than that of  $\text{LiNO}_3$  ( $600^\circ\text{C}$ ) and  $\text{LiNO}_2$  ( $350^\circ\text{C}$ ).<sup>26</sup> To eliminate the nitrate or nitrite from  $\text{Li}_2\text{SO}_4$  and to further verify the origin of the detected ammonia, we then annealed  $\text{Li}_2\text{SO}_4$  in Ar atmosphere at  $800^\circ\text{C}$  for 4 h. The XRD pattern of the as-annealed  $\text{Li}_2\text{SO}_4$  can be well assigned to monoclinic  $\text{Li}_2\text{SO}_4$  (JCPDS No.: 20-0640) (Figure S8). We further tested the concentration of nitrate and nitrite in the annealed  $\text{Li}_2\text{SO}_4$  using spectrophotometric methods. As shown in **Figure 4a and 4b**, both the absorbance values at 220 nm for  $\text{NO}_3^-$  and 540 nm for  $\text{NO}_2^-$  significantly decrease after annealing at high temperature. Furthermore, the concentration of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  does not change with the concentration of  $\text{Li}_2\text{SO}_4$  after high-temperature annealing (Figure S9 and S10), indicating the successful elimination of nitrate and nitrite in  $\text{Li}_2\text{SO}_4$ . The above results indicate that high-temperature treatment is highly effective for eliminating the nitrate



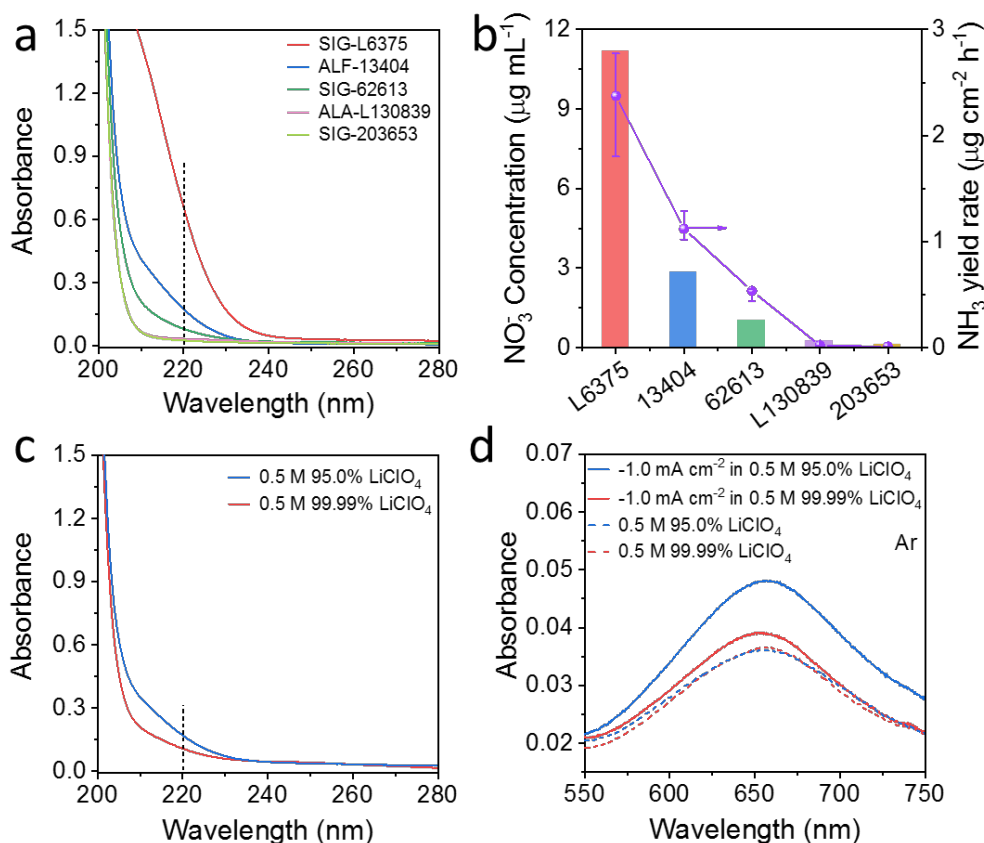
and nitrite while keeping  $\text{Li}_2\text{SO}_4$  unchanged. We further conducted electrolysis at a constant current density of  $-1.0 \text{ mA cm}^{-2}$  in 0.5 M as-annealed  $\text{Li}_2\text{SO}_4$  using Ti foil under otherwise identical conditions. No ammonia can be detected in either Ar or  $\text{N}_2$  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  $\text{Li}_2\text{SO}_4$ , as-annealed  $\text{Li}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  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  $\text{NO}_x$  free. Therefore, we conclude that the detected ammonia is produced from the reduction of nitrate and nitrite in the pristine  $\text{Li}_2\text{SO}_4$ .



**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  $\text{Li}_2\text{SO}_4$  before (grey lines) and after (red lines) annealing treatment. (c and d) UV-vis spectra for the 0.5 M annealed  $\text{Li}_2\text{SO}_4$  electrolytes before (grey lines) and after (other lines) electrolysis with bare Ti foil at  $-1.0 \text{ mA cm}^{-2}$  for 1 and 2 h in Ar and  $\text{N}_2$ .

*Identification of NO<sub>x</sub><sup>-</sup> contamination in various lithium salts.* As Li<sub>2</sub>SO<sub>4</sub> is a commonly used electrolyte in NRR, especially for the investigation of electrolyte effect on NRR performance, the trace amount of NO<sub>x</sub><sup>-</sup> 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<sub>x</sub><sup>-</sup> concentration in several Li<sub>2</sub>SO<sub>4</sub> products with various brands and product codes (**Table 1**). The concentration of nitrate and nitrite is revealed to vary significantly among different Li<sub>2</sub>SO<sub>4</sub> 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<sup>-2</sup> in Ar for 1 h in different Li<sub>2</sub>SO<sub>4</sub> 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 NO<sub>3</sub><sup>-</sup> contamination. We realize that not all Li<sub>2</sub>SO<sub>4</sub> chemicals contain nitrate or nitrite contamination, since no obvious NO<sub>3</sub><sup>-</sup> is detected in the fresh electrolyte and no ammonia yield is achieved after electrolysis using some untreated Li<sub>2</sub>SO<sub>4</sub> products (Sigma-Aldrich, 203653; Aladdin, L130839) (**Figure 5b**). The nitrate and nitrite in Li<sub>2</sub>SO<sub>4</sub> most probably originate from lithium carbonate, which is the upstream product for most of commercial lithium salts.<sup>27</sup> In fact, the lithium carbonate chemical (Sigma-Aldrich, 431559), even though with a high purity of 99.99%, is labeled with a NO<sub>3</sub><sup>-</sup> content of 5 mg kg<sup>-1</sup>. Generally, the lithium carbonate is industrially produced from either spodumene or continental brines.<sup>27-28</sup> The spodumene route starts with a heating process at 1100°C to change α-spodumene to β-spodumene,<sup>28</sup> 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,<sup>29</sup> is generally realized by a series of evaporation, adsorption, solvent extraction and membrane processes.<sup>28, 30</sup> 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  $\text{NO}_x^-$  contamination, such as  $\text{LiClO}_4$ , another commonly used electrolyte in NRR. As shown in **Figure 5c**, nitrate is detected in 0.5 M  $\text{LiClO}_4$  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%  $\text{LiClO}_4$  electrolyte due to its much higher content of  $\text{NO}_3^-$  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  $-1.0 \text{ mA cm}^{-2}$  in Ar for 1 h in 0.5 M  $\text{Li}_2\text{SO}_4$  solutions with different brands and product codes (SIG: Sigma-Aldrich, ALF: Alfa Aesar, ALA: Aladdin). (c) UV-vis spectra for determining nitrate in different  $\text{LiClO}_4$  solutions. (d) UV-

vis spectra for indophenol blue indicator stained electrolytes before (dashed lines) and after (solid lines) electrolysis with bare Ti foil at  $-1.0 \text{ mA cm}^{-2}$  in Ar for 1 h in different  $\text{LiClO}_4$  solutions.

**Table 1.** The labeled  $\text{NO}_3^-$  content in various lithium salts and detected  $\text{NO}_3^-$  concentration in their 0.5 M solution.

Chemical	Brand	Product code	Assay	Labeled $\text{NO}_3^-$ content <sup>a</sup>	$[\text{NO}_3^-]$ in 0.5 M solution ( $\mu\text{g mL}^{-1}$ ) <sup>b</sup>
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	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	$\geq 99.0\%$	$\leq 10 \text{ mg kg}^{-1}$	/
$\text{Li}_2\text{SO}_4$	Sigma-Aldrich	203653	$\geq 99.99\%$	N.A.	Not detected
$\text{Li}_2\text{SO}_4$	Sigma-Aldrich	L6375	$\geq 98.5\%$	N.A.	11.19
$\text{Li}_2\text{SO}_4$	Sigma-Aldrich	62613	$\geq 98.0\%$	N.A.	1.02
$\text{Li}_2\text{SO}_4$	Alfa Aesar	13404	$\geq 99.7\%$	N.A.	2.82
$\text{Li}_2\text{SO}_4$	Aladdin	L130839	$\geq 98.5\%$	N.A.	Not detected
$\text{LiClO}_4$	Sigma-Aldrich	431567	$\geq 99.99\%$	N.A.	1.39
$\text{LiClO}_4$	Sigma-Aldrich	205281	$\geq 95.0\%$	N.A.	2.38
$\text{Li}_2\text{CO}_3$	Sigma-Aldrich	431559	$\geq 99.99\%$	$\leq 5 \text{ mg kg}^{-1}$	/
$\text{Li}_2\text{CO}_3$	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  $\text{NO}_3^-$  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  $\text{NO}_x^-$  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.<sup>31-35</sup> 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  $\text{Li}^+$  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.

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## ASSOCIATED CONTENT

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

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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).

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