

# Facts or Artifacts: Pitfalls in Quantifying Sub-ppm Levels of Ammonia Produced from Electrochemical Nitrogen Reduction

Suchi Smita Biswas,<sup>§</sup> Arunava Saha,<sup>§</sup> and Muthusamy Eswaramoorthy\*Cite This: *ACS Omega* 2022, 7, 1874–1882

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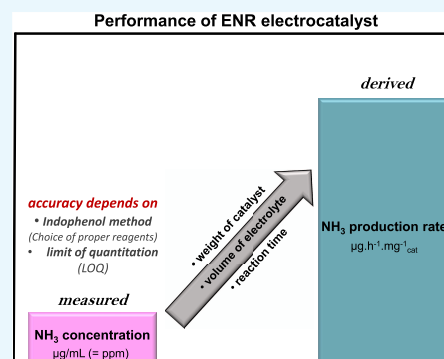


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**ABSTRACT:** Synthesis of ammonia through electrochemical nitrogen reduction (ENR) is emerging as one of the attractive research areas in recent years, notwithstanding the enormous challenges it faces in quantification of ammonia at very low concentrations. Several reports claiming high production rate are unwittingly compromised by the accuracy of analyzing a very low concentration (<1 ppm) of ammonia in the electrolyte post-ENR reaction using the indophenol method. Therefore, in this work, we have highlighted the significance of selecting and standardizing a right protocol encompassing admissible levels of oxidants and a complexing agent, citrate (to mitigate the effect of interfering metal ions), through elaborate control experiments. In addition, the importance of setting the lowest limit of ammonia concentration that can be accurately quantified by the indophenol method is also justified. Further, the experimental observations were summarized into a protocol, which was followed to re-evaluate the performance of two well-claimed electrocatalysts for ENR reported recently in the literature.



## 1. INTRODUCTION

Researchers around the globe are in search of an energy-efficient alternative to the century-old Haber Bosch process for ammonia production. Recent progress made in the generation of electricity from renewable sources generated a great deal of interest in electrochemical ammonia synthesis from nitrogen and water under ambient conditions.<sup>1–4</sup> However, the inert nature (941 kJ/mol bond dissociation energy) and low solubility (20 ppm at 20 °C, 1 atm) of N<sub>2</sub> in water coupled with the competing hydrogen evolution reaction are the major challenges for the electrochemical nitrogen reduction (ENR) reaction in an aqueous medium.<sup>5–7</sup> Several reports in recent years claim an ammonia production rate anywhere between 2 and 120 µg<sub>NH<sub>3</sub></sub> h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup> using metals, metal oxides, chalcogenides, and carbon as electrocatalysts.<sup>8–13</sup> Nevertheless, it is being realized lately that the isolation of ENR ammonia from contaminants is an insurmountable task to deal with in this reaction. Interference of atmospheric NH<sub>3</sub>, NO<sub>x</sub> contamination, and the presence of reducible N species in the catalysts are some of the major contributors to the false-positive reports in this field.<sup>14–17</sup> As a natural corollary, many tall claims made in the field of electrochemical nitrogen reduction (ENR) in recent years are obfuscated with these experimental errors and require a revisit.

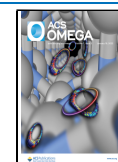
Although there are a few excellent articles that underline the need to adopt careful experimental protocols to eliminate NO<sub>x</sub> and NH<sub>3</sub> from the electrochemical system prior to reactions,<sup>15,18,19</sup> in-depth analysis of spectrometric quantification of ammonia by the indophenol method (in an aqueous medium) has been overlooked in this field of research for quite

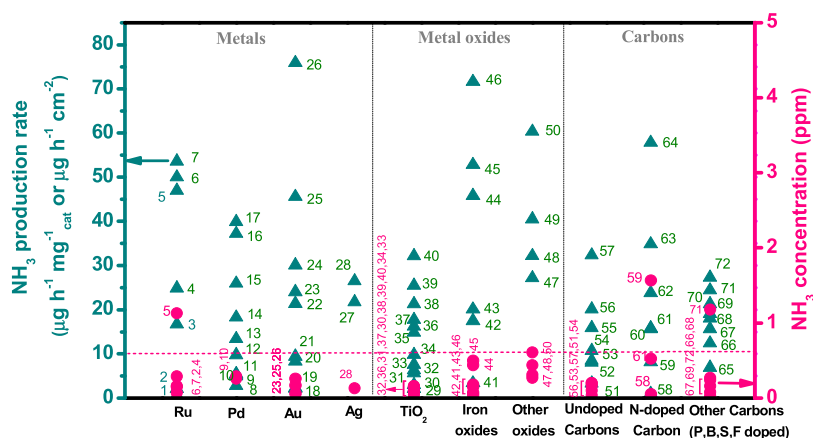
some time. To draw attention to this oversight, we have juxtaposed in Figure 1 the ammonia production rate as reported and the actual concentration of ammonia produced. The concentration of ammonia was extracted from the absorbance maxima value of the ultraviolet–visible (UV–vis) absorption data of the indophenol method provided in some of these reports (details in Table S1). It is evident from Figure 1 that the actual concentration of ammonia produced is below 0.6 ppm for most of the reported catalysts. It also reveals a huge variation in the ammonia production rate even for a small change in the measured concentration. For example, the production rate showed a variation from 0.97 µg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup> (for N and P codoped carbon, S.No. 58 in Table S1)<sup>20</sup> to 50 µg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup> (for Ru/rGO, S.No. 6 in Table S1)<sup>21</sup> for a concentration difference of 0.02 ppm. Such a large variation for a slight change in concentration actually resulted from the conversion factor (from the concentration to the production rate in µg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup> or in some cases µg h<sup>-1</sup> cm<sup>-2</sup>), which involves multiplication of volume of the electrolyte and division by the amount of catalyst used and the reaction time. This conversion factor resulted in reporting a wide range of yields despite similar concentrations, as the volume of

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**Figure 1.** Performance mapping of ENR electrocatalysts from the literature. The reported ammonia production rates of highly explored metal, metal oxide, and carbon-based electrocatalysts are shown in turquoise blue triangles. Very few catalysts with production rate above  $80 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$  are not presented in this graph but included in the reference.<sup>13</sup> The pink circles denote the extracted ammonia concentration from the UV–vis absorption data available for some of the catalysts (Table S1 for calculation details). The horizontal dotted line (pink color) indicates that the concentration of ammonia produced for most of the catalysts lies below 0.6 ppm.

electrolyte and the amount of catalyst used varied from one report to the other.

It underlines the importance of following stringent protocols to accurately quantify ammonia concentration in the electrolyte. Although isotopic labeling experiments help validate the ammonia production devoid of contaminants,<sup>14,22</sup> the cost and not-so-easy accessibility of  $^{15}\text{N}_2$  are some of the limitations to its extensive use. The most widely used technique to quantify ammonia in the aqueous-phase ENR reaction is the well-known indophenol method.<sup>23</sup> Although this is an age-old method, there is no uniformity in the procedures (in terms of the order of addition of reagents, addition of the complexing agent, and the amount of oxidant used) adopted in the literature, and the various protocols used compound the problem of accurate estimation of ammonia<sup>24,25</sup> at sub-ppm-level concentrations in the ENR reaction.

In our work, we have highlighted the importance of documenting ammonia produced in terms of “concentration” (in the electrolyte) along with the normalized production rate in the ENR reaction. The significance of selecting and standardizing the right protocol encompassing an admissible level of oxidant and a complexing agent, citrate (to mitigate the effect of interfering metal ions), is discussed elaborately with definitive control experiments. Above all, the efficacy of setting the lowest limit of ammonia concentration that can be accurately quantified by the indophenol method is highlighted in this work. Summarizing our observations, we proposed a standardized protocol that was subjected to verification on the performance of two well-claimed electrocatalysts for ENR reported recently in the literature ( $\text{Au}_3\text{Pd}/\text{NF}$  and  $\text{ZnS}/\text{NF}$ ). The critical analysis addressed here will establish more reliability in quantification and documentation of the amount of ammonia produced from ENR in an aqueous medium.

## 2. EXPERIMENTAL SECTION

**2.1. Reagents and Materials.** Salicylic acid ( $\geq 99.0\%$ ), sodium hypochlorite ( $\text{NaClO}$  with available chlorine 4.00–4.99%), sodium nitroferricyanide, sodium citrate,  $\text{NH}_4\text{Cl}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , sulfadiazine, *N*-(1-naphthyl)ethylenediamine dihydrochloride, vanadium(III) chloride,  $\text{HAuCl}_4$ ,  $\text{Na}_2\text{PdCl}_4$ , and  $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$  were purchased from Sigma-Aldrich Chemical

Co., Ltd. Pluronic F-127, potassium permanganate ( $\text{KMnO}_4$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), and thiourea were obtained from Alfa-aesar. Tetrahydrofuran (THF) ( $>99.5\%$ ),  $\text{C}_2\text{H}_5\text{OH}$ , 25% ammonia solution ( $\text{NH}_4\text{OH}$ ),  $\text{H}_2\text{SO}_4$  (98%), and  $\text{HCl}$  (37%) were purchased from Merck. Ni foam was procured from Fuel Cell Store.

**2.2. Characterization and Measurements.** X-ray diffraction (XRD) analysis was performed using the Bruker D8 advance eco instrument with a  $\text{Cu K}\alpha$  radiation source ( $\lambda = 1.54 \text{ \AA}$ ; step size: 0.02; current: 30 mA; and voltage: 40 kV). Field emission scanning electron microscopic (FESEM) images of the samples were obtained via a Nova-Nano SEM-600 (FEI, The Netherlands). UV–vis measurements were performed using the Perkin Elmer Lambda 900 UV–vis instrument.

**2.3. Synthesis of  $\text{Au}_3\text{Pd}/\text{Ni}$  Foam ( $\text{Au}_3\text{Pd}/\text{NF}$ ).**<sup>26</sup> A piece of Ni foam ( $1 \text{ cm} \times 2 \text{ cm}$ ) was treated with 3 M  $\text{HCl}$  to remove any oxide layer. Then, it was washed with Milli-Q water and ethanol under sonication and dried in an oven.  $\text{Au}_3\text{Pd}/\text{NF}$  was synthesized by following the reported procedure. First, Pluronic F-127 (10 mg) was dissolved in THF (3 mL). Then, 1.5 mL of  $\text{C}_2\text{H}_5\text{OH}$  was added to it. To this mixture, 1.5 mL of an aqueous solution of  $\text{HAuCl}_4$  (20 mM) and 0.5 mL of an aqueous solution of  $\text{Na}_2\text{PdCl}_4$  (20 mM) were added. Ni foam ( $1 \text{ cm} \times 2 \text{ cm}$ ) was dipped in this solution for 20 min. A visible color change of the solution was observed from golden yellow to colorless (Figure S11a).  $\text{Au}_3\text{Pd}/\text{NF}$  was obtained after washing with water and drying at an ambient condition at  $60 \text{ }^\circ\text{C}$ .

**2.4. Synthesis of the  $\text{ZnS}/\text{Ni}$  Foam ( $\text{ZnS}/\text{NF}$ ) Catalyst.**<sup>27</sup> A piece of Ni foam was pretreated according to the above procedure for removal of any oxide layer. Then, 1 mmol of  $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$  and 3 mmol of thiourea were dissolved in 30 mL of Milli-Q water under continuous stirring. This solution was then transferred to a 50 mL Teflon-lined stainless steel autoclave, and the piece of Ni foam was dipped in it. The autoclave was kept at  $160 \text{ }^\circ\text{C}$  for 6 h. The obtained  $\text{ZnS}/\text{NF}$  (Figure S14a) was washed with a mild acidic solution (0.05 M  $\text{H}_2\text{SO}_4$ ) until excess ammonia was not found in the supernatant of the solution post washing (Figure S15). It was further rinsed with Milli-Q water and absolute ethanol and dried in an oven at  $60 \text{ }^\circ\text{C}$ .

**Table 1. Stepwise Procedure for Four Different Indophenol Methods Adopted for Ammonia Quantification in ENR<sup>a</sup>**

procedure	analyte volume	step 1	step 2	step 3	incubation time (h)	mole ratio of salicylate: NaClO	references
P1	2 mL	2 mL (5 wt % salicylic acid, 5 wt % citrate in 1 M NaOH)	1 mL (0.05 M NaClO)	0.2 mL (1 wt % cat.)	2	1:0.07	16
P2	500 $\mu$ L	500 $\mu$ L (0.5 M NaClO)	50 $\mu$ L (5 wt % salicylic acid, 5 wt % citrate in 1 M NaOH)	10 $\mu$ L (0.5 wt % cat.)	3	1:14	29
P3	4 mL	50 $\mu$ L (0.02 M NaClO in 0.75 M NaOH)	50 $\mu$ L (1 wt % cat.)	500 $\mu$ L (6.4 wt % sodium salicylate in 0.32 M NaOH)	1	1:0.005	26
P4	4 mL	50 $\mu$ L (0.75 M NaClO in 0.75 M NaOH)	500 $\mu$ L (6.4 wt % sodium salicylate in 0.32 M NaOH)	50 $\mu$ L (1 wt % cat.)	1	1:0.2	30

<sup>a</sup>All of the reagents are added into the analyte consecutively as mentioned below.

### 2.5. Standardization of the Indophenol Procedure.

Among several indophenol methods available in the literature for ammonia quantification in ENR, we have selected four different procedures (labeled as P1, P2, P3, and P4) for quantifying ammonia in blank Milli-Q water and in 0.3 ppm ammonia standard solution (prepared using  $\text{NH}_4\text{Cl}$ ). Salicylic acid ( $\geq 99.0\%$ ), sodium hypochlorite (NaClO with available chlorine 4.00–4.99%), and a catalyst, sodium nitroferrocyanide, were used as common indophenol reagents in all of the procedures. Only in procedures P1 and P2, sodium citrate was additionally used. Furthermore, the concentration of reagents and their sequence of addition in the analyte are procedure-dependent and are given in Table 1. One must follow the steps mentioned in Table 1 for each procedure with freshly prepared indophenol reagents. As an example, in procedure P1, first 2 mL of coloring agent (5 wt % salicylic acid and 5 wt % sodium citrate in 1 M NaOH) was added into 2 mL of analyte, followed by addition of 1 mL of an oxidizing agent solution (0.05 M NaClO) and 200  $\mu$ L of catalyst (1 wt % sodium nitroferrocyanide) in sequence. The solution with the analyte and indophenol reagents was mixed thoroughly and stored in the dark (without any light) at room temperature for 2 h. This was followed by a UV–visible absorption measurement (Perkin Elmer Lambda 900) using a 10 mm quartz cuvette to obtain the spectrum with absorption maxima ( $A_{\lambda_{\text{max}}}$ ) at 645 nm.

The maximum absorbance value ( $A_{\lambda_{\text{max}}}$ ) obtained from the UV–vis spectrum corresponds to the ammonia concentration present in the analyte. The analytes used in this work are prepared in Milli-Q water, which inherently contains a certain amount of ammonia.

Therefore, to remove the background ammonia contribution (Milli-Q water and indophenol reagent chemicals) from the analyte, we subtracted the  $A_{\lambda_{\text{max}}}$  of the blank from the analyte's value (denoted  $\Delta\text{Absorbance}$ ).

$$\begin{aligned} \Delta\text{Absorbance}_{(\text{analyte}-\text{blank})} \\ = \text{Absorbance of analyte}_{\lambda_{\text{max}}} - \text{Absorbance of blank}_{\lambda_{\text{max}}} \end{aligned} \quad (1)$$

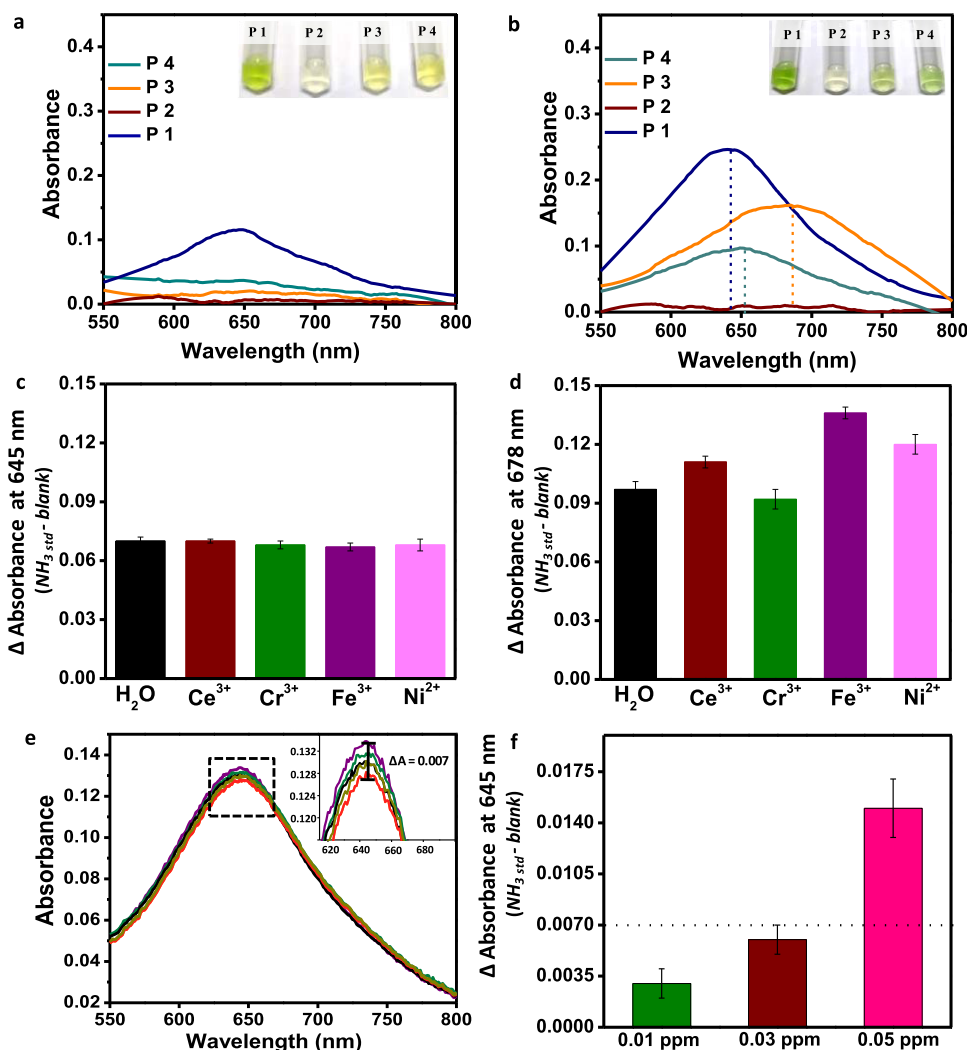
The indophenol method and procedures P1 (with citrate) and P3 (without citrate) were selected to quantify ammonia in a 0.2 ppm ammonia solution (using  $\text{NH}_4\text{Cl}$ ) containing 0.1 mM metal ions ( $\text{Ce}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$ ). The 0.1 mM metal ion solutions were prepared using  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . Herein, the blank solution contains Milli-Q water with a 0.1 mM metal ion.

The calibration curve was obtained using procedure P1 with different concentrations of an ammonia standard (prepared with  $\text{NH}_4\text{Cl}$ ), with  $\text{NH}_4^+$  concentrations varying from 0 to 1 ppm in 0.05 M  $\text{H}_2\text{SO}_4$  and 0.1 M  $\text{Na}_2\text{SO}_4$  separately. The absorbance values (at  $\lambda_{\text{max}} = 645$  nm) of the ammonia standards are incorporated in the calibration curve after subtracting the contribution of the blank from each of them as given in eq 1.

Ammonia solution for the containment test, in Figure S10, was prepared by serial dilution of a commercial 25% ammonia solution ( $\text{NH}_4\text{OH}$ ) using a 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution. The final concentration of ammonia obtained after serial dilution was calculated from the calibration plot (Figure S5b) to be 0.3 ppm.

**2.6. Quantification of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  by the Griess Method.**<sup>28</sup> The Griess method is used for the determination of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  ions' concentration in the electrolyte. The diazotizing reagent was obtained by adding 1 mL of concentrated HCl (37%) and 0.1 g of sulfadiazine (SULF) in a volumetric flask, which was filled up to 10 mL with water. The coupling reagent was prepared by dissolving 0.01 g of *N*-(1-naphthyl)ethylenediamine dihydrochloride (NED) in 10 mL of  $\text{H}_2\text{O}$ . All of the Griess reagents were stored in a refrigerator (4 °C) for further use. For the detection of  $\text{NO}_2^-$  ion quantity, first 0.50 mL of 0.1 M HCl was added to 0.5 mL of a sample. Further, 25  $\mu$ L of SULF and 25  $\mu$ L of NED were added sequentially, resulting in a pink coloration of the solution upon incubating for 20 min at ambient temperature. The UV–vis measurement was taken immediately. For quantification of  $\text{NO}_3^-$  ions, a similar protocol was used like for the  $\text{NO}_2^-$  ion with the addition of extra 50  $\mu$ L of a 0.02 wt % vanadium(III) chloride solution (prepared in 6 M HCl) at the end. Further, the mixture was incubated at 60 °C in a water bath for 25 min and cooled to room temperature before the UV–vis measurement.

**2.7. Electrochemical Measurements.** All of the electrochemical measurements were carried out in an airtight two-chamber glass H-cell separated by a Nafion 117 membrane (Figures S6 and S7). A three-electrode system was used with an electrocatalyst on conducting Ni foam, an aqueous Ag/AgCl (1 M KCl) electrode (CHI 111), and a platinum wire (CHI Instruments Inc.) as the working, reference, and counter electrodes, respectively. Prior to the electrochemical experiment,  $\text{N}_2/\text{Ar}$  was purged in the electrolyte (0.1 M  $\text{Na}_2\text{SO}_4$ ) of the cathode chamber at 20 mL/min for 30 min. During the electrochemical reaction, the catholyte (electrolyte in the cathode chamber) was continuously purged with  $\text{N}_2/\text{Ar}$  gas



**Figure 2.** Optimization of the indophenol method for ammonia quantification. UV–visible absorption spectra of (a) Milli-Q water and (b) Milli-Q water containing 0.3 ppm ammonia (prepared using NH<sub>4</sub>Cl) were analyzed with four different indophenol procedures used in the literature as tabulated in Table 1. The inset provides the optical image of the analyte after incubating with indophenol reagents according to the adopted procedure. The presence of metal ions (0.1 mM) in the 0.2 ppm ammonia standard showed a variation in the increase of the absorbance value ( $\Delta A$ ) with respect to the blank at  $\lambda_{\text{max}}$  by (c)  $\pm 4\%$  for procedure P1 in which sodium citrate was used and (d)  $+40\%$  (Fe<sup>3+</sup>) and  $-11\%$  (Cr<sup>3+</sup>) for procedure P3 in which no citrate was used. (e) Successive UV–vis scan of indophenol-stained Milli-Q water, following procedure P1 (the inset shows the maximum variation of 0.007 in the absorbance value at  $\lambda_{\text{max}} = 645$  nm). (f) Change in the absorbance value ( $\Delta A$ ) for ammonia calibration standards (0.01, 0.03, and 0.05 ppm) with respect to the blank (Milli-Q water). The horizontal dotted line lies at  $\Delta A = 0.007$ , below which the concentration of ammonia cannot be estimated accurately.

with the same flow rate of 20 mL/min. Linear sweep voltammetry (LSV) and chronoamperometry (CA) were performed with a potentiostat (Biologic Science Instruments, Inc., 760E). The applied potential measured against the Ag/AgCl (1 M KCl) reference electrode was converted to a reversible hydrogen electrode (RHE) after calibrating it in 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. Electrolysis of the catalyst in the Ar medium was performed first, and after performing chronoamperometry in the Ar medium, the same working electrode was used for electrolysis in the nitrogen medium.

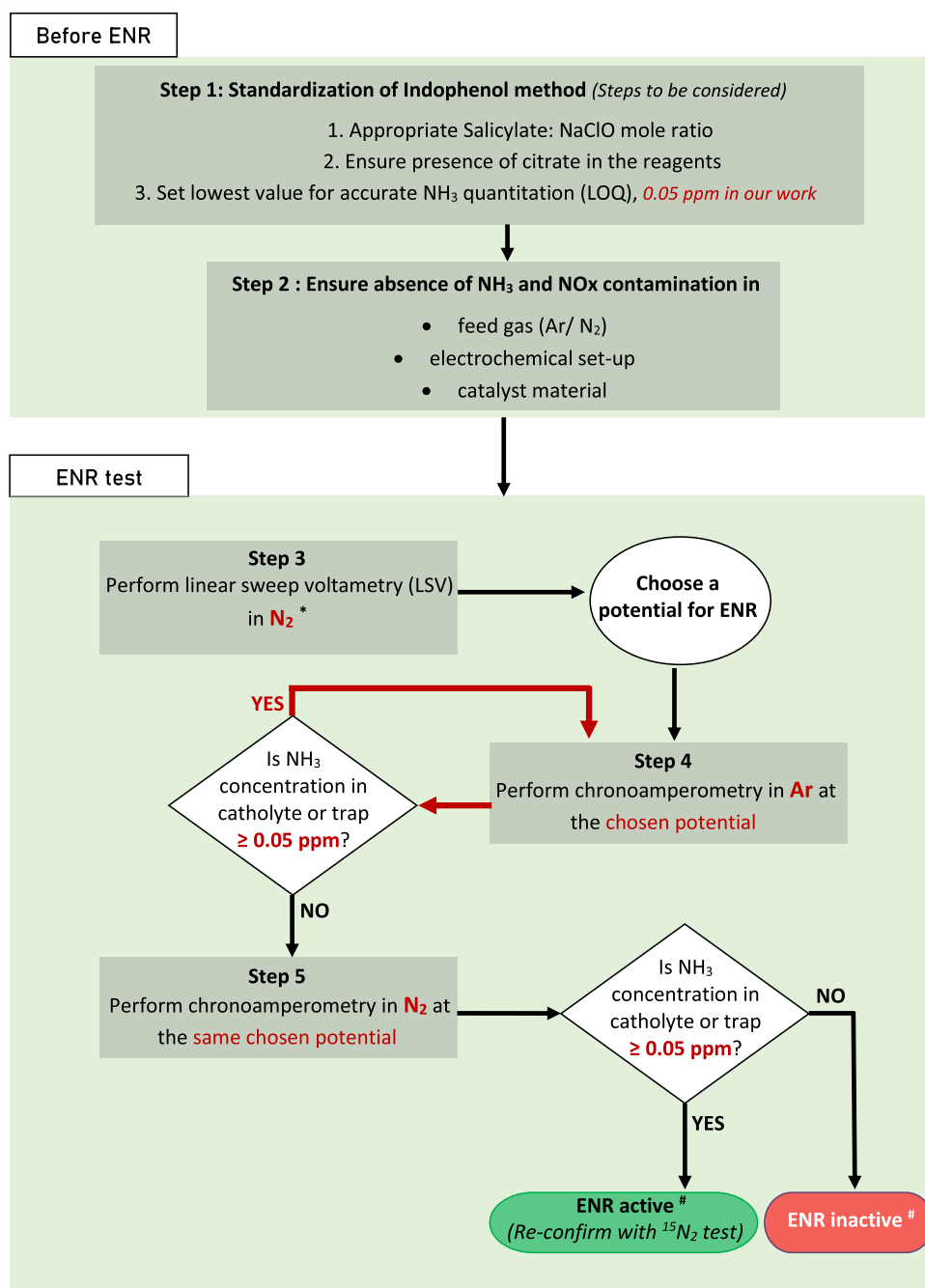
The initial volume of the electrolyte in both cathode and anode chambers was 23 mL. A total of 1.9 mL of aliquots for ammonia detection were collected from the purged electrolyte (30 min of purging) of the cathode, the anode chamber, and the trap prior to electrochemical measurements, and the same after the electrochemical process. To 1.9 mL of electrolyte, 100  $\mu$ L of 2 M H<sub>2</sub>SO<sub>4</sub> was added to stabilize the soluble ammonia

(volatility of ammonia increases with pH), and it was stored in a refrigerator at 4 °C. The cathode and anode chambers were continuously agitated with a Teflon-lined magnetic stirrer at 500 rpm during all of the electrochemical measurements. Then, a 12 mL solution of 0.05 M H<sub>2</sub>SO<sub>4</sub> was put as a trap to contain the ammonia at the outlet of the cathode chamber.

The ammonia estimation by the indophenol method (procedure P1) was done for each set of electrochemical reaction within 4 h to avoid ammonia contamination upon storage.

For all of the purposes in this work, fresh Milli-Q water with less than 12 h of storage time was used (to avoid increase in ammonia contamination upon storage).

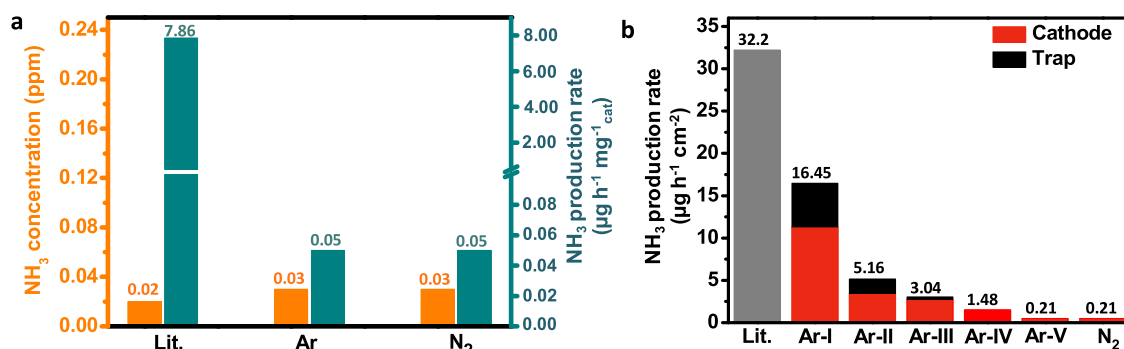
**2.8. Calibration of Reference Electrodes and Conversion to RHE.** The calibration Ag/AgCl (1 M KCl) reference electrode was performed in a standard three-electrode system. A polished and activated Pt wire (CHI

Scheme 1. Protocol for Performing ENR<sup>a</sup>

<sup>a</sup>The stepwise procedure highlights the necessity of choosing the appropriate indophenol method along with establishment of the LOQ (lowest limit of quantitation) prior to electrochemical ENR analysis. In addition to it, emphasis is also given toward performing prolonged electrochemical reduction in Ar at the chosen potential until no ammonia is detected in the electrolyte (the loop is marked with red-colored arrows in the scheme) before performing electroreduction of N<sub>2</sub>. This will take care of the reducible N species or NH<sub>3</sub> inherently present in the catalyst material, which are not removed by the conventional precatalysis treatment (exemplified below with the case study of ZnS/NF). The details of each step are provided in the [Supporting Information](#). \*Until stabilized polarization curves (LSV) are obtained. #Check the ENR activity at other potentials starting from step 4.

Instruments Inc.) was used as the working electrode, and a high-surface-area Pt coil (CHI Instruments Inc.) was used as the counter electrode. The Ag/AgCl (1 M KCl) electrode was used as the reference electrode. The electrolyte (0.1 M Na<sub>2</sub>SO<sub>4</sub>) was prepurged and saturated with high-purity H<sub>2</sub> (VICI DBS hydrogen generator, 99.999% purity) for 1 h prior to the experiments. Cyclic voltammetry (CV) was then run at a scan rate of 1 mV s<sup>-1</sup> with continuous H<sub>2</sub> bubbling near the

working electrode (Pt wire) (Figure S9). The potential at which the current crossed zero is taken to be the thermodynamic potential for the hydrogen electrode reactions. In this case, the average potential of the two lines crossing zero current (hydrogen oxidation and hydrogen reduction) was calculated. In 0.1 M Na<sub>2</sub>SO<sub>4</sub>, the zero current point is at -0.521 V, so  $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.521 \text{ V}$ .



**Figure 3.** Revisiting the ENR activity of the electrocatalyst. The ammonia concentrations generated in the catholyte and trap after electrochemical reduction in nitrogen (N<sub>2</sub>) and argon (Ar) gas using (a) Au<sub>3</sub>Pd/NF at -0.1 V vs RHE and (b) ZnS/NF at -0.5 V vs RHE are presented along with their reported data, denoted “Lit.” The ammonia yield, which is calculated from the ammonia concentration, is also provided in the graphs. It must be noted that according to our protocol (Scheme 1), the ammonia concentration generated below 0.05 ppm post electrolysis is considered insignificant. In our work, Au<sub>3</sub>Pd/NF produced 0.03 ppm (inconsiderable) ammonia concentration post electrolysis in both Ar and N<sub>2</sub> atmospheres. In the case of ZnS/NF, the concentration of ammonia generated after electrolysis in the argon atmosphere was >0.05 ppm until four consecutive cycles, after which an insignificant amount of ammonia was produced in both Ar and N<sub>2</sub> atmospheres. It must be noted that the ammonia production rate in the case of ZnS/NF was reported as  $5.27 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$ , which is equal to  $32.2 \text{ } \mu\text{g h}^{-1} \text{ cm}^{-2}$ .

### 3. RESULTS AND DISCUSSION

**3.1. Pitfalls in Ammonia Quantification by the Indophenol Method.** The indophenol method generally uses a coloring agent (phenol/salicylic acid), an oxidant (NaClO), and a catalyst (nitroprusside) to detect ammonia in the form of indophenol, as described in Figure S1.<sup>23</sup> In the literature, there are four sets of procedures commonly used to estimate the ammonia produced in ENR, which differed from one another with respect to the mole ratio of salicylate to NaClO employed, the order of addition of reagents, and the use of sodium citrate.<sup>16,26,29,30</sup> To understand the influence of these factors further, we have selected all four indophenol procedures for quantification analysis (Table 1). To start with, we estimated the ammonia inherently present in Milli-Q water by these procedures, and the UV-vis absorption results are shown in Figure 2a. Among all of the procedures employed, only one (procedure P1) showed a distinct absorption maximum at 645 nm, which was stable for more than 2 h (Figures 2a and S2). Next, a known amount of ammonium chloride was added to the Milli-Q water (equivalent to 0.3 ppm of ammonia solution) and the quantification was repeated for all four procedures. Among the four procedures, procedure P2 (with a high NaClO/salicylate mole ratio, 14:1) failed to show any UV-vis absorption maxima ( $\lambda_{\text{max}}$ ) (Figure 2b). The absence of color for procedure P2 in the inset (Figure 2b) further confirms the invalidity of this procedure to estimate ammonia at lower concentrations. In the other three procedures, a concomitant increase in the absorbance value with respect to blank Milli-Q water was observed at their  $\lambda_{\text{max}}$ . Furthermore, the relevance of citrate addition (scavenger of interfering metal ions in the indophenol method<sup>31</sup>) is exemplified in quantifying 0.2 ppm ammonia standard in the presence of Ce<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, and Ni<sup>2+</sup> metal ions (experimental details are provided in the experimental section, Section 2.5) using the procedures P1 (with citrate) and P3 (without citrate). The experimental data (Figures 2c,d and S3) show only  $\pm 4\%$  variation in absorbance maxima for all of the cation-containing standards analyzed by procedure P1, whereas a large variation in absorbance maxima, +40% (Fe<sup>3+</sup>) to -11% (Cr<sup>3+</sup>), was observed for procedure P3. Thus, based on the above control experiments, we have adopted the robust

indophenol procedure P1 in our quantification studies to avoid any false results associated with these metal ions.

The presence of a trace amount of ammonia from the surrounding and possibly from indophenol reagents<sup>14,16</sup> (inherent) results in variable absorbance maxima for blank Milli-Q water, which cannot be nullified (Figure S4a). To avoid such fluctuations cropping up in the measurement of ammonia concentration, we have used the difference in the absorbance value ( $\Delta A$  at 645 nm) obtained for the electrolyte before and after ENR, rather than their actual absorbance values (according to eq 1, experimental Section 2.5).

The  $\Delta A$  value (at 645 nm) obtained for the addition of a known amount of ammonium chloride in the electrolyte was used for the calibration curve (Figure S5) in our method.

It is to be noted that the  $\Delta A$  value below 0.007 does not have any significance as successive UV-vis scans (without repositioning or refilling the cuvette) of Milli-Q water stained with indophenol reagents themselves show a variation of  $\Delta A = 0.007$  (at 645 nm, Figure 2e). Such a variation in the  $\Delta A$  value for successive UV-vis scans was observed even for the 0.3 ppm ammonia standard (Figure S4b), suggesting it to be the inherent instrument precision limit (0.007).<sup>32</sup> It is to be noted that in other labs the observed inherent instrument precision may differ from 0.007 and may also vary with absorbance. In our case, the observations disregard the  $\Delta A$  value below 0.007 obtained for any analyte.

It is important to note that the calibration standards prepared with ammonia concentration below 0.05 ppm have absorbance values ( $\Delta A$ ) less than the instrument precision value, i.e., 0.007 (Figure 2f). Here, we realize the limitation in accurately estimating the ammonia concentration below 0.05 ppm in an aqueous medium and set it as the lower limit of quantitation (LOQ) for the ammonia concentration (precise calculation for LOQ along with the limit of detection (LOD) is provided in the Supporting Information). In other words, ammonia concentration below 0.05 ppm was not considered as a positive result for ENR.

**3.2. Electrochemical Nitrogen Reduction Studies.** Based on the above experimental findings, we have proposed a stepwise protocol for performing ENR (Scheme 1) and have revisited the ENR activity of two recently reported electrocatalysts, Au<sub>3</sub>Pd alloy and zinc sulfide on nickel foam (NF)<sup>26,27</sup>

with our optimized electrochemical setup (see the Supporting Information for details, Figures S6–S8 and S10).

The Au<sub>3</sub>Pd/NF electrocatalyst,<sup>26</sup> synthesized by a simple galvanic replacement reaction as reported in the literature, was characterized using XRD and FESEM imaging (Figure S11). The absence of NO<sub>x</sub> and ammonia contamination from Au<sub>3</sub>Pd/NF was confirmed by carrying out electrochemical reduction in argon (Figure S12). Estimation of ammonia in the catholyte showed more or less the same absorbance maxima (at λ<sub>max</sub> = 645 nm) as the one obtained before electrolysis (Figure S13a). Quantitation of ammonia after carrying out the electrochemical nitrogen reduction (chronoamperometry performed at −0.1 V vs RHE in 0.1 M Na<sub>2</sub>SO<sub>4</sub>) showed no significant change in the absorbance maxima (ΔA < 0.007) as compared to the reaction carried out in an argon flow (Figure S13b with a detailed analysis provided in Table S2). As the concentration of ammonia measured after the ENR is lower than the LOQ (<0.05 ppm), we considered this as an inactive catalyst for electrochemical nitrogen reduction to ammonia (Figure 3a). In contrast, the report claimed the ammonia production rate to be 7.85 μg h<sup>−1</sup> mg<sub>cat</sub><sup>−1</sup> (for Au<sub>3</sub>Pd/NF synthesized using the Pluronic F-127 surfactant).<sup>26</sup> Interestingly, the concentration of ammonia in the electrolyte calculated from its calibration curve is below 0.05 ppm although the derived production rate is huge (Figure 3a).

The unusually high production rate in spite of the low concentration of ammonia is due to the amplification factor arising from the volume of the electrolyte and the amount of catalyst used (details are provided in the Supporting Information).

The ZnS nanostructure grown on the nickel foam (ZnS/NF)<sup>27</sup> is another electrocatalyst we have tested for ENR activity (Figure S14). Since the synthesis of ZnS/NF involved the nitrogen-based precursor (thiourea), it was subjected to an acid wash to remove any occluded ammonia produced during synthesis (Figure S15). The acid-washed ZnS/NF electrocatalyst was first tested in an argon environment (20 mL/min flow) while applying a constant potential of −0.5 V vs RHE (as reported in the literature) for 2 h (Figure S16b). The catholyte after the reaction was analyzed by the indophenol method, which showed ammonia concentration above 1 ppm. However, with subsequent runs, the production rate of ammonia decreases gradually and goes below 1 μg h<sup>−1</sup> cm<sup>−2</sup> (below 0.05 ppm, ΔA ~ 0.007) in the 5th cycle (Figures 3b and S17). Further electrochemical reduction performed under nitrogen with the same electrode (after the catalyst was subjected to 5 cycles under argon) did not produce any ammonia (below 0.05 ppm), which is in sharp contrast to the ammonia production rate of 32.2 μg h<sup>−1</sup> cm<sup>−2</sup> reported in the literature (see Figure 3b and Table S3 for more information).

## 4. CONCLUSIONS

In conclusion, through some definitive control experiments, we have standardized the protocol to quantify ammonia in an aqueous electrolyte at a very low concentration in the ENR reaction using the indophenol method. Our observation suggests that the choice of a proper indophenol procedure (with an appropriate salicylate/NaClO ratio, inclusion of citrate) is a decisive factor in accurately determining the concentration of ammonia at sub-ppm levels. It is also evident from our investigations that the quantitation of ammonia by the indophenol method below a 0.05 ppm (LOQ) concentration in the catholyte falls in the range of experimental

errors and converting this concentration into production rate will be misleading and has to be avoided. The protocol we have established would help researchers screen the catalysts in the first place before proceeding to costlier <sup>15</sup>N<sub>2</sub> tests for further confirmation. Since the ammonia produced from ENR is exceedingly low, we suggest that the performance metric of an electrocatalyst needs to be mentioned in terms of concentration of ammonia along with the normalized production rate. It is because the ammonia concentration is the direct quantity we measure using the UV–vis spectrometric method (particularly by indophenol method) and it has limitations in measuring at very low concentrations. In addition, we suggest that researchers in this field always provide the obtained UV–vis spectra (with the absorbance value) and also document the electrolyte volume and the amount of catalyst loaded for the ENR process to remove any ambiguity when others try to reproduce the performance of a reported catalyst. As this field is in its infancy stage and many state-of-the-art protocols to ascertain the production of ammonia are still emerging, it is imperative to provide all minute experimental details along with every possible pitfall we encounter in this analysis to assess the performance of a catalyst devoid of false positives.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c05263>.

Table listing the ammonia production rate and the corresponding ammonia concentration of ENR electrocatalysts from the literature; schematic of the indophenol reaction mechanism; stability of the product formed from the indophenol method; comparison of indophenol procedures P1 and P3; limitations of the indophenol method; calibration plot; calculation for the limit of detection and limit of quantitation; optimization of the electrochemical setup; details of the customized cell setup; schematic of the full electrochemical setup; NO<sub>x</sub>- and NH<sub>3</sub>-free feed gas; ammonia containment test; calibration of the reference electrode; stepwise protocols to evaluate the ENR activity of a catalyst; characterization; electrochemical performance and spectrometric analysis of electrolytes of the Au<sub>3</sub>Pd/NF electrocatalyst; electrochemical performance and spectrometric analysis of electrolytes of the ZnS/NF electrocatalyst; calculation of the ammonia production rate (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Muthusamy Eswaramoorthy – *Nanomaterials and Catalysis Laboratory, Chemistry and Physics of Materials Science, School of Advanced Materials (SAMat), JNCASR, Bengaluru 560064, India; International Centre for Materials Science, JNCASR, Bengaluru 560064, India; [orcid.org/0000-0002-5015-3094](https://orcid.org/0000-0002-5015-3094); Email: [eswar@jncasr.ac.in](mailto:eswar@jncasr.ac.in)*

### Authors

Suchi Smita Biswas – *Nanomaterials and Catalysis Laboratory, Chemistry and Physics of Materials Science, School of Advanced Materials (SAMat), JNCASR, Bengaluru 560064, India*

Arunava Saha – *Nanomaterials and Catalysis Laboratory, Chemistry and Physics of Materials Science, School of*

Advanced Materials (SAMat), JNCASR, Bengaluru 560064, India

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acsomega.1c05263>

### Author Contributions

<sup>§</sup>S.S.B. and A.S. contributed equally.

### Notes

The authors declare no competing financial interest.

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