Supplementary information for:

Revisiting amorphous molybdenum sulfide's activity for the electro-driven reduction of dinitrogen and N-containing substrates

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Content

S1. Bibliographic analysis

Table S1: Main catalytic figures and conditions reported for dinitrogen reduction reaction (NRR) promoted by molybdenum sulfide derivatives.

Material	Loading WE mater.	Electrolyte	Bias (V *vs.* RHE)	Rate ($\mu mol.cm^{-2}.h^{-1}$)	Rate ($\mu mol.mg_{MoSx}^{-1}.h^{-1}$)	FE (%)
MoS_2 nanoflowers (defect-free)[1]	0.4 $mg.cm^{-2}$ CC + Nafion	0.1 M Na_2SO_4	-0.4	0.32	0.79	2.2
MoS_2 nanoflowers (defect-rich)[1]	0.4 $mg.cm^{-2}$ CC + Nafion	0.1 M Na_2SO_4	-0.4	0.68	1.7	8.3
MoS_2 nanosheets[2]	*a,b*	0.1 M Na_2SO_4	-0.5	0.29	*a,b*	1.2
MoS_2 nanosheets[2]	*a,b*	0.1 M HCl	-0.5	0.31	*a,b*	0.1
MoS_2 nanosheets on BC fiber[c,3]	10 $mg.cm^{-2}$ CC + Nafion	0.1 M Na_2SO_4 pH 3	-0.2	0.2	0.31	0.5
MoS_2 nanosheets on BC fibers[c,3]	10 $mg.cm^{-2}$ CC + Nafion	0.1 M Li_2SO_4 pH 3	-0.2	1.6	2.5	9.8
2H-MoS_2[4]	1 $mg.cm^{-2}$ CP + Nafion	0.01 M HCl pH 2	-0.2	0.02[d]	0.02[d]	*e*
1T-MoS_2[4]	1 $mg.cm^{-2}$ CP + Nafion	0.01 M HCl pH 2	-0.2	0.02[d]	0.02[d]	*e*
MoS_2 nanosheets[5]	1 $mg.cm^{-2}$ CP + Nafion	0.1 M Na_2SO_4	-0.3	0.15	0.15	5.2
MoS_2 nanosheets[5]	1 $mg.cm^{-2}$ CP + Nafion	0.1 M HCl pH 1	-0.3	0.1	0.1	0.1
MoS_2 nanosheets[5]	1 $mg.cm^{-2}$ CP + Nafion	0.1 M NaOH pH 13	-0.3	0.88	0.88	2
MoS_2@rGO[6]	0.1 $mg.cm^{-2}$ CP	0.1 M $LiClO_4$	-0.45	0.15	1.46[f]	4.6
N-doped MoS_2 nanoflowers[7]	0.7 $mg.cm^{-2}$ GC	0.1 M Na_2SO_4	-0.3	2.9	4.1	9.1
MoS_2 nanoflowers[7]	0.7 $mg.cm^{-2}$ GC	0.1 M Na_2SO_4	-0.3	0.2[d]	0.3[d]	0.4[d]
Co-doped MoS_{2-x}[8]	*a,b*	0.01 M $H2_SO_4$	-0.3	*e*	0.6	10
MoS_{2-x}[8]	*a,b*	0.01 M H_2SO_4	-0.3	*e*	0.32	1.7
2H-MoS_2[9]	*a*	0.1 M HCl pH 1	-0.34	0.2	*a*	0.1
Fe doped 2H-MoS_2[9]	*a*	0.1 M HCl pH 1	-0.34	0.82[d]	*a*	0.3[d]
MoS_2 nanodots @rGO[10]	0.8 $mg.cm^{-2}$ CC + Nafion (0.4 mg MoS_2)	0.1 M Na_2SO_4 pH 10	-0.35	0.4[d]	0.5[d,f]	27.9

MoS_2 nanodots @rGO[10]	0.8 mg.cm^{-2} CC + Nafion (0.4 mg MoS_2)	0.1 M Na_2SO_4 pH 10	-0.75	0.8	1[f]	2[d]
15%-wt N-coordinated MoS_2/C_3N_4[11]	[b] CP + Nafion	0.1 M Na_2SO_4	-0.5	[b]	1.2[g]	6.9
$MoS_2@C_3N_4$[11]	[b] CP + Nafion	0.1 M Na_2SO_4	-0.5	[b]	0.6[g]	3.8
MoS_2[11]	[b] CP + Nafion	0.1 M Na_2SO_4	-0.5	[b]	0.4	2.8
3%-wt 1T-MoS_2/g-C_3N_4[12]	0.7 mg.cm^{-2} GC + Nafion	0.1 M HCl pH 1	-0.3	1.2	1.8[g]	20.5
10%-wt 1T-$MoS_2@Ti_3C_2$[13]	0.7 mg.cm^{-2} GC + Nafion	0.1 M HCl pH 1	-0.3	1.2	1.8[h]	10.9
1T-MoS_2[13]	0.7 mg.cm^{-2} GC + Nafion	0.1 M HCl pH 1	-0.3	0.5	0.7	5.6
amorphous MoS_3[14]	0.2 mg.cm^{-2} CC	0.5 M Li_2SO_4	-0.3	0.61	3	12.8
MoS_2[14]	[b] CC	0.5 M Li_2SO_4	-0.3	[b]	0.61	3.9
$FeMo_3S_4$ nanorods[15]	0.2 mg.cm^{-2} CC + Nafion	0.5 M $LiClO_4$	-0.3	0.77	3.8	19.2

WE mater. : working electrode material; CC: carbon cloth ; BC: bacteriocelulose; CP: carbon paper;
[a] hydrothermally grown MoS_2 nanosheets on working electrode; [b] no loading indication; [c] calcinated MoS_2 coated bacteriocellulose fibers; loading 64 mg MoS_2.g^{-1}; [d] estimated on the figures; [e] not reported; [f] µmol.mg$_{MoS2@rGO}^{-1}$.h^{-1}; [g] µmol.mg$_{MoS2@C3N4}^{-1}$.h^{-1}; [h] µmol.mg$_{MoS2@Ti3C2}^{-1}$.h^{-1}.

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S2. Materials & Equipment

S2.1 Materials

Potassium persulfate, ammonium tetrathiomolybdate, ethanol, carbon disulfide, diethyl ether, concentrated aqueous hydrochloric acid (37%), dibasic potassium phosphate, potassium dihydrogen phosphate, hydroxylamine, sodium azide, salicylic acid, sodium nitroprusside dihydrate, sodium hydroxide, citric acid, diluted aqueous sodium hypochlorite solution (~10-15%), 4-(dimethylamino)benzaldehyde, hydrazine monohydrate, sodium nitrite, sulfanilamide (SULF) acidic

nitrite, n-(1-naphthyl)ethylenediamine (NED) were purchased from Aldrich. All reagents were ACS reagent grades and used as received. 0.1 M aqueous ammonia standard solution (NH_3, H4001-01) and alkaline ionic strength adjuster buffer (ISA, H4014-00) were obtained from Hanna Instruments. Milli-Q water (H_2O) was purified through a Millipore system. N_2 (99.998%) or Ar (99.9999%) were purchased from Air Products and used without additional purification.

S2.2 Equipment

The electrochemical studies were conducted on a Biologic SP-300 workstation. The electrochemical cell (BMM-EC 15mL water-based), glassy carbon working electrodes (GC 25/25/ CUSTOM, 1 mm or 3 mm) and Ag/AgCl/3M reference electrode (Ag/AgCl 70mm) were obtained from Redox-me. The flow of the feeding gas was controlled using Bronkhorst EL-FLOW mass-flow meters. The GC working electrodes were polished using a Struers LaboPol-1 polishing machine. The catalytic ink suspensions were homogenized in a Bandelin Sonorex sonication bath. The Ammonia selective electrode (HI4101/Hanna Instruments,) was connected to a Mettler Toledo (FiveEasy-FE20) pH meter. UV-Visible spectra were recorded on a Shimadzu UV-1800 UV spectrophotometer using the dual beam mode. Hydrogen was quantified using a Micro Gas Chromatograph S3000 (SRA Instruments) with a diamond LV Ms5A 14m module which was operated via the Soprane chrome interface

S3 Methods

S3.1 Preparation of amorphous molybdenum sulfide (*a*-MoS_x)[11]

1.3 g of ammonium tetrathiomolybdate $[MoS_4](NH_4)_2$ was firstly dissolved in 250 mL Milli-Q water to form a deep-red solution and then 2.7 g $K_2S_2O_8$ was added, the mixture was stirred in a closed round-bottomed flask in Ar for 3 hours resulting in the formation of a dark brown suspension. The product was collected and then washed by centrifugation with 3 x 15 mL Milli-Q water; 3 x 15 mL ethanol ; 3 x 15 mL carbon disulfide; 3 x 15 mL diethyl ether . The obtained black solid was then dried by natural evaporation under dried under an Ar stream and kept under an Ar atmosphere. The powder was stored under Ar and used for subsequent reactions without further purification.

S3.2 Direct reduction of dinitrogen (N_2)

S3.2.1 Working electrode preparation

The catalytic ink was typically prepared by sonicating 2 mg of *a*-MoS_x in 200 µL of isopropanol for 30 minutes to obtain a homogenous suspension. When the Nafion ionomer was incorporated, 1 µL of a commercial Nafion solution at 5% (wt/v) was added to the mixture prior sonication. The working electrodes were prepared by drop-casting 3 x 10 µL of the ink on a freshly polished GC electrode (1

cm^2) and dried in air to obtain a loading of 0.3 mg *α*-MoS_x per square centimeter. For WE coated only with Nafion, a similar protocol was followed without incorporating the *α*-MoS_x in the Nafion/isopropyl alcohol solution.

S3.2.2 Electrochemical measurements

Potential-controlled electrolysis were carried out in the three-electrode configuration using a single-compartmented cell (15 ml). A Pt wire isolated by a frit (P4) was used as counter electrode (CE), and an Ag/AgCl/3 M KCl electrode (0.18V vs RHE) as reference electrode (RE). Bare-, Nafion-, or *α*-MoS_x-coated GC were used as WE for the control and NRR experiments as summarized in Table S2.

The experiments were performed under ambient conditions (room temperature, atmospheric pressure), under a continuous flow of N_2 (Ar) calibrated at 10 mL/min. Two different electrolyte solutions were used: 0.1 M HCl (pH = 1) and 0.1 M potassium phosphate buffer (K_2HPO_4–KH_2PO_4 8.5–91.5%; pH = 5.8). The potentials reported in this work are converted to RHE scale using the following relation:

$$E\,(RHE) = E\,(applied) + E^0\,(Ag/AgCl/3M\ KCl) + 0.059 \times pH$$

with pH equals 1 and 5.8 for 0.1 M HCl and 0.1 M KPi buffer, respectively. During the course of the electrolysis the WE was poised at –0.3 V vs RHE. 1 mL samples of the electrolyte were taken at fixed times (0h, 2h, 4h…) and kept for the colorimetric determination of NH_3. The initial volume of electrolyte introduced in the cell was 10 mL for each experiments (controls and NRR). For selected experiments, the final ammonia concentration present in the electrolyte was also determined using an ammonia-selective electrode (see below).

S3.2.3 Control experiments

5 control conditions were investigated (Table S2). The evolution of the background ammonia concentration in the electrolyte was followed over time upon: A) continuously purging 10 mL of the selected electrolyte with N_2 (10 mL/min) for 20 minutes ("t = 0") to 25 hours (control series HCl-1/KPi-1 for 0.1 M HCl or 0.1 M KPi, respectively); B) running a CA under the standard conditions on bare GC for up to 25 h (control series HCl-2/KPi-2 for 0.1 M HCl or 0.1 M KPi, respectively); C) running a CA under the standard conditions on Nafion-coated GC for up to 25 h (control series HCl-3/KPi-3 for 0.1 M HCl or 0.1 M KPi, respectively); D) continuously purging 10 mL of the electrolyte with N_2 (10 mL/min) in the complete three-electrode configuration using 0.3 mg of Nafion coated *α*-MoS_x on GC, for 20 minutes ("t = 0") to 25 hours (control series HCl-4/KPi-4 for 0.1 M HCl or 0.1 M KPi, respectively); E) running a

CA under the standard conditions on 0.3 mg of Nafion coated *a*-MoS_x on GC for up to 25 h under Ar (series HCl-5/KPi-5 for 0.1 M HCl or 0.1 M KPi, respectively).

Table S2: Summary of the NRR and control groups tested. HCl-1/HCl-7: experiments run in 0.1 M HCl (pH = 1) electrolyte. KPi-1/KPi-7: experiments run in 0.1 M KPi buffer (pH = 5.8).

Series	**a-MoSx loading** (mg/cm^2)	**Additive and solvent**	**Potential applied** (V vs. RHE)	**Feeding gas**	**Experiment time**
HCl-1/KPi-1	-	-	-	N_2	>20 h
HCl-2/KPi-2	-	-	-0.3	N_2	>20 h
HCl-3/KPi-3	-	1 µL Naf + 200 µL IPA	-0.3	N_2	>20 h
HCl-4/KPi-4	0.3	1 µL Naf + 200 µL IPA	O.C.P.	N_2	>20 h
HCl-5/KPi-5	0.3	1 µL Naf + 200 µL IPA	-0.3	Ar	>20 h
HCl-6/KPi-6	0.3	200 µL IPA	-0.3	N_2	>20 h
HCl-7/KPi-7	0.3	1 µL Naf + 200 µL IPA	-0.3	N_2	>20 h

Naf: commercial 5% Nafion solution. IPA: isopropyl alcohol. OCP: open circuit potential (full setup without connecting the potentistat)

S3.2.4 Data correction

Small variations of the concentration of adventitious ammonia can significantly affect the absorbance of the samples in the salicylate assay, even at time zero (t = 0) where virtually no ammonia is expected (Figure S2). During the course of the electrolysis, the total volume of electrolyte decreases due to the successive sampling. This induces an overestimation of any variation of the apparent ammonia concentration between successive measurements. To eliminate this bias the data reported for the CA in the discussion are, thus, corrected as follow:

$$[NH_3]_{ic} = \frac{\left([NH_3]_1 \times Vs_1 + \cdots + [NH_3]_{i-1} \times Vs_{i-1} + [NH_3]_i \times (Vs_i + Vel_i)\right)}{(Vs_1 + \cdots + Vs_{i-1} + Vs_i + Vel_i)}$$

where $[NH_3]_{ic}$ is the corrected value of the concentration of the ammonia for sample *i*, $[NH_3]_i$ is the apparent concentration of ammonia measured for the sample *i,* Vs_i the volume of sample *i* and Vel_i the volume of the remaining electrolyte after taking the i^{th} aliquot.

S3.3 Reduction of other N-containing substrates (N_2H_4, NH_2OH, NO_2^-, NO_3^-, N_3^-)

S3.3.1 Reactivity screening

The instant response of the current density recorded after addition of the selected substrate (N_2H_4, NH_2OH, NO_3^-. NO_2^-, N_3^-) was used to identify reduction of the latter by *a*-MoS_x. In these initial tests a

thin film of *a*-MoS_x was deposited on a 3 mm diameter GC electrode which was used as WE. The latter was poised at -0.2 V *vs*. RHE in 2 mL of 0.1 M KPi electrolyte (pH = 5.8), and 100 µL of a 1 M solution of the selected substrate was added to the cathode compartment to yield a 50 mM solution of the substrate in the electrolyte. Subsequent additions of 100 µL aliquots of the substrate were then realized to confirmed the observed evolution of the current density at the WE. During these initial tests, only NH_2OH and N_3^- led to an immediate increase of current density (Figure S10).

The reactivity of *a*-MoS_x towards NH_2OH and $N_3^-$was then investigated in more details performing potential-controlled electrolysis in 10 mL of 0.1 M KPi electrolyte (pH = 5.8) containing 10 mM of the selected substrate, under a constant flow of Ar (10 mL/min). The electrolysis were conducted on bare *a*-MoS_x films (0.3 mg/cm^2) deposited on 1 cm^2 GC electrode using the same experimental set up as described in section S3.2.2.

S3.3.2 Electro-driven N_3^- reduction

Extended electrolysis of Ar-saturated 10 mM solutions of NaN_3 in KPi buffer (pH = 5.8) were conducted using pristine *a*-MoS_x films (0.3 mg/cm^2) deposited on 1 cm^2 GC electrode as WE using the same setup as described in section S3.2.2 The solution was first purged with Ar for 20 min before starting the electrolysis. Aliquots of the electrolyte were taken at defined times and the concentration of ammonia was determined using the salicylate assay.

Extended electrolysis of Ar-saturated 10 mM solutions of NaN_3 in KPi buffer (pH = 5.8) was also run using bare GC as WE (1 cm^2) following the same protocol as just described. Aliquots of the electrolyte were taken at defined times and the concentration of ammonia was determined using the salicylate assay.

Direct NaN_3 reaction on *a*-MoS_x was tested by soaking 0.3 mg of *a*-MoS_x in 10 mL of a 10 mM solution of NaN_3 in 0.1 M KPi buffer (pH = 5.8) at room temperature for 30 h. Aliquots of the electrolyte were taken at defined times and the concentration of ammonia was determined using the salicylate assay.

When NaN_3 reduction was coupled with direct H_2 detection, a custom-made cell (ca. 40 mL) was used to allow an optimal connection with the micro gas-chromatograph apparatus. In these experiments the WE consisted on a 1 cm^2 GC electrode coated with pristine *a*-MoS_x (0.3 mg). A Pt wire isolated by a frit (P4) was used as counter electrode (CE), and an Ag/AgCl/3 M KCl electrode (0.18V *vs*. RHE) as reference electrode (RE). 25 mL 0.1 M potassium phosphate buffer (pH = 5.8) was introduced in the cell and continuously purged with Ar at 5 mL/min and the composition of the head space was regularly sampled and analyzed with the micro gas-chromatograph. When the electrolyte was saturated with Ar, the WE was poised at -0.2 V (t = 0) and kept at constant potential for 6h30. At t = 2h30, a solution of 1 M of NaN_3 in 0.1 M KPi (pH = 5.8) was added (250 µL) to reach 10 mM of NaN_3 in the cathode

compartment. A sample of 1 mL of the electrolyte was taken at t = 4 h30 to provide an intermediate measurement of the concentration of ammonia and hydrazine produced during the electrolysis.

S4. Quantification of NH_3, NO_2^-, NO_3^- and N_2H_4

S4.1 Ammonia determination

S4.1.1 Colorimetric titration of ammonia (NH_3)

Method

For this assay we used the method proposed by Bower and Holm-Hansen[22]. This approach relies on the spectrophotometric quantification of a quinone-imine derivative, that results from the reaction of chloramine on salicylic acid in alkaline conditions, which exhibits a specific absorption band centered around 650 nm. Importantly the reaction time and overall procedure of the assays were optimized for our specific conditions to ensure reliable measurements (see details below). For each sample of electrolyte (1 mL) collected during the course of the NRR and control experiments, three independent measurements were done. The concentration of ammonia reported for each sample corresponds to the mean value calculated form these measurements.

Reagents preparation and storage

The assay requires the preparation of three reagents.

Reagent ①: 9.5 g (68.8 mmol) of salicylic acid, 2.75 g (68.8 mmol) of sodium hydroxide and 7 mg (0.023 mmol) of sodium nitroprusside dihydrate are dissolved in 25 mL of water. This solution is stable at 5 °C, in the dark, for up to 3 months.

Reagent ②: 6.53 g (34.0 mmol) of citric acid and 5.85 g (146.3 mmol) of sodium hydroxide are dissolved in 100 mL of water. This solution is stable and can be stored several months without degradation.

Reagent ③: 0.5 mL of sodium hypochlorite solution (Commercial bleach∼10-15% NaOCl) is added to 9.5 mL of ②. This solution must be prepared freshly, just before use.

Assays conditions

a) 0.1 M HCl electrolyte

The samples (1 mL) collected during the course of the control or NRR studies were split into 3 fractions of 0.3 mL, which were treated separately. Each fraction was first neutralized with the addition of 0.3 mL of aqueous 0.1 M NaOH. Next 80 μL of reagent ① was added and the mixture was homogenized,

before the addition of 135 μL of reagent ③. The resulting samples were reacted in dark for 90 minutes before measuring the absorbance at 650 nm using UV-Visible spectroscopy.

b) 0.1 M KPi buffer

The samples (1 mL) collected during the course of the control or NRR studies were diluted by the addition 0.5 mL mQ water, then the solutions were split into 3 fractions of 0.5 mL, which were treated separately. Each fraction was directly mixed with 100 μL of reagent ① followed by the addition of 200 μL of reagent ③. The resulting samples were reacted in dark for 90 minutes before measuring the absorbance at 650 nm using UV-Visible spectroscopy.

UV-Vis measurements

The spectra were recorded between 500 nm and 1000 nm using cuvettes of 1 cm of optical pathway. The spectrophotometer was used in dual beam mode using mQ water as reference. When necessary the baseline was corrected at 1000 nm to adjust the absorbance to ±0.0010 before recording the spectra. For the reduction of N_3^-, when the concentration of ammonia exceeded 0.5 mM the samples were diluted with mQ water to keep the value of the absorbance at 650 nm below 2. In the latter case the dilution facor was then considered to calculate the initial concentration of ammonia in the sample. For an accurate analysis of the assays, the time required for reaching a stable reading of the absorption at 650 nm (complete conversion) was investigated. As shown on figure S1a the absorbance of samples in HCl evolves greatly up to 40 min before reaching a stable plateau. In the same conditions the assay executed in 0.1 M KPi reaches a stable reading much faster. In the following assays a reaction time of 90 min was selected for all the samples.

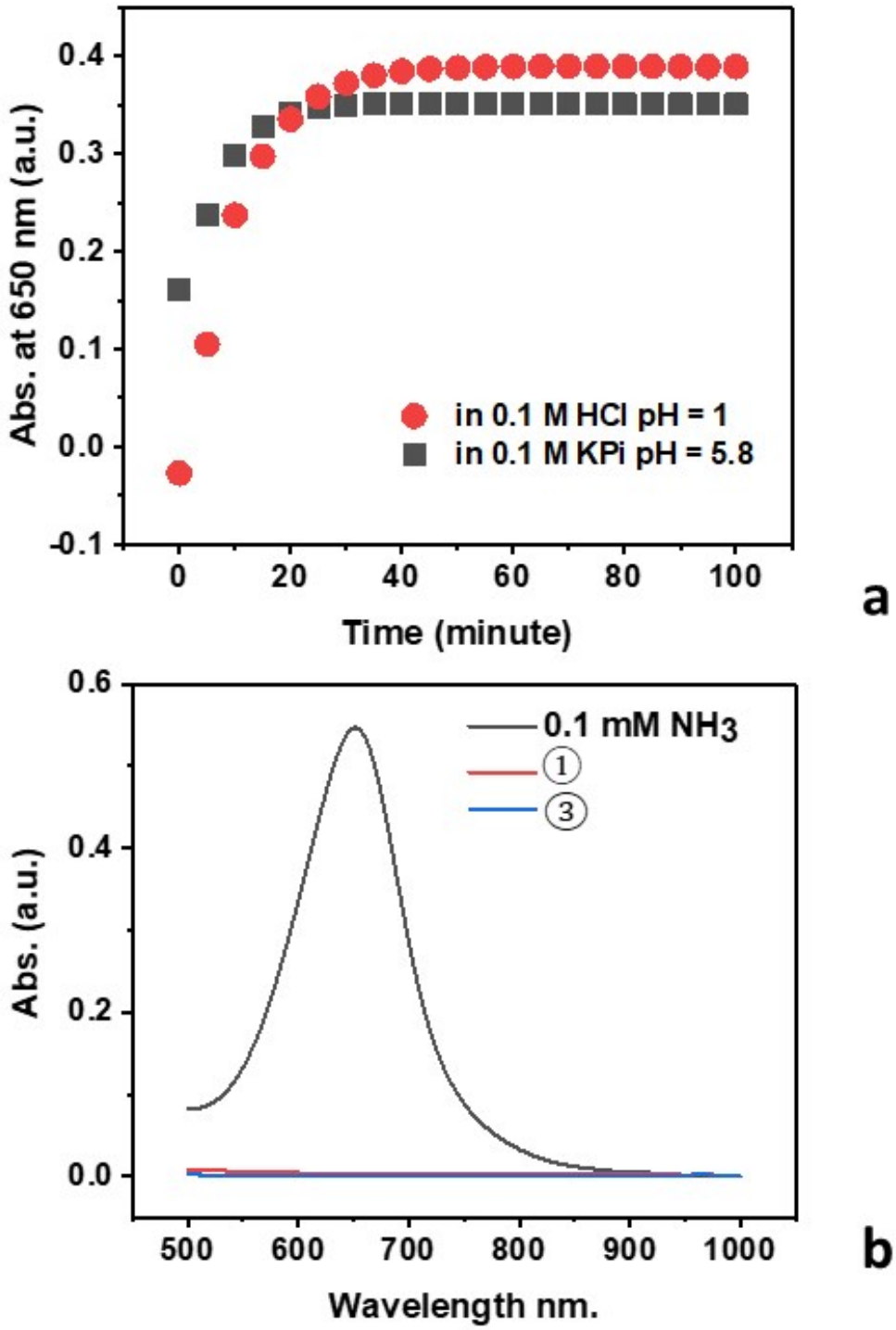


Figure S1: a) Evolution of the absorbance at 650 nm recorded for a representative sample prepared by treating 0.3 mL of a solution of 0.02 mM NH_3 in 0.1 M HCl and 0.1 M KPi as described above. The absorbance was recorded every 5 min. b) UV-Vis spectra of: a solution of 0.1 mM ammonia in 0.1 M HCl treated accordingly to the procedure described above after 90 min of reaction time (black curve), the reagent ① (red curve), and reagent ③ (blue curve).

Calibration curves and quantification of the ammonia concentration

To ensure accurate measurements, the limit of detection and linearity range of the assay in our specific conditions were established from known dilutions of an aqueous ammonia standard solution in 0.1 M HCl and 0.1 M KPi (Figure S3).

A good linearity (R^2 = 0.994/0.999) was obtained for concentrations of ammonia comprised between 0.001 mM and 0.2 mM. We note that Bower and Holm-Hansen report a lower limit of detection of about one order of magnitude lower than in our test (0.0003 mM). We attribute this difference to the presence of 0.03 mM – 0.1 mM (0.02 mM – 0.04 mM) of NH_3 as a trace contaminant in the 0.1 M HCl (0.1 M KPi) electrolyte, thus, limiting the precision of the colorimetric method in our conditions.

In order to ensure an accurate determination of the ammonia concentration present in the samples collected during NRR (N_3RR) and control experiments, a fresh calibration curve was established for each individual series of measurements (using the appropriate electrolyte). The calibration curves were built from at least three experimental points, each of which determined from three independent measurements. In the case of NRR (N_3RR) and control studies, the individual calibration curves were built for a limited range of concentrations: 0.1 mM, 0.05 mM and “0” mM (or 1 mM; 0.5 mM; “0” mM for N_3RR).

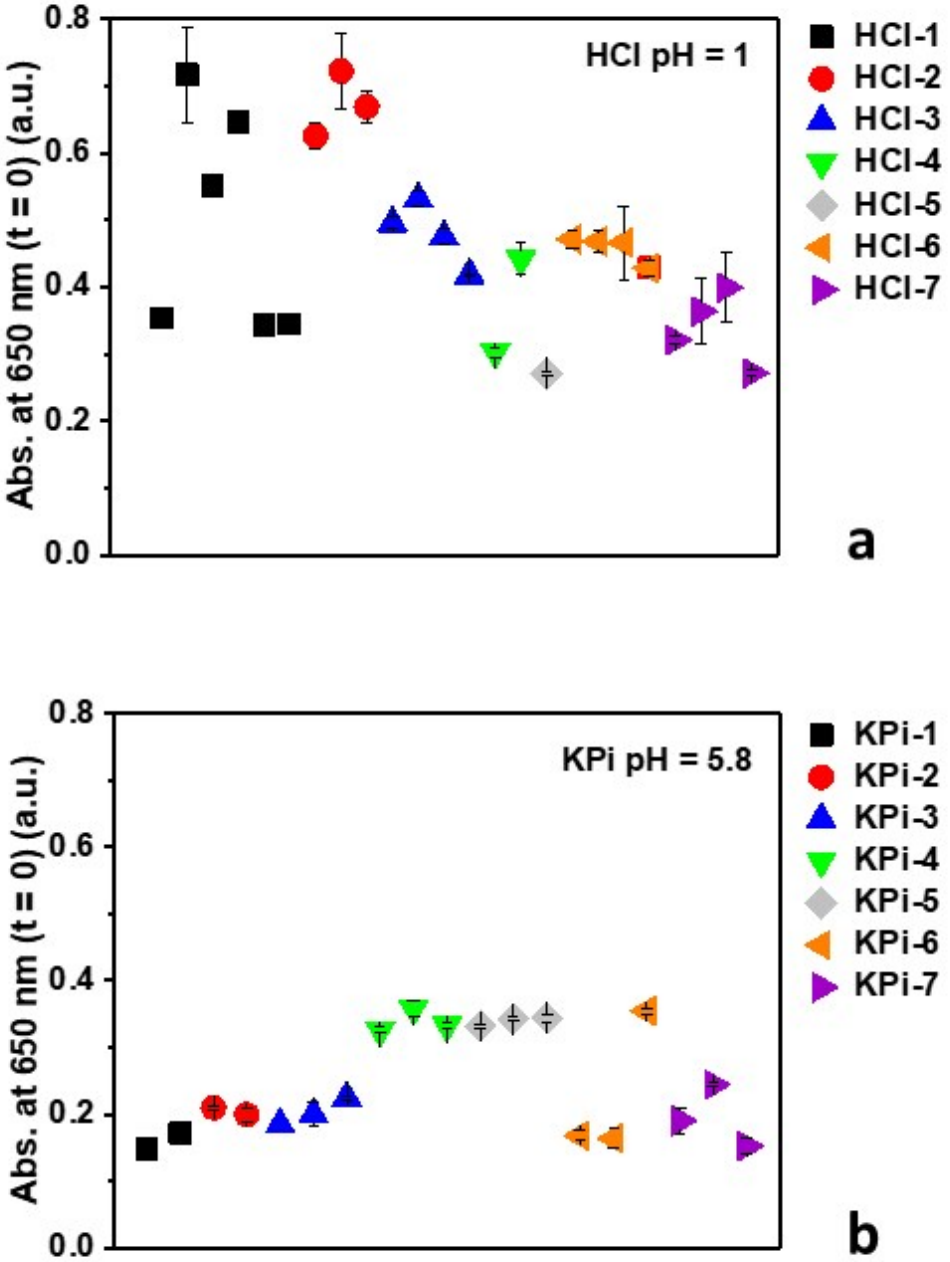


Figure S2: Absorption at 650 nm measured with the salicylate assay for samples from controls and experimental series at time zero in 0.1 M HCl (a) and 0.1 M KPi (b). Cf. to Table S2 and section S3.2.3 for the description of the experimental conditions tested in each series.

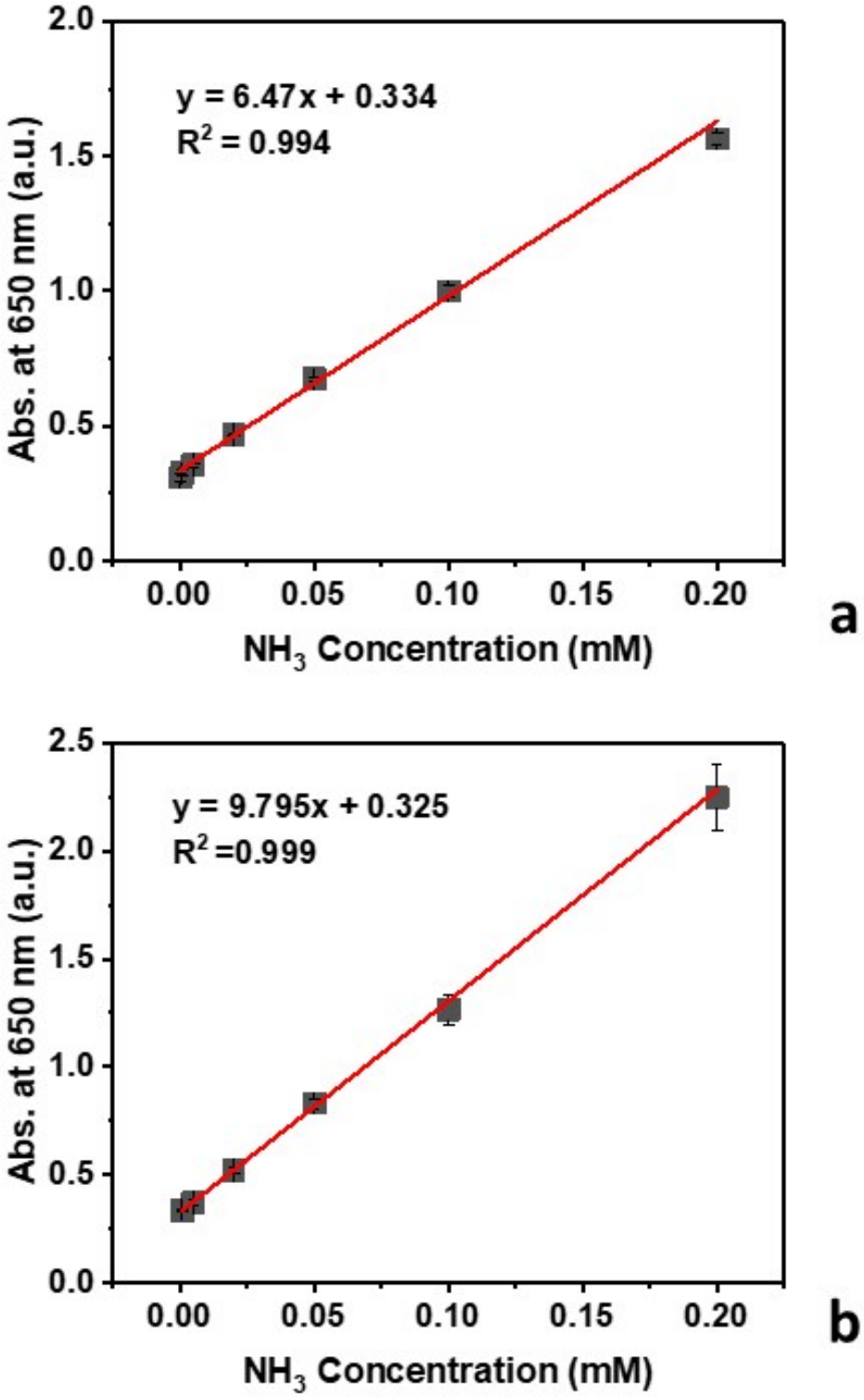


Figure S3: Typical calibration curves obtained for the salicylate assay in 0.1 M HCl (a) and 0.1 M KPi (b) using known dilution of a standard NH_3 solution (dilution to: 0.001 mM, 0.005 mM, 0.05 mM, 0.1 mM and 0.2 mM).

S4.1.2 Potentiometric titration of ammonia (Ammonium selective electrode)

Method

The use of an ammonia selective electrode provided an independent method to cross-check the salicylate assays for selected NRR/N_3RR and control experiments. The initial and final concentrations of ammonia present in the electrolytes were tested. Each measurement corresponds to a single readout of the potential of the electrode after full equilibration in the samples of interest. Before each series of measurements, a calibration curve was established by dilution of an aqueous 0.1 M standard ammonia solution in the appropriate electrolyte (see below for the detailed compositions).

Note: this method is very sensitive, so any movement of the electrode should be strictly avoided during the measurements. Regular controls of the integrity of the membrane is necessary and the latter must be renewed at the first sign of aging (pinholes, scratches…)

Assay conditions

For the measurements, the electrode is equilibrated in the sample of interest at room temperature, under gentle stirring (100 r/s), until a stable reading is observed. Between two subsequent measurements, the electrode is well rinsed with mQ water and carefully dried with a soft tissue.

a) 0.1 M HCl electolyte

The samples (0.1 M HCl, 1 mL) are neutralized by addition of an equimolar solution of NaOH in MiliQ water (0.1 M NaOH, 1 mL). The commercial ionic strength adjustment buffer (40 µL, HI4014-00) is added in portion of 2% of the total volume of the sample. The mixture is well stirred before measurement.

b) 0.1 M KPi buffer

The commercial ionic strength adjustment buffer (20 µL, HI4014-00) is added in portion of 2% of the samples (0.1 M KPi, 1 mL). The mixture is well stirred before measurement.

Calibration curves and quantification of the ammonia concentration

To ensure accurate measurements, the limit of detection and linearity range of the assay were established in our specific conditions from known dilutions of an aqueous ammonia standard solution in 0.1 M HCl, and 0.1 M KPi buffer (Figure S4).

A good linearity (R^2 = 0.998/0.999) was obtained for concentrations of ammonia comprised between 0.002 mM and 5 mM in 0.1M HCl; and between 2 mM and 100 mM in 0.1 M KPi.

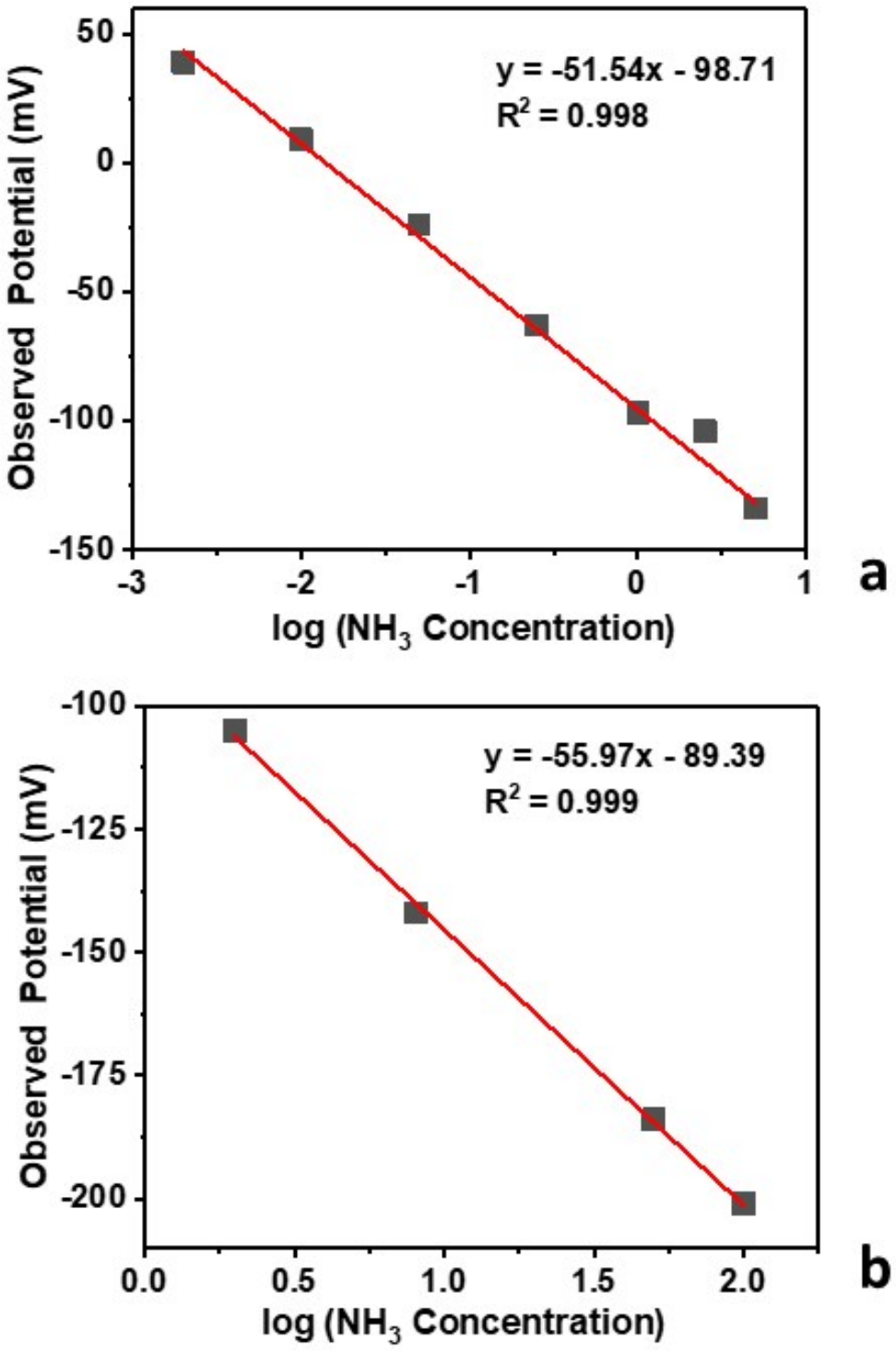


Figure S4: Calibration curves of the ammonia selective electrode using 0.002 mM, 0.01 mM, 0.05 mM, 0.25 mM, 1 mM, 2.5 mM, and 5 mM ammonia standards prepared in 0.1 mM HCl (a); and using 2 mM, 8 mM, 50 mM, and 100 mM ammonia standards prepared in 0.1 M KPi (b)

S4.2 Colorimetric titration of hydrazine (N_2H_4)

Method

The determination of the concentration of hydrazine was done following the approach introduced by Watt and Chrisp.[3] This procedure is based on the quantification of a yellow dye resulting from acid catalyzed condensation of hydrazine with 4-(Dimethylamino)benzaldehyde and exhibiting a specific absorption band centered at 455 nm. The yellow color develops immediately and the absorbance measured at 455 nm stabilizes after 10 min. It remains stable for up to 12 h.[33]

For this assay, each sample (0.5 mL) collected during the electrolysis was diluted by 1 mL of a 1 M HCl solution, and divided in three samples of 0.5 mL which are then treated independently. The concentration of hydrazine reported for each sample corresponds to the mean value calculated form these measurements.

Reagents preparation and storage

The color reagent was prepared by adding 0.2 g 4-(Dimethylamino)benzaldehyde (1.34 mmol) and 1 mL concentrated hydrochloric acid (37%) into 10 mL Ethanol.

Assay conditions

0.1 M HCl electrolyte/ 0.1 M KPi buffer

The sample (0.5 mL) collected during the electrolysis are diluted by 1 mL 1 M HCl solution, then divided into three parts. Each 0.5 mL sample is mixed with 0.5 mL of the color reagent then reacted for 20 min before measuring the absorbance at 455 nm using UV-Visible spectroscopy.

Calibration curves and quantification of the ammonia concentration

To ensure accurate measurements, the limit of detection and linearity range of the assay in our specific conditions were established from known dilutions of hydrazine hydrate standard solution in 0.1 M KPi (Figure S5). A good linearity (R^2 = 0.997) was obtained for concentrations of ammonia comprised between 0.005 mM and 0.5 mM.

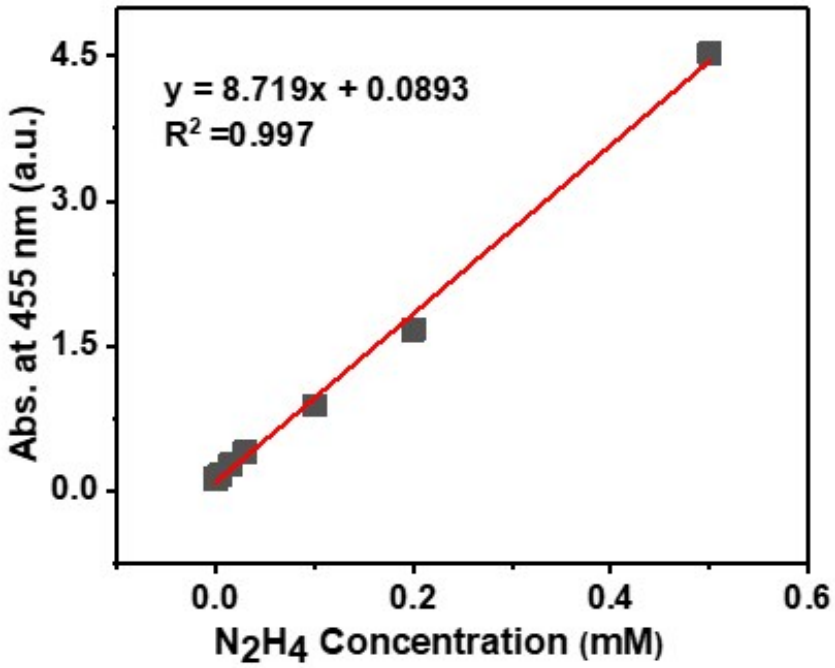


Figure S5: Calibration curve for the determination the concentration of hydrazine using Watt and Chrisp method in 0.1 M KPi, using 0.005 mM, 0.015 mM, 0.03 mM, 0.1 mM, 0.2 mM, and 0.5 mM hydrazine standards in 0.1 M KPi.

S4.3 Colorimetric titration of nitrite and nitrate (NO_2^-, NO_3^-)

Method

The determination of the concentration of adventitious NOx contaminants possibly present in the electrolyte, and susceptible to lead to the accumulation of ammonia under reductive conditions, was investigated via the method proposed by Griess *and coll*.[44] The procedure is based on the spectrophotometric quantification of an azo dye formed upon reaction of the *in situ* generated diazonium salt of the sulfanilamide (SULF) on n-(1-naphthyl)ethylenediamine (NED), which exhibits a specific absorption band centered at 540 nm. The nitrate (NO_3^-) is firstly reduced to nitrite (NO_2^-) by vanadium (III). Importantly we optimized the reaction time protocol to increase the sensitivity of the method for our specific conditions and ensure reliable measurements. (see details below). For each sample, three independent measurements were done. The concentration reported for each sample corresponds to the mean value calculated form these measurements.

Reagents preparation and storage

SULF (2% w/v in 5% HCl): 10 mL of concentrated HCl solution (37%) are firstly diluted in 64 mL of H_2O to obtain a 5% HCl solution. 1.48 g (8.6 mmol) of sulfanilamide are dissolved in the previous HCl solution. This solution is stable at 5 °C, in the dark, for up to several months.

NED (0.1% w/v in H_2O): 30 mg of n-(1-naphthyl)ethylenediamine (0.1 mmol) are dissolved in 30 mL H_2O. This solution is stable at 5 °C, in the dark, for up to several months.

Vanadium solution: 40 mg (0.2 mmol) of vanadium (III) chloride are dissolved in 5 mL 1M HCl solution. This solution is stable at 5 °C, in the dark, for less than 2 weeks.

Assay conditions

0.1 M HCl electrolyte/ 0.1 M KPi buffer

200 µL of the electrolyte is mixed with 200 µL of 1M HCl solution (or 200 µL of the Vanadium solution for NO_3^- titration, in which case the mixture is reacted 20 minutes before the next step). 100 µL SULF is then added followed by the addition of 100 µL of NED. The resulting samples are reacted in dark for 60 minutes before measuring the absorbance at 540 nm using UV-Visible spectroscopy.

Calibration curves and quantification of the NO_x^- concentration

To ensure accurate measurements, the limit of detection and linearity range of the assay in our specific conditions were established from known dilutions of $NaNO_2$ / KNO_3 standard solutions in 0.1 M KPi (Figure S6).

Good linearity (R^2 = 0.997) is observed for nitrite concentrations between 0.001 mM and 0.1 mM (Figure S6a). In the case of nitrate (Figure S6b*)* a linear region (R^2 = 0.997) is obtained for concentrations between 0.001 mM and 0.1 mM.

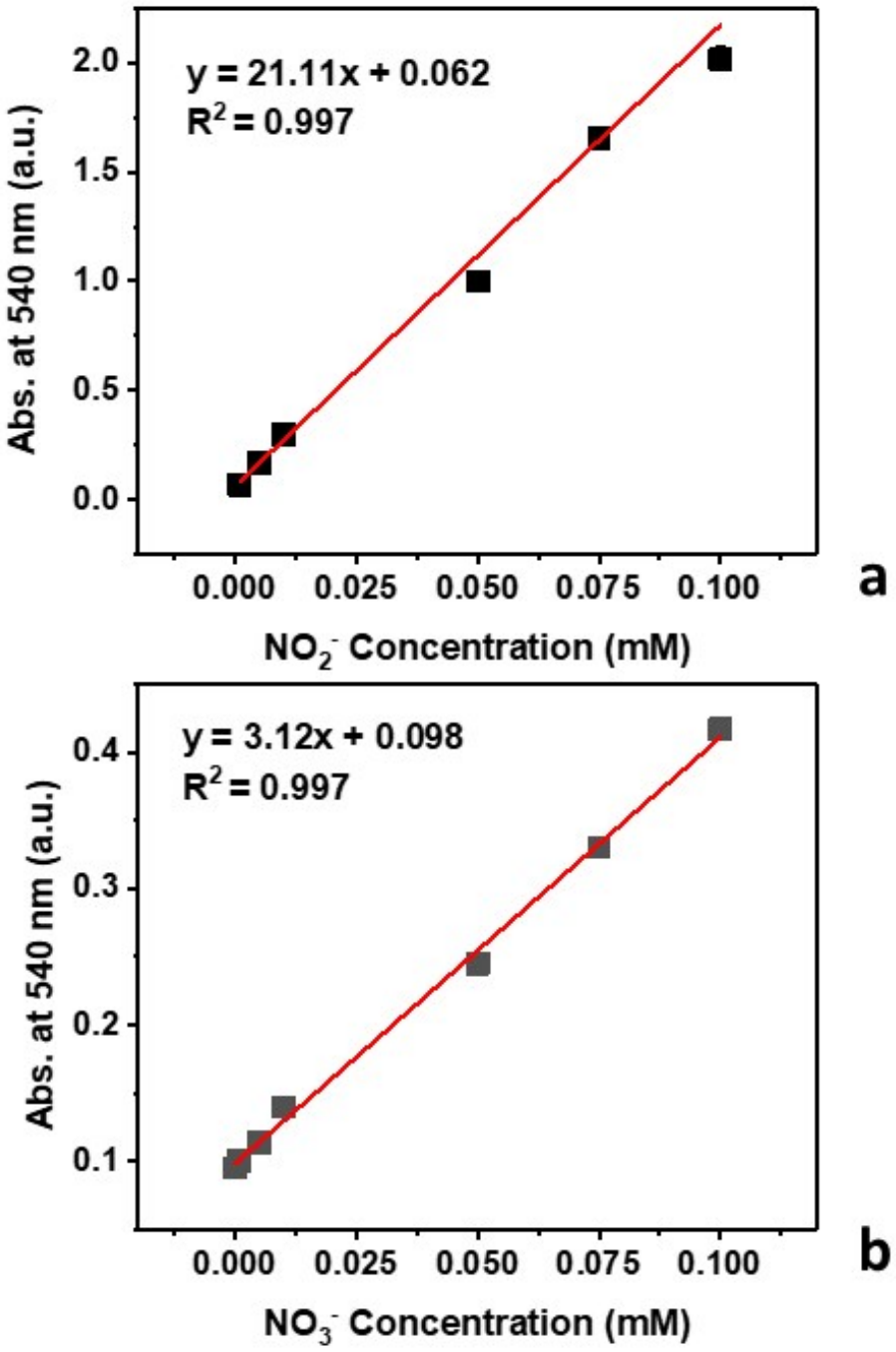


Figure S6: Typical calibration curves used for the determination of the concentration of nitrite (a) and nitrate (b) ions using the Griess assay.

S5 Results & Data analysis

Table S3: Dispersion of the variation of the background ammonia concentrations measured for control series HCl-1/KPi-1 – HCl-5/KPi-5 with respect to t = 0. Bin size: 2 µM, the values indicated in red correspond to punctual variation higher than 10 µM with respect to time zero.

HCl-1 – HCl-5			KPi-1 – KPi-5		
Bin Center	Count	Cumulative Count	Bin Center	Count	Cumulative Count
-9	1	1	-17	1	1
-7	1	2	-15	0	1
-5	3	5	-13	0	1
-3	3	8	-11	0	1
-1	11	19	-9	1	2
1	7	26	-7	2	4
3	5	31	-5	2	6
5	6	37	-3	7	13
7	3	40	-1	3	16
9	2	42	1	8	24
11	2	44	3	5	29
			5	1	30

Table S4: Comparison the concentration of NH_3 measured using the salicylate method (SM) and ion selective electrode (ISE) for azide reduction (N_3RR).

Time (h)	SM Concentration (mM)	ISE Concentration (mM)
0	0.00	0.00
2	1.06	1.39
4.5	1.78	2.47
19.5	2.91	2.70
21.5	2.97	3.09

Table S5: Influence of KPi concentration on Griess Assay. 0.001mM NO_3^- samples were prepared in different KPi buffer with concentration 0, 0.1, 0.2 M.

Concentration of KPi (M)	Abs. at 540 nm (a.u.)	s
0	0.10701	0.01167
0.1	0.12039	0.01936
0.2	0.12254	0.01129

s standard deviation (*vide infra*)

The concentration of KPi buffer has a limited influence on the absorbance at 540 nm for the Griess assay between 0. M and 0.2 M.

Table S6: Evolution of the concertation of NO_2^- and NO_3^- species measured in 0.1 M KPi buffer (pH = 5.8) under a constant flow of N_2 (purity 99.998%, 10 mL/min).

Reference	1 µM NO_2^- in 0.1M KPi	s	1 µM NO_3^- in 0.1M KPi	s
Abs. (a.u.) @ $\lambda_{540\ mn}$	0.07	0.03	0.12	0.02
Time (h)	Abs. at 540 nm (a.u.) NO_2^-	s	Abs. at 540 nm (a.u.) NO_3^-	s
0	0.03	0.01	0.095	0.008
2	0.03	0.01	0.105	0.006
4	0.07	0.02	0.09	0.01
6	0.06	0.05	0.108	0.004
24	0.06	0.03	0.0801	0.0003

s: standard deviation

$$s = \sqrt{\frac{\sum_{i}^{n}(x_i - \bar{x})^2}{(n-1)}}$$

Table S7: N_2H_4 concentration reached at the end of potential-controlled electrolysis (–0.2 V *vs.* RHE) of 10 mM solution of sodium azide in argon saturated 0.1 M KPi run on pristine *a*-MoS_x-coated electrodes.

Series	Concentration of N_2H_4 (mM)	Time (h)
N_3RR-3-a	0.019	21
N_3RR-3-b	0.012	6
N_3RR-3-c	0.006	4

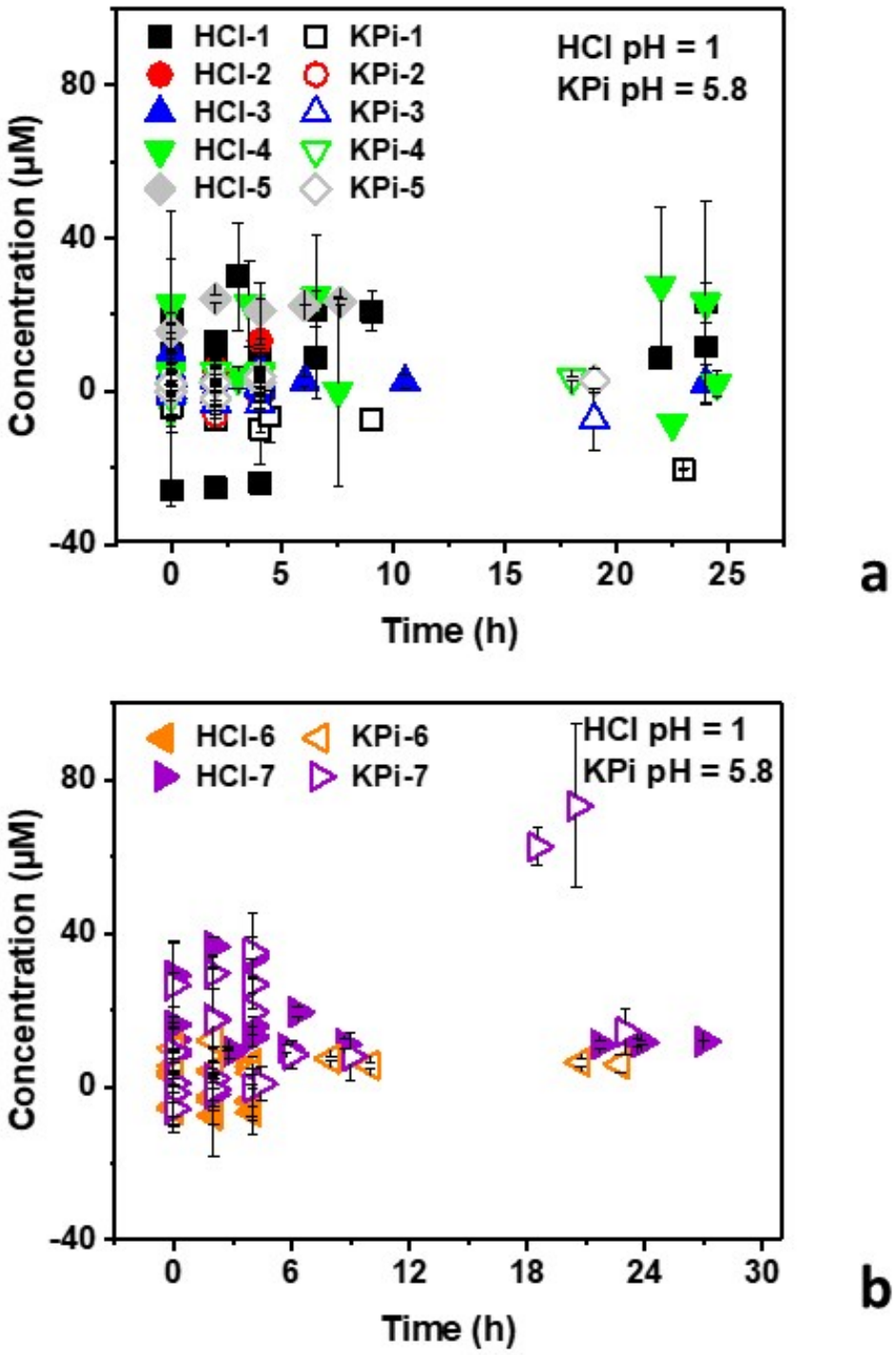
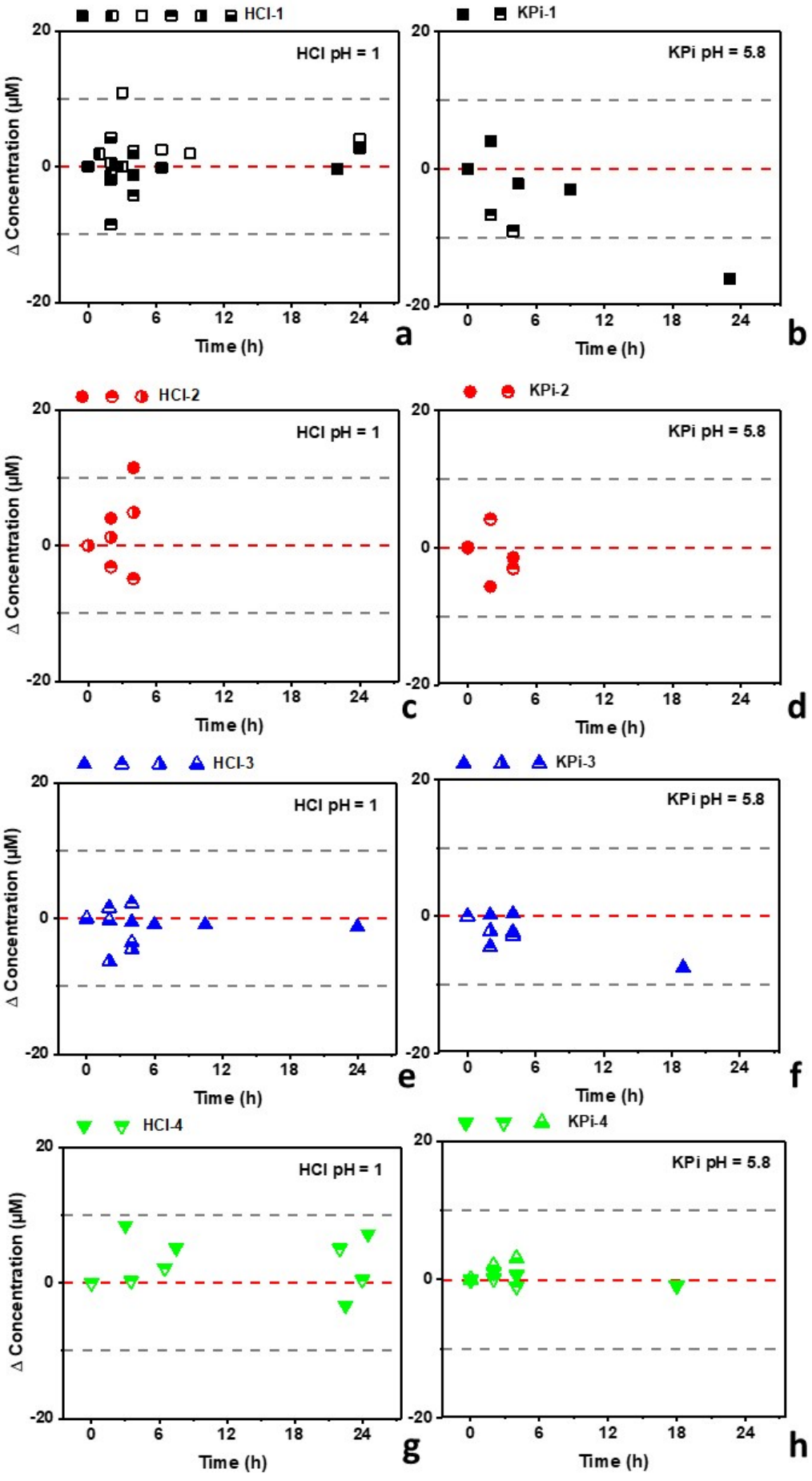


Figure S7: Apparent concentration of ammonia measured for the control groups (a) and experimental groups (b) over time. The values of the concentrations reported between successive samples are corrected according to the equation given in section S3.2.4. The concentrations reported here are the values obtained directly using the linear relationship determined form the individual calibration curve established for each series. Negatives values are due to a lower background ammonia concentration initially present in the experimental samples compared to the electrolyte used for establishing the calibration individual calibration curve.


HCl-1
HCl pH = 1
KPi-1
KPi pH = 5.8
HCl-2
HCl pH = 1
KPi-2
KPi pH = 5.8
HCl-3
HCl pH = 1
KPi-3
KPi pH = 5.8
HCl-4
HCl pH = 1
KPi-4
KPi pH = 5.8
Δ Concentration (μM)
Time (h)
20
0
-20
0
6
12
18
24
a
b
c
d
e
f
g
h

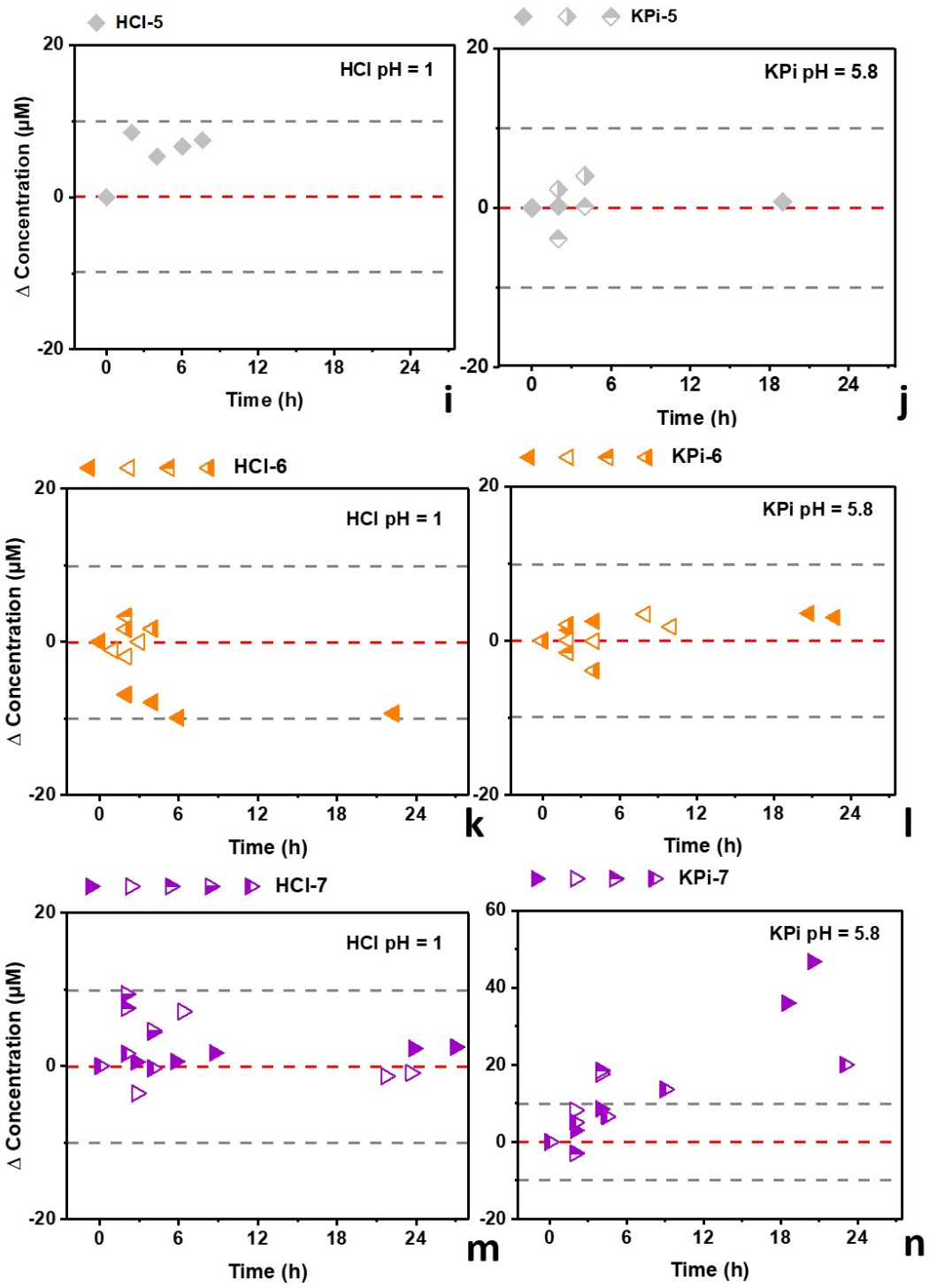


Figure S8: Evolution of the apparent NH_3 concentration over time for each individual control (a-j) and NRR experiments (k-n). The distinct filling patterns within each series indicates measurements executed on samples collected from independent runs.

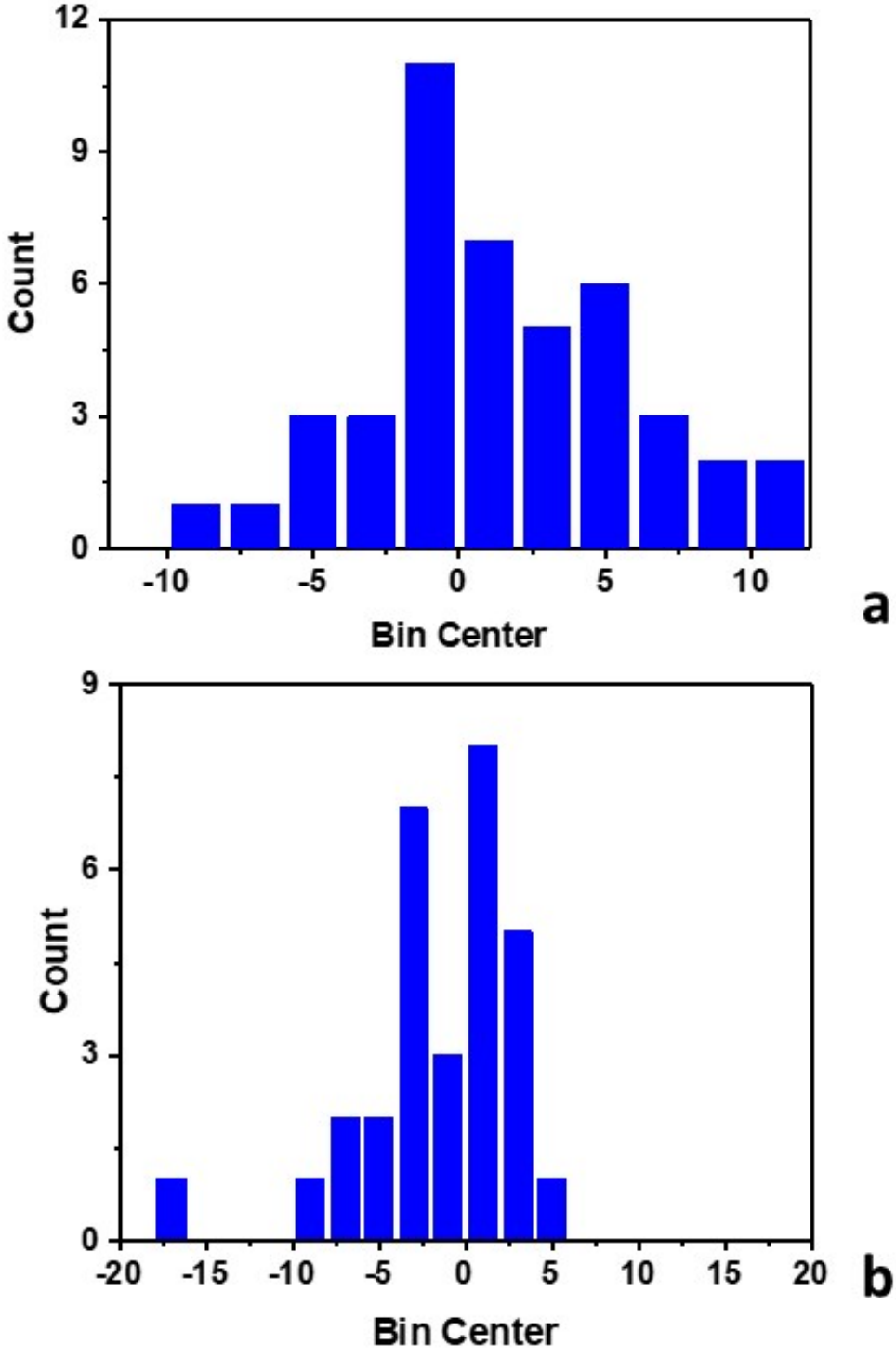


Figure S9: Frequency distribution histograms of the apparent concentration measured with the salicylate assay for samples from controls series in 0.1 M HCl (a) and 0.1 M KPi (b) electrolytes.

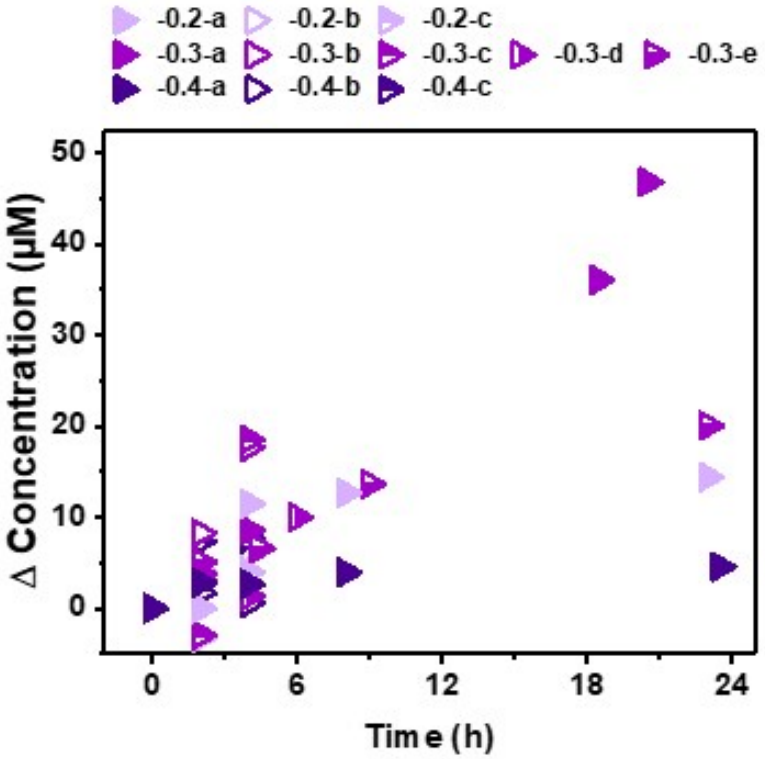


Figure S10: Evolution of the apparent concentration of NH_3 in the electrolyte during potential-controlled electrolysis in N_2-saturated 0.1 M KPi buffer (pH = 5.8) using Nafion-coated *a*-MoS_x thin-films deposited on glassy carbon electrodes (KPi-7). The working electrode was polarized at –0.2 V, –0.3 V, or –0.4 V *vs*. RHE. The distinct filling patterns within each series indicates measurements executed on samples collected from independent runs.

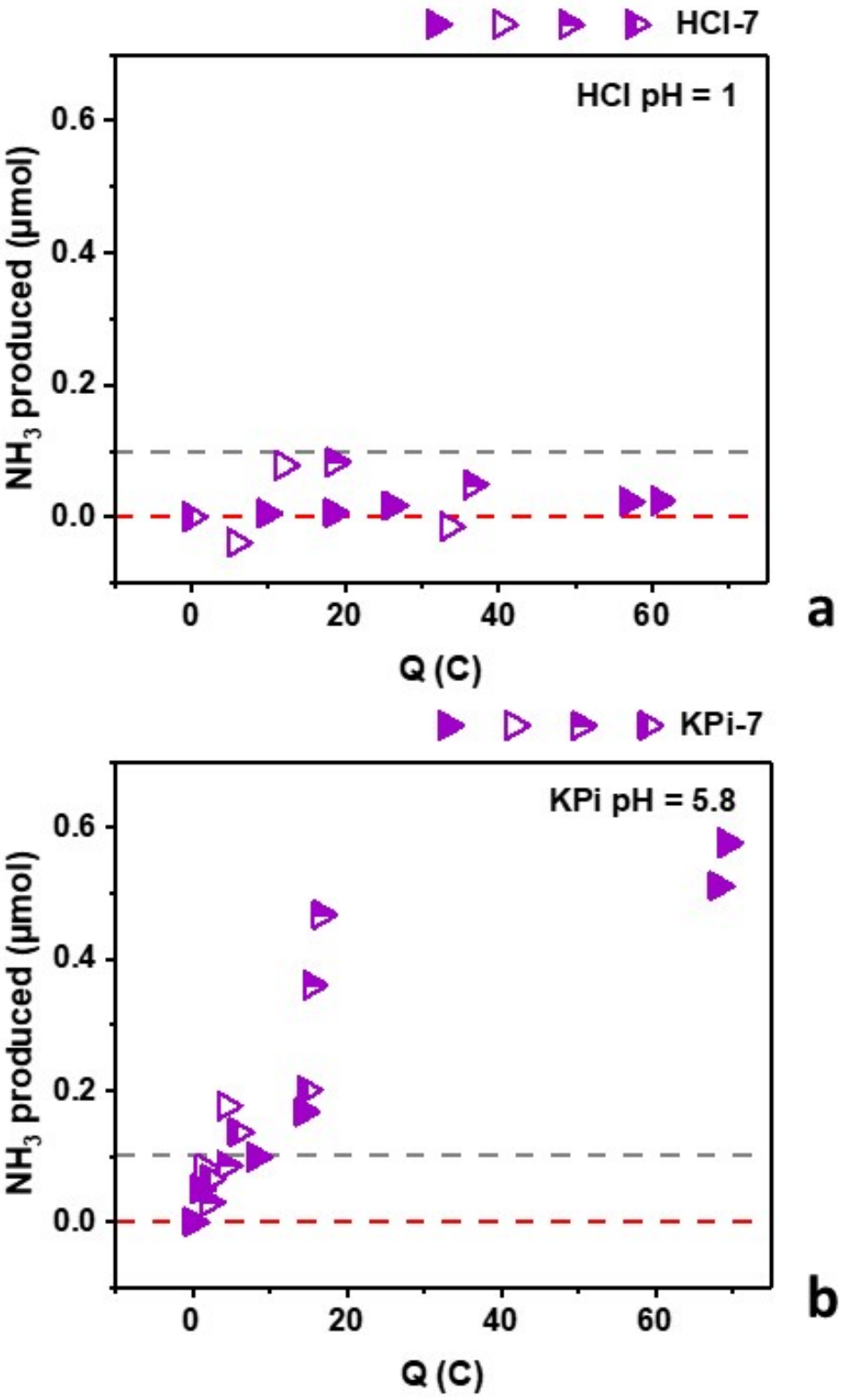


Figure S11: Evolution of the quantity of ammonia measured in the electrolyte as a function of the total charge passed during chronoamperometry measurements recorded on thin films of *a*-MoS_x incorporating Nafion, in 0.1 M HCl (a) and 0.1 M KPi (b) buffer electrolyte. The working electrode was polarized –0.3 V *vs*. RHE. The distinct filling patterns within each series indicates measurements executed on samples collected from independent runs.

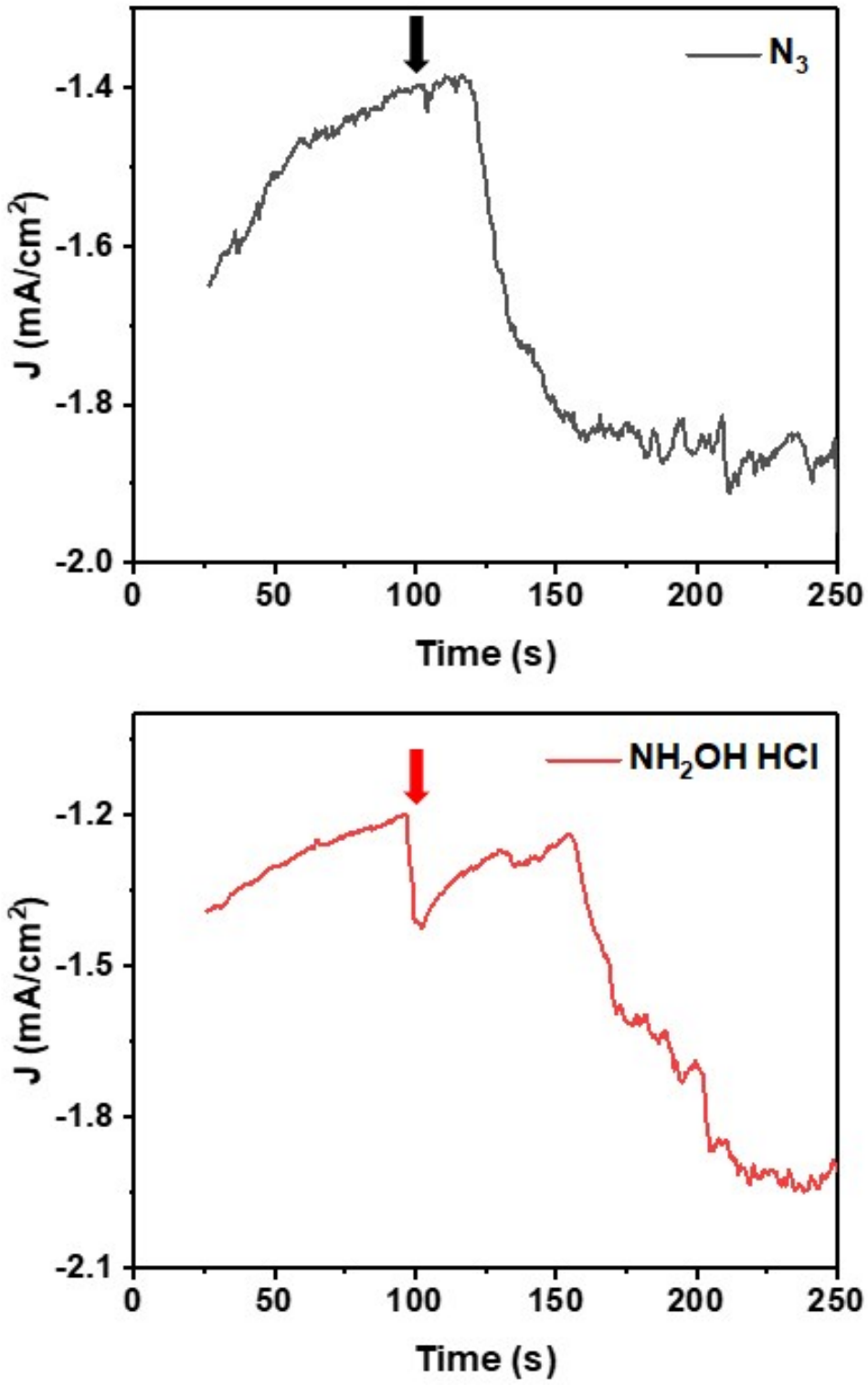


Figure S12: Evolution of the current density recorded during the potential-controlled electrolysis of 2 mL 0.1 M KPi (pH = 5.8), run at –0.2 V *vs*. RHE on a thin film of *a*-MoS_x. The arrow indicates the addition of 20 µL of a 1 M sodium azide (black curve, t = 100 s) solution or 1 M hydroxylamine hydrochloride solution (red curve, t = 100 s).

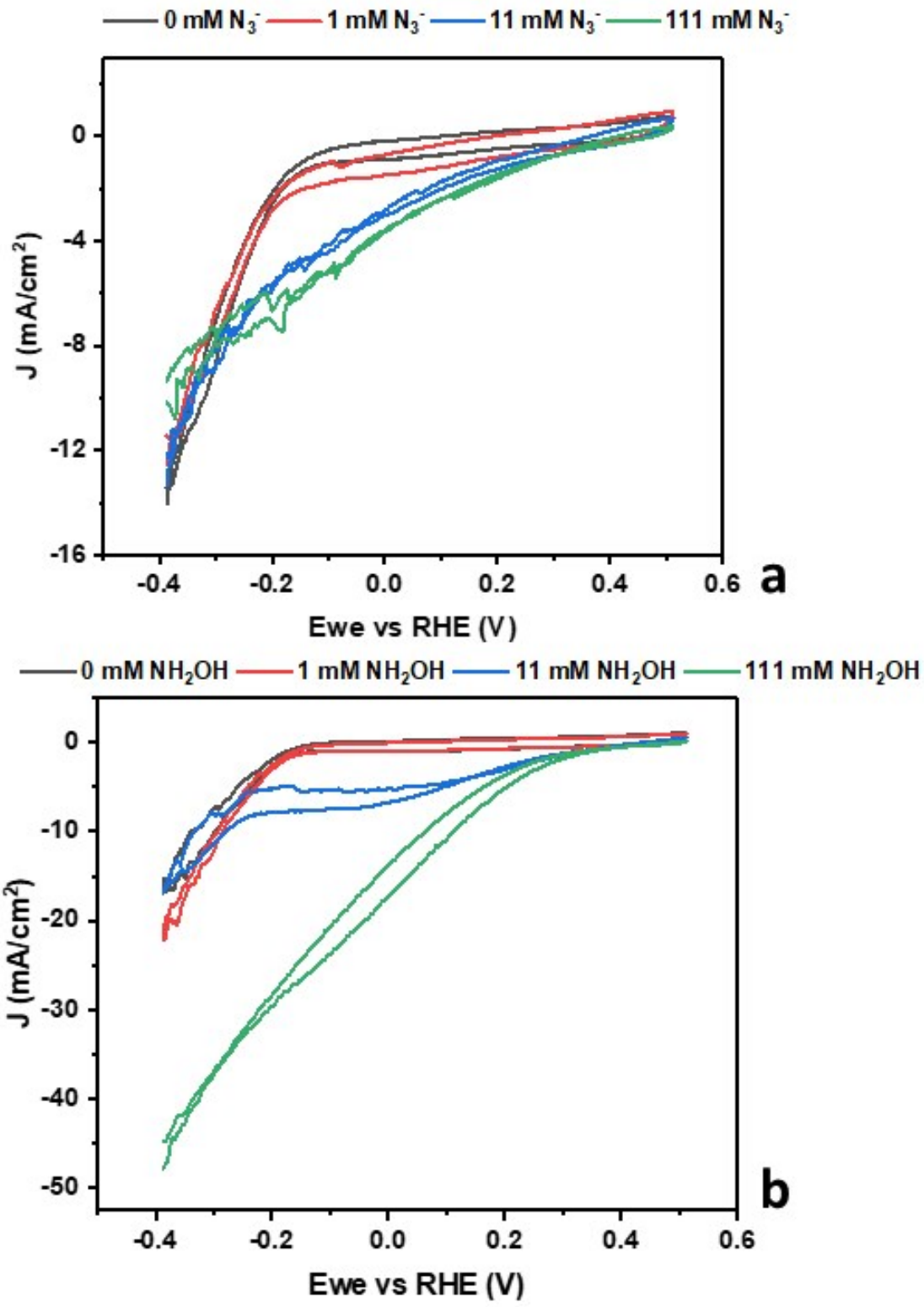


Figure S13: cyclic voltammograms recorded from -0.4 V to 0.6 V *vs*. RHE, with an increasing concentration of sodium azide (a) or hydroxylamine (b) substrates in 0.1 M KPi (pH = 5.8). Scan rate 2 mV/s.

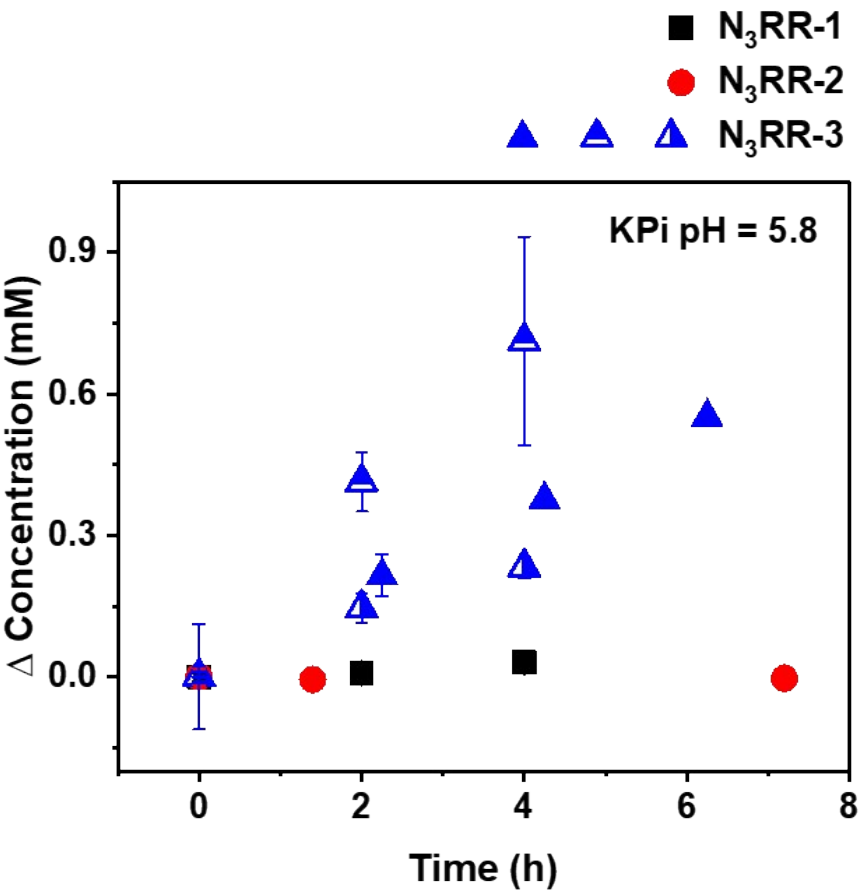


Figure S14: Evolution of the apparent concentration of NH_3 measured during potential-controlled electrolysis (–0.2 V *vs.* RHE) of a 10 mM solution of sodium azide in argon saturated 0.1 M KPi over bare glassy carbon (series N_3RR-1) or *a*-MoS_x coated (N_3RR-3) electrodes. Series N_3RR-2 shows the evolution of the ammonia concentration measured in a 10 mM solution of sodium azide in 0.1 M KPi over time, in presence of an *a*-MoS_x coated electrode in the absence of an applied bias (open circuit potential). The distinct filling patterns within series indicates measurements executed on samples collected from independent runs.

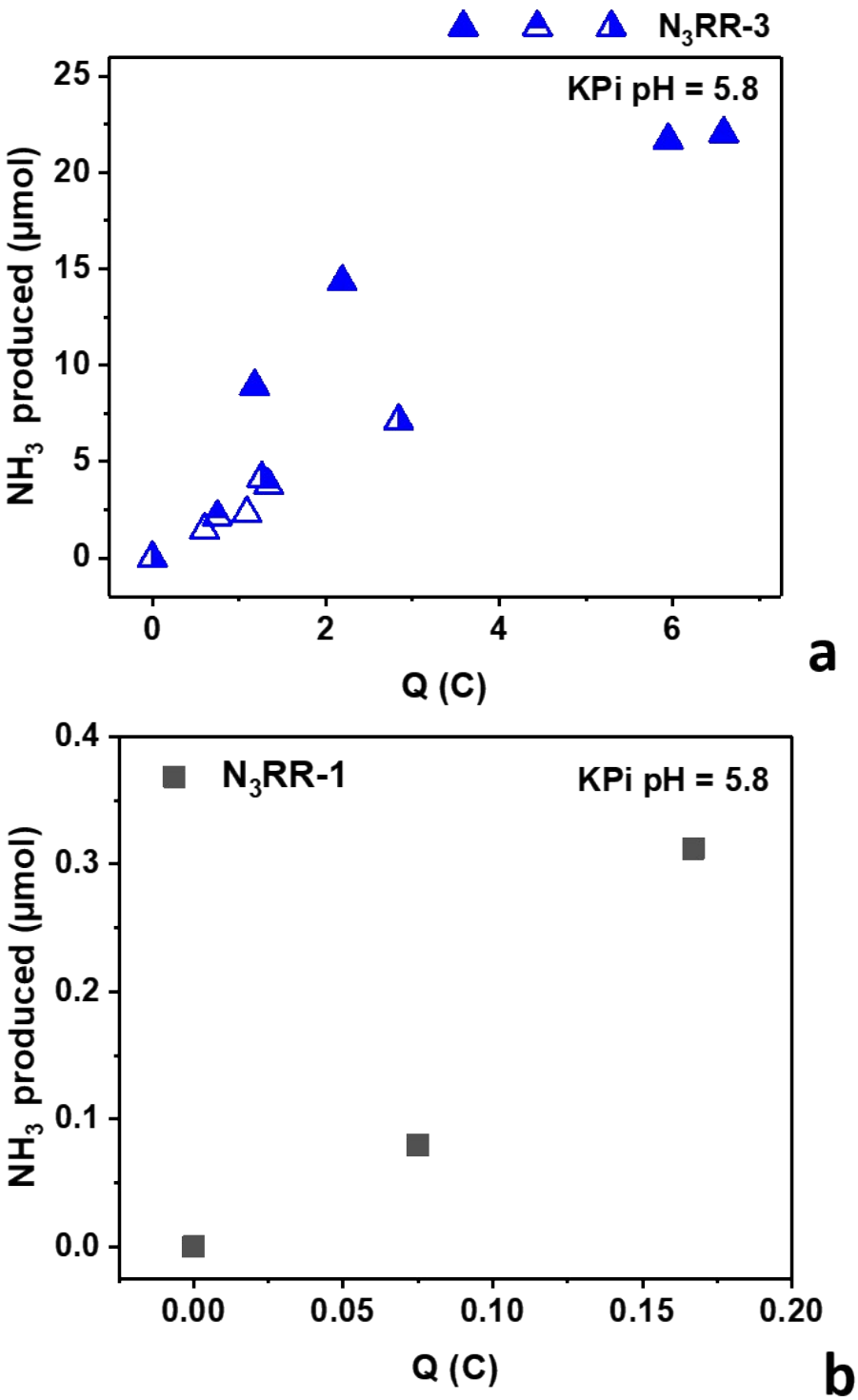


Figure S15: Evolution of the quantity of ammonia produced as a function of the charge passed during the CA of pristine *α*-MoSx films (N_3RR-3, a) or bare GC (N_3RR-1, b) in the presence of 10 mM of NaN_3, in 0.1 M KPi electrolyte (pH = 5.8), potential applied –0.2V *vs*. RHE. The distinct filling patterns within series indicates measurements executed on samples collected from independent runs.

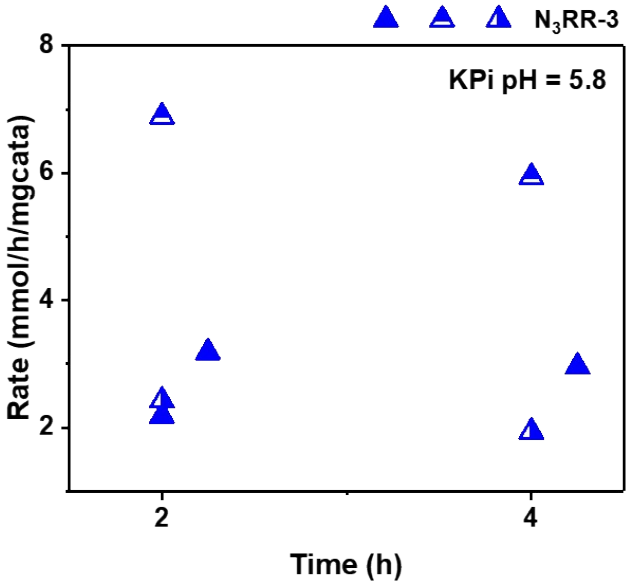


Figure S16: Evolution of the apparent ammonia production rate measured over time, during potential-controlled electrolysis (–0.2 V *vs.* RHE) of 10 mM solutions of sodium azide in argon saturated 0.1 M KPi run on pristine *a*-MoS_x-coated electrodes. The distinct filling patterns within each series indicates measurements executed on samples collected from independent runs.

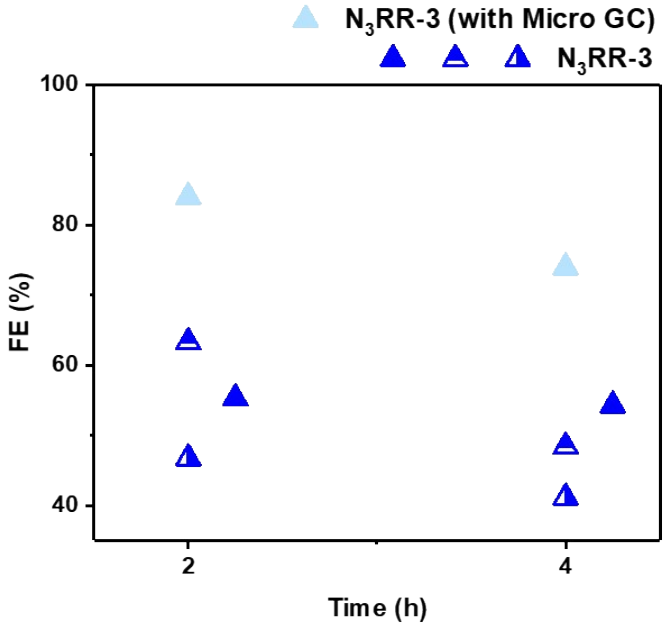


Figure S17: Evolution of the faradaic efficiency over time, during potential-controlled electrolysis (–0.2 V *vs.* RHE) of 10 mM solutions of sodium azide in argon saturated 0.1 M KPi run on pristine *a*-MoS_x-coated electrodes. The distinct filling patterns within each series indicates measurements executed on samples collected from independent runs.

S6 References

(1) Tran, P. D.; Tran, T. V.; Orio, M.; Torelli, S.; Truong, Q. D.; Nayuki, K.; Sasaki, Y.; Chiam, S. Y.; Yi, R.; Honma, I.; Barber, J.; Artero, V., *Nat. Mater.* 2016, **15** (6), 640–646.
(2) Bower, C. E.; Holm-Hansen, T. *Can. J. Fish. Aquat. Sci.* 1980, **37** (5), 794–798.
(3) Watt, G. W.; Chrisp, J. D. *Anal. Chem.* 1952, **24** (12), 2006–2008.
(4) Griess, P. Bemerkungen Zu Der Abhandlung Der HH. Weselsky, *Berichte Dtsch. Chem. Ges.* 1879, **12** (1), 426–428.