Supplementary information for

Enhancing the Rate and Efficiency of Electrochemical Ammonia Synthesis from N_2 in Concentrated Divalent Electrolytes

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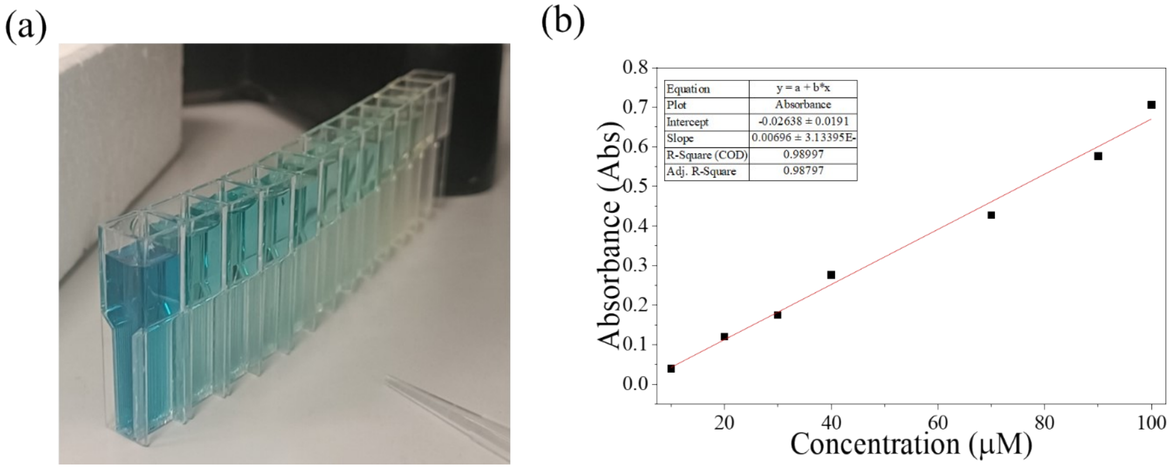
S1: Calibration curves of ammonia standards using the indophenol blue method.

Ammonia standard solutions of various concentrations were prepared by dissolving ammonium chloride (NH_4Cl) in 1 mM sulfuric acid (H_2SO_4). The standards were subsequently analyzed colorimetrically using the indophenol blue method. Following reagent addition and color development, the absorbance of each sample was measured at 655 nm using a UV-Visible spectrophotometer. A calibration curve was constructed by plotting the absorbance values against the corresponding ammonia concentrations.



Equation	y = a + b*x
Plot	Absorbance
Intercept	-0.02638 ± 0.0191
Slope	0.00696 ± 3.13395E-
R-Square (COD)	0.98997
Adj. R-Square	0.98797

Figure S1: (a) Photographs of various ammonia standards from lower concentrations (yellow to higher concentrations (blue), and (b) Calibration curve of ammonium chloride of different known concentrations in 1 mM H_2SO_4. Slope = 0.0069 Abs/μM and $R^2 = 0.989$.

As the direct quantification of ammonia using the indophenol blue method is not feasible in concentrated electrolytes, an indirect approach was employed. The electrolyte was heated at 110 °C for 10 min, and the evolved ammonia was transported by a continuous nitrogen flow (50 cc min^{-1}) into a 1 mM H_2SO_4 trapping solution. The trapped ammonia was subsequently quantified using the indophenol blue method. The extracted ammonia was found to be ~10 % of the original concentration of the NH_3 standard solution.

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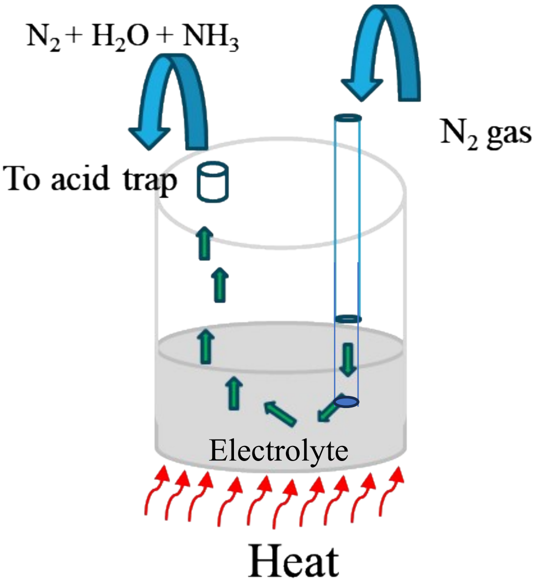

Figure S2: A schematic of ammonia quantification in a concentrated electrolyte.

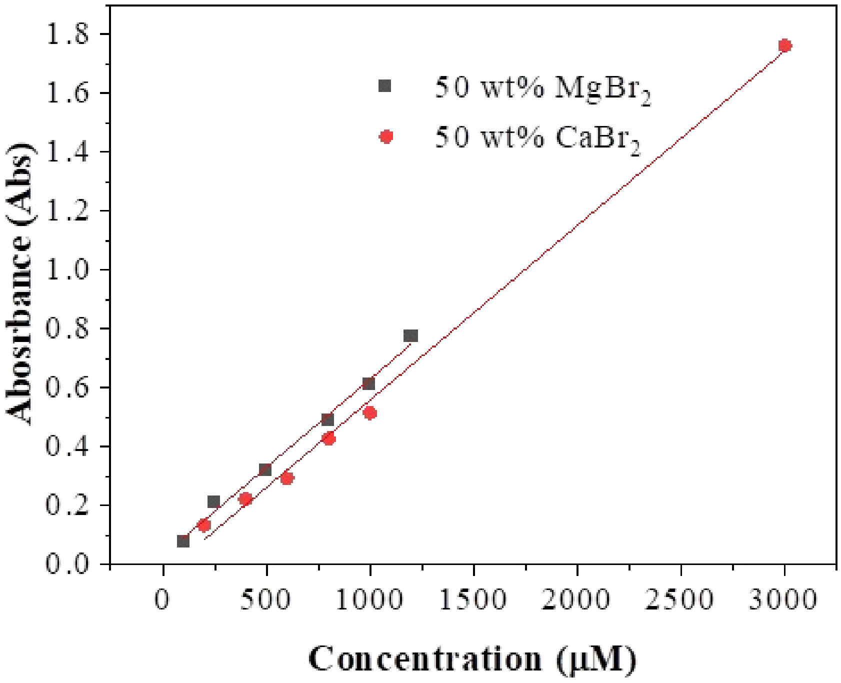

Figure S3: Calibration curve of ammonium chloride of different known concentrations in 50 wt.% $CaBr_2$ and 50 wt.% $MgBr_2$ by heating and trapping in 1mM H_2SO_4. Correction factor =

10.66 (Slope = 5.92×10^{-4} Abs/µM) and $R^2 = 0.999$ for 50 wt.% $CaBr_2$ and Correction factor = 10.66 (slope = 5.98×10^{-4} Abs/µM) and $R^2 = 0.999$ for 50 wt.% $MgBr_2$.

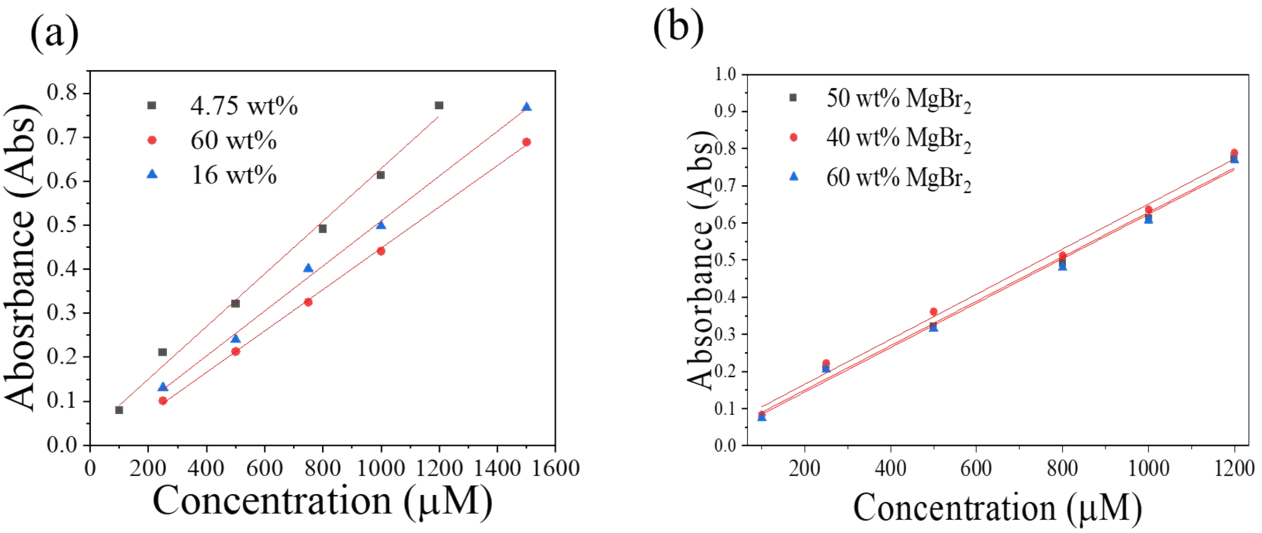

Figure S4: Calibration curves for ammonia quantification, constructed using standard solutions spanning various concentrations in (a) $CaBr_2$ and (b) $MgBr_2$.

Table S1: Calibration of ammonia standards over a wide range of concentrations in 50 wt% $CaBr_2$.

Concentration of NH_3 standard in 50 wt% $CaBr_2$ (µM)	Concentration of ammonia extracted (µM)	% of ammonia extracted
50	5.69	11.4
100	10.92	10.9
200	22.46	11.2
1000	112.31	11.2
2000	213.69	10.7
4000	395.38	9.9
10000	1153.84	11.5
20000	2378.46	11.9

40000	5052.30	12.6
		Avg = 11.2; S. D. = ±0.76 (6.7%)

Table S2: Calibration of ammonia standards over a wide range of concentrations in 50 wt% $MgBr_2$.

Concentration of NH_3 standard in 50 wt% $MgBr_2$ (µM)	**Concentration of ammonia extracted (µM)**	**% of ammonia extracted**
50	6.11	12.2
100	12.52	12.5
200	23.36	11.7
1000	152.12	15.2
2000	221.34	11.1
4000	451.59	11.3
10000	1123.63	11.2
20000	2632.41	13.2
40000	5547.72	13.9
		Avg = 12.5; S.D = ±1.15 (9.6%)

At low, medium, and high concentrations of ammonia standards in 50 wt% $CaBr_2$ and $MgBr_2$, the extracted ammonia shows a linear trend.

Ammonia standards were acidified by the addition of 1 mL of 1 M HCl to 1 mL of each standard solution to ensure complete protonation of ammonia to ammonium (NH_4^+). The resulting samples were analysed by proton nuclear magnetic resonance (^1H NMR) spectroscopy using maleic acid as an internal standard for baseline referencing. The integrated signal intensity of the ammonium resonance was plotted against the corresponding ammonia concentrations to construct a calibration curve.

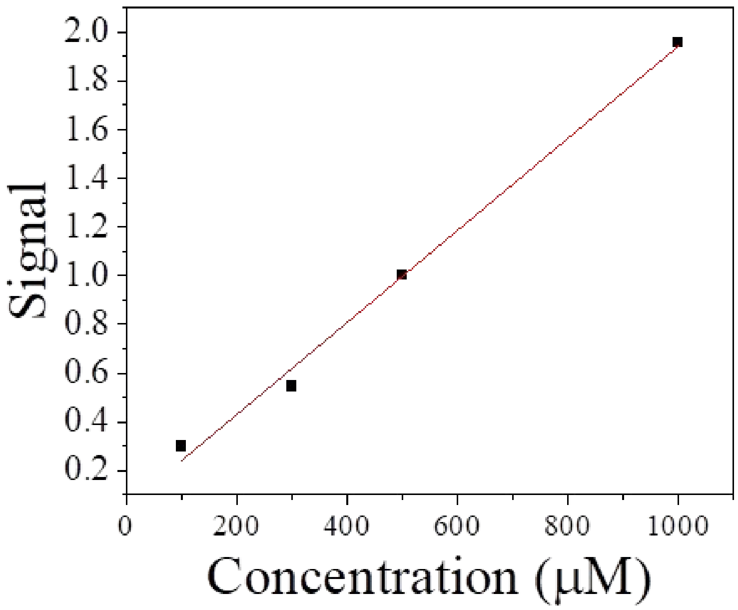

Figure S5: Calibration curve of ammonia standards in 50 wt.% $MgBr_2$ by ^1H NMR by using maleic acid as a standard. $R^2 = 0.99$ and slope = 0.0019/μM.

S2: Calculation of "free water" available in different concentrations of $CaBr_2$ and $MgBr_2$

Assuming that the hydration number of the calcium ion[1] in $CaBr_2$ and the bromide ion[2] is 6 at room temperature, although at higher concentrations, the hydration number decreases slightly to 5.5[3].

For a 60 wt.% $CaBr_2$ solution (equivalent to 7.5 M, based on a total mass of 100 g), with a composition of 60 g $CaBr_2$ and 40 g H_2O. This corresponds to ionic concentrations of 0.3 M Ca^{2+} and 0.6 M Br^- when normalized against the total solution volume. The corresponding molarity of water in this system is approximately 2.22 M. Given that complete solvation of each Ca^{2+} and Br^- ion requires six water molecules, and considering that crystalline $CaBr_2 \cdot 6H_2O$ already contains approximately 5.5 water molecules per ion pair, the total water needed for solvation in the solution is estimated as:

(0.3 M Ca^{2+} + 0.6 M Br^-) × 5.5 = 4.95 M.

Thus, the theoretical water deficiency is calculated as:

I2.22 M (available) − 4.95 M (required)I = 2.73 M,

indicating that the solution contains a deficit of 2.72 M of water molecules, hence does not contain a sufficient number of water molecules to solvate all ions present fully.

A similar analysis for a 50 wt.% $CaBr_2$ solution (based on 100 mL total volume) yields 0.25 M Ca^{2+} and 0.5 M Br^- ions, and a water concentration of approximately 2.77 M. The water required for complete solvation in this case is:

(0.25 + 0.5) M × 5.5 = 4.12 M,

resulting in a theoretical water deficit of:

I 2.77 M − 4.12 M I = 1.36 M.

These results indicate that both 60 wt.% and 50 wt.% $CaBr_2$ electrolytes are deficient in free water molecules necessary for complete ion solvation.

For comparison, similar calculations for less concentrated solutions show an excess of free water, in a 16 wt.% $CaBr_2$ solution (1 M), the free water concentration is approximately 3.34 M, while in a 4.75 wt.% $CaBr_2$ solution (0.25 M), the free water concentration increases to approximately 4.96 M, indicating sufficient hydration for ion solvation.

Mg^{2+} ions, which possess a higher solvation energy compared to Ca^{2+} ions, exhibit a larger primary hydration number of six under identical conditions of concentration, temperature, and pressure[4]. As a result, the estimated free water deficit in a 50 wt.% $MgBr_2$ solution is approximately 1.82 M, indicating an even greater deficit of available water molecules for complete ion solvation relative to the corresponding $CaBr_2$ solution.

S3: Removal of ammonia from commercial $CaBr_2$

Due to ammonia contamination in commercial $CaBr_2$, the prepared electrolyte was heated for 10 min, and the outlet gas was trapped in 1 mM H_2SO_4 and analyzed to quantify the ammonia. After 10 min, the water lost was added back to the electrolyte, and the mixture was heated again until the ammonia in the trap was negligible.

Table S3: Ammonia removal from commercial $CaBr_2$ salt.

Boil cycle no.	**Absorbance of the trap**	**Concentration of ammonia (µM)**
1	1.06	1614
2	0.86	1308
3	0.079	120
4	0.054	82
5	0.043	73

The lowest possible ammonia contamination obtained was taken for baseline subtraction.

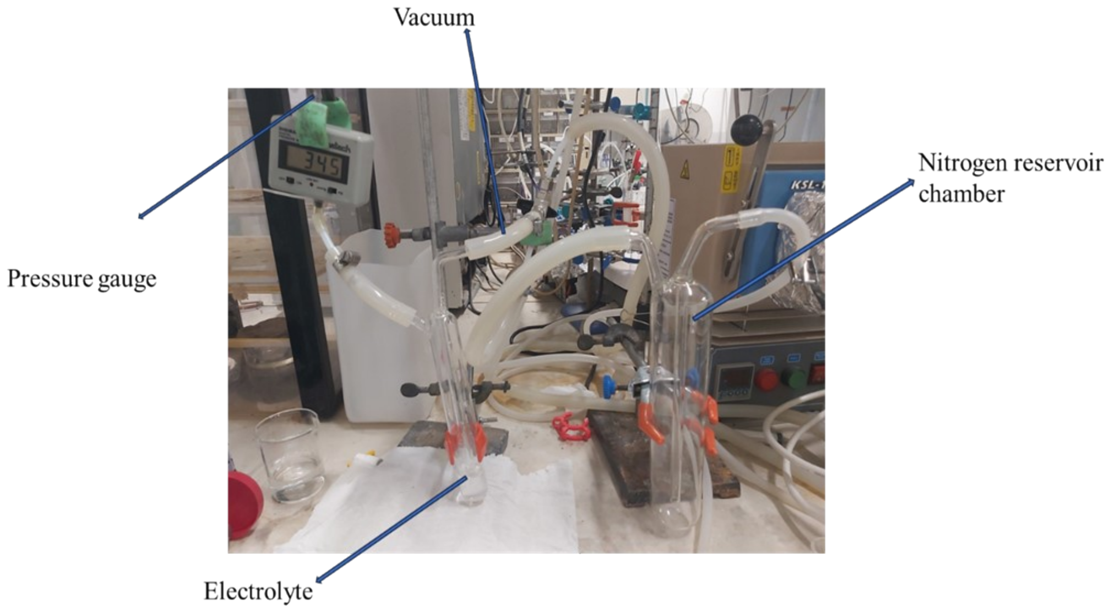

Figure S6: Apparatus for testing nitrogen solubility in electrolytes.

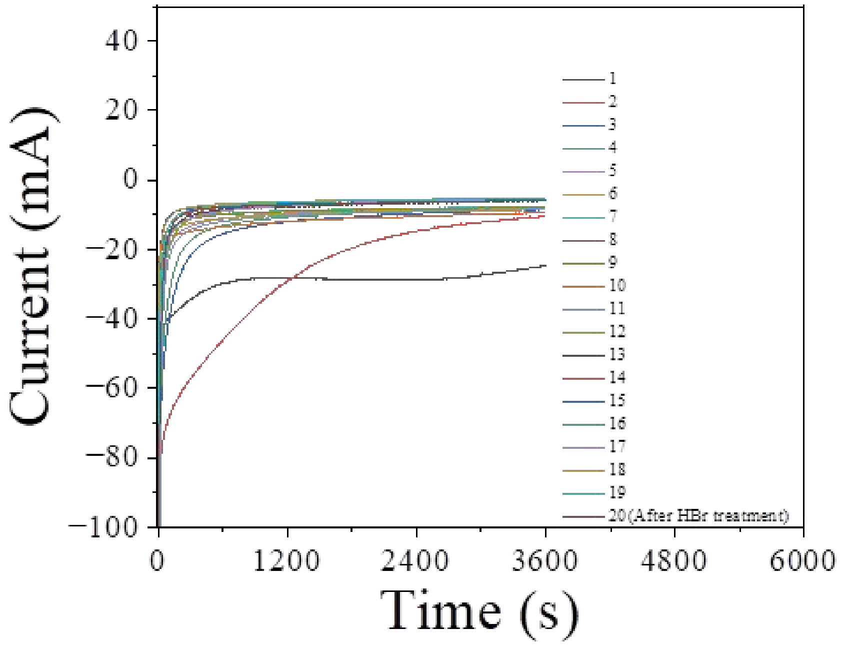

Figure S7: Chronoamperometry cycles using N_2-purged 50 wt.% $CaBr_2$ circulated through both the cathode and anode at -0.15 V vs. RHE for 1 h, performed for stability test.

Table S4: ICP AES analysis of Pt and Ru in the electrolyte before, after 1 h, and 3 h of CA in the same electrolyte at -0.15 V.

Element	Fresh electrolyte	Electrolyte used for 1 h CA	Electrolyte used for 3 CA
Pt	<0.001 ppm	0.317 ppm (0.08% of total catalyst)	0.597 ppm (0.15%)
Ru	0.013 ppm	0.142 ppm (0.03%)	0.230 ppm (0.05%)

S4: Control experiments to determine the source of NH_3.

Presence of NO_2^- was ruled out by using p-dimethylaminobenzaldehyde in 90:10 volume % ethanol: HCl, and showed no NO_2^- in 50 wt% $CaBr_2$[5]. NO_3^- couldn't be qualitatively analysed because $CaBr_2$ shows a peak near 240 nm in UV-Vis spectroscopy, which interferes with the NO_3^- region. So, the electrolyte was analysed for NO_2^- produced by NO_3^- reduction during the electrolysis of 50 wt% $CaBr_2$ at -0.35 V vs RHE. The use of p-dimethylaminobenzaldehyde in a 90:10 volume percent ethanol: hydrochloric acid solution showed no absorbance peak at 420 nm in UV-visible spectroscopy, revealing no detectable traces of the impurity after extended reduction, consistent with the absence of significant concentrations of this ion in the electrolyte. This indicates that hydrazine is not present following electrolysis[6]. The qualitative analysis of hydrazine during the reduction of 50 wt% $CaBr_2$ and 50 wt% $MgBr_2$ at potentials -0.15 V, -0.25 V, -0.35V, -0.45 V, -0.55 V, and -0.65 V vs RHE revealed no trace of hydrazine. To quantify the contribution from all reactive nitrogen sources, before each experiment, the electrolysis was performed using Ar-purged 50 wt.% $CaBr_2$ at -0.35 V vs RHE for 1 hour, and analysis of the electrolyte and the trap showed a total ammonia amount of 6.46 µg, which is negligible.

The results of $^{15}N_2$-labelled experiments showing the qualitative and quantitative detection of $^{15}NH_3$ by NMR are shown in Figure S9 below.

Electrolysis of 20 mL of 50 wt% $CaBr_2$ electrolyte for 1 hour at −0.35 V vs. RHE, at an ammonia production rate of 81 µg $h^{-1}cm^{-2}$, yields a total ammonia concentration of 1760 µM in the bulk electrolyte. Of this, 10% is captured in the acid trap, corresponding to a collected ammonia concentration of 176 µM. Figure S8 (a) shows ^{15}NMR signal of 176 µM $^{15}NH_4OH$ standard prepared in 1 mM H_2SO_4. This value is in close agreement with the ^{15}N NMR of the trap after heating and extracting $^{15}NH_3$ from 50 wt% $CaBr_2$ after 1 hour of electrolysis at -0.35 V vs RHE, shown in Figure S8 (b), thereby providing qualitative and quantitative confirmation of the measured ammonia production rate.

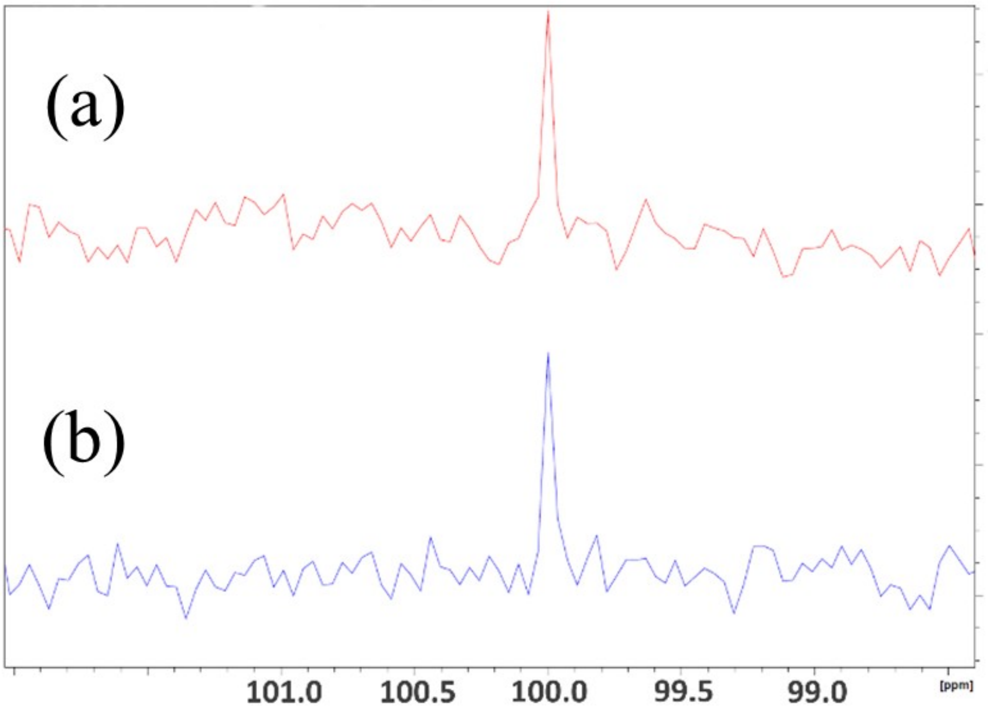

Figure S8. ^{15}N NMR spectrum of (a) labelled ammonia standard $^{15}NH_4OH$ (176 μM) in the 1mM H_2SO_4, and (b) the trap solution after eNRR at -0.35 V vs RHE for 1 hour in $^{15}N_2$ gas purged electrolyte solution.

References

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