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Fundamental Investigation of Electrochemical Urea Synthesis

*Effect of cell design, electrolyte nature, and analytical tools
on the outcome of nitrate ions and CO₂ co-reduction*

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Summary

Electrochemical processes are gaining recognition as a transformative alternative to conventional chemical manufacturing, which remains one of the most carbon-intensive industrial sectors due to its reliance on fossil fuels as both feedstocks and energy sources. By contrast, electrochemical pathways can directly leverage renewable electricity (*e.g.*, wind, solar) and abundant, low-carbon feedstocks (*e.g.*, water, CO₂), offering a viable route toward sustainable chemical production.

Significant progress has already been made in fundamental electrochemical transformations such as water splitting for green hydrogen production and CO₂ reduction (CO₂RR), with several systems advancing toward industrial implementation. Building on these advances, current efforts focus on complex electrosynthetic reactions that enable the carbon-heteroatom bonds formation. In this context, the catalytic electrosynthesis of C-N bonds has emerged as a particularly promising direction with urea representing a key target molecule due to its high global demand and potential for carbon-neutral production. Currently, urea is the most widely used synthetic nitrogen fertilizer, and its conventional synthesis occurs *via* the Haber-Bosh and Bosh-Meiser processes, energy-intensive and fossil fuel-based reactions, accounting for more than 2% of global energy consumption. Therefore, the Electrochemical Urea Synthesis (EUS), through the co-reduction of waste-derived carbon sources and nitrogen species, could provide a novel and sustainable alternative.

Progress in EUS research is hindered by the lack of rigorous and reproducible experimental protocols. Most of the findings supporting the feasibility of EUS, using the most common co-reduction approach (typically, the combination of CO₂RR and nitrate reduction reaction, NO₃RR) have been achieved in limited and non-scalable systems (*i.e.*, the use of H-cell, in which CO₂RR is intrinsically limited) and not in an industrially relevant configuration and environment. Furthermore, since the reported results are derived from analytical methodologies susceptible to inaccuracies, not only is there a lack of protocols for the precise quantification of urea, and consequently for the assessment of the faradaic efficiency of the systems, but also of reliable benchmarks (*e.g.*, the EUS activity/selectivity of basic catalytic systems like zero-valent metals).

This PhD thesis has two main objectives: to develop and validate a reliable analytical protocol for the accurate detection and quantification of EUS systems,

and to identify and evaluate the operational conditions under which urea could be feasibly synthesized electrochemically.

To achieve the first objective, an in-depth analysis of the methods currently employed for urea detection and quantification in EUS was carried out. These techniques were found to suffer from major limitations, including inaccuracy and poor reproducibility, susceptibility to interferers and high limit of detection or long acquisition times. To overcome these drawbacks, a robust, interference-free, and time-efficient chromatographic method was developed as an *ad hoc* analytical procedure, specifically designed to minimize false positives and negatives.

Building on this analytical foundation, the second objective focused on investigating the feasibility of EUS itself. The newly established quantification protocol was coupled with electrochemical testing to reassess the EUS activity, *via* $\text{CO}_2 + \text{NO}_3^-$ co-reduction, of polycrystalline Cu, the first EUS-active catalyst reported by Shibata et al. back in 1995, under near-neutral pH conditions (*i.e.*, $\text{KHCO}_3 + \text{KNO}_3$ aqueous electrolyte) in both static H-cell and three-compartment flow-cell setups. The results revealed that GDE-based setup enhanced EUS efficiency.

To further explore the reaction landscape, Cu, Ag, and Au gas diffusion electrodes (GDEs) were also tested in flow-cells under alkaline conditions (*i.e.*, $\text{KOH} + \text{KNO}_3$ aqueous electrolyte), where the hydrogen evolution reaction (HER) is suppressed, thereby promoting CO_2RR and NO_3RR and their potential coupling. However, even under these optimized conditions, no traces of urea were detected, demonstrating the infeasibility of EUS *via* CO_2 and NO_3^- co-reduction under the experimental conditions applied in this study.

Based on these results, the final stage of the project explored an alternative, anodic (oxidative) pathway for urea synthesis. In this approach, C-N coupling is envisioned to occur through the oxidation of ammonia into reactive nitrogen intermediates under controlled anodic potentials, while CO serves as the carbon source for subsequent coupling.

Contents

Introduction.....	1
1.1 The origin of Electrochemistry	1
1.2 Electrocatalysis.....	3
1.3 Electrochemical cells.....	4
1.4 CO ₂ Reduction Reaction	6
1.5 NO ₃ Reduction Reaction	10
1.6 Electrochemical synthesis of urea	12
1.7 References	14
Quantification Techniques.....	18
2.1 Optimization of the HPLC/UV-Vis method for urea detection/quantification.....	18
2.1.1. Urea detection/quantification on HiPlex column	27
2.2 Modified DAMO-TSC method (M-DAMO-TSC).....	28
2.3.1. Gas chromatography (GC)	31
2.3.2. HPLC method for CO ₂ RR products detection/quantification	32
2.3.3. ¹ H-NMR.....	34
2.3.4. Colorimetric methods	35
2.4. References	42
EUS assessment in near-neutral electrolytes	45
3.1 Materials and methods	45
3.1.1. Electrode preparation and characterization	45
3.1.2. Electrochemical testing	46
3.1.3. Electrochemical Definitions	50
3.1.4. Quantification of products.....	52
3.1.5. Extended rationale of the study: choice of catalyst and reaction conditions	57
3.2. H-cell testing	59
3.2.1. Preparation of WE and calibration of RE for H-cell testing	59

3.2.2. Open Circuit Potential (OCP).....	60
3.2.3. Galvanostatic Electrochemical Impedance Spectroscopy (GEIS)	61
3.2.4. HER, CO ₂ RR, NO ₃ RR and EUS assessment	62
3.2.5. Urea detection in post-electrolysis samples	69
3.2.6. Urea migration and diffusion through the AEM and/or degradation under operative conditions.....	74
3.2.7. pH variations upon electrolysis	75
3.2.8. Cu foil electrode characterization.....	76
3.2.9. Conclusions	77
3.3. Flow-cell testing.....	78
3.3.1. Calibration of RE.....	78
3.3.2. HER, CO ₂ RR, NO ₃ RR and EUS assessment	79
3.3.3. Chronopotentiometric scans & related electrolyte pH and product distribution.....	82
3.3.4. Cu/PTFE electrode characterization.....	89
3.3.5. Conclusions	91
3.4. References	92
EUS assessment in alkaline electrolyte	97
4.1. Materials and methods	97
4.1.1. Electrode preparation and characterization	98
4.1.2. Electrochemical testing	98
4.1.3. Urea quantification	99
4.2. HER, CO ₂ RR, NO ₃ RR and EUS assessment	100
4.2.1. Cu GDE	100
4.2.2. Ag GDE.....	103
4.2.3. Au GDE	106
4.3. Consideration o product analysis.....	109
4.4. Me/PTFE electrode characterization	110
4.5. Conclusions	112
4.5. References	113
EUS assessment through NH ₃ oxidation	114

5.1 Materials and Methods	115
5.1.1. Electrochemical testing	115
5.1.2. Quantification of products	116
5.2. Discussion	116
5.3. Conclusions	119
5.4. References	120
Conclusions.....	121
Appendix.....	123

List of Figures

Figure 1 Representative scheme of a three-electrode single compartment cell with a) the counter electrode, b) reference electrode and (c) working electrode.....	4
Figure 2 Representative scheme of an H-cell (left) and flow-cell (right) with (a) counter electrode, (b) separator, (c) reference electrode and (d) working electrode.	5
Figure 3 Carbon cycle.....	6
Figure 4 Thermodynamic potential of CO ₂ RR in an aqueous electrolyte solution (ref. 23).	8
Figure 5 Nitrogen cycle.	10
Figure 6 Thermodynamic potential of NO ₃ RR in an aqueous electrolyte solution (ref. 28).	11
Figure 7 Urea synthesis through the coupling of the Haber-Bosch and the Bosch-Meiser processes.	12
Figure 8 HPLC Agilent Infinity 1260 workstation, equipped with a quaternary pump, standard autosampler, thermostatted column compartment, Diode Array Detector (DAD/UV-Vis) operating in the range between 190 to 950 nm and a Refractive Index Detector (RID).	19
Figure 9 Sample chromatograms collected during the first attempt of isocratic urea separation in mock EUS samples. Column: Poroshell 120 HILIC-Z. Mobile phase A = H ₂ O. Mobile phase B = ACN. Flow: 0.750 mL min ⁻¹ . Gradient: isocratic, A/B = 20/80. Re-equilibration: none. Injection: 2.5 µL. Column temperature: 30°C. Detection: UV, 195 nm, 20 Hz.	20
Figure 10 Sample chromatograms collected during the first attempt of gradient urea separation. Column: Poroshell 120 HILIC-Z. Mobile phase A = H ₂ O. Mobile phase B = ACN. Flow: 0.500 mL min ⁻¹ . Gradient: 5/95 to 50/50 in 9 minutes, then isocratic 50/50 for 8 minutes. Re-equilibration: 10 minutes at the initial 5/95 eluent composition. Injection: 2.5 µL. Column temperature: 30°C. Detection: UV, 195 nm, 20 Hz. Insets to highlight the typical shape of chromatograms (left) and the	

presence of asymmetric, small peaks when a plain bicarbonate solution is injected (right). 21

Figure 11 Tentative urea calibration (urea standard samples prepared in 0.2 M KHCO_3 + 0.02 M KNO_3). Column: Poroshell 120 HILIC-Z. Mobile phase A = H_2O . Mobile phase B = ACN. Flow: 0.500 mL min^{-1} . Gradient: from 5/95 to 50/50 in 9 minutes (linear gradient), then isocratic 50/50 for 8 minutes. Re-equilibration: 10 minutes at the initial 5/95 eluent composition. Injection: 2.5 μL . Column temperature: 30°C. Detection: UV, 195 nm, 20 Hz.....22

Figure 12 Preliminary check of urea separation using a buffered elution gradient. Column: Poroshell 120 HILIC-Z. Mobile phase A = 10 mM formic acid in H_2O . Mobile phase B = 10 mM formic acid in ACN. Flow: 0.500 mL min^{-1} . Gradient: from 5/95 to 50/50 in 9 minutes (linear gradient), then isocratic 50/50 for 8 minutes. Re-equilibration: 10 minutes at the initial 5/95 eluent composition. Injection: 2.5 μL . Column temperature: 30°C. Detection: UV, 195 nm, 20 Hz. 23

Figure 13 Check for interferers in the formic acid-buffered gradient elution method. Experimental conditions are identical to those reported in the previous Figure 9. Product mixes contain 5000 ppm of the most common individual CO_2RR and NO_3RR products and possible EUS by-products dissolved in 0.2 M KHCO_3 + 0.02 M KNO_3 . The CO_2RR mix contains formic acid (formate ions), acetic acid (acetate ions), formaldehyde, acetaldehyde, methanol, ethanol, isopropanol and 1-propanol. The NO_3RR mix contains nitrite ions, ammonia (ammonium ions), hydrazine, hydroxylamine. The EUS by-products mix contains: formamide and acetamide. 24

Figure 14 Complete calibration data, obtained by HPLC analyses of urea standards (from 0.5 to 40000 ppm, dissolved in EUS electrolyte) according to the optimized methodology reported in Figure 9. a) Chromatograms collected during the preliminary screening (up to 5000 ppm) at different urea concentrations (top) and related magnifications of urea peak region (bottom). b) Replicates of the calibration curve, with concentrations of urea reaching the saturation of the detector. c) Linear (up to 1000 ppm) and asymptotic (from 1000 to 40000 ppm) fitting of the averaged calibration data (full red circles). Average peak area obtained from control standards at 5, 7.25, 10, 250 and 2500 ppm are represented in full green circles. The inset magnifies the linear region of the calibration curve.....25

Figure 15 Chromatograms obtained on the same 100 ppm urea standard in different days, with freshly prepared (not standardized preparation procedure) eluent. Operative conditions are reported in Figure 12. 26

Figure 16 Urea elution peaks obtained under typical CO ₂ RR products analysis conditions on Hi-Plex H (see Section 2.3.2. “High-Performance Liquid Chromatography (HPLC)” for details). The number of counts (DAD/UV-Vis, operating at 195 nm) is indicated in the figure to highlight the small size of the signal.	28
Figure 17 Comparison of (a) DAMO-TSC and M-DAMO-TSC spectra and (b) calibration lines obtained on standard urea samples. Insets in (b) show the identical color intensity obtained in clean urea samples reacted according to the classic DAMO-TSC method (top left) and nitrite-containing urea samples treated according to the M-DAMO-TSC method (bottom left). Note: vials in the insets have the blank sample on their left and urea-containing samples with decreasing concentration from left to right.	29
Figure 18 Typical symptoms of NO ₂ ⁻ interference in the urea quantification by the classic DAMO-TSC method: increase in the absorbance and/or false positives together with shifts in the λ_{max} at low concentration (dashed and full red traces) and false negatives at high concentration (dashed and full blue traces).	30
Figure 19 Sample FID (top) and TCD (bottom) gas chromatograms obtained during the calibration of the GC. Stars indicate peaks stemming from column events (e.g., valve switches).	31
Figure 20 Sample calibration curves obtained for the most common gaseous CO ₂ RR products on polycrystalline Cu. Full data (including less common gaseous products of the individual reactions, e.g., C ₂ H ₆ and N ₂) available in the following Table. H ₂ calibration line refers to H ₂ Peak 1 data.	32
Figure 21 a) Identification of the retention time of each analyte at different detectors (RID, DAD @ 210 nm, and DAD @ 280 nm), obtained by injecting 25 mL of concentrated analytes solutions (ca. 1000 ppm) in H ₂ O. b) Individual CO ₂ RR byproducts mixtures, prepared in the presence or absence of the typical components of the electrolyte used in this study. c) Representative calibration plot (inset is a magnification of the low analyte concentration region), obtained from the integration of RID peaks area. Regressed calibration lines are not shown to provide a more readable figure. Other calibration plots are not reported for the sake of conciseness but are available to the reader upon reasonable request to the corresponding author.	33
Figure 22 ¹ H-NMR spectra collected on standard urea samples in representative electrolyte.	35

Figure 23 a) Absorption spectra collected upon the application of the Griess method on standard nitrite samples in $\text{KHCO}_3 + \text{KNO}_3$ based electrolyte and b) the resulting calibration line, regressed according to the Lambert-Beer equation. In the inset, a picture of the cuvettes containing the blank electrolyte (first from the left) and the calibration samples, reacted according to the Griess method. 36

Figure 24 a) Absorption spectra collected upon application of the indophenol blue method on standard ammonia samples in $\text{KHCO}_3 + \text{KNO}_3$ based electrolyte and b) the resulting calibration line, regressed according to the Lambert-Beer equation. In the inset, a picture of the cuvettes containing the blank electrolyte (first from the left) and the calibration samples, reacted according to the indophenol blue method. 37

Figure 25 a) Absorption spectra collected upon the application of the Watt and Chrisp method on standard hydrazine samples in $\text{KHCO}_3 + \text{KNO}_3$ based electrolyte and b) the resulting calibration line, regressed according to the Lambert-Beer equation. In the inset, a picture of the cuvettes containing the blank electrolyte (first from the left) and the calibration samples, reacted according to the Watt and Chrisp method. 38

Figure 26 a) Absorption spectra collected upon the application of the DAMO-TSC method on standard urea samples in $\text{KHCO}_3 + \text{KNO}_3$ based electrolyte and b) the resulting calibration line, regressed according to the Lambert-Beer equation. In the inset, a picture of the cuvettes containing the blank electrolyte (first from the left) and the calibration samples, reacted according to the DAMO-TSC method. 38

Figure 27 Stability check of common individual NO_3RR by-products (and also urea) in the electrolyte (0.2 M $\text{KHCO}_3 + 0.02$ M KNO_3). Samples of different analytes (a) urea; b) NO_2^- ; c) NH_3 ; d) N_2H_4) at different concentrations have been tested as soon as they were prepared (red dashed lines) and after being stocked at RT for two days (black full lines). 39

Figure 28 Assessment of colorimetric interferences in post-electrolysis-like samples a) to standard solutions containing a single byproduct; b) to standard solutions containing both the target analyte and one additional species. 40

Figure 29 Schematics of the electrochemical setup used for H-cell EUS studies: (a) CO_2 gas cylinder; (b) Ar gas cylinder; (c) CO_2 mass flow controller (MFC); (d) Ar mass flow controller (MFC); (e) three-way gas valve; (f) H-cell; (g) acid scrubber (containing e.g., 1M H_2SO_4); (h) gas dryer; (i) gas outlet mass flow meter (MFM); (j) in-line gas chromatograph (GC). In the inset, magnification of the H-cell

configuration: (1) Ni mesh CE; (2) Anion Exchange Membrane (AEM); (3) gas inlet; (4) Ag/AgCl RE; (5) Cu foil WE (with holder); (6) gas outlet. 47

Figure 30 Scheme of the electrochemical setup for EUS testing. (a) CO₂ gas cylinder; (b) Ar gas cylinder; (c) CO₂ mass flow controller (MFC); (d) Ar mass flow controller (MFC); (e) three-way gas valve; (f) three- compartment flow cell; (g) dual-channel peristaltic pump; (h) anolyte reservoir; (i) catholyte reservoir; (j) acid scrubber (containing e.g. 1M H₂SO₄) (k) gas dryer (l) gas outlet mass flow meter (MFM); (m) in-line gas chromatograph (GC). Magnification at the bottom: simplified exploded view of the flow-cell. (1) Gas inlet; (2) gas outlet; (3) Cu/PTFE WE; (4) Ag/AgCl RE; (5) catholyte inlet; (6) catholyte outlet; (7) AEM; (8) Ni mesh CE; (9) anolyte inlet; (10) anolyte outlet.....50

Figure 31 a) Typical current versus time profile obtained from the electropolishing procedure of the Cu foil used as WE in H-cell tests. b) Sample calibration of the RE (3 M KCl Ag/AgCl), obtained measuring its OCP in 0.5 M H₂SO₄ (pH 0) versus an RHE. Inset: magnification used to appreciate the variation of the voltage, in the range of tenths of mV. 60

Figure 32 Open Circuit Potential (OCP) traces collected on the Cu foil WE under different reaction environments (i.e., with different electrolytes and gas feeds, details in Table 2). 61

Figure 33 Polycrystalline Cu electrochemical testing under HER conditions (i.e., 0.2 M KHCO₃, Ar). a) CV curve (10th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -4 mA cm⁻², 0.8 mA cm⁻² amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz), c) CP scan at -12.5 mA cm⁻² and d) related product distribution. 63

Figure 34 Polycrystalline Cu electrochemical testing under CO₂RR conditions (i.e., 0.2 M KHCO₃, CO₂). a) CV curve (10th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -6 mA cm⁻², 1.2 mA cm⁻² amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz), c) CP scans at different current densities and d) related product distribution. 64

Figure 35 Polycrystalline Cu electrochemical testing under NO₃RR conditions (i.e., 0.2 M KHCO₃ + 0.02 M KNO₃, Ar). a) CV curve (10th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -6 mA cm⁻², 1.2 mA cm⁻² amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz), c) CP scans at different current densities and d) related product distribution. 65

Figure 36 Polycrystalline Cu electrochemical testing under NO ₃ RR conditions (i.e., 0.2 M KHCO ₃ + 0.02 M KNO ₃ , Ar). a) CV curve (10 th scan, scan rate 100 mV s ⁻¹), b) GEIS (collected at -6 mA cm ⁻² , 1.2 mA cm ⁻² amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz), c) CP scans at different current densities and d) 17-hours long CP scan at -5 mA cm ⁻²	67
Figure 37 Product distribution at different current densities.	68
Figure 38 Tentative detection of urea by the classic DAMO-TSC method in post-electrolysis H-cell samples. a) HER catholytes; b) CO ₂ RR catholytes; c) NO ₃ RR catholytes; d) NO ₃ RR anolytes; e) EUS catholytes; f) EUS anolytes.	70
Figure 39 Tentative detection of urea by the modified M-DAMO-TSC method in post-electrolysis H-cell samples. a) NO ₃ RR catholytes; b) NO ₃ RR anolytes; c) EUS catholytes; d) EUS anolytes.	71
Figure 40 Spectrophotometric test conducted on post-electrolysis samples, 17-hours long CP at -5 mA cm ⁻² , EUS conditions. a) Griess test showing the absence of nitrite ions due to the complete conversion of nitrate ions to b) ammonia, detected by the indophenol blue method (D.F. stands for dilution factor). c) DAMO-TSC and d) M-DAMO-TSC tests, demonstrating the absence of either urea or nitrite-based false positives.	72
Figure 41 HPLC chromatographs (left side) and corresponding colorimetric tests according to the Griess method (right). a) Catholytes and b) anolytes collected after 1-hour long CP scans at different current densities under EUS conditions. The acronym DF in right figures stands for Dilution Factor. c) Catholyte and anolyte collected after a 17-hours long CP scan at -5 mA cm ⁻² under EUS conditions.	73
Figure 42 HPLC chromatograms of (a) catholytes and (b) anolytes before and after the urea migration (red traces) and diffusion (blue traces) experiments. Insets magnify the region in which the urea peak is expected.	74
Figure 43 pH variations of the a) catholytes and b) anolytes during CP scans in different environments and at different current densities. 1-hour long CP traces collected under individual c) HER and d) NO ₃ RR conditions and corrected by the initial (gray trace or final (red traces) pH values.	76
Figure 44 Basic characterization of Cu foils electrodes used for H-cell testing. a) XRD patterns collected on pristine, electropolished, and post-electrolysis (EUS conditions) WEs. SEM images of b) pristine, c) electropolished, and d) post-electrolysis Cu foils.	77

Figure 45 Sample calibration of the RE (3 M KCl Ag/AgCl, eDAQ leakless), obtained measuring its OCP in 0.5 M H₂SO₄ (pH 0) versus an RHE. Inset: downward drift of the RE potential when the calibration time is lengthened 79

Figure 46 Cu/PTFE electrochemical testing under HER conditions (i.e., 0.2 M KHCO₃, Ar) in flow cell configuration. a) CV curve (5th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -5.65 mA, 1.4 mA amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.5 Hz). 80

Figure 47 Cu/PTFE electrochemical testing under CO₂RR conditions (i.e., 0.2 M KHCO₃, CO₂) in flow cell configuration. a) CV curve (5th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -5.65 mA, 1.4 mA amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.5 Hz). 80

Figure 48 Cu/PTFE electrochemical testing under NO₃RR conditions (i.e., 0.2 M KHCO₃ + 0.02 M KNO₃, Ar) in flow cell configuration. a) CV curve (5th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -5.65 mA, 1.4 mA amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.5 Hz). 81

Figure 49 Cu/PTFE electrochemical testing under EUS conditions (i.e., 0.2 M KHCO₃ + 0.02 M KNO₃, Ar) in flow cell configuration. a) CV curve (5th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -5.65 mA, 1.4 mA amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.5 Hz). 81

Figure 50 Long CP scans, collected in flow cell configuration, EUS conditions, at different current densities. 83

Figure 51 Final pH measured in post-electrolysis catholytes (full triangles) and anolytes (hollow triangles). Dashed lines represent the initial pH values measures in for catholytes (CO₂ feed, bottom) and anolytes (no gas feed, top).....84

Figure 52 HPLC chromatograms collected according to the developed HILIC method on post-electrolysis flow cell samples. a) Catholytes analyses and b) anolyte analysis, with insets magnifying the region of nitrite (left) and urea (right) peaks. 85

Figure 53 GC, HPLC, and colorimetric analyses carried out on the post-electrolysis electrolytes collected after long CP scans in flow-cell configuration, EUS conditions. a) Peak area of the detected products at different times and at different current densities, evidencing the fluctuations in the production rates. b) HPLC analyses (HiPlex method, for CO₂RR products detection) of catholytes, evidencing

the presence of (mainly) formate ions. Colorimetric tests for the detection and quantification of c) ammonia and d) nitrites. D.F. stands for dilution factor. 87

Figure 54 Spectra collected on the post-electrolysis catholytes obtained from flow-cell testing. The detection/quantification method applied was the M-DAMO-TSC one.....88

Figure 55 Basic characterization of the Cu/PTFE electrodes used for flow-cell testing. a) XRD patterns collected on the bare support (PTFE) and on the pristine and post-electrolysis electrode. PE and PEO stand for polyethylene and polyethylene oxide, constituents of the backing layer of the PTFE membrane. Pristine Cu/PTFE b) SEM image and c) XRF analysis. (d) XRF analysis of the used Cu/PTFE. 90

Figure 56 (a) Absorption spectra collected upon the application of the DAMO-TSC method on standard urea samples in KOH + KNO₃ based electrolyte and (b) the resulting calibration line, regressed according to the Lambert-Beer equation. ...100

Figure 57 Open Circuit Potential (OCP) traces collected on the Cu/PTFE WE under different reaction environments (i.e., with different electrolytes and gas feeds, details in Table 3). 101

Figure 58 Cu/PTFE electrochemical testing under various conditions. a) CV curve (5th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -10 mA cm⁻², 2.8 mA cm⁻² amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz). 102

Figure 59 a) CP scans under EUS conditions at different current density, b) Tentative detection of urea by the classic DAMO-TSC method in post-electrolysis samples and c) HPLC chromatogram collected according to the developed HILIC method on post-electrolysis catholyte.....103

Figure 60 Open Circuit Potential (OCP) traces collected on the Ag/PTFE WE under different reaction environments (i.e., with different electrolytes and gas feeds, details in Table 3). 104

Figure 61 Ag/PTFE electrochemical testing under various conditions. a) CV curve (5th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -10 mA cm⁻², 2.8 mA cm⁻² amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz) 105

Figure 62 CP scans under EUS conditions at different current density and b) Tentative detection of urea by the classic DAMO-TSC method in post-electrolysis samples.....	106
Figure 63 Open Circuit Potential (OCP) traces collected on the Au/PTFE WE under different reaction environments (i.e., with different electrolytes and gas feeds, details in Table 3).	107
Figure 64 Au/PTFE electrochemical testing under various conditions. a) CV curve (5 th scan, scan rate 100 mV s ⁻¹), b) GEIS (collected at -10 mA cm ⁻² , 2.8 mA cm ⁻² amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz).	108
Figure 65 CP scans under EUS conditions at different current density and b) Tentative detection of urea by the classic DAMO-TSC method in post-electrolysis samples.....	108
Figure 66 HPLC chromatograms collected according to the developed HILIC method on post-electrolysis flow cell catholytes under EUS conditions.....	109
Figure 67 Absorption spectra obtained applying DAMO-TSC method on a) catholytes obtained from CP scans under EUS conditions for each metal electrode and b) standard nitrite samples.	110
Figure 68 Basic characterization of the Me/PTFE electrodes used for flow-cell testing. XRD patterns collected on the bare support (PTFE) and on the pristine and post-electrolysis a) Cu/PTFE, b) Ag/PTFE and c) Au/PTFE electrodes. SEM image of c) Cu/PTFE, d) Ag/PTFE and e) Au/PTFE electrodes.....	111
Figure 69 a) Open Circuit Potential (OCP) traces collected on Pt coil WE under oxidative EUS condition. b) CV curve (10 th scan, scan rate 100 mV s ⁻¹), c) GEIS (collected at 10 mA cm ⁻² , 2 mA cm ⁻² amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz), d) CP scans at different current densities	117
Figure 70 Absorption spectra obtained applying DAMO-TSC method on catholytes obtained from CP scans at various current densities in the days following the electrochemical test.....	118
Figure 71 Absorption spectra obtained applying DAMO-TSC method on catholytes obtained from CP scans at various current densities after heating at 50 °C for 1 hour.	119

List of Tables

Table 1 Faradaic Efficiencies of CO ₂ Reduction Products on Metal Electrodes in CO ₂ -Saturated 0.1 M KHCO ₃ (pH = 6.8) (ref.24).....	9
Table 2 Electrolytes and gas feeds used to investigate individual and co-reduction processes. The initial electrolyte pH is intended after saturation with the gas of choice.....	48
Table 3 Electrolytes and gas feeds used to investigate individual and co-reduction processes. The initial electrolyte pH is intended after saturation with the gas of choice.....	99
Table 4 Response factors (i.e., slope) and related statistics regressed from GC calibration data. * Indicates the peaks selected for the quantification of products. The choice was based on the statistical parameters and the easiness of integration (i.e., quality of the local baseline).....	123

Chapter 1

Introduction

1.1 The origin of Electrochemistry

Electrochemistry is a branch of physical chemistry concerned with the study of the reciprocal interactions between chemical processes and electrical phenomena. Its origins can be traced back to the late 18th century, when Luigi Galvani (1737-1798) observed that the frog legs contracted when touched with two different metals, an effect which he attributed to a form of “animal electricity” (1). Soon after, Alessandro Volta (1745-1827) proposed an alternative explanation, arguing that the phenomenon described by Galvani was not due to electricity generated within the animal, but rather to the electric current produced when dissimilar metals were brought into contact in a conductive medium; he termed this phenomenon “*Galvanism*” (2).

Building on this assumption and his further investigations, in 1800 Volta developed the Voltaic pile, a pioneering device, commonly known as the first battery, composed of a stacked arrangement of alternating metallic discs separated by paper or cloth soaked in brine (1). This invention quickly became an indispensable tool for experimental research. Humphry Davy (1778-1829) was the first to exploit its potential systematically; applying the continuous current, it supplied to the electrolysis of various chemical compounds, thereby achieving the first isolation of several highly reactive metals. These results not only expanded the inventory of known elements but also provided direct evidence that electrical energy could drive chemical transformations, establishing electrolysis as a central method in the emerging field of electrochemistry (3).

Building on Davy’s achievements, his student Michael Faraday (1791-1867) formulated in 1834 the fundamental laws of electrolysis. He demonstrated that the mass of material transformed at an electrode is directly proportional to the electric charge passed, and that the relative masses produced by the same charge correspond to the equivalent weights of the substances involved (4).

The late 19th century represented a decisive turning point, marked by the theoretical contributions of Svante Arrhenius (1859-1927) and Walther Nernst (1864-1941). Arrhenius, relying on conductance studies of Friedrich Kohlrausch, proposed his theory of electrolytic dissociation (1884), introducing the concept of ions as the carriers of current in solution and thereby providing a molecular basis for Faraday's laws. Nernst, a few years later, established a rigorous thermodynamic treatment of electrochemical systems. In 1889, he derived the equation that estimate the cell potential under non-equilibrium conditions, relating electrode potentials to ionic concentrations, as follow (1-5).

$$E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln \left(\frac{a_O}{a_R} \right) \text{ (Equation 1)}$$

Where R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the operative temperature expressed in kelvin (K), a_O and a_R are the activity coefficients of the oxidant and reductant, respectively.

The theoretical standard cell voltage, E_{cell}^0 , represents the overall driving force of a redox reaction to proceed spontaneously and it is defined by the difference between the standard reduction potential of the cathode, $E_{cathode}^0$, and the standard reduction potential of the anode, E_{anode}^0 , as:

$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0 \text{ (Equation 2)}$$

E_{cell}^0 can also be expressed as a function of the standard Gibbs free energy change of the overall electrochemical reaction (1 atm, 298 K), ΔG^0 , the number of electrons transferred in the redox reaction, n , and Faraday constant (96485 C mol^{-1}), F , as follows (6):

$$E_{cell}^0 = -\frac{\Delta G^0}{nF} \text{ (Equation 3)}$$

Throughout the 20th century, electrochemistry has become indispensable in modern applications, ranging from energy conversion and storage technologies, such as batteries and fuel cells, to environmental remediation, electrosynthesis, and biosensing, thereby supporting sustainable development and innovation across multiple sectors (7).

1.2 Electrocatalysis

Electrocatalysis merges the principles of catalysis and electrochemistry to establish how electrode materials control the energy required to drive electrochemical reactions. The applied cell potential (ΔV) includes the thermodynamic voltage necessary for the reaction and additional contributions such as the electrocatalytic overpotential (η), representing the additional driving force needed to achieve practical reaction rates. Minimizing this overpotential is critical for reducing the energy barrier for charge transfer, enabling higher current densities at lower voltages and thus improving the overall energy efficiency of the process (8). Central to this advancement is the rational engineering of catalytic interfaces that govern reactant adsorption and the formation of key intermediates, which strongly influence both the kinetics and selectivity of electrode reactions (9-10). Catalyst design must account not only for the selectivity, but also for Sabatier's principle: intermediates must bind strongly enough to be activated, but not so strongly that their release is inhibited (11). Transition metals and their alloys, mainly in their zerovalent or oxide forms, are widely used as electrocatalysts because of their partially filled *d*-orbitals, which enable versatile interactions with reactants, while atomic-scale features such as terraces, steps, and defects profoundly affect activity and selectivity (10).

Today, electrocatalysis underpins many of the most promising sustainable pathways for energy conversion and chemical manufacturing. Water electrolysis, through the hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode, enables, respectively, the production of clean hydrogen as a low-carbon alternative to fossil fuels, and oxygen for applications such as metal anode regeneration in metal-air batteries. The electrochemical reduction of CO₂ (CO₂RR) and CO (CORR) provides transformative opportunities to close the carbon cycle by converting greenhouse gases into fuels and valuable chemicals. Similarly, the electrocatalytic oxidation of organic molecules represents another sustainable route to synthesize fine chemicals while also enabling the degradation of pollutants in wastewater. Nitrogen electrocatalysis has recently emerged as another key frontier, aiming to develop sustainable alternatives to thermochemical nitrogen conversion. The nitrogen reduction reaction (NRR) seeks to produce ammonia under mild conditions, displacing the conventional energy-intensive Haber-Bosch process. Complementary nitric oxide (NOR) and nitrate reduction (NO₃RR) reactions focus on the removal of nitrogen pollutants and the recovery of reactive nitrogen species

(12). Conversely, ammonia oxidation (NH_3OR) is recognized as a cornerstone for sustainable hydrogen production and efficient nitrogen valorisation (13). Together, these processes exemplify the overarching goals of electrocatalysis: to deliver catalysts that are active, stable, and selective under practical conditions, enabling the transition toward sustainable energy and chemical technologies.

1.3 Electrochemical cells

The study of electrochemical processes is carried out using electrochemical cells that provide a controlled environment in which oxidation and reduction reactions can be analyzed, offering insights into both fundamental reaction mechanisms and practical applications. Among the different cell configurations, the three-electrode single compartment setup is the most widely employed at the laboratory scale, especially when the objective is to examine a single half-reaction (Figure 1).

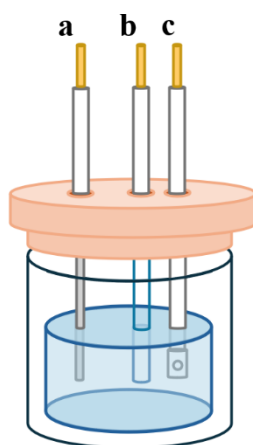


Figure 1 Representative scheme of a three-electrode single compartment cell with a) the counter electrode, b) reference electrode and (c) working electrode.

In this configuration, the working electrode (WE), the counter electrode (CE), and the reference electrode (RE) are immersed into the electrolyte, responsible for ion transport and system's electrical neutrality, available in aqueous, molten salt or solid forms, and connected to a potentiostat responsible for controlling and measuring the applied potential and current. When the circuit is closed, electrons flow from the electrode with the lower positive standard reduction potential, which undergoes oxidation and is therefore denoted as the negative electrode or anode, to the electrode with the higher positive standard reduction potential, which undergoes reduction and is designated as the positive electrode or cathode. Therefore, within the electrocatalytic cell, cations migrate through the electrolyte toward the cathode surface, while anions move toward the anode surface (14). The reference electrode

is essential to accurately monitor the potential of the working electrode without being affected by the current exchange between the working and counter electrodes (15).

While single-compartment three-electrode cells are fundamental for mechanistic studies, alternative configurations are required to better mimic practical electrochemical systems and prevent parasitic recombination reactions. In this context, the most widely employed electrocatalytic cell configurations for half-single reactions studies are H-cells and flow-cells, which are designed with physically separated cathodic and anodic chambers by an ion-conducting separator (Figure 2).

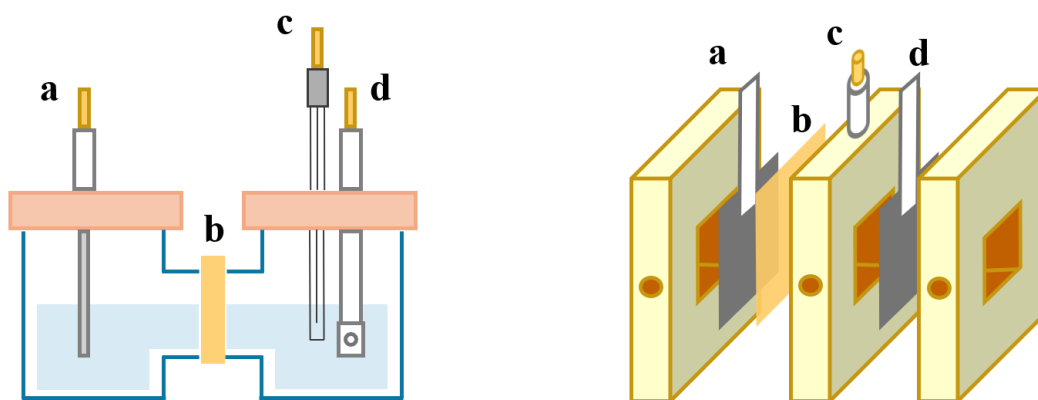


Figure 2 Representative scheme of an H-cell (left) and flow-cell (right) with (a) counter electrode, (b) separator, (c) reference electrode and (d) working electrode.

The separator ensures physical separation of the electrodes, preventing short-circuiting, while still maintaining continuous ionic conductivity within the cell (5). Separators can be porous diaphragms, solid electrolytes or membranes. The membranes are broadly classified according to the type of charge carrier they selectively transport. Cation exchange membranes (CEMs) conduct positively charged species such as H^+ while rejecting anions, making them particularly suitable for acidic environments and proton-coupled electrochemical reactions. In contrast, anion-exchange membranes (AEMs) allow the transport of negatively charged species such as OH^- , supporting alkaline conditions. A third category, bipolar membranes (BPMs), consists of laminated cation- and anion-conducting layers. The selection of the membrane depends on the pH of the electrolyte employed (14).

H-type cells are widely used in fundamental electrochemical research as they are easy to handle and adaptable to various electrodes. However, these systems suffer

from severe mass transport limitations, especially in the case of CO₂RR studies, that restrict the achievable current densities and therefore fail to reproduce conditions relevant to industrial application. By contrast, flow-cells overcome these limitations by continuously circulating reactants and products across the electrodes, thus enhancing mass transfer, and enabling operation at industrially relevant current densities. Furthermore, their modular design allows laboratory-scale units to be readily scaled into stacked configurations, which is essential for commercial electrolyzer applications (16, 17).

1.4 CO₂ Reduction Reaction

The electrochemical reduction of carbon dioxide (CO₂RR) has emerged as a promising strategy to mitigate rising CO₂ emissions while simultaneously producing valuable fuels and chemicals. By coupling renewable electricity with electrochemical conversion, CO₂RR offers a sustainable pathway to close the carbon cycle and reduce dependence on fossil resources (Figure 3) (18, 19, 20).

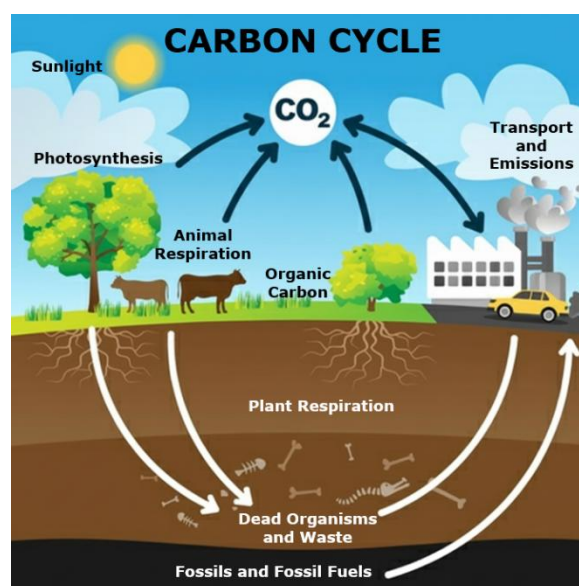
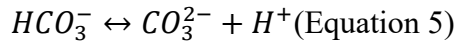
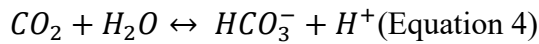


Figure 3 Carbon cycle.

Despite being thermodynamically feasible, CO₂RR is hindered by sluggish reaction kinetics due to the chemical inertness of the CO₂ molecule, which possesses a highly stable linear structure and strong C=O double bonds (~750 kJ/mol). The activation of CO₂ requires the initial formation of a surface-bound CO₂⁻ intermediate through a one-electron transfer step, a process associated with a high activation barrier and slow charge-transfer kinetics (18). As a result, CO₂RR

typically proceeds at sluggish rates and demands significant overpotentials to achieve practical current densities. Under such strongly reductive conditions, the hydrogen evolution reaction (HER), a simple process involving two protons and two electrons, readily competes for available electrons and active sites, often dominating at cathodic current and reducing the overall selectivity toward carbon-based products. To enhance CO₂RR selectivity relative to HER, neutral electrolytes are commonly employed, as the reduced proton activity suppresses HER while still permitting CO₂RR to occur. However, in aqueous media, the thermodynamic equilibria among CO₂, bicarbonate and carbonate species (18) is described by



Carbonates and bicarbonates are not catalytically active species in CO₂RR, and their formation through acid-base neutralization results in poor CO₂ utilization.

Beyond electrolyte composition, the design of the electrolyzer strongly influences product selectivity and the overall efficiency of the CO₂ reduction process. In this context, the use of a flow cell, rather than a conventional H-cell, enables the exploitation of a gas diffusion electrode (GDE), which enhances CO₂ deployment at the catalyst surface and thereby improves mass transport, ultimately leading to higher current densities. In such configuration, the GDE consists of a porous catalyst layer (CL) supported by a diffusion medium, typically a PTFE-treated hydrophobic carbon structure comprising a macroporous gas diffusion layer (GDL) and a microporous layer (MPL) that ensures CO₂ transport to the CL, provides mechanical stability, and enables electronic conductivity. The CL is formed by depositing catalyst particles mixed with an ionic binder onto the MPL, where the binder maintains particle cohesion and facilitates ionic conductivity (21).

Depending on the reaction pathway and the electrocatalyst employed, a wide range of products can be obtained, including two-electron reduction products such as carbon monoxide (CO) and formic acid (HCOOH), as well as more deeply reduced multi-electron products such as methanol (CH₃OH), methane (CH₄), and C₂⁺ hydrocarbons, alcohols and acids (Figure 4) (22).

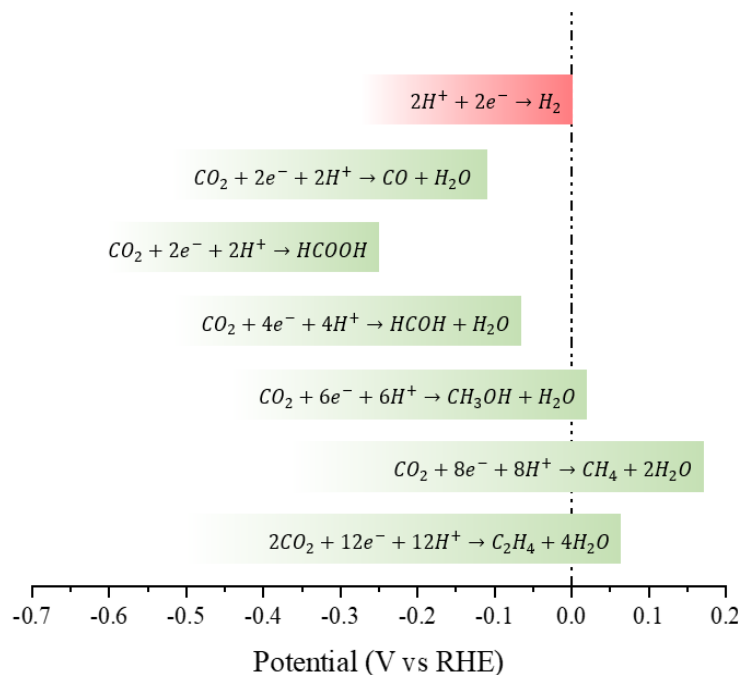


Figure 4 Thermodynamic potential of CO₂RR in an aqueous electrolyte solution (ref. 23).

The choice of electrocatalyst plays a decisive role in steering product selectivity during CO₂RR (Table 1). Noble metals such as Au and Ag are commonly reported to favor CO formation, a behavior that has been associated with weak *CO binding and limited hydrogen adsorption. Copper, on the other hand, uniquely enables the formation of multi-carbon products, although this capability is accompanied by a broad distribution of reaction pathways and reduced selectivity toward individual products.

Table 1 Faradaic Efficiencies of CO₂ Reduction Products on Metal Electrodes in CO₂-Saturated 0.1 M KHCO₃ (pH = 6.8) (ref.24).

Metal	E (V vs RHE)	CH₄ (%)	C₂H₄ (%)	EtOH (%)	CO (%)	HCOO⁻ (%)	H₂ (%)
Hg	-1.12	0	0	0	0	99.5	0
Ti	-1.21	0	0	0	0	0	99.7
Cd	-1.24	1.13	0	0	13.9	78.4	9.4
Au	-0.65	0	0	0	87.1	0.7	10.2
Ag	-0.98	0	0	0	81.5	0.6	12.4
Zn	-1.15	0	0	0	79.4	6.1	9.9
Pd	-0.81	2.9	0	0	28.3	2.8	26.2
Cu	-1.05	33.3	25.5	5.7	1.3	9.4	20.5
Ni	-1.09	1.8	0.1	0	0	1.4	88.9
Fe	-0.52	0	0	0	0	0	94.8
Pt	-0.68	0	0	0	0	0.1	95.7

1.5 NO₃ Reduction Reaction

Nitrate contamination has become a critical environmental concern due to the extensive use of nitrogen-based fertilizers that undergo microbial oxidation converting ammonia and ammonium into nitrate species that readily leach into groundwater (Figure 5) (25).

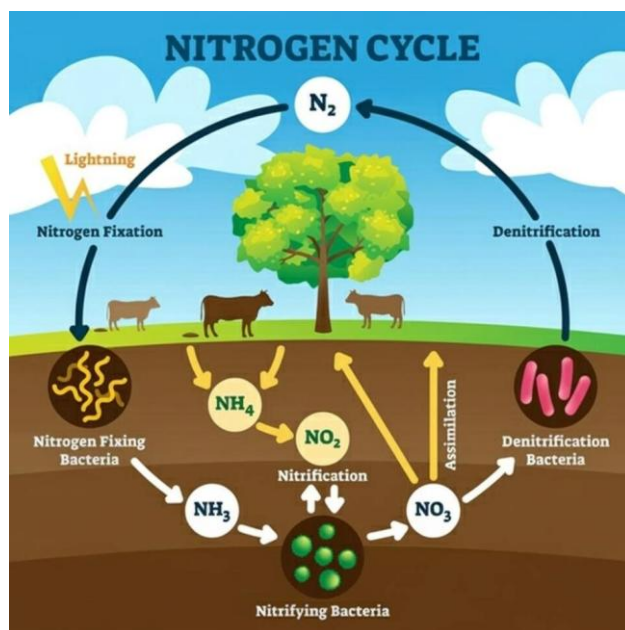


Figure 5 Nitrogen cycle.

As a result, excessive agricultural fertilizer use has led to widespread nitrate accumulation in soil and freshwater systems, posing serious environmental and public health risks (26, 27).

Among the different strategies for nitrate removal, the electrochemical reduction of nitrate (NO₃RR) has emerged as a promising approach since it can simultaneously eliminate harmful nitrates and convert them into valuable products by using renewable electricity. The electrochemical reduction of nitrate is a complex multi-electron, multi-proton process that can follow different reaction pathways. Depending on the number of electrons transferred and the catalyst employed, nitrate may be reduced to nitrite (NO₂⁻), ammonium (NH₄⁺), or nitrogen gas (N₂).

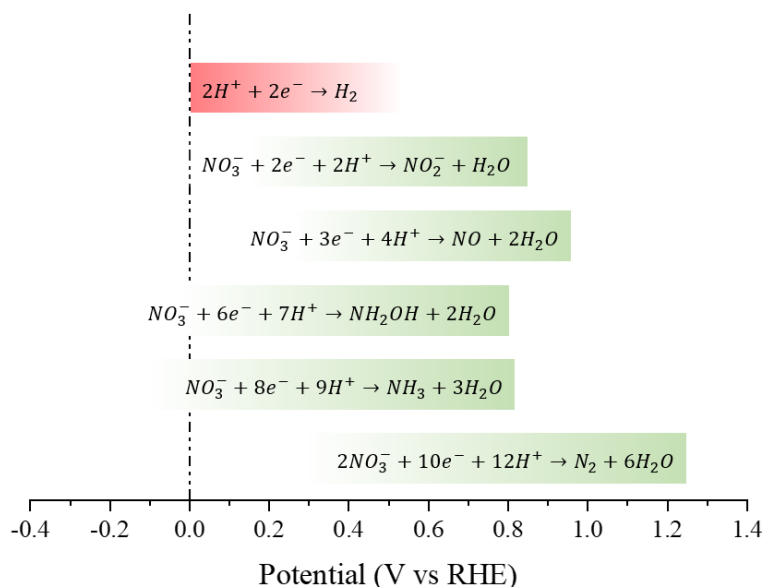


Figure 6 Thermodynamic potential of NO₃RR in an aqueous electrolyte solution (ref. 28).

While ammonium and ammonia are industrially relevant products, nitrogen gas is considered the most environmentally benign outcome, as it closes the nitrogen cycle (29). Thermodynamically, nitrate reduction is favorable but the multi-step nature of NO₃RR gives rise to a variety of intermediates and parallel pathways, making it difficult to steer the reaction toward a single desired product. High faradaic efficiency and good selectivity are typically achieved at less cathodic potential, where parasitic HER is minimized. Therefore, the design of the catalyst plays a crucial role in determining the process selectivity (30).

Noble metals, such as Pt, Pd, Rh, and Ru, through facet control, strain engineering, and heterostructure design, can achieve very high selectivity for NH₃ while suppressing parasitic HER. Single-atom catalysts (SACs), such as Fe, Cu, Ni, or Mo, also favor NH₃ over N₂ owing to the greater exposure of isolated active sites that effectively inhibit N-N coupling. Transition-metal-based catalysts (Cu, Co, Fe, Ni, Bi) and their alloys constitute the most versatile group. Among them, Cu and its heterostructures are particularly selective for NH₃, while Fe and Co can also deliver high selectivity when combined with defect engineering or conductive supports. Finally, bimetallic alloys (e.g., Cu-Ni, Cu-Fe, Co-Cu) exploit synergistic effects that tune intermediate adsorption, achieving faradaic efficiencies above 95%, whereas metal oxides and perovskites with abundant oxygen vacancies can further enhance NH₃ selectivity, though typically with lower activity compared to pure metals (31).

1.6 Electrochemical synthesis of urea

Urea is the most widely used nitrogen-based fertilizer in agriculture (32) due to its high nitrogen content (46%), chemical stability, solubility, low toxicity, and ease of mixing (33).

In the last decades, urea has played a key role in increasing crop production and feeding a growing population (34). However, since its conventional synthesis relies on the energy-intensive, fossil fuel-driven Haber-Bosch and Bosch-Meiser processes, collectively responsible for over 2% of global energy consumption (32), the electrochemical synthesis of urea may represent a sustainable alternative to this approach (35).

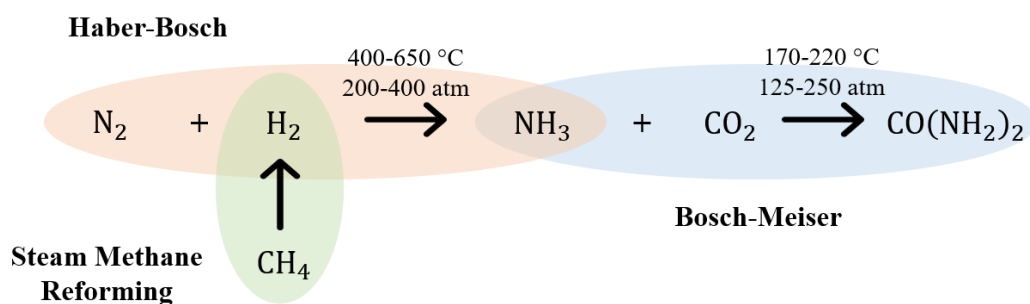


Figure 7 Urea synthesis through the coupling of the Haber-Bosch and the Bosch-Meiser processes.

The electrochemical synthesis of urea was first demonstrated by Shibata in 1995. In the study (36-39), urea was successfully synthesized under ambient temperature and pressure conditions through the simultaneous reduction of CO_2 and nitrogen oxides (e.g. NO_3^- or NO_2^-) at gas-diffusion electrodes testing a wide range of catalysts. Initial investigations with Cu, Ag, and Au catalysts showed that urea could be formed in an electrolytic cell, using 0.2 M KHCO_3 0.02 M KNO_2 electrolyte and providing CO_2 in the cathode gas-chamber, with current efficiencies up to 37% (37). Subsequent work expanded the catalyst library to include transition and post-transition metals (Cr, Mo, Mn, Ru, Co, Rh, Ir, Ni, Pd, Pt, Zn, Cd, In, Sn, Pb, etc.), revealing that urea formation predominantly occurs on cadmium achieving the highest efficiency of ~55% at -1.0 V vs SHE (38). Parallel investigations using nitrate ions instead of nitrite confirmed urea production but generally at lower faradaic efficiencies due to the reduced production of ammonia-like intermediates (39). To further improve selectivity, metallophthalocyanine (M-Pc) catalysts were tested in 0.2 M KHCO_3 0.02 M KNO_2 electrolyte, providing CO_2 in the cathode gas-chamber. This study highlighted the role of molecular catalysts in stabilizing $^*\text{CO}$ and $^*\text{NH}_{2(\text{ads})}$ like intermediates (40). Collectively, these studies

provided the mechanistic basis that urea is formed via coupling between $\ast\text{CO}$ (from CO_2 reduction) and $\ast\text{NH}_2$ (from $\text{NO}_2^-/\text{NO}_3^-$ reduction), and established gas-diffusion electrodes as an effective platform for exploring electrocatalytic urea synthesis.

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Chapter 2

Quantification Techniques

Progress in electrochemical urea synthesis (EUS) research is constrained by the absence of rigorous and reproducible experimental protocols. To date, most demonstrations of EUS feasibility have been performed in limited, non-scalable systems such as H-cells, rather than in configurations or environments representative of industrial relevant conditions (1-3). Moreover, many reported results rely on analytical methods prone to inaccuracy, resulting in a critical lack of standardized protocols for precise urea quantification and, consequently, for the reliable determination of faradaic efficiency (4). In response, the urea quantification methods commonly reported in the literature (*i.e.*, DAMO-TSC method) were critically assessed, highlighting their inadequacy, and a robust interference-free and time-effective protocol, based on High Performance Liquid Chromatography (HPLC), was developed to enable accurate and reproducible urea determination.

2.1 Optimization of the HPLC/UV-Vis method for urea detection/quantification

Given the small, markedly polar nature of urea, we employed hydrophilic interaction chromatography (HILIC). Initial experiments utilized an Agilent Infinity 1260 chromatograph (Figure 8) equipped with an Agilent InfinityLab Poroshell 120 HILIC-Z column (2.1×100 mm, $2.7 \mu\text{m}$). Column specifications, conditioning, operational parameters, and storage procedures follow manufacturer guidelines (Agilent *COLUMN USER GUIDE for Normal-Phase and HILIC Columns*).

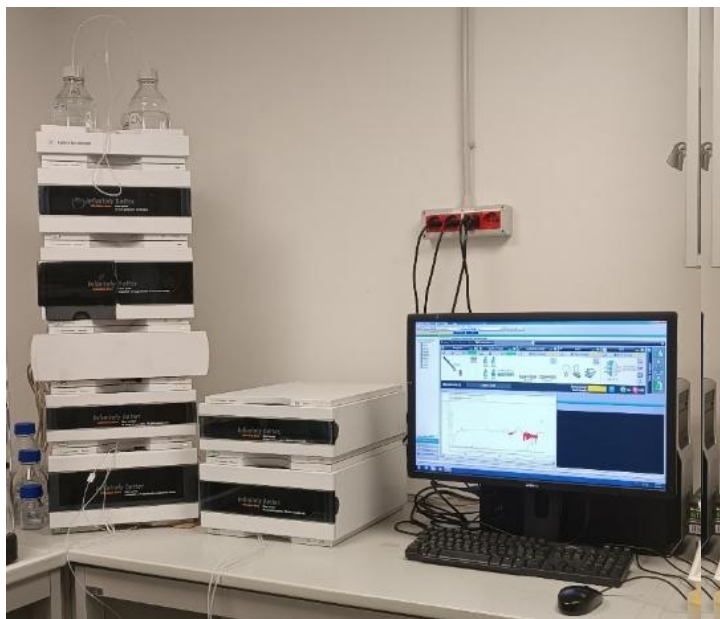


Figure 8 HPLC Agilent Infinity 1260 workstation, equipped with a quaternary pump, standard autosampler, thermostatted column compartment, Diode Array Detector (DAD/UV-Vis) operating in the range between 190 to 950 nm and a Refractive Index Detector (RID).

Due to the lack of established protocols for separating urea from bicarbonate- and nitrate-containing aqueous solutions using this column and the limited procedural detail available in the literature, at first an isocratic elution condition (20/80 water/acetonitrile) was implemented. Urea was detected by DAD/UV-Vis at 195 nm. Representative sample chromatograms are provided in Figure 9.

Neither water nor KHCO_3 solution (black and red traces, respectively) produced detectable signals at 195 nm. In contrast, nitrate ions, which exhibit strong absorption in the near UV region (blue trace, Figure 9), yielded a peak at *ca.* 5.45 minutes. A mock EUS sample (urea, *ca.* 100 ppm, in 0.2 M KHCO_3 + 0.02 M KNO_3) displayed a peak at the same retention time, reflecting overlapping contributions from both urea and nitrate. These results indicate that the high polarity of the 20/80 water/acetonitrile eluent does not permit adequate resolution of the analytes.

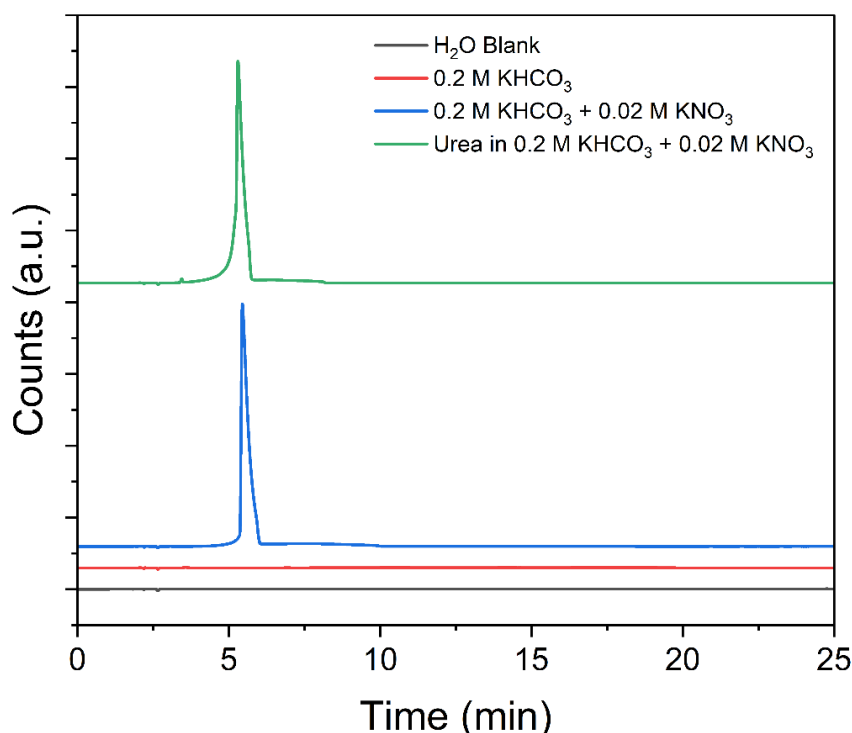


Figure 9 Sample chromatograms collected during the first attempt of isocratic urea separation in mock EUS samples. Column: Poroshell 120 HILIC-Z. Mobile phase A = H₂O. Mobile phase B = ACN. Flow: 0.750 mL min⁻¹. Gradient: isocratic, A/B = 20/80. Re-equilibration: none. Injection: 2.5 µL. Column temperature: 30°C. Detection: UV, 195 nm, 20 Hz.

To improve separation, we initially considered lowering the A/B ratio to 5/95, which would extend the retention time of polar species and potentially achieve baseline resolution. However, under isocratic conditions such an approach would result in impractically long runs. Therefore, in the second optimization step, we adopted a gradient strategy: starting from 5/95, the eluent composition was ramped to 50/50. In line with HILIC separation principles and column specifications, retention diminishes when the water fraction reaches $\geq 50\%$ (as reported in column manuals and in literature) (5). At this stage, an isocratic step at A/B ratio of 50/50 was introduced to ensure complete elution of residual species. The mobile phase was then returned to the initial 5/95 A/B ratio, followed by a 10-minute post-run to allow system re-equilibration. Additional parameters (*e.g.*, flow rate) were likewise optimized. Chromatograms of control samples and a urea standard obtained under these conditions are presented in Figure 10.

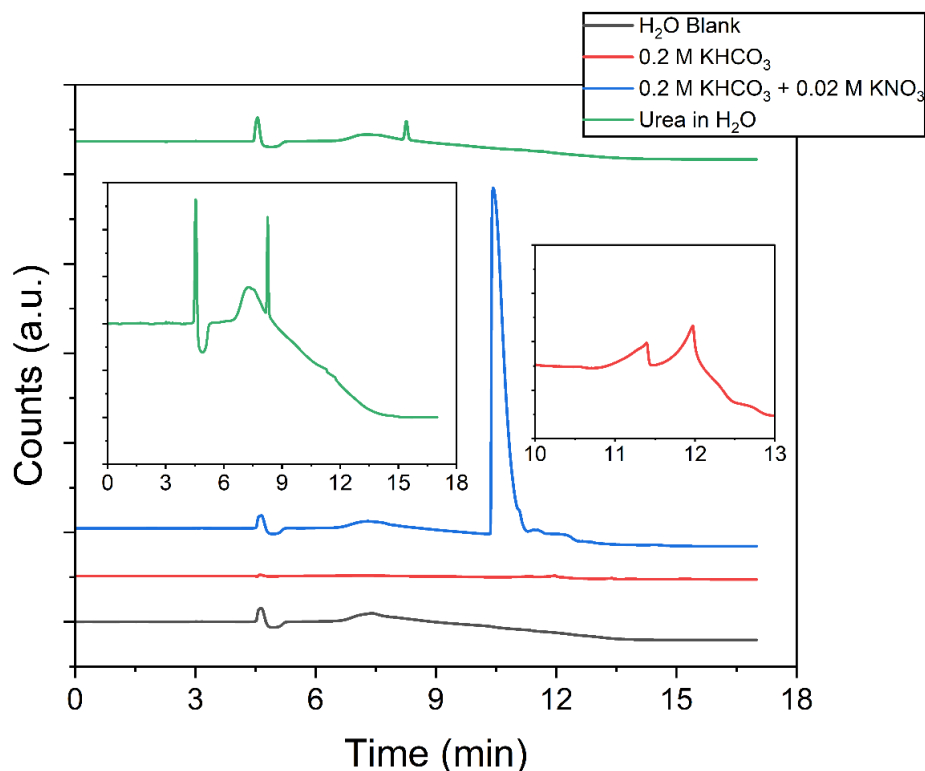


Figure 10 Sample chromatograms collected during the first attempt of gradient urea separation. Column: Poroshell 120 HILIC-Z. Mobile phase A = H_2O . Mobile phase B = ACN. Flow: $0.500 \text{ mL min}^{-1}$. Gradient: 5/95 to 50/50 in 9 minutes, then isocratic 50/50 for 8 minutes. Re-equilibration: 10 minutes at the initial 5/95 eluent composition. Injection: $2.5 \mu\text{L}$. Column temperature: 30°C . Detection: UV, 195 nm, 20 Hz. Insets to highlight the typical shape of chromatograms (left) and the presence of asymmetric, small peaks when a plain bicarbonate solution is injected (right).

Figure 10 illustrates that the chromatograms obtained under gradient elution can be divided into three distinct regions. The first region is mostly flat, with a signal at *ca.* 4.6 minutes attributed to the injection process. In the second region, the baseline increases showing a maximum at *ca.* 7.3 minutes, followed by a nearly linear decline. At *ca.* 14 minutes, the baseline stabilizes, consistent with the isocratic step initiated at 9 minutes. These features, clearly visible in the left inset of Figure 10 and consistently observed across all samples, reveal characteristic signals in the presence of the analytes of interest. Specifically, KHCO_3 solutions yield small, asymmetric peaks between 11 and 12 minutes (right inset, Figure 10), nitrate ions elute at *ca.* 10.4 minutes (blue trace), and urea elutes at *ca.* 8.25 minutes (green trace), producing a sharp, well-defined, and readily integrable peak within the linearly descending portion of the baseline.

Encouraged by these results, we proceeded to construct a calibration curve for urea under the optimized conditions. Standard solutions of urea (from 0.5 to 5000 ppm) were prepared in 0.2 M KHCO_3 + 0.02 M KNO_3 solutions and sequentially injected. The corresponding chromatograms are presented in Figure 11.

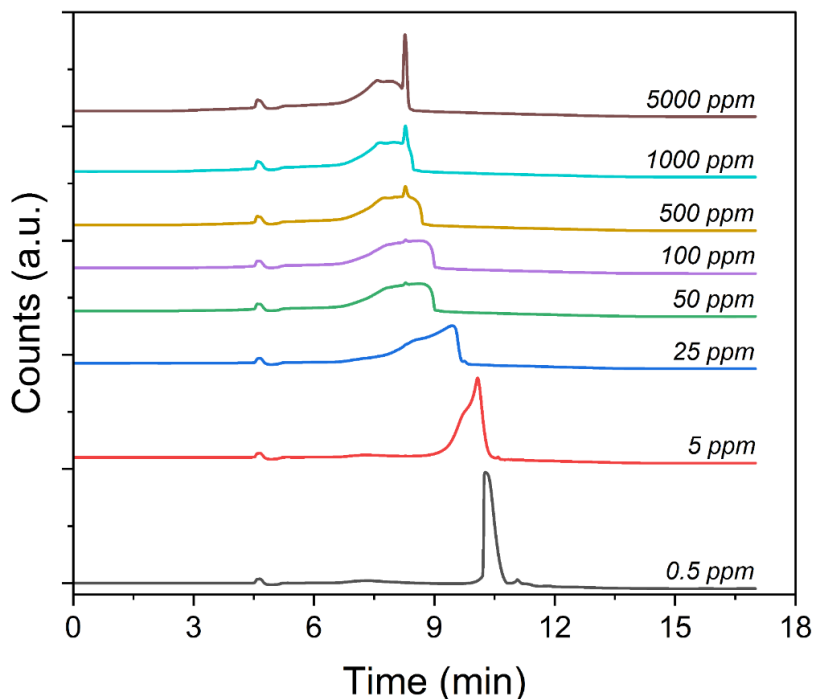


Figure 11 Tentative urea calibration (urea standard samples prepared in 0.2 M KHCO_3 + 0.02 M KNO_3). Column: Poroshell 120 HILIC-Z. Mobile phase A = H_2O . Mobile phase B = ACN. Flow: 0.500 mL min^{-1} . Gradient: from 5/95 to 50/50 in 9 minutes (linear gradient), then isocratic 50/50 for 8 minutes. Re-equilibration: 10 minutes at the initial 5/95 eluent composition. Injection: 2.5 μL . Column temperature: 30°C. Detection: UV, 195 nm, 20 Hz.

Two key observations can be drawn from Figure 11. First, under the employed elution and detection conditions, urea becomes barely detectable only at concentrations between 50 and 100 ppm. This detection limit does not meet the sensitivity required by the EUS community. Second, repeated injections result in broadening and shifting of the nitrate peak toward shorter retention times, which interferes with urea detection. This behavior indicates progressive poisoning of the column active sites, likely due to the high concentrations of nitrate and bicarbonate injected. The final isocratic step (minutes 9 to 17) is therefore insufficient to fully regenerate the column. While dilution of the samples prior to injection could mitigate this effect, such an approach would also dilute the analyte, thereby reducing detectability and hindering quantitative analysis.

In the third optimization step, we maintained the procedural framework but modified the nature of the eluents. Increasing the ionic strength of the mobile phase through the addition of a buffering agent can promote desorption of analytes and impurities from the column, reduce retention times, and improve peak shape (Agilent Technical Overview: *Hydrophilic Interaction Chromatography Method Development and Troubleshooting*). However, the use of buffers may interfere with detection, particularly in the near UV range where common additives (formic or acetic acid and their salts) absorb at *ca.* 210 nm. With this consideration in mind, we evaluated formic acid as a buffering agent. Accordingly, mobile phase A was prepared as a 10 mM aqueous solution of formic acid, and mobile phase B as a mixture of 100 mL 100 mM formic acid in water with 900 mL acetonitrile (hereafter referred to as 10 mM formic acid in ACN). Initial separation and detection tests with both urea-containing and blank water/electrolyte samples yielded promising results, as shown in Figure 12.

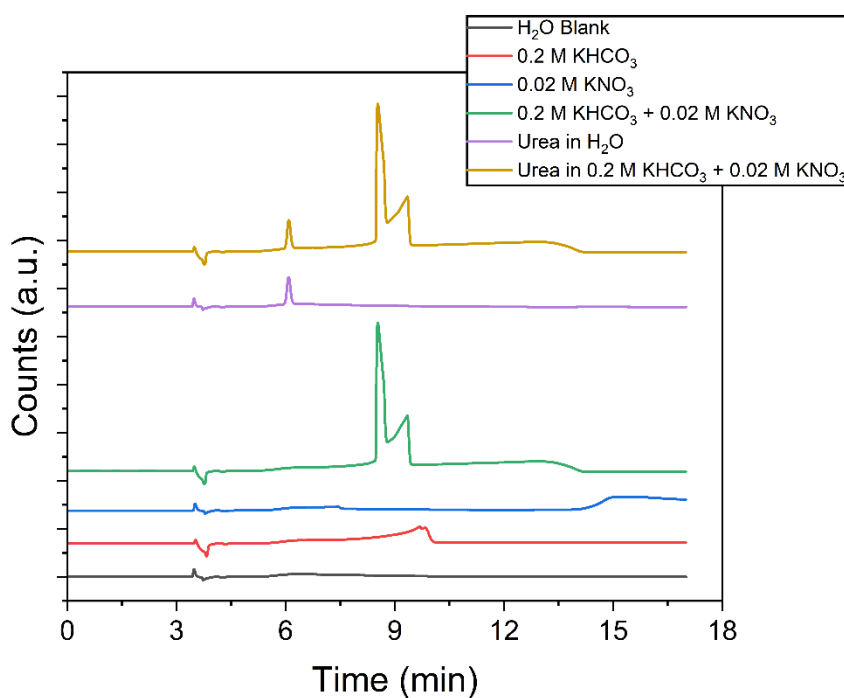


Figure 12 Preliminary check of urea separation using a buffered elution gradient. Column: Poroshell 120 HILIC-Z. Mobile phase A = 10 mM formic acid in H₂O. Mobile phase B = 10 mM formic acid in ACN. Flow: 0.500 mL min⁻¹. Gradient: from 5/95 to 50/50 in 9 minutes (linear gradient), then isocratic 50/50 for 8 minutes. Re-equilibration: 10 minutes at the initial 5/95 eluent composition. Injection: 2.5 µL. Column temperature: 30°C. Detection: UV, 195 nm, 20 Hz.

In the presence of detectable analytes (e.g., urea, nitrate), the expected buffer-induced decrease in retention time was confirmed (Figure 12), with urea eluting at

ca. 6.4 minutes. Notably, bicarbonate and nitrate ions yielded distinct chromatographic behaviors depending on whether they were injected individually or together. Sole bicarbonate (red trace) produced the asymmetric peaks previously discussed (Figure 10), though with reduced retention time, consistently with the higher ionic strength of the eluent. Sole nitrate (blue trace) showed no significant feature in this region. However, injection of the blank EUS electrolyte (0.2 M KHCO_3 + 0.02 M KNO_3) produced a two-peak system around 8-10 minutes. Tests suggest these peaks correspond to nitrate and bicarbonate, respectively although the origin of this co-dependent behavior remains unresolved.

To evaluate possible interferences from other relevant analytes, standard solutions of common individual CO_2RR and NO_3RR products, as well as representative C-N containing species (*i.e.*, potential EUS by-products), were prepared and analyzed. The principal results are summarized in Figure 13.

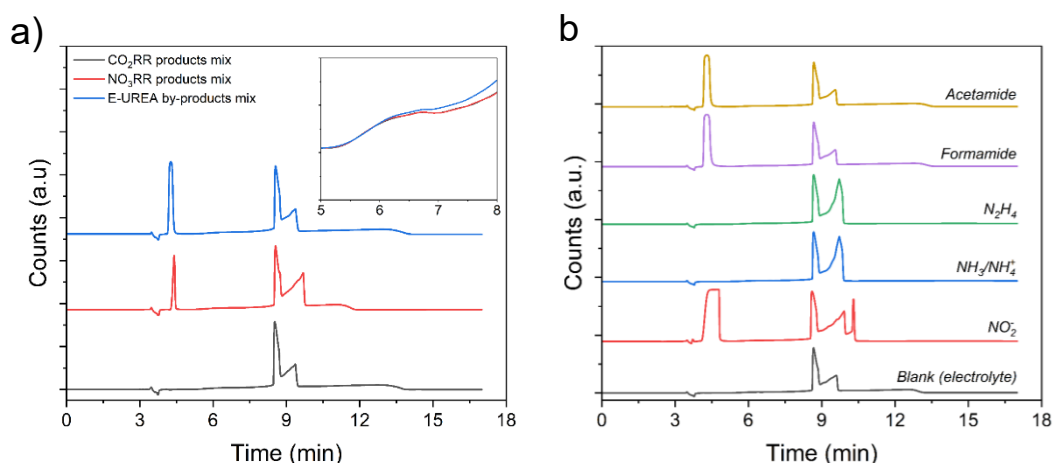


Figure 13 Check for interferers in the formic acid-buffered gradient elution method. Experimental conditions are identical to those reported in the previous Figure 9. Product mixes contain 5000 ppm of the most common individual CO_2RR and NO_3RR products and possible EUS by-products dissolved in 0.2 M KHCO_3 + 0.02 M KNO_3 . The CO_2RR mix contains formic acid (formate ions), acetic acid (acetate ions), formaldehyde, acetaldehyde, methanol, ethanol, isopropanol and 1-propanol. The NO_3RR mix contains nitrite ions, ammonia (ammonium ions), hydrazine, hydroxylamine. The EUS by-products mix contains: formamide and acetamide.

Injection of a CO_2RR product mixture produced no additional peaks, likely due to the poor detectability of these species at 195 nm (see Section 2.1.1. “HPLC/UV-Vis detection on HiPlex column”). In contrast, the NO_3RR product mixture yielded an additional peak at ca. 4.4 minutes and enhanced intensity of the asymmetric peak immediately following the nitrate signal. The EUS by-products mixture displayed only a peak at ca. 4.4 minutes, similar to that observed for the NO_3RR mixture, with no further noteworthy features. Individual injections of NO_3RR products and

potential EUS by-products (Figure 13b) allowed consistent assignment of the *ca.* 4.4-minute peak to nitrite, formamide, and/or acetamide, while the increase in the asymmetric peak was attributed to hydrazine and/or ammonium ions.

As no overlap with the urea peak was observed in Figure 13, we repeated the calibration procedure described for Figure 13 under buffered gradient elution conditions. This approach yielded robust, well-resolved, and readily integrable data (Figure 14).

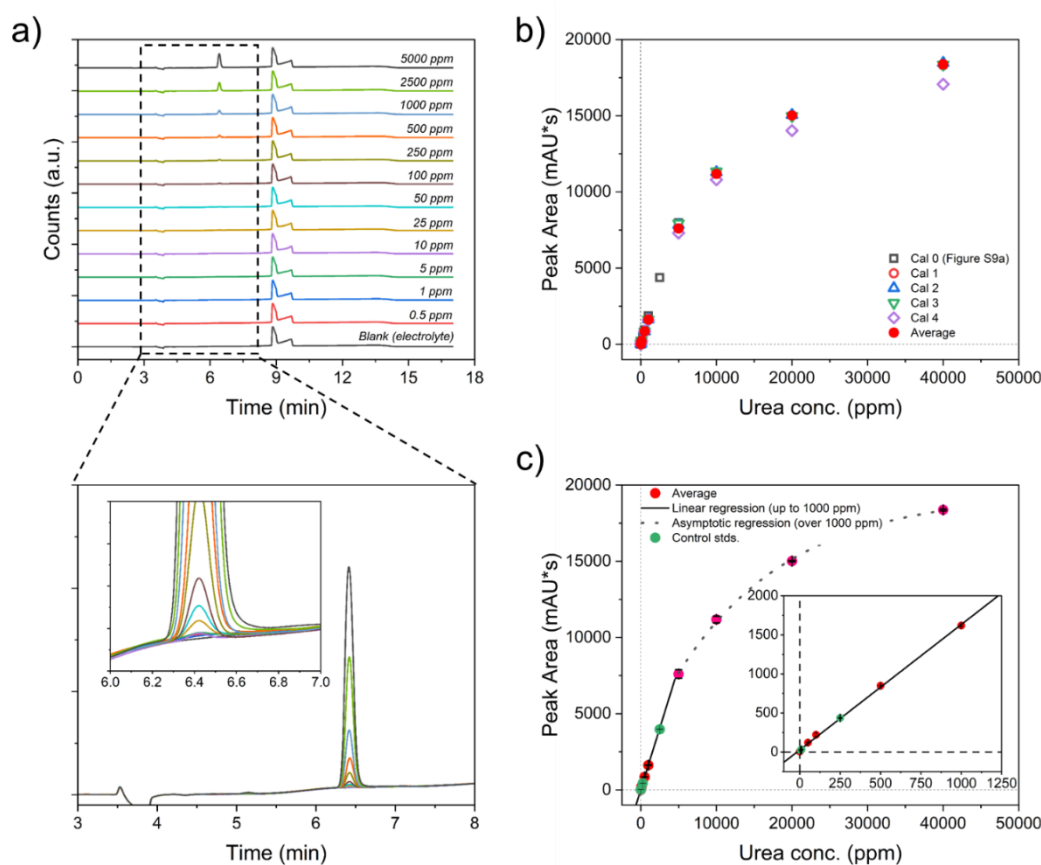


Figure 14 Complete calibration data, obtained by HPLC analyses of urea standards (from 0.5 to 40000 ppm, dissolved in EUS electrolyte) according to the optimized methodology reported in Figure 9. a) Chromatograms collected during the preliminary screening (up to 5000 ppm) at different urea concentrations (top) and related magnifications of urea peak region (bottom). b) Replicates of the calibration curve, with concentrations of urea reaching the saturation of the detector. c) Linear (up to 1000 ppm) and asymptotic (from 1000 to 40000 ppm) fitting of the averaged calibration data (full red circles). Average peak area obtained from control standards at 5, 7.25, 10, 250 and 2500 ppm are represented in full green circles. The inset magnifies the linear region of the calibration curve.

Standards at 0.5 and 1 ppm produced no detectable urea peaks (red and blue chromatograms in Figure 14a). The 5 ppm urea standard was the first to yield a

clear peak at 6.4 minutes. To obtain reliable statistical parameters for calibration, four additional calibration curves were collected, extending also to higher urea concentrations (> 5000 ppm, up to 40000 ppm).

As expected, an asymptotic response was observed at higher concentrations (Figure 14c, dashed line), while linearity was maintained for urea concentrations up to 1000 ppm (Figure 14c, solid line). The robustness of the calibration was subsequently validated by repeatedly injecting control standards (green filled circles, Figure 14c) with concentrations within the same range as the calibration standards but at distinct values and for multiple times (4x). Statistical data for the determination of the limit of detection (LoD) and limit of quantification (LoQ) were obtained by averaging the peak areas from calibration samples and blanks. Using the signal-to-noise (S/N) ratio, defined as the ratio between the sample peak area and the blank peak area, we identified an LoD of 5 ppm ($S/N = 3.59$) and, from calibration data, an LoQ of 19.9 ppm ($S/N = 10$).

The calibration procedure proved to be robust and reproducible, yielding consistent chromatograms and peak areas across multiple standard injections performed on different days. However, noticeable shifts in analyte retention times were observed when the eluent preparation was not standardized (Figure 15).

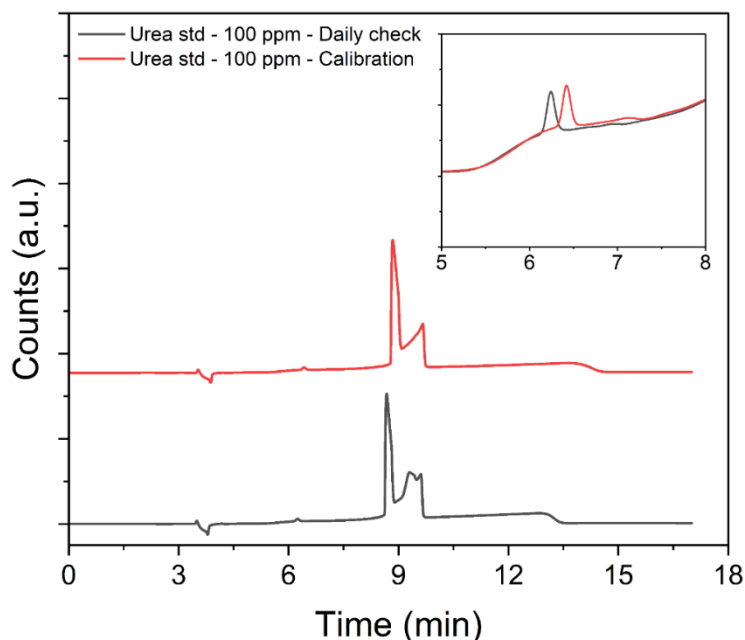


Figure 15 Chromatograms obtained on the same 100 ppm urea standard in different days, with freshly prepared (not standardized preparation procedure) eluent. Operative conditions are reported in Figure 12.

This sensitivity is inherent to HILIC operation, where even minor variations in eluent composition can result in retention time shifts, as documented in technical references (e.g., Agilent Technical Overview, *Hydrophilic Interaction Chromatography Method Development and Troubleshooting*). Accordingly, we recommend strict standardization of eluent preparation procedures and the inclusion of standard sample runs at the beginning of each analytical batch.

In summary, the optimized HPLC/UV-Vis method enables unbiased and accurate quantification of urea in post-reaction EUS electrolytes in the range from 20 to 1000 ppm (that corresponds to 330 μM to 17 mM), with qualitative detection achievable down to *ca.* 5 ppm. Each analytical run, including elution and post-run re-equilibration, requires 27 minutes. Although the developed HPLC method is free from interferences, its detection and quantification limits are higher than those of conventional or modified DAMO-TSC methods. Nonetheless, simple calculations demonstrate that this approach remains compatible with the requirements of EUS. By appropriately selecting current density, electrode area, electrolyte volume, and the acquisition time of CP scans, the expected urea concentration (at a fixed faradaic efficiency informed by literature values) can be raised above the detection and quantification thresholds of the method.

2.1.1. Urea detection/quantification on HiPlex column

During optimization of the HPLC method for separation and quantification of CO_2RR liquid products on a HiPlex H column (see Section 2.3.2. “*HPLC method for CO_2RR products detection/quantification*”), we unexpectedly observed that the column also retains and separates urea. Under the same conditions employed for CO_2RR product analysis, urea exhibited strong retention and eluted at *ca.* 190 minutes (Figure 16; detection by DAD/UV-Vis at 195 nm). However, the extended retention time resulted in a markedly broad peak, complicating both identification and integration, particularly at low concentrations (black trace, Figure 16).

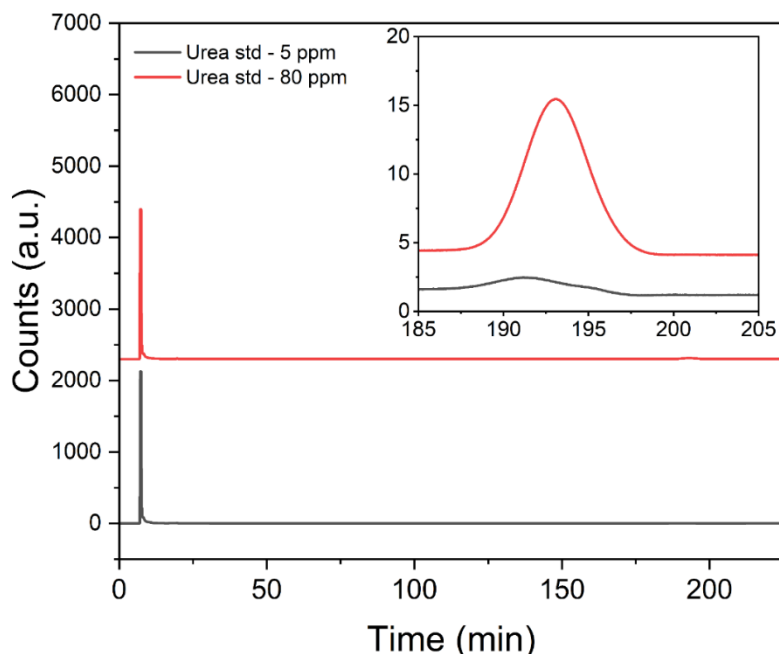


Figure 16 Urea elution peaks obtained under typical CO₂RR products analysis conditions on Hi-Plex H (see Section 2.3.2. “High-Performance Liquid Chromatography (HPLC)” for details). The number of counts (DAD/UV-Vis, operating at 195 nm) is indicated in the figure to highlight the small size of the signal.

Hi-Plex columns are mechanically fragile and cannot tolerate high flow rates or support gradient elution (see the user manual, 5991-6743EN *Agilent HiPlex data sheet*). As a result, the urea peak could not be shifted to shorter retention times. Considering the extended acquisition time and the difficulty of peak integration, this separation approach was not pursued further.

2.2 Modified DAMO-TSC method (M-DAMO-TSC)

The DAMO-TSC colorimetric assay offers a simple and relatively rapid means of urea quantification; however, its applicability to EUS post-reaction electrolytes is limited by significant interference effects (6). These shortcomings, extensively documented by several groups (2, 3, 7-12), including ours (4), primarily arise from the presence of nitrite ions, a common by-product of NO₃RR. At high concentrations ($\geq ca.$ 1.5 mM), nitrite ions suppress color development, resulting in false negatives. More critically for EUS applications, low concentrations of NO₂⁻ (0 to $ca.$ 1.5 mM) can induce false positives, as first reported by Wei et al. (12) and subsequently confirmed in multiple studies.

To address this issue, in 2023, Chen et al. (13) introduced a modified DAMO-TSC method (M-DAMO-TSC), in which nitrite interference is suppressed by reaction with sulfamic acid under acidic conditions. Sulfamic acid, a standard reagent for nitrite ions abatement in wastewater, is also employed in related contexts, such as nitrate quantification in nitrite-containing solutions (14). We successfully reproduced the findings of Chen et al., confirming that M-DAMO-TSC, implemented here without adding HCl in the nitrite reduction step (see the Section 3.1.4.4.4. “Urea - M-DAMO-TSC method”), (i) does not alter the sensitivity of the classic DAMO-TSC method (Figure 17) and (ii) eliminates the characteristic indicators of NO_2^- interference (Figure 18), including anomalous absorbance changes in urea standards and λ_{max} shifts to lower values (12), thereby restoring a robust and reliable peak for urea quantification.

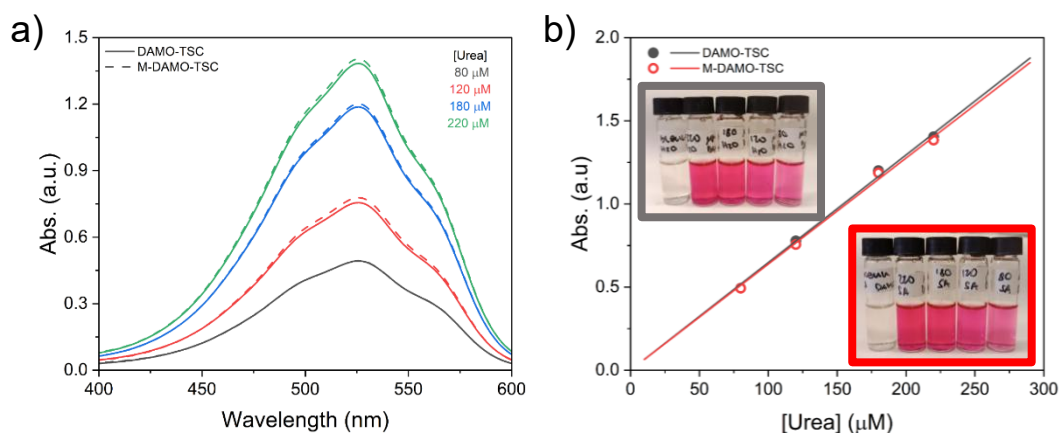


Figure 17 Comparison of (a) DAMO-TSC and M-DAMO-TSC spectra and (b) calibration lines obtained on standard urea samples. Insets in (b) show the identical color intensity obtained in clean urea samples reacted according to the classic DAMO-TSC method (top left) and nitrite-containing urea samples treated according to the M-DAMO-TSC method (bottom left). Note: vials in the insets have the blank sample on their left and urea-containing samples with decreasing concentration from left to right.

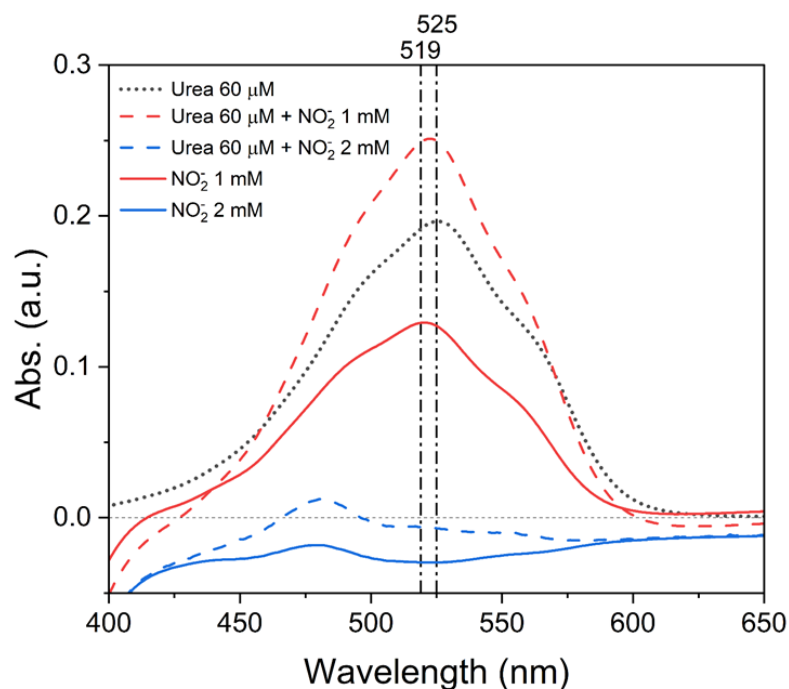


Figure 18 Typical symptoms of NO_2^- interference in the urea quantification by the classic DAMO-TSC method: increase in the absorbance and/or false positives together with shifts in the λ_{max} at low concentration (dashed and full red traces) and false negatives at high concentration (dashed and full blue traces).

Building on these positive results, we adopted the M-DAMO-TSC method as a complementary approach for urea quantification, thereby providing an independent validation of the results obtained by HPLC/UV-Vis. Notably, this colorimetric technique extends the lower detection and quantification range for urea down to 0.1 ppm (13), surpassing the sensitivity of the HPLC method.

It should be noted, however, that the M-DAMO-TSC method selectively removes nitrite ions from post-reaction electrolytes, while other potential interferents (*e.g.*, cyanates) remain unaddressed. Furthermore, Tiange et al. highlighted five critical challenges associated with DAMO-TSC assays in post-reaction electrolytes, including time-dependent variation in the absorbance of the urea-derived chromophore and sensitivity of the signal to light exposure (8). The introduction of sulfamic acid does not mitigate these issues, and thus M-DAMO-TSC remains susceptible to the same sources of error.

2.3 Calibration of most common EUS by-products

Although the primary focus of this work is the assessment of urea production, for which a dedicated HPLC/UV-Vis method has been developed, additional by-products of the EUS process (*i.e.*, products of HER, CO₂RR, and NO₃RR) were also detected by integrating established analytical approaches for each reaction (see, *e.g.*, refs. 15, 16).

Detection and quantification of these by-products were performed as detailed in the dedicated Section 3.1.4. “*Quantification of products*”. Representative chromatograms and/or spectra, along with the corresponding calibration curves, are reported below.

2.3.1. Gas chromatography (GC)

An inline GC was employed to detect H₂ and N₂, obtained from parasitic HER and NO₃RR respectively, and the major gaseous products of CO₂RR. Under the operating conditions described, the Thermal Conductivity Detector (TCD) also exhibited sensitivity to N₂ (Figure 19), a potential product of NO₃RR. However, no N₂ formation was observed in experiments where NO₃RR occurred, consistent with the documented tendency of Cu-based catalysts to favor NO₂⁻ and NH₃ production (17, 18).

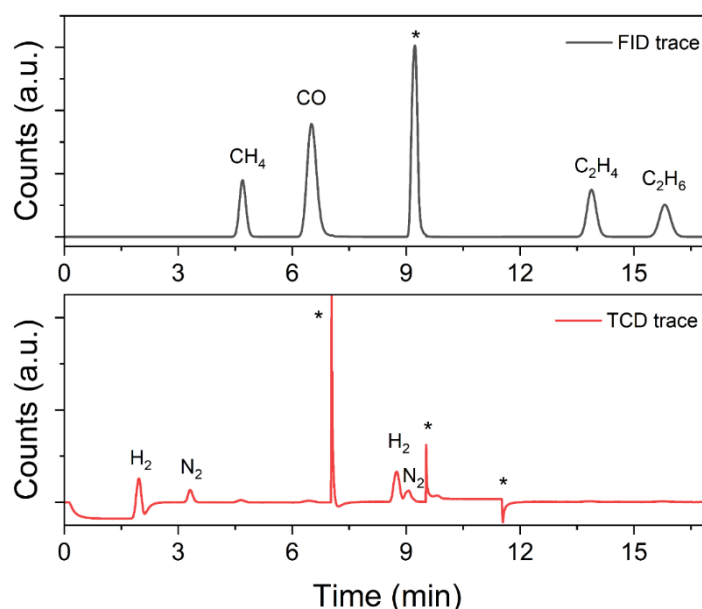


Figure 19 Sample FID (top) and TCD (bottom) gas chromatograms obtained during the calibration of the GC. Stars indicate peaks stemming from column events (*e.g.*, valve switches).

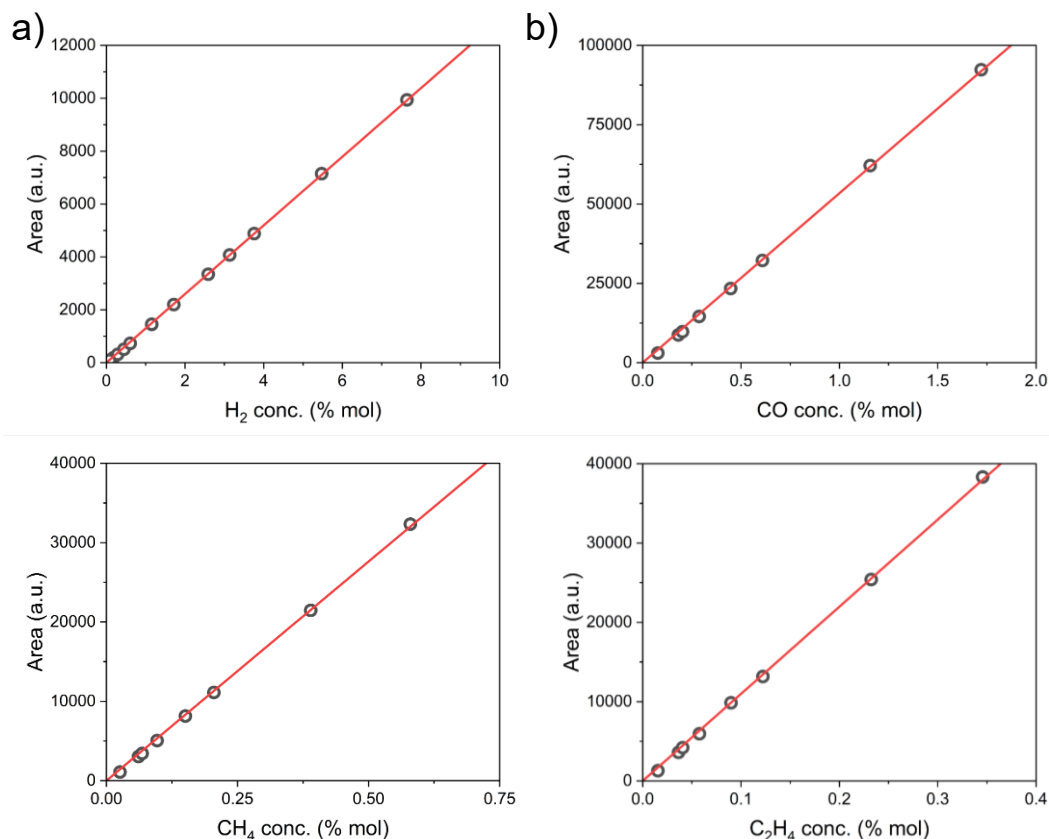


Figure 20 Sample calibration curves obtained for the most common gaseous CO₂RR products on polycrystalline Cu. Full data (including less common gaseous products of the individual reactions, e.g., C₂H₆ and N₂) available in the following Table. H₂ calibration line refers to H₂ Peak 1 data.

Response factors (*i.e.*, slope) and related statistics regressed from GC calibration data are reported in Table 4 in Appendix.

2.3.2. HPLC method for CO₂RR products detection/quantification

Liquid-phase CO₂RR products were quantified using a combined HPLC/UV-Vis and Refractive Index Detector (RID) approach on a HiPlex H column, following the conditions described in the Section 3.1.4.2.1. “CO₂RR liquid product analysis” and the protocol reported by Iglesias van Montfort et al. (15). Retention times and peak areas of the analytes, measured across detectors (Figure 21a), were found to be independent of the electrolyte matrix (see RID chromatograms, Figure 21b).

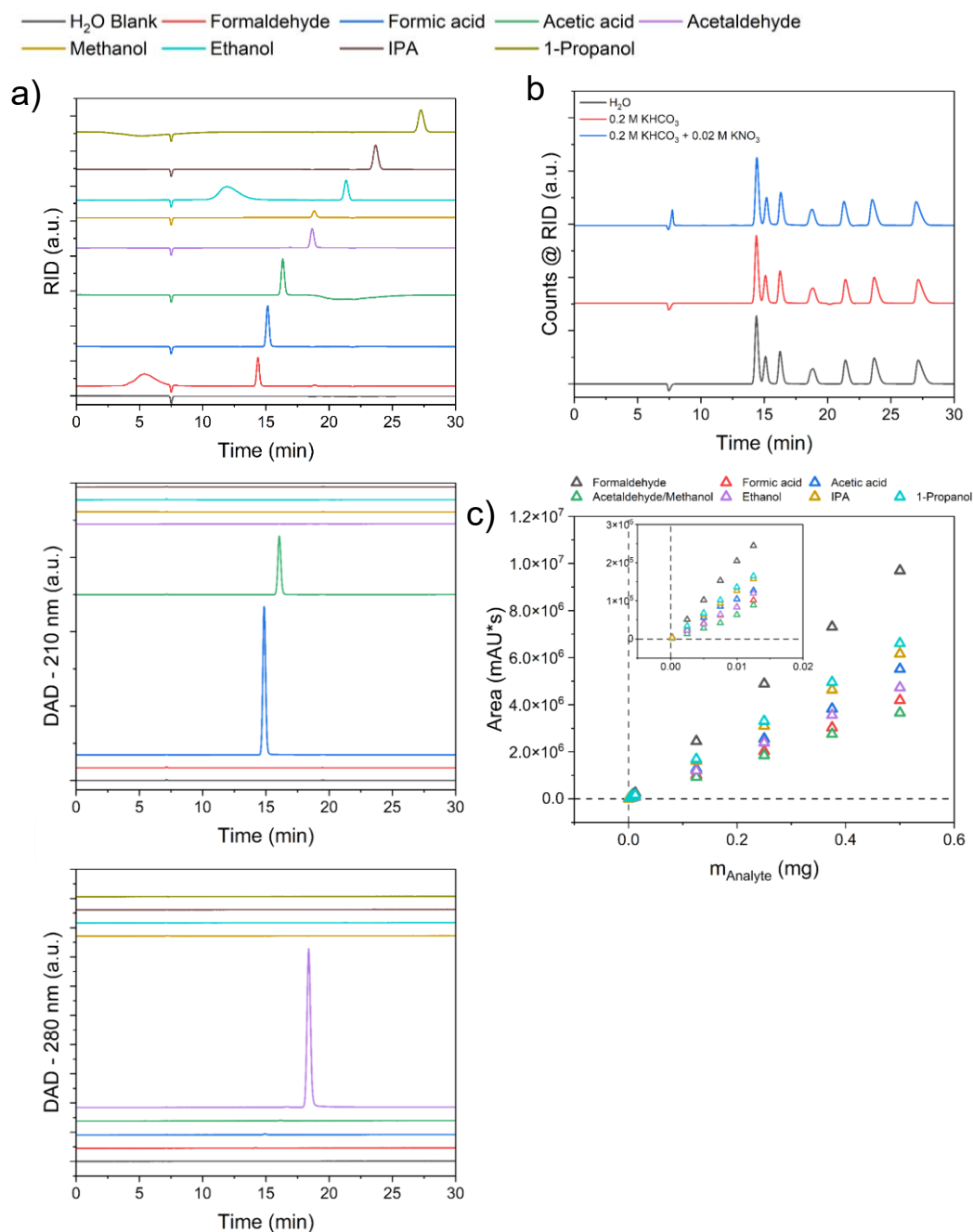


Figure 21 a) Identification of the retention time of each analyte at different detectors (RID, DAD @ 210 nm, and DAD @ 280 nm), obtained by injecting 25 mL of concentrated analytes solutions (ca. 1000 ppm) in H₂O. b) Individual CO₂RR byproducts mixtures, prepared in the presence or absence of the typical components of the electrolyte used in this study. c) Representative calibration plot (inset is a magnification of the low analyte concentration region), obtained from the integration of RID peaks area. Regressed calibration lines are not shown to provide a more readable figure. Other calibration plots are not reported for the sake of conciseness but are available to the reader upon reasonable request to the corresponding author.

It should be emphasized that the separation and detection of some products, was not optimal under the current chromatographic conditions. Acetaldehyde and methanol co-elute on the RID, although acetaldehyde could still be readily detected and quantified using the DAD at 280 nm. Ethanol, and also methanol partially, exhibited signal interference associated with (bi)carbonate-related noise, consistent with the observations of Iglesias van Montfort et al. (15). As the primary focus of this work was urea detection and given that these compounds are not directly involved in its formation, further optimization of these separations was not pursued. Nonetheless, we acknowledge that improved chromatographic resolution might have revealed trace amounts of alcohols, which could partially account for the missing faradaic efficiency in the individual CO₂RR balance (Section 3.2.4.2. “CO₂RR conditions”).

2.3.3. ¹H-NMR

¹H-NMR has been widely applied for identification and quantification of liquid-phase products in CO₂RR studies. We recently optimized an external standard method for this purpose, as reported in our previous work (19). In the present study, however, given the primary focus on urea detection and quantification, ¹H-NMR was not employed to cross-validate the CO₂RR liquid-product distributions obtained by HPLC.

It is worth noting that ¹H-NMR can, in principle, be used for ammonia and urea quantification, though several limitations exist (as discussed in our prior Viewpoint (4)). For urea specifically, detection is complicated by the exchangeable nature of its protons, necessitating pH adjustment, and by a relatively high detection limit (2, 8). Figure 22 presents a tentative calibration on urea standards, illustrating the relatively high LoD achievable on routine 600 MHz instrumentation with practical acquisition times.

Urea concentration was determined *via* the external standard PULCON (Pulse Length Based Concentration Determination) method (20). Broad NH₂ signals at 5.62 ppm were integrated and compared with those of an external standard (10.118 mM solution of DiMethyl Sulfone (DMS, TraceCERT® certified purity 99.73%, uncertainty 0.09%) prepared in blank solution. Peak areas were normalized to the number of contributing protons (*i.e.*, 4H for urea and 6H for DMS, respectively). Given the relatively high limit of detection of the technique, the calibration curve is not reported.

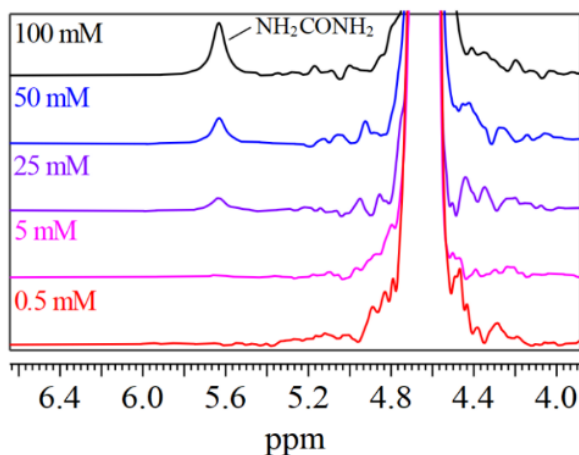


Figure 22 ^1H -NMR spectra collected on standard urea samples in representative electrolyte.

2.3.4. Colorimetric methods

The detection and quantification of individual NO_3RR products in this work were performed using widely adopted colorimetric methods (with the exception of N_2), as outlined in Section 3.1.4.4. “*Colorimetric methods*”. While we acknowledge the inherent limitations of these methods, they represent the most practical and accessible approach for the present study, whose primary objective was to evaluate urea formation on Cu-based catalysts.

To address these challenges, we are actively developing and implementing more robust and precise detection strategies, with particular emphasis on chromatographic quantification of ionic species (such as NO_2^- and NH_4^+). Certain potential NO_3RR products (*e.g.*, hydroxylamine, N_xO_y gaseous species) were excluded from consideration, given their negligible formation on Cu-based catalysts under near-neutral operating conditions. Moreover, no detectable N_2 formation was observed in our gas chromatography analyses.

2.3.4.1. NO_2^- - Griess method

Calibration curves were established by measuring the absorption spectra of solutions containing varying initial concentrations of nitrite ions in the reference electrolyte employed in the study (*e.g.*, 0.2 M KHCO_3 + 0.02 M KNO_3). During calibration, the Griess method exhibited a progressive blue shift in the absorption maximum (λ_{max}), from the conventional 540 nm down to approximately 530 nm, with increasing NO_2^- concentration (Figure 23a). Nevertheless, calibration curves obtained using either the conventional wavelength or the shifted λ_{max} were effectively overlapped (Figure 23b), confirming the robustness of the regression. In agreement with established principles of absorbance spectroscopy, samples exhibiting high absorbance values (≥ 2) deviated from Lambert-Beer linearity; these data points (highlighted as red crosses in Figure 23b) were excluded from the regression analysis.

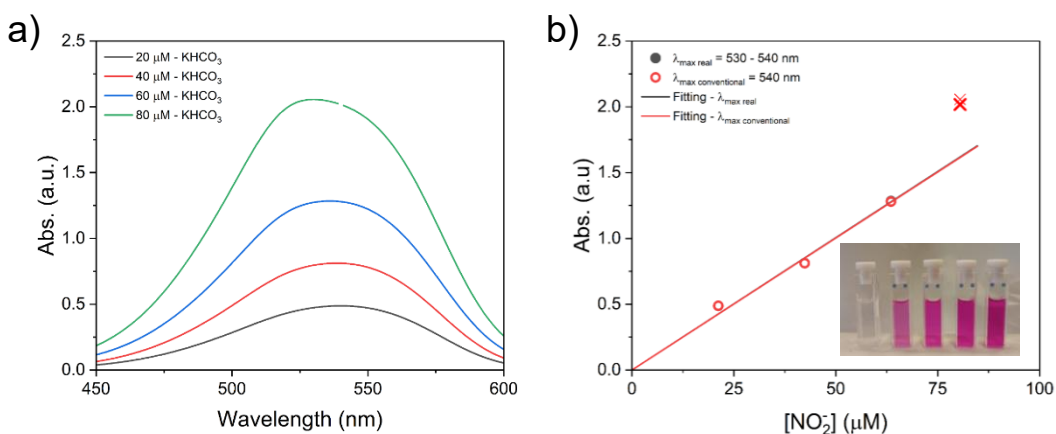


Figure 23 a) Absorption spectra collected upon the application of the Griess method on standard nitrite samples in KHCO_3 + KNO_3 based electrolyte and b) the resulting calibration line, regressed according to the Lambert-Beer equation. In the inset, a picture of the cuvettes containing the blank electrolyte (first from the left) and the calibration samples, reacted according to the Griess method.

2.3.4.2. NH_3 – Indophenol blue method

Calibration curves for ammonia were obtained by measuring the absorption spectra of solutions with varying initial concentrations of NH_3 in the reference electrolyte (*i.e.* 0.2 M KHCO_3 + 0.02 M KNO_3). Based on previous calibrations in other media (*e.g.*, 1 M KOH) and consistent with literature reports, the absorbance maximum of the peak was expected at *ca.* 652 nm. In this study, however, the spectra displayed a slight red shift to 661 nm (Figure 24a), which proved negligible with respect to absorbance-concentration correlations (Figure 24b). Notably, post-electrolysis samples did not exhibit any such shift. Given that calibration standards were

prepared from ammonium chloride (NH_4Cl , purity > 99.5%, Sigma-Aldrich), we attribute the observed shift to the presence of chloride anions, absent in post-reaction electrolytes. Importantly, while the slope differences between regressions at the conventional and shifted wavelengths were minimal, this behavior underscores the susceptibility of colorimetric methods to matrix-dependent interferences and highlights the need for more reliable analytical approaches for quantification of electrolysis byproducts.

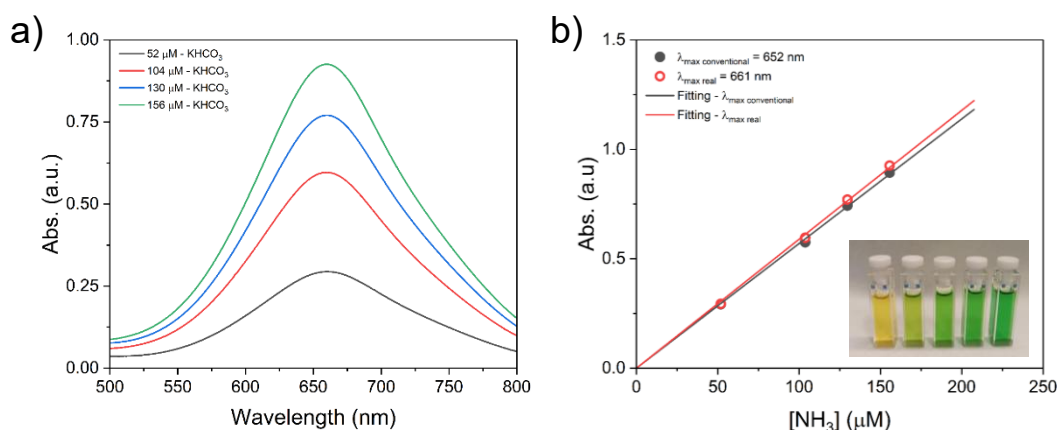


Figure 24 a) Absorption spectra collected upon application of the indophenol blue method on standard ammonia samples in $\text{KHCO}_3 + \text{KNO}_3$ based electrolyte and b) the resulting calibration line, regressed according to the Lambert-Beer equation. In the inset, a picture of the cuvettes containing the blank electrolyte (first from the left) and the calibration samples, reacted according to the indophenol blue method.

2.3.4.3. N_2H_4 – Watt and Chrisp method

For hydrazine quantification, calibration curves were obtained from solutions of known hydrazine concentration prepared in the reference electrolyte (*i.e.* 0.2 M $\text{KHCO}_3 + 0.02$ M KNO_3). In this case, the spectra were fully consistent with those expected from the standard Watt and Chrisp method, with no significant deviations observed. The reaction produced the characteristic yellow coloration, yielding an asymmetric absorption peak with a maximum at 458 nm (Figure 25a) (21). Linear regression of the absorbance data provided a robust and reliable calibration curve (Figure 25b).

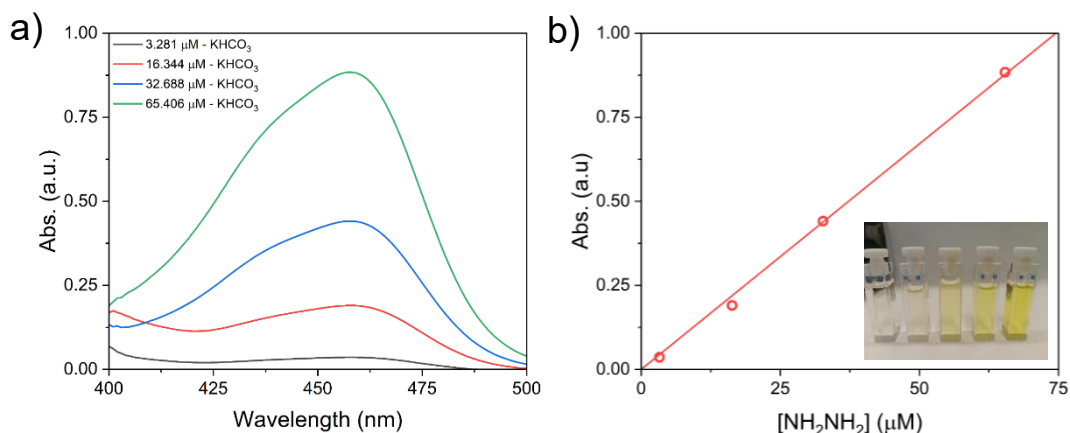


Figure 25 a) Absorption spectra collected upon the application of the Watt and Chrisp method on standard hydrazine samples in $\text{KHCO}_3 + \text{KNO}_3$ based electrolyte and b) the resulting calibration line, regressed according to the Lambert-Beer equation. In the inset, a picture of the cuvettes containing the blank electrolyte (first from the left) and the calibration samples, reacted according

2.3.4.4. Urea – DAMO-TSC method

Although the classical DAMO-TSC method is widely regarded as urea-specific, it was not employed for urea quantification in this study. Instead, the sulfamic acid-modified variant (M-DAMO-TSC), described earlier in Section 2.2. “*Modified DAMO-TSC Method (M-DAMO-TSC)*”, was selected as the preferred colorimetric approach. For completeness, Figure 26 presents the calibration spectra and regression obtained under the conditions of the classical DAMO-TSC method.

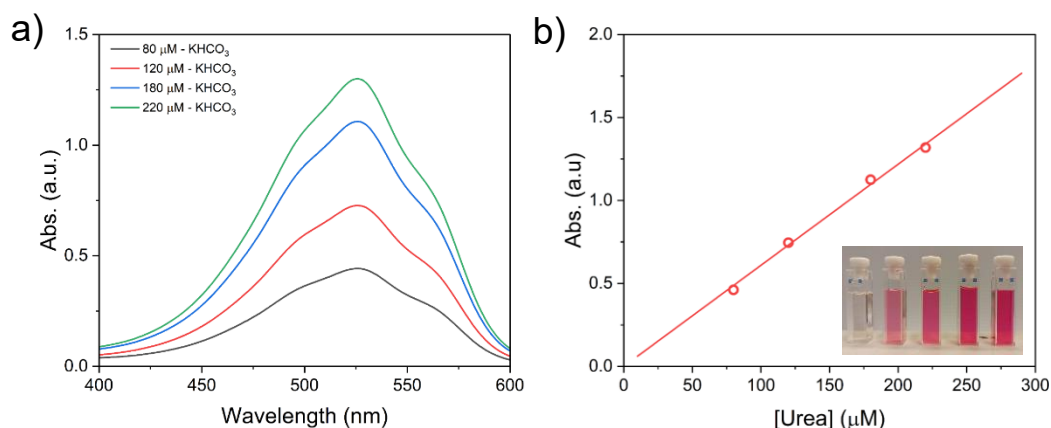


Figure 26 a) Absorption spectra collected upon the application of the DAMO-TSC method on standard urea samples in $\text{KHCO}_3 + \text{KNO}_3$ based electrolyte and b) the resulting calibration line, regressed according to the Lambert-Beer equation. In the inset, a picture of the cuvettes containing the blank electrolyte (first from the left) and the calibration samples, reacted according to the DAMO-TSC method.

The resulting absorption profile, with a λ_{max} at 525 nm (Figure 26a), and the slope of the calibration line (Figure 26b) are in good agreement with values commonly reported in the literature.

2.3.4.5. Additional analytes stability check

Given that both electrochemical measurements and colorimetric analyses are time-consuming, it was not always feasible to perform CP scans and product quantification on the same day. To ensure data reliability, we evaluated the stability of the analytes in the electrolyte using aged standard solutions. Apart from hydrazine (Figure 27d), analyte concentrations remained unchanged after storage for two days at room temperature (Figure 27).

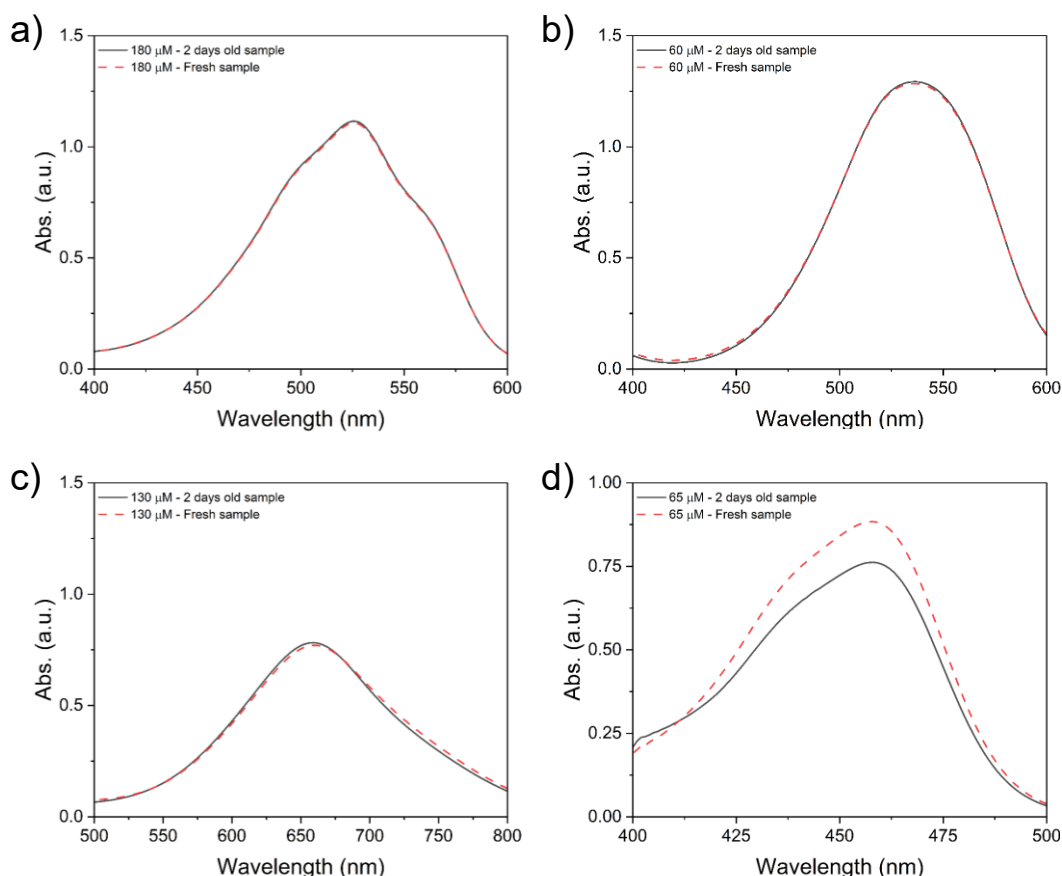


Figure 27 Stability check of common individual NO_3RR by-products (and also urea) in the electrolyte ($0.2 \text{ M KHCO}_3 + 0.02 \text{ M KNO}_3$). Samples of different analytes (a) urea; b) NO_2^- ; c) NH_3 ; d) N_2H_4) at different concentrations have been tested as soon as they were prepared (red dashed lines) and after being stocked at RT for two days (black full lines).

2.3.4.6. Assessment of colorimetric interferences in post-electrolysis-like samples

Colorimetric methods, specific to individual NO₃RR products, were also systematically evaluated in samples representative of real post-electrolysis conditions. Each method was first applied to standard solutions containing a single byproduct (Figure 28a) and subsequently to solutions containing the target analyte in the presence of one additional species at a time (Figure 28b). The concentrations of the interfering analytes in Figure 28b were selected based on calculations assuming 100% Faradaic efficiency, representing the worst-case scenario in which the system predominantly generates a single byproduct.

a)		Interferer								
		Urea	NH ₃	NO ₃ ⁻	NO ₂ ⁻	NH ₂ NH ₂	NH ₂ OH	MeOH	EtOH	HCOO ⁻
Target (applied method)	Urea									
	NH ₃									
	NO ₃ ⁻									
	NO ₂ ⁻									
	NH ₂ NH ₂									
	NH ₂ OH									

b)		Interferer								
		Urea	NH ₃	NO ₃ ⁻	NO ₂ ⁻	NH ₂ NH ₂	NH ₂ OH	MeOH	EtOH	HCOO ⁻
Target (applied method)	Urea									
	NH ₃									
	NO ₃ ⁻									
	NO ₂ ⁻									
	NH ₂ NH ₂									
	NH ₂ OH	N.Q.	N.Q.	N.Q.	N.Q.	N.Q.		N.Q.	N.Q.	N.Q.

	Target peak is present	Target peak, correct Abs.
	No peak from the interferer	Decrease Abs.
	Shifted peak, not problematic	Increased Abs.
	Shifted peak, problematic	Shift in λ _{max}
	Peak of the interferer at target's λ _{max}	Broad band, kills the peak
	Broad band, kills the peak	Peak disappears

Figure 28 Assessment of colorimetric interferences in post-electrolysis-like samples a) to standard solutions containing a single byproduct; b) to standard solutions containing both the target analyte and one additional species.

As previously discussed, among the species evaluated, nitrite ions emerged as the most significant interferences. At high concentrations ($\geq ca. 1.5$ mM), nitrite ions suppress color development, resulting in false negatives, and at low concentrations (0 to $ca. 1.5$ mM), NO₂⁻ can induce false positives. However, although nitrite ions

can be readily removed by applying the M-DAMO-TSC method, the presence of other possible byproducts leads to suppression of the urea signal, further demonstrating the high susceptibility of these methods to interference and their limited reliability for accurate product quantification.

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Chapter 3

EUS assessment in near-neutral electrolytes

3.1 Materials and methods

The following sections detail the methodologies for electrode preparation and characterization, electrochemical testing, and quantitative analysis of reaction products.

3.1.1. Electrode preparation and characterization

3.1.1.1. Cu foil electrode (H-cell)

A Cu foil strip (2×1 cm, 0.25 mm thickness, CAS: 7440-50-8, Sigma-Aldrich) was cut and sequentially cleaned by sonication in Milli-Q water, ethanol, and acetone, followed by drying under an Ar or N₂ stream. Kapton tape was then applied to the clean Cu strip to expose a total electrochemically active area of 2 cm² (1×1 cm on each side). The prepared Cu foil was immersed in a single compartment, two-electrode electrochemical cell containing 15 mL of 85 wt.% H₃PO₄ (CAS: 7664-38-2, Sigma-Aldrich), using a Cu mesh (CAS: 7440-50-8, Alfa Aesar) as the counter electrode. Electropolishing of the Cu foil was performed by applying a cell voltage of 1.2 V for 10 minutes. Following the electropolishing step, the sample was rinsed with Milli-Q water and immediately used for H-cell EUS testing.

3.1.1.2. Cu/PTFE electrode (flow-cell)

Cu/PTFE electrodes were prepared by depositing Cu onto PTFE membranes (Sterlitech® Aspire QL822, 0.45 μm pore size) using electron-beam evaporation (Kenosistec KE500ET combined e-beam/thermal evaporator) at a deposition rate of 50 Å s⁻¹. The resulting Cu film, with a final thickness of approximately 300 nm, provided uniform coverage of the PTFE substrate and ensured sufficient electrical conductivity for subsequent catalytic applications.

3.1.1.3. Reference electrodes calibration

Prior to use in either H-cell or flow-cell configurations, all reference electrodes were calibrated by measuring their Open Circuit Potential (OCP) in 0.5 M H₂SO₄ (pH 0) against a Reference Hydrogen Electrode (RHE, HydroFlex®, Gaskatel).

3.1.1.4. X-Ray Diffraction (XRD) Analysis

XRD measurements were carried out under ambient conditions and at room temperature, with the Cu foil or Cu/PTFE electrode supported on a zero-diffraction single-crystal substrate. Data acquisition was performed using a PANalytical Empyrean diffractometer equipped with a 1.8 kW Cu K α ceramic X-ray tube and a PIXcel3D 2 $\times$ 2 area detector, operating at 45 kV and 40 mA. The diffraction patterns were processed and analyzed using HighScore Plus version 4.1 (PANalytical).

3.1.1.5. Scanning Electron Microscopy (SEM)

Electron micrographs were acquired using a FEI Helios NanoLab DualBeam 650 system operated at a landing voltage of 5 kV and a probe current of 50 pA.

3.1.2. Electrochemical testing

3.1.2.1. H-cell setup

Experiments were performed in a gas-tight, low-volume, double compartment H-cell (Pine Research, Low Volume Separated Cell - AF01CKT1008) in a three-electrode configuration. The cathodic compartment housed the working electrode (WE, Cu foil, 2 cm², mounted in a custom holder), the reference electrode (RE, Ag/AgCl, 3 M KCl, 3.5 mm outer diameter, Pine Research), a gas inlet for bubbling and a gas outlet. The anodic compartment contained the counter electrode (CE), consisting of an oversized Ni mesh to ensure negligible polarization losses (1).

The gas inlet was supplied with either high-purity Ar or CO₂, depending on the experiment (both delivered through Bronkhorst F-201CV-100-RGD-22-V mass flow controllers), at a flow rate of 14 sccm, in accordance with Shibata's works (2). Prior to each test, the electrolyte was purged with the selected gas for a minimum of 15 minutes to ensure saturation and removal of dissolved air. The outlet stream passed sequentially through a gas dryer (SRI Gas Stream Dryer, part# 8670-5850), a universal Mass Flow Meter (EL-Flow Prestige Bronkhorst, FG-111B-AGD-22-V-DA-000 model) equipped with a B2 Bright display, and finally to the in-line gas

chromatograph (GC). A schematic representation of the setup is provided in Figure 29.

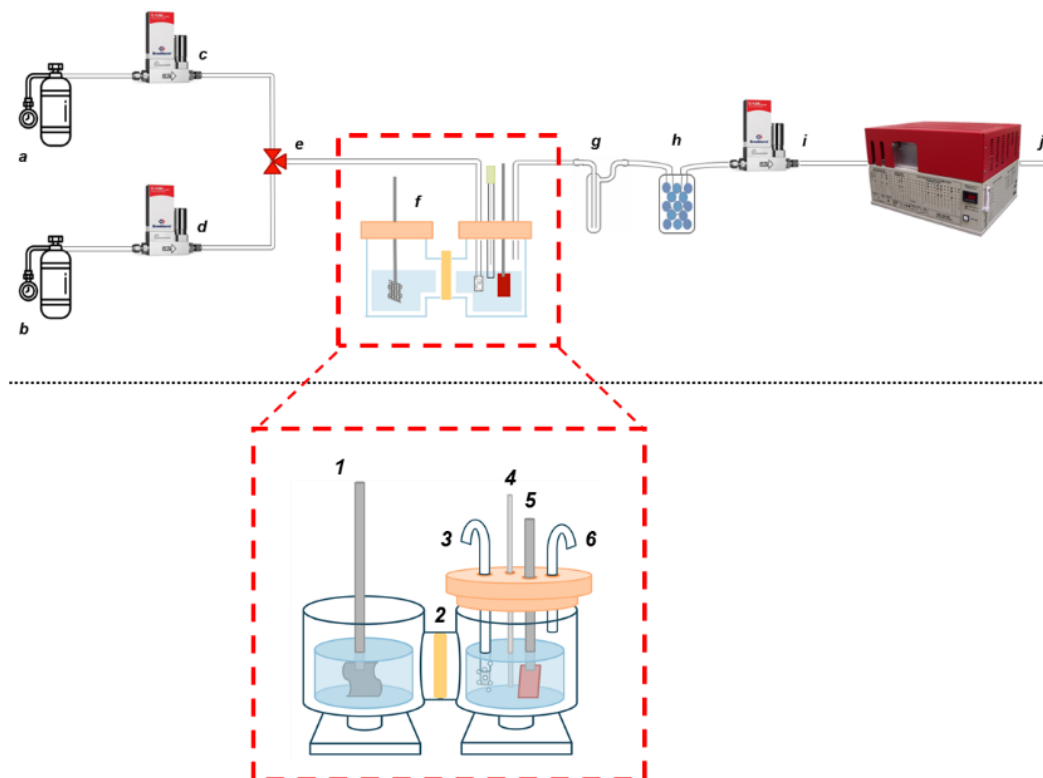


Figure 29 Schematics of the electrochemical setup used for H-cell EUS studies: (a) CO₂ gas cylinder; (b) Ar gas cylinder; (c) CO₂ mass flow controller (MFC); (d) Ar mass flow controller (MFC); (e) three-way gas valve; (f) H-cell; (g) acid scrubber (containing e.g., 1M H₂SO₄); (h) gas dryer; (i) gas outlet mass flow meter (MFM); (j) in-line gas chromatograph (GC). In the inset, magnification of the H-cell configuration: (1) Ni mesh CE; (2) Anion Exchange Membrane (AEM); (3) gas inlet; (4) Ag/AgCl RE; (5) Cu foil WE (with holder); (6) gas outlet.

Both compartments were filled with 20 mL of electrolyte, the composition of which depended on the specific experimental conditions. All electrolytes were prepared using Milli-Q water and treated with Chelex 100 resin (Bio-Rad, catalog no. 210011676) prior to use, following standard procedures (3) to remove trace metal impurities. The initial and final pH values of the electrolytes were measured with a SensION+ PH3 pH meter equipped with a Crison glass electrode (0-14 pH range); results are reported in Table 2 and Figures 43 and 51.

The two compartments were separated by a Fumasep FAB-PK-130 Anion Exchange Membrane (AEM), which was cleaned and activated according to the manufacturer's recommended procedure.

The standard electrochemical procedure comprised several sequential steps: monitoring of the Open Circuit Potential (OCP) of the working electrode (WE), electrode conditioning by cyclic voltammetry (CV), acquisition of Galvanostatic Linear Sweep Voltammetry (G-LSV) curves, determination of the uncompensated resistance (R_u) via Galvanostatic Electrochemical Impedance Spectroscopy (GEIS), and long-term (1 to 18 h) chronopotentiometric (CP) scans at various current densities. All operational parameters for each electrochemical technique (*e.g.*, scan rate, current range) are reported in the corresponding figure captions of the electrochemical traces.

Chronopotentiometric scans were employed to evaluate product distribution, specifically, urea formation, from individual and coupled reduction reactions on polycrystalline Cu under different current densities. Each CP experiment was conducted using freshly prepared electrolyte and following a thorough cell cleaning procedure involving immersion in an acid bath for 20 minutes, followed by sequential rinsing with tap water, ethanol, acetone, and Milli-Q water. During CP operation, gas-phase products were detected and quantified using an in-line GC (multiple runs), while liquid-phase samples were collected at the end of each scan for colorimetric and HPLC analyses.

The complete electrochemical protocol, including CP scans, was performed under four distinct conditions, alternating between individual and combined reactant feeds (Table 2).

Table 2 Electrolytes and gas feeds used to investigate individual and co-reduction processes. The initial electrolyte pH is intended after saturation with the gas of choice.

<i>Expected reaction</i>	<i>Electrolyte</i>	<i>Gas feed</i>	<i>Initial electrolyte pH</i>
HER	0.2 M KHCO ₃	Ar	8.69
CO ₂ RR (+ <i>parasitic HER</i>)	0.2 M KHCO ₃	CO ₂	7.20
NO ₃ RR (+ <i>parasitic HER</i>)	0.2 M KHCO ₃ + 0.02 M KNO ₃	Ar	8.69
EUS (CO ₂ RR + NO ₃ RR) (+ <i>parasitic HER</i>)	0.2 M KHCO ₃ + 0.02 M KNO ₃	CO ₂	7.20

This approach enabled the assessment of catalyst activity and selectivity for the individual reactions (*i.e.*, HER, CO₂RR and NO₃RR), as well as under co-reduction conditions (*i.e.*, CO₂RR + NO₃RR). Operative blanks for product identification were obtained by replicating the CP scans under identical conditions but without applying electrical bias (*i.e.*, open-circuit operation).

3.1.2.2. Flow-cell setup

Experiments were conducted in a three-compartment flow-cell, designed based on the geometry reported by Burdyny's group (4) and previously described in our earlier work (5). The cell employed a Cu/PTFE working electrode (gas diffusion electrode, GDE; exposed geometric area: 1.13 cm²) following the design principles proposed by Dinh et al. (6). The reference electrode (RE) was an Ag/AgCl (3 M KCl, eDAQ leakless, Green Leaf Scientific) identical to that used in the H-cell configuration, but with a reduced outer diameter of 2 mm. The same counter electrode (CE) and ion-exchange membrane utilized in the H-cell setup were employed here as well.

All operational parameters were maintained identical to those adopted in H-cell testing, with both anolyte and catholyte flow rates set to 7.5 mL min⁻¹. This value was selected as a representative average of the 5-10 mL min⁻¹ cm⁻² range commonly reported in literature, ensuring mass-transport enhancement and operational stability in the flow-cell configuration (7). A schematic representation of the flow-cell configuration is provided in Figure 30.

The electrochemical procedures described above were also applied to the flow-cell configuration. In this case, chronopotentiometric (CP) experiments were conducted exclusively under EUS testing conditions using a 0.2 M KHCO₃ + 0.02 M KNO₃ electrolyte and a CO₂ gas feed with the objective of evaluating urea formation.

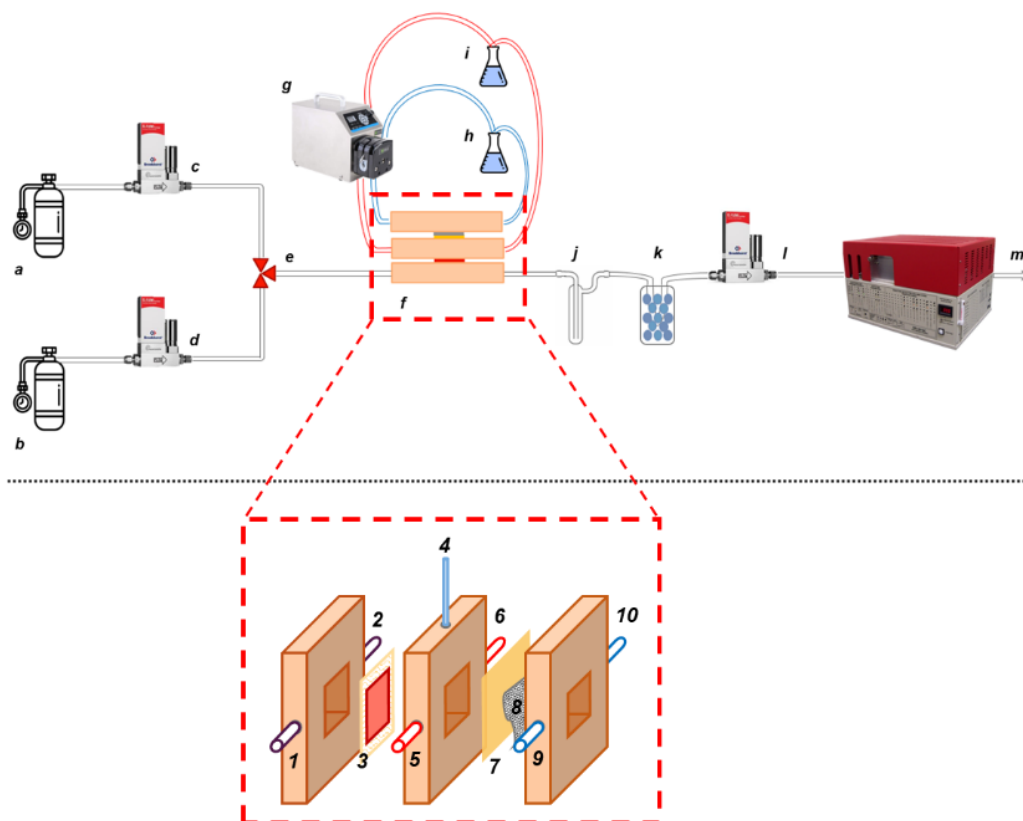


Figure 30 Scheme of the electrochemical setup for EUS testing. (a) CO₂ gas cylinder; (b) Ar gas cylinder; (c) CO₂ mass flow controller (MFC); (d) Ar mass flow controller (MFC); (e) three-way gas valve; (f) three-compartment flow cell; (g) dual-channel peristaltic pump; (h) anolyte reservoir; (i) catholyte reservoir; (j) acid scrubber (containing e.g. 1M H₂SO₄) (k) gas dryer (l) gas outlet mass flow meter (MFM); (m) in-line gas chromatograph (GC). Magnification at the bottom: simplified exploded view of the flow-cell. (1) Gas inlet; (2) gas outlet; (3) Cu/PTFE WE; (4) Ag/AgCl RE; (5) catholyte inlet; (6) catholyte outlet; (7) AEM; (8) Ni mesh CE; (9) anolyte inlet; (10) anolyte outlet.

3.1.3. Electrochemical Definitions

3.1.3.1. Potential correction

Unless otherwise specified, all potentials reported in this work are referenced to the RHE and corrected for ohmic losses according to the following equation:

$$E \text{ vs RHE} = E_{RE} + E_{RE}^0 + 0.059 \times pH - IR_u \text{ (Equation 6)}$$

Where E_{RE} is the measured potential versus the reference electrode during the measurement, E_{RE}^0 is the standard potential of the reference electrode (determined

as described in Section 3.1.1.3. “*Reference electrode calibration*”), I is the current recorded during the measurement, and R_u is the uncompensated resistance of the electrochemical system. Since the electrolyte pH may vary during CP scans, the implications of using either the initial or final pH values in the above equation are discussed in the dedicated Section 3.2.7. “*pH variations upon electrolysis*”.

3.1.3.2. Uncompensated resistance determination.

R_u was estimated as the real component of the impedance at high frequency (*i.e.*, 50 kHz) obtained from galvanostatic electrochemical impedance spectroscopy (GEIS) measurements. The experimental GEIS data are discussed in detail in the Section 3.2.3. “*Galvanostatic Electrochemical Impedance Spectroscopy (GEIS)*.”

3.1.3.3. Faradaic efficiency calculations.

Following quantification of each product by GC, HPLC, or colorimetric analysis, the Faradaic efficiency for each product was determined according to Faraday’s law:

$$FE_{Product} = \frac{Q_{Product}}{Q_{Tot}} = \frac{n_{Product} \times F \times mol_{Product}}{I_{CP} \times t_{CP}} \text{ (Equation 7)}$$

where $n_{Product}$ is the number of electrons transferred per mole of product, F is the Faraday constant (96485 C mol⁻¹), $mol_{Product}$ is the number of moles of product formed during the CP scan (as determined by GC/HPLC/colorimetric tests), and I_{CP} and t_{CP} are the applied current and total duration of the CP run, respectively.

3.1.4. Quantification of products

3.1.4.1. Gas Chromatography

Gaseous products generated from the individual HER, CO₂RR, and NO₃RR experiments were analyzed using an SRI 8610C gas chromatograph (Multiple Gas Analyzer #5) equipped with a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID) coupled with a methanizer. Argon was employed as the carrier gas. Prior to the experiments, both detectors were calibrated using a customized gas mixture containing the typical gaseous products of CO₂RR (*e.g.*, CO, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈) and H₂ originating from the parasitic HER. Representative chromatograms and calibration curves are provided in Figures 19-20.

3.1.4.2. HPLC

All HPLC analyses were performed using an Agilent Infinity 1260 system equipped with a quaternary pump, standard autosampler, thermostatted column compartment, Diode Array Detector (DAD/UV-Vis, operating range 190-950 nm), and a Refractive Index Detector (RID).

3.1.4.2.1. CO₂RR liquid product analysis

Liquid products from the CO₂RR were separated on an Agilent Hi-Plex H column (300 × 7.7 mm) operated at 50 °C in isocratic mode, using 5 mM H₂SO_{4(aq)} as the mobile phase at a flow rate of 0.6 mL min⁻¹. Chromatographic runs lasted 30 minutes, ensuring the elution of all common CO₂RR products (*e.g.*, C₃ alcohols, typically rare, eluting at *ca.* 27 min). Calibration standards were injected in volumes ranging from 2.5 to 100 µL, while experimental samples were analyzed at consistent injection volumes to ensure linearity (*e.g.*, doubling of peak area for doubled injection volume). For consistency in Faradaic efficiency calculations, 25 µL injections were employed. Both catholyte and anolyte samples were analyzed to quantify potential crossover species such as formate ions. Product detection was performed using the DAD/UV-Vis channels (210 and 280 nm) and/or RID (T = 40 °C), depending on analyte characteristics (see Figure 21). A detailed description of this separation and detection protocol can be found in the work of Burdyny et al. (8).

Unexpected urea elution observed on the Hi-Plex H column is discussed in Section 2.1.1. “*Urea detection/quantification on Hi-Plex column*” (Figure 16). In that case,

the method described above was adapted by extending the chromatographic run to 240 minutes and by adding a DAD/UV-Vis detection channel at 195 nm.

3.1.4.2.2. Urea detection and quantification

For optimized urea separation, an Agilent InfinityLab Poroshell 120 HILIC-Z column (2.1×100 mm, $2.7 \mu\text{m}$) was employed. A detailed stepwise optimization of the analytical method was carried out (see Section 2.1. “*Optimization of the HPLC/UV-Vis method for urea detection/quantification*”). In the optimized protocol, the column was thermostatted at 30°C and operated with two mobile phases; mobile phase A is a 10 mM formic acid solution in Milli-Q water, while mobile phase B is a 10 mM formic acid in $\text{H}_2\text{O}/\text{ACN} = 10/90$ (prepared by adding 900 mL of acetonitrile to 100 mL of 100 mM formic acid solution).

Gradient elution was performed at a flow rate of 0.5 mL min^{-1} , starting from A/B = 5/95 at 0 min and linearly progressing to 50/50 within 9 minutes, followed by an 8-minute isocratic step at 50/50. The total analytical runtime was therefore 17 minutes. A 10-minute post-run step restored the gradient to the initial A/B = 5/95, resulting in a total cycle time of 27 minutes per injection. Injection volumes for both calibration standards and EUS samples were set at $2.5 \mu\text{L}$. Both catholyte and anolyte fractions were analyzed. Urea detection was performed using the DAD/UV-Vis channel at 195 nm, while absorbance at 210 and 280 nm was simultaneously monitored to assess potential interference from CO_2RR liquid products. The RID could not be employed under these conditions, as it is incompatible with gradient elution.

3.1.4.3. ^1H -NMR

Samples were prepared by adding 5% DMSO-d_6 (used as the lock solvent) to 2 mL of the liquid sample and subsequently transferred into 5 mm NMR SampleJet tube (Bruker) for analysis. DMSO-d_6 was employed in place of D_2O to prevent proton-deuterium exchange of the urea protons in deuterated water.

NMR spectra were acquired using a Bruker Avance III 600 MHz spectrometer equipped with a cryoprobe (5 mm QCI probe) and a z-shielded pulsed-field gradient coil. Automatic optimization was performed for probe tuning, matching, and resolution, while the 90° pulse was manually calibrated for each individual sample. Following the 90° excitation pulse, 16 transients were collected without dummy scans, using 65536 digit points, with a relaxation delay of 30 s, over a spectral width of 20.83 ppm, with the offset centered at 6.18 ppm.

Prior to Fourier transform application, an exponential function equivalent to 0.3 Hz was applied to smooth the FIDs. The resulting spectra were manually phased and automatically baseline corrected. Chemical shifts were referenced to the residual non-deuterated DMSO-d₅ peak, set at 2.50 ppm.

3.1.4.4. Colorimetric methods

The most common products arising from the individual NO₃RR and urea formation reactions were detected and quantified using well-established colorimetric and analytical methods reported in the literature. The procedures adopted for each analyte are briefly summarized below. Concentrations reported in the calibration curves correspond to those of the original standard solutions and do not account for the dilution effects introduced by the analytical method themselves (*e.g.*, due to the addition of several milliliters of reagents during sample preparation).

3.1.4.4.1. NO₂⁻ - Griess Method

The quantification of nitrite ions was performed using the Griess spectrophotometric method, which is based on a quantitative diazotization reaction. In this method, nitrite ions react with the diazotizing agent sulfanilamide (SULF) under acidic conditions to form a transient diazonium salt. This intermediate then couples with N-(1-naphthyl)ethylenediamine (NED) to yield a stable azo dye that exhibits a characteristic absorption maximum at 540 nm (9).

The diazotizing reagent (SULF solution) was prepared by dissolving 100 mg of sulfanilamide in 10 mL of an acidic solution consisting of 1 mL concentrated hydrochloric acid (37 wt.%) and 9 mL deionized water. The coupling reagent (NED solution) was prepared by dissolving 10 mg of NED in 10 mL of deionized water, following the procedure reported by MacFarlane et al. (9).

For a typical Griess assay (whether for calibration curve preparation or post-electrolysis sample analysis), 1.5 mL of sample are mixed with 1.5 mL of 1.1 M HCl solution, followed by the sequential addition of 75 µL of the SULF solution and 75 µL of the NED solution. The mixture is then incubated for 20 minutes at ambient temperature to allow the coupling reaction to reach completion and for the characteristic pink coloration of the azo dye to fully develop.

Subsequently, UV-Vis absorption spectra were recorded using quartz cuvettes with a 10 mm optical path length, and the nitrite concentration was determined from the absorbance intensity at 540 nm.

3.1.4.4.2. NH_3 – Indophenol Blue Method

The Berthelot spectrophotometric method, also known as the indophenol blue method, was employed for the quantification of ammonia and ammonium ions. This colorimetric technique is based on a three-step reaction that results in the quantitative formation of the indophenol blue chromophore from ammonia (10).

In a typical procedure, 2 mL of the ammonia-containing sample are mixed with 2 mL of a 1 M KOH solution containing 5 wt.% salicylic acid and 5 wt.% sodium citrate. Subsequently, 1 mL of 0.06 M $\text{NaClO}_{(\text{aq})}$ and 0.2 mL of a 1 wt.% aqueous solution of sodium nitroferricyanide are added. The reaction mixture is incubated at ambient temperature for 2 hours to ensure complete color development.

After incubation, UV-Vis absorption spectra were recorded using quartz cuvettes with a 10 mm optical path length, and the absorbance corresponding to indophenol blue formation was used to determine the ammonia concentration.

3.1.4.4.3. N_2H_4 – Watt and Chrisp Method

Hydrazine was quantified spectrophotometrically following the Watt and Chrisp method (11), which is based on the formation of a yellow-colored compound resulting from the reaction between hydrazine and *p*-dimethylaminobenzaldehyde. The color reagent was prepared by dissolving 0.4 g of *p*-dimethylaminobenzaldehyde in 20 mL of ethanol, followed by the addition of 2 mL of concentrated hydrochloric acid (37 wt.%) as described by Watt and Chrisp (11).

In a typical assay, 1 mL of the sample solution is mixed with 2 mL of the color reagent and 2 mL of 1 M HCl. The mixture is then incubated for 10 minutes at ambient temperature to allow complete color development.

UV-Vis absorption spectra were subsequently recorded using quartz cuvettes with a 10 mm optical path length, and the absorbance intensity of the hydrazone product was used to determine the hydrazine concentration.

3.1.4.4.3. Urea – DAMO-TSC Method

The DAMO-TSC method was employed for the indirect spectrophotometric quantification of urea. This technique relies on the reaction between urea and diacetyl, generated *in situ* through the thermal degradation of diacetylmonoxime (DAMO), in the presence of thiosemicarbazide (TSC) which acts as a color stabilizer and enhancer (12).

The assay involves two reagent mixtures: an acidic ferric chloride solution and a DAMO-TSC solution. The acidic solution was prepared by dissolving 2 mg of ferric chloride in a strongly acidic aqueous medium composed of concentrated phosphoric acid (2 mL, 85 wt.%), concentrated sulfuric acid (6 mL, 95-98 wt.%), and 12 mL of deionized water. The DAMO-TSC solution was obtained by dissolving 100 mg of DAMO and 2 mg of TSC in 20 mL of deionized water.

In a typical test, 1 mL of the urea-containing sample is mixed with 2 mL of the acidic ferric chloride solution and 1 mL of the DAMO-TSC solution. The resulting mixture is then heated at 100 °C for 15 minutes to promote the formation of a pink-colored complex. After cooling to room temperature, UV-Vis absorption spectra were collected using quartz cuvettes with a 10 mm optical path length, and the absorbance of the resulting chromophore was used to determine the urea concentration.

3.1.4.4.4. Urea – M-DAMO-TSC Method

The sulfamic acid-modified DAMO-TSC method (M-DAMO-TSC) was employed to suppress nitrite interference (13) in EUS post-reaction electrolytes, as demonstrated by Chen et al. (14). This approach follows the same principles as the conventional DAMO-TSC method but introduces an additional preliminary step to chemically reduce nitrite ions under acidic conditions, thereby preventing their contribution to false-positive color development (13).

In the standard procedure, nitrite ions are quantitatively converted to N_2 by adding 300 μ L of 10 M HCl and 100 μ L of a 4 wt.% sulfamic acid solution to 1 mL of the sample. The resulting mixture is left to react for 20 minutes at room temperature, after which the conventional DAMO-TSC protocol is applied for urea quantification.

In our experiments, however, it was observed that the M-DAMO-TSC method produced reliable results even in the absence of sample acidification during the nitrite reduction step. Accordingly, the procedure by Chen et al. was slightly modified by substituting the 300 μ L of 10 M HCl with 300 μ L of deionized water.

3.1.5. Extended rationale of the study: choice of catalyst and reaction conditions

3.1.5.1 Choice of Catalyst

The selection of polycrystalline copper as catalyst and a near-neutral KHCO_3 -based electrolyte is motivated by the seminal work of Shibata et al. (2) and by more recent theoretical studies by Wan et al. (15). In their pioneering investigations, Shibata and Furuya demonstrated the feasibility of EUS through the co-reduction of CO_2 and NO_3^- (or NO_2^-) in 0.2 M KHCO_3 + 0.02 M KNO_3 (or KNO_2) aqueous electrolytes, further hypothesizing a correlation between the CO_2 to CO and $\text{NO}_2^-/\text{NO}_3^-$ to NH_3 selectivity of Cu in individual CO_2RR and NO_3RR and the efficiency of urea synthesis under co-reduction conditions (2). This correlation was later extended to other catalysts, zero-valent transition metals, phthalocyanines, and borides; in subsequent studies by the same authors (2, 16-20).

While more recent EUS mechanistic studies (15, 21, 22) have refined our understanding of EUS, Shibata and Furuya's original hypothesis remains fundamental: the $^*\text{CO}_{(\text{ads})}$ and $^*\text{NH}_{2(\text{ads})}$ are key intermediates in C-N bond formation leading to urea. Nonetheless, the current state of knowledge on CO_2RR mechanisms challenges this interpretation. Among all zero-valent metals investigated by Shibata and Furuya, only Cu exhibits an optimal $^*\text{CO}$ (and $^*\text{H}$) binding energy that enables further reduction of CO intermediates (23, 24). This property uniquely allows Cu to produce multi-electron CO_2RR products beyond the two-electron reduction level (23, 25).

Others CO selective catalysts (*e.g.* Ag) do not retain CO on their surfaces (14), and co-reduction systems coupling NO_3RR with CO_2RR have not yielded urea in subsequent studies (2, 16-20). Therefore, the general correlation proposed by Shibata and Furuya for other metals, those that either bind $^*\text{CO}$ too weakly or too strongly, appears to break down. When the adsorption energies of $^*\text{H}$ and N-containing intermediates are also considered (as shown in Figure 2 of Wan et al. (14)), Cu emerges as the only promising candidate for EUS among simple zero-valent metals.

Despite the inconsistencies between the early mechanistic assumptions and the current understanding of CO_2RR , Cu remains the most suitable model system for urea electrosynthesis via $\text{CO}_2 + \text{NO}_3^-$ co-reduction.

It is important to acknowledge that Shibata and Furuya's urea quantification relied on the urease-indophenol blue method (26-28), which is now recognized to be susceptible to analytical inaccuracies and potential interferences. These methodological limitations may have contributed to some of the inconsistencies or questionable correlations reported in their studies. Accordingly, a key motivation of the present work is to rigorously re-examine these foundational experiments using state-of-the-art analytical techniques, thereby assessing their reproducibility under well-defined and controlled electrochemical conditions (15).

3.1.5.2. Choice of Electrolyte

To ensure comparability with the early reports of Shibata and Furuya, we employed the same near-neutral electrolyte composition (0.2 M KHCO_3 + 0.02 M KNO_3), even though this choice is suboptimal for industrially relevant EUS operation due to its limited ionic conductivity (29). This approach enables a direct assessment of the reproducibility of the original results and provides first-hand evidence of the challenges associated with low-conductivity, near-neutral electrolytes (*e.g.*, pH variations under operative conditions, reactants depletion).

3.1.5.3. Choice of Electrochemical Cell Configuration

Experiments were carried out in both H-cell and flow-cell configurations to align with current trends in EUS research and to enable a comparative evaluation of catalyst performance. While Shibata and Furuya employed GDE-based setup in their work (2, 16-20), most contemporary studies rely on conventional H-cells. The limitations of the latter design have been discussed extensively by several groups (30), including ours (29). Accordingly, evaluating a model catalyst, such as polycrystalline Cu, in both H-cell and flow-cell configurations allows to (i) evaluate its activity and selectivity for EUS and (ii) assess how the cell and electrode configuration influences the process performance.

It is noteworthy that our flow-cell experiments were not designed to reproduce exactly those of Shibata and Furuya. Indeed, in their configuration, the electrochemical system was membrane-free, static and implemented the hydrogen oxidation reaction (HOR) at the anode. In contrast, our approach utilizes a compartmentalized design, implemented in both H-cell and flow-cell configurations, where the cathodic and anodic chambers were separated by an Anion Exchange Membrane (AEM, Fumasep FAB-PK-130). This modification was motivated by (i) the slightly alkaline pH of the starting electrolytes, (ii) the need to evaluate the limitations of colorimetric urea detection methods (*e.g.*, nitrite

crossover through the AEM leading to false-positive signals in the anolyte, see Section 3.2.5 “*Urea detection in H-cell post-electrolysis samples*”), and (iii) the chemical and mechanical instability of Nafion-based membranes in the presence of ammonia (generated during NO₃RR on Cu) (31).

In our systems, the Oxygen Evolution Reaction (OER) was implemented at the anode, in line with most EUS studies published after the Shibata and Furuya’s series. Although it is not yet clear whether this substitution affects urea formation or detection, we hypothesize that Shibata and Furuya’s use of HOR at the anode was intended to prevent urea electrooxidation (UOR), which could occur in their membrane-free setup through diffusion of urea to the anode. In that configuration, the lower anodic potential of HOR relative to OER would minimize urea degradation. In contrast, our use of an AEM effectively prevents urea crossover to the anodic compartment, thereby eliminating the risk of anodic urea oxidation and minimizing the influence of the anodic half-reaction on overall product distribution (see Section 3.2.6. “*Urea Migration and Diffusion through the AEM*”).

3.2. H-cell testing

3.2.1. Preparation of WE and calibration of RE for H-cell testing

A representative current-time trace recorded during the electropolishing (CA at 1.2 V vs Cu counter electrode) of the Cu foil working electrode (WE) employed in the H-cell studies is reported in Figure 31a. The current exhibits an exponential decay profile, reaching a steady-state plateau after approximately 8 minutes of operation, consistent with surface smoothing and oxide removal.

Figure 31b displays a representative calibration curve for the reference electrode (RE) used in the H-cell experiments. The measured standard potential (E^0) was found to be in close agreement with the theoretical value (222.5 mV vs RHE), and the stable potential signal further confirms the reliability and reproducibility of the reference electrode under the experimental conditions adopted.

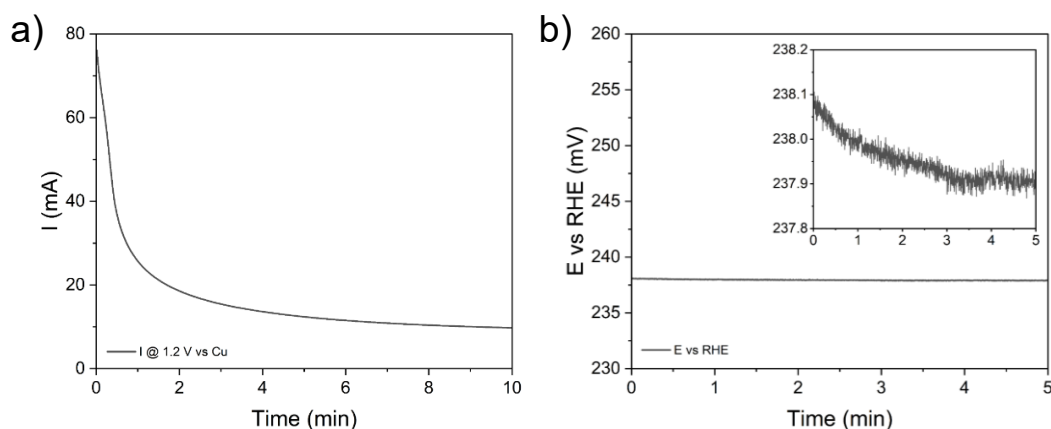


Figure 31 a) Typical current versus time profile obtained from the electropolishing procedure of the Cu foil used as WE in H-cell tests. b) Sample calibration of the RE (3 M KCl Ag/AgCl), obtained measuring its OCP in 0.5 M H_2SO_4 (pH 0) versus an RHE. Inset: magnification used to appreciate the variation of the voltage, in the range of tenths of mV.

3.2.2. Open Circuit Potential (OCP)

The Open Circuit Potential of the WE was monitored under various reaction environments (Figure 32). The recorded traces exhibit stability over time, with potential values exceeding the standard reduction potential of the Cu^{2+}/Cu^0 couple ($E^0_{Cu^{2+}/Cu^0} = 340$ mV vs RHE) (32), thereby indicating a thermodynamic tendency of the copper surface toward corrosion. Although such considerations remain preliminary at the current Technology Readiness Level (TRL), these results suggest that any future electrolyzer designed for EUS would require specific operational strategies to prevent copper corrosion or dissolution during open circuit conditions, *e.g.*, when the system might go idling because of the lack of green electricity offer. To address this, the system could implement cathodic protection through a small holding potential or ensure the absence of electrolyte within the cathodic compartment during open-circuit conditions.

Interestingly, the presence of either CO_2 (red trace) and nitrate ions (blue trace), introduced into the electrolyte by bubbling or dissolution, leads to a comparable decrease in the measured OCP, implying a partial protective effect on the electrode surface. Indeed, under EUS conditions (green trace), where both CO_2 and NO_3^- are simultaneously present, their combined influence results in a further decrease of the potential, suggesting a synergistic stabilization effect.

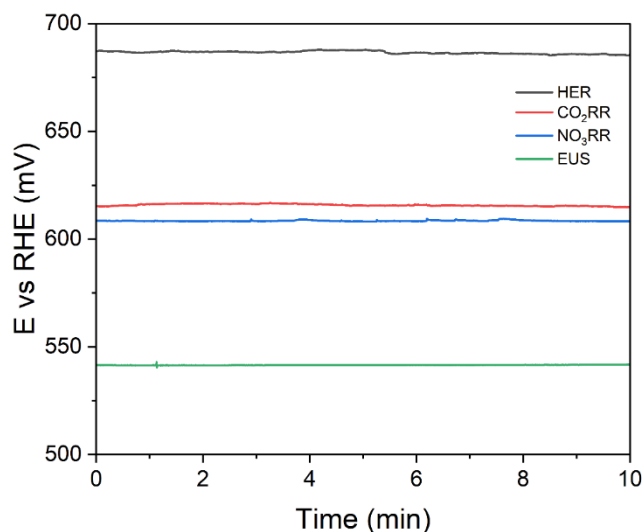


Figure 32 Open Circuit Potential (OCP) traces collected on the Cu foil WE under different reaction environments (i.e., with different electrolytes and gas feeds, details in Table 2).

3.2.3. Galvanostatic Electrochemical Impedance Spectroscopy (GEIS)

As discussed in the Section 3.1.3.2. “Uncompensated resistance determination”, GEIS measurements were performed to determine the uncompensated system resistance (R_u), which is required for accurate ohmic drop correction. The GEIS spectra collected under various reaction environments are presented in Figures 33b–36b.

In all cases, the Nyquist plots display two distinct semicircles, with the high-frequency intercept occurring at Z' values greater than $0 \, \Omega$. When nitrate ions are present in the electrolyte, under NO_3RR and EUS conditions, a minor diffusional contribution becomes discernible in the low-frequency region.

Given that a comprehensive impedance analysis lies beyond the scope of the present work, no model-based fitting was applied. Instead, the uncompensated resistance (R_u) was directly extracted as the real component (Z') measured at high frequency (50 kHz). Overall, we notice that the electrochemical behavior of the system under the four different conditions can be qualitatively described by an equivalent circuit of the type $R_1(R_2Q_1)(R_3Q_2)$. In this model, R_1 represents the uncompensated resistance, R_u , while the two parallel circuits (R_2Q_1) and (R_3Q_2) are tentatively assigned to the kinetics of interfacial electrochemical reactions and to secondary processes, such as diffusion or surface adsorption, respectively.

3.2.4. HER, CO₂RR, NO₃RR and EUS assessment

To elucidate the fundamental electrochemical behavior and selectivity of the individual reactions involved in EUS (*i.e.*, HER, CO₂RR and NO₃RR), voltammetric measurements were performed, and the corresponding product distributions were analyzed following 1-hour chronopotentiometric (CP) experiments conducted under varying reactant conditions (presence or absence of each species).

3.2.4.1. HER conditions

Under HER conditions, the CV scan of polycrystalline Cu displays an almost featureless cathodic profile, with an onset potential between -0.5 and -0.6 V vs RHE (Figure 33a). This behavior is consistent with the limited HER activity of Cu at near-neutral pH (24). The CP trace, collected at a constant current density of -12.5 mA cm⁻², initially stabilizes around -0.9 V vs RHE and gradually approaches -1.0 V vs RHE, in good agreement with the voltammetric data once capacitive contributions are accounted for (Figure 33c).

As expected, H₂ was the only gaseous product detected during the CP, with a FE_{H₂} of approximately 93% (Figure 33d). The observed lack in charge balance may arise from a redox contribution of the working electrode itself (*i.e.*, the reduction of surface CuO_x species to metallic Cu⁰ during electrolysis) or, most likely, from analytical limitations in accurately quantifying H₂. The latter issue likely stems from the diluted nature of the gas stream exiting the H-cell, a consequence of both the relatively low current density and the limited geometric surface area of the working electrode.

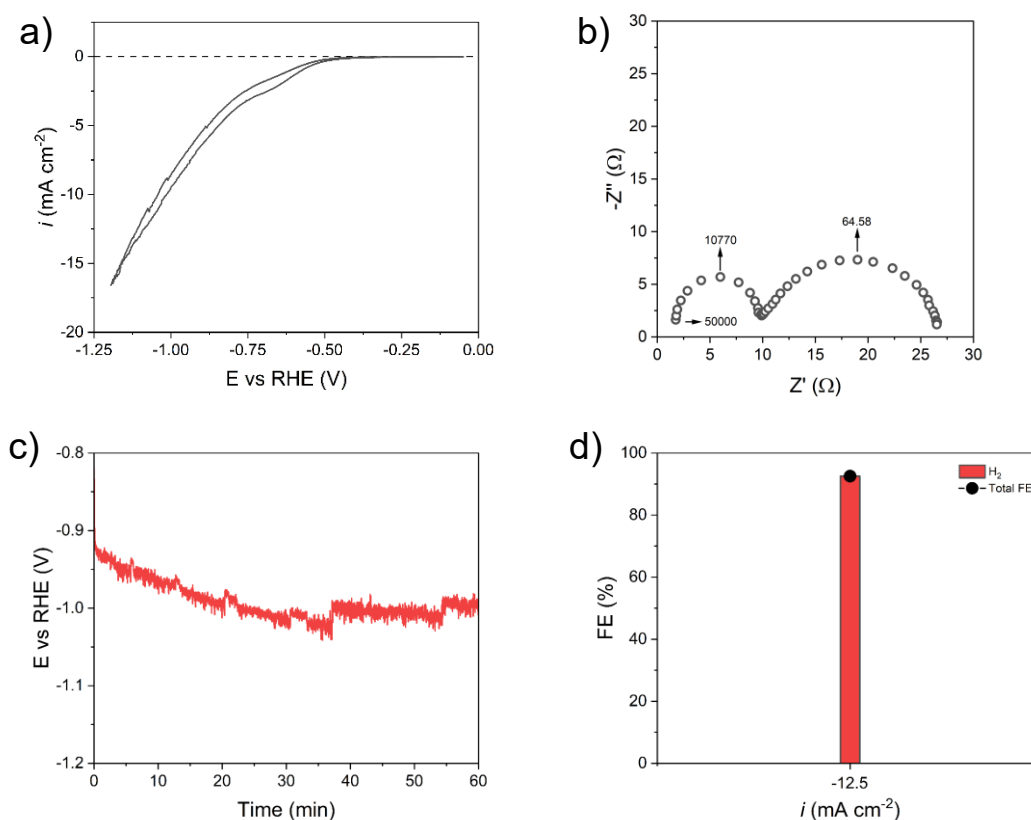


Figure 33 Polycrystalline Cu electrochemical testing under HER conditions (i.e., 0.2 M KHCO₃, Ar). a) CV curve (10th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -4 mA cm⁻², 0.8 mA cm⁻² amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz), c) CP scan at -12.5 mA cm⁻² and d) related product distribution.

3.2.4.2. CO₂RR conditions

The results obtained for the CO₂RR are consistent with previously reported data (23, 33). As shown in Figure 34a, the CV scan does not display any distinct redox features, and the onset potential closely matches that recorded under HER conditions. Given the near-neutral pH of the electrolyte and the intense competition from HER (34), it is not possible to clearly decouple the individual contributions of CO₂RR and HER to the overall cathodic current. Nevertheless, the comparison between the cathodic branches of HER and CO₂RR obtained CV scans clearly indicates that H-cells, operated with near-neutral electrolytes, are suboptimal systems for investigating EUS.

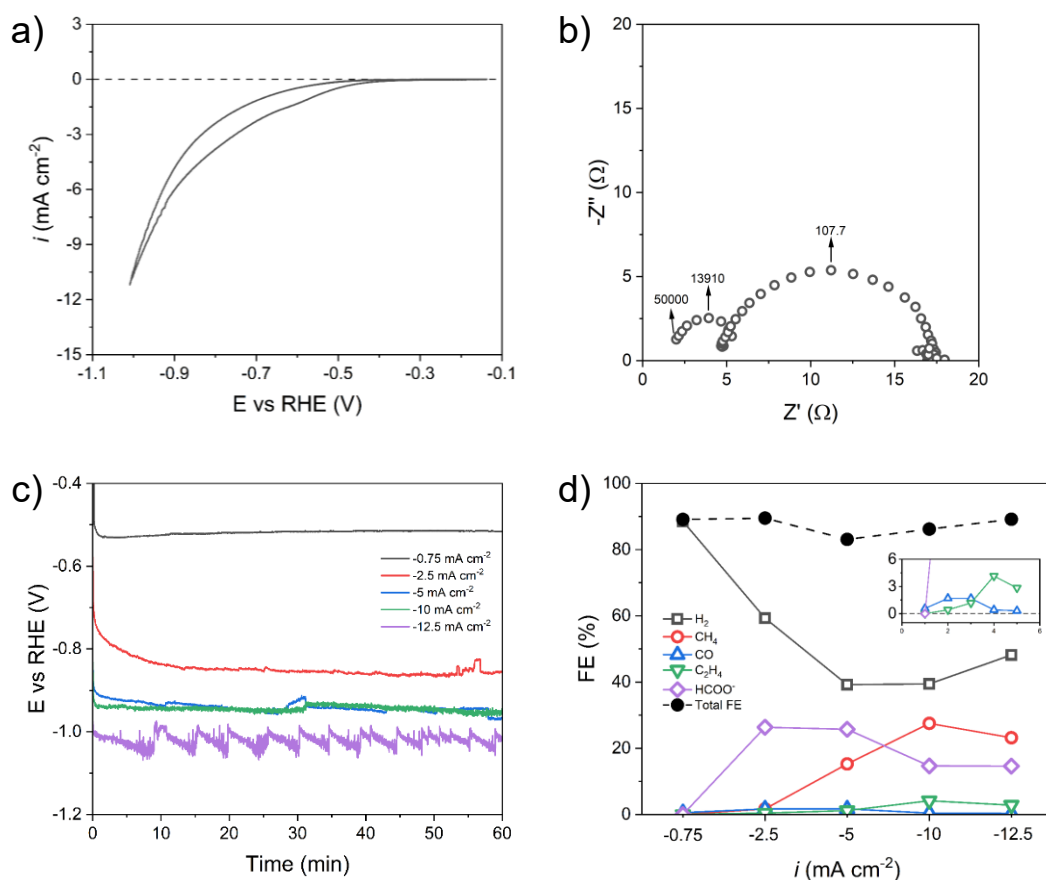


Figure 34 Polycrystalline Cu electrochemical testing under CO₂RR conditions (i.e., 0.2 M KHCO₃, CO₂). a) CV curve (10th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -6 mA cm⁻², 1.2 mA cm⁻² amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz), c) CP scans at different current densities and d) related product distribution.

CP measurements (Figure 34c) yielded a product mixture typical of polycrystalline copper catalysts, comprising both H₂ and CO₂RR-derived species (23, 33). A slight deviation from the benchmark distribution reported by the Jaramillo group in 2012 (33) was observed, most notably a lower FE_{C₂H₄} than expected (Figure 34d). This discrepancy is likely attributable to differences in experimental conditions, such as electrolyte concentration, electrode geometric area, and, most importantly, cell design.

Finally, a Faradaic efficiency deficit of approximately 10% was observed. This missing charge is plausibly due to analytical limitations in ethanol detection (as discussed in Section 2.3.2. “High-Performance Liquid Chromatography (HPLC)”) and/or the intrinsic challenges associated with accurately quantifying products in highly diluted post-electrolysis samples, both in the gas and liquid phases.

3.2.4.3. NO₃RR conditions

The main results of the individual NO₃RR studies are summarized in Figure 35. The CV scan (Figure 35a) exhibits a complex profile featuring multiple peaks and diffusion-limited plateaus, in line with observations previously reported by the Koper group (35), who investigated NO₃RR on copper single crystals under both acidic and alkaline conditions. Given the polycrystalline nature of the working electrode and the near-neutral pH of the electrolyte, the voltammetric response obtained can be regarded as a “hybrid” of the behaviors described for the individual crystallographic facets.

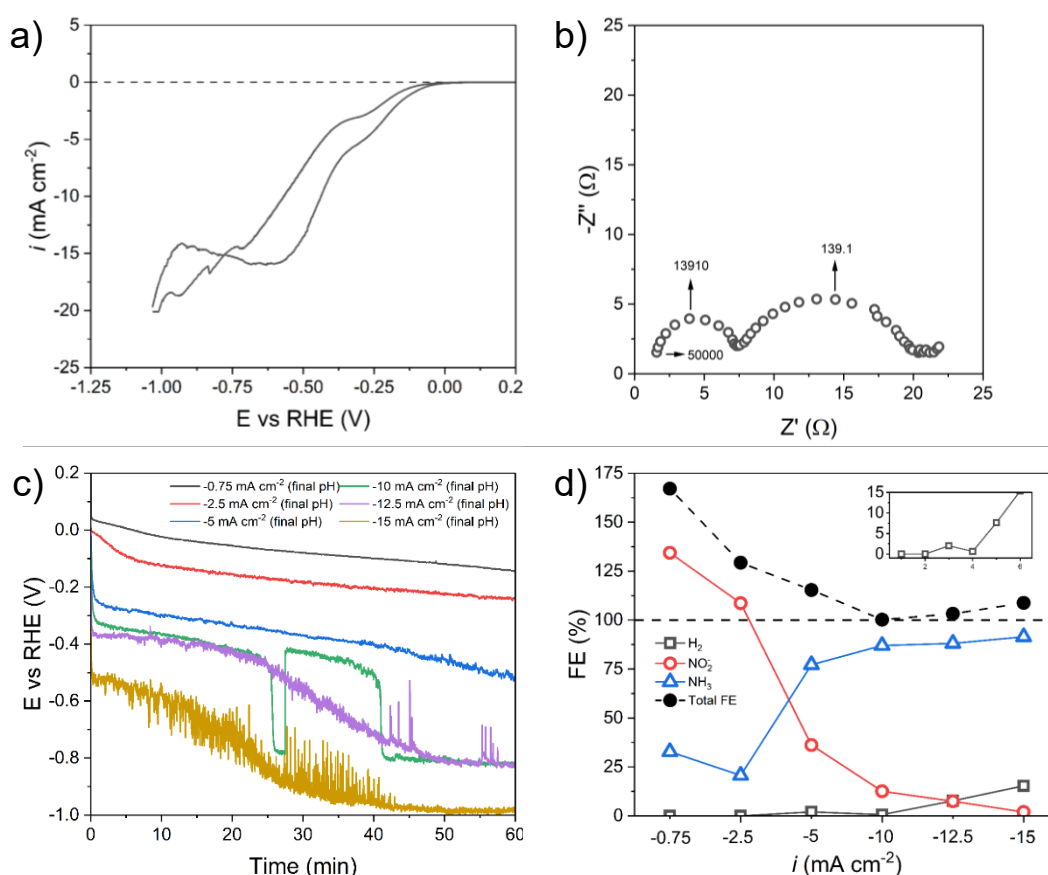


Figure 35 Polycrystalline Cu electrochemical testing under NO₃RR conditions (i.e., 0.2 M KHCO₃ + 0.02 M KNO₃, Ar). a) CV curve (10th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -6 mA cm⁻², 1.2 mA cm⁻² amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz), c) CP scans at different current densities and d) related product distribution.

CP measurements performed at varying current densities (Figure 35c) display significantly less cathodic potential values compared to those observed for HER and CO₂RR, reflecting the more favorable thermodynamics and kinetics of the NO₃RR (Section 1.5 “NO₃ Reduction Reaction”, Figure 6). Notably, all CP traces

exhibit a downward trend in potential over time, which becomes more pronounced at higher current densities. For measurements conducted at $|i| \geq 10 \text{ mA cm}^{-2}$, a distinct inflection point is observed, after which the potential stabilizes at a lower steady-state value. Although this behavior was not investigated in detail, it can be reasonably attributed to the progressive depletion of nitrate ions near the electrode surface and/or a shift in product selectivity as the reaction proceeds.

The corresponding product distributions (Figure 35d) also mirror the hybrid behavior reported by Pérez-Gallent et al. (35), with nitrite and ammonia emerging as the main products at low and high current densities, respectively. The parasitic HER contribution becomes significant only at $|i| > 10 \text{ mA cm}^{-2}$.

An apparent Faradaic efficiency exceeding 100% was occasionally observed, particularly for CP scans performed at low current densities. This artifact is attributed to the limited precision and reproducibility inherent to colorimetric quantification methods. Contributing factors include the low analyte concentrations in several samples, possible spectral interferences from by-products or dissolved metal cations, inaccuracies arising from sample dilution (especially for concentrated samples yielding absorbance values above 1.5-2), and small variations in procedural timing (*e.g.*, color development duration, light exposure, or dye aging).

3.2.4.4. EUS conditions

EUS experiments were performed under CO_2 and NO_3^- co-reduction conditions, with the resulting data presented in Figure 36. The CV scans (Figure 36a) can be interpreted as a superposition of the individual behavior observed for CO_2RR and NO_3RR processes. The resulting features reflect the simultaneous occurrence and mutual competition of the two reduction processes, while also highlighting the persistent contribution of the parasitic hydrogen evolution reaction (HER). Identifying a potential region in which both CO_2RR and NO_3RR proceed concurrently in the absence of HER is challenging, given the complexity of the traces and the overlapping nature of the reaction pathways.

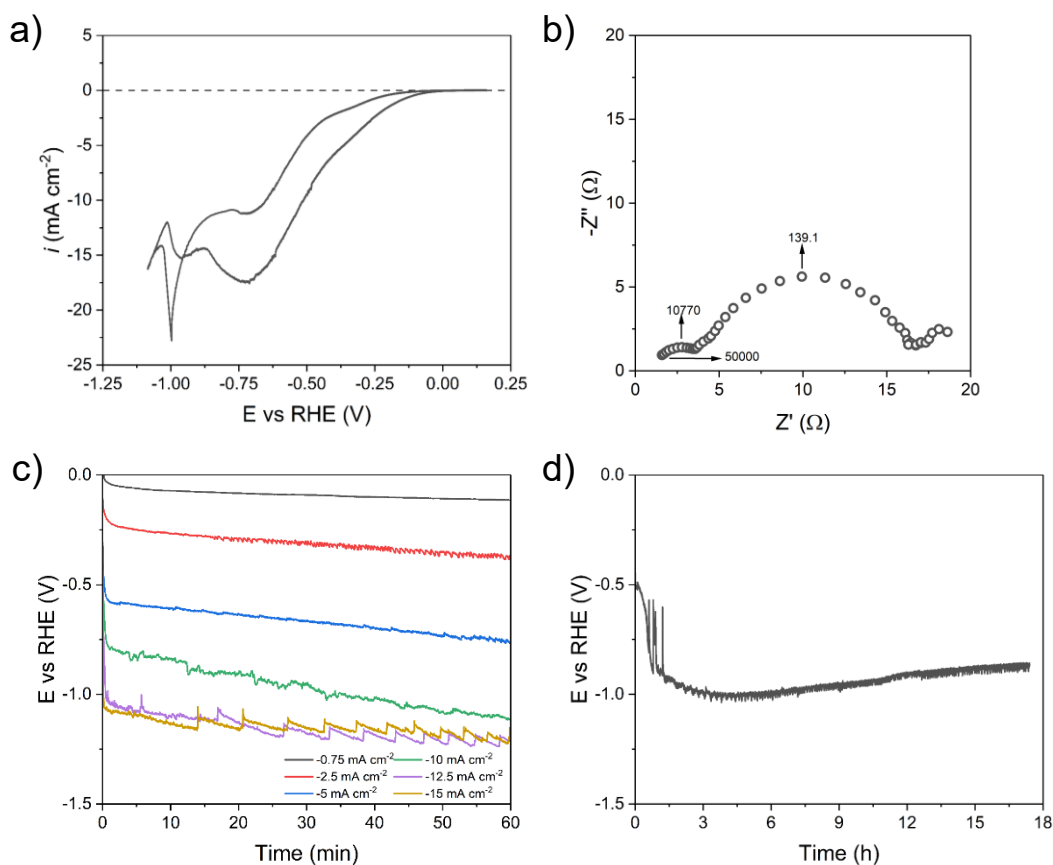


Figure 36 Polycrystalline Cu electrochemical testing under NO_3RR conditions (i.e., $0.2 \text{ M KHCO}_3 + 0.02 \text{ M KNO}_3$, Ar). a) CV curve (10^{th} scan, scan rate 100 mV s^{-1}), b) GEIS (collected at -6 mA cm^{-2} , 1.2 mA cm^{-2} amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz), c) CP scans at different current densities and d) 17-hours long CP scan at -5 mA cm^{-2} .

It should be noted, however, that at low applied potentials, several data points appear distorted, likely due to diffusional limitations and/or the potentiostat reaching its voltage compliance limit under the particularly inefficient

configuration employed (*i.e.*, low electrolyte conductivity, relatively large electrode spacing, and near-neutral OER conditions at the anode). These points are reported for completeness, though their accuracy is limited and the overall curve shape clearly indicates the presence of measurement artifacts.

The chronopotentiometric (CP) profiles (Figure 36c) similarly reflect a combination of the markedly cathodic potentials typical of CO₂RR and the progressive potential drift observed during NO₃RR.

Assuming that urea formation proceeds through the surface coupling of C- and N-based intermediates, this observation emphasizes the inherent limitations of H-cell systems and, more generally, of all setups in which CO₂ is introduced through dissolution in the electrolyte, for reliable EUS testing (29, 30). Nonetheless, in the current density range between -5 and -15 mA cm⁻², the product distribution shows appreciable amounts of *CO_(ads)-derived species (*e.g.*, CO, CH₄, C₂H₄ (24)) together with ammonia originating from NO₃RR. According to the mechanistic correlation proposed by Shibata and Furuya (2, 16-20) and supported by recent DFT studies (15, 21), these observations suggest that urea formation could, in principle, occur under such conditions.

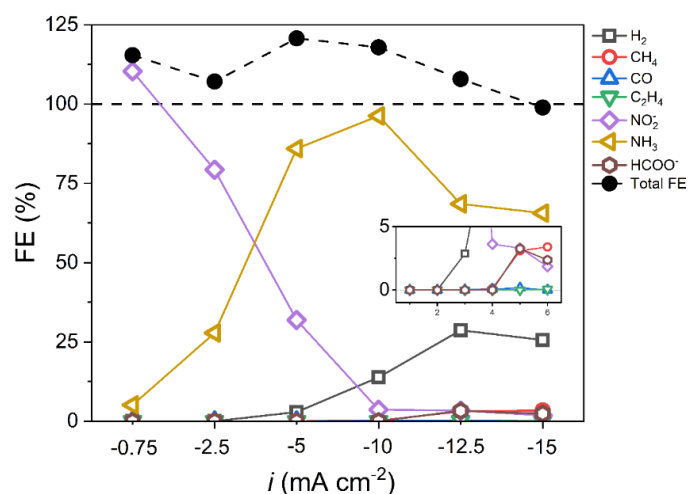


Figure 37 Product distribution at different current densities.

However, no urea was detected by either HPLC/UV-Vis or the modified DAMO-TSC (M-DAMO-TSC) methods, even after extended 17-hour chronopotentiometric runs (CP trace in Figure 36d, analytical data in Figures 39-42).

3.2.5. Urea detection in post-electrolysis samples

Post-electrolysis samples from H-cell experiments were analyzed for urea using all the rapid analytical methods discussed in this work, namely, the DAMO-TSC, modified DAMO-TSC (M-DAMO-TSC), and HPLC/UV-Vis protocols. As expected, the application of the DAMO-TSC method to samples obtained under HER and CO₂RR conditions yielded no detectable signals (Figures 38a and 38b). In contrast, when NO₃RR was taking place, either as an individual process or concurrently with CO₂RR (Figures 38c-38f), false-positive responses, due to the presence of nitrite ions generated during NO₃RR as previously discussed (16, 28, 31), were consistently observed.

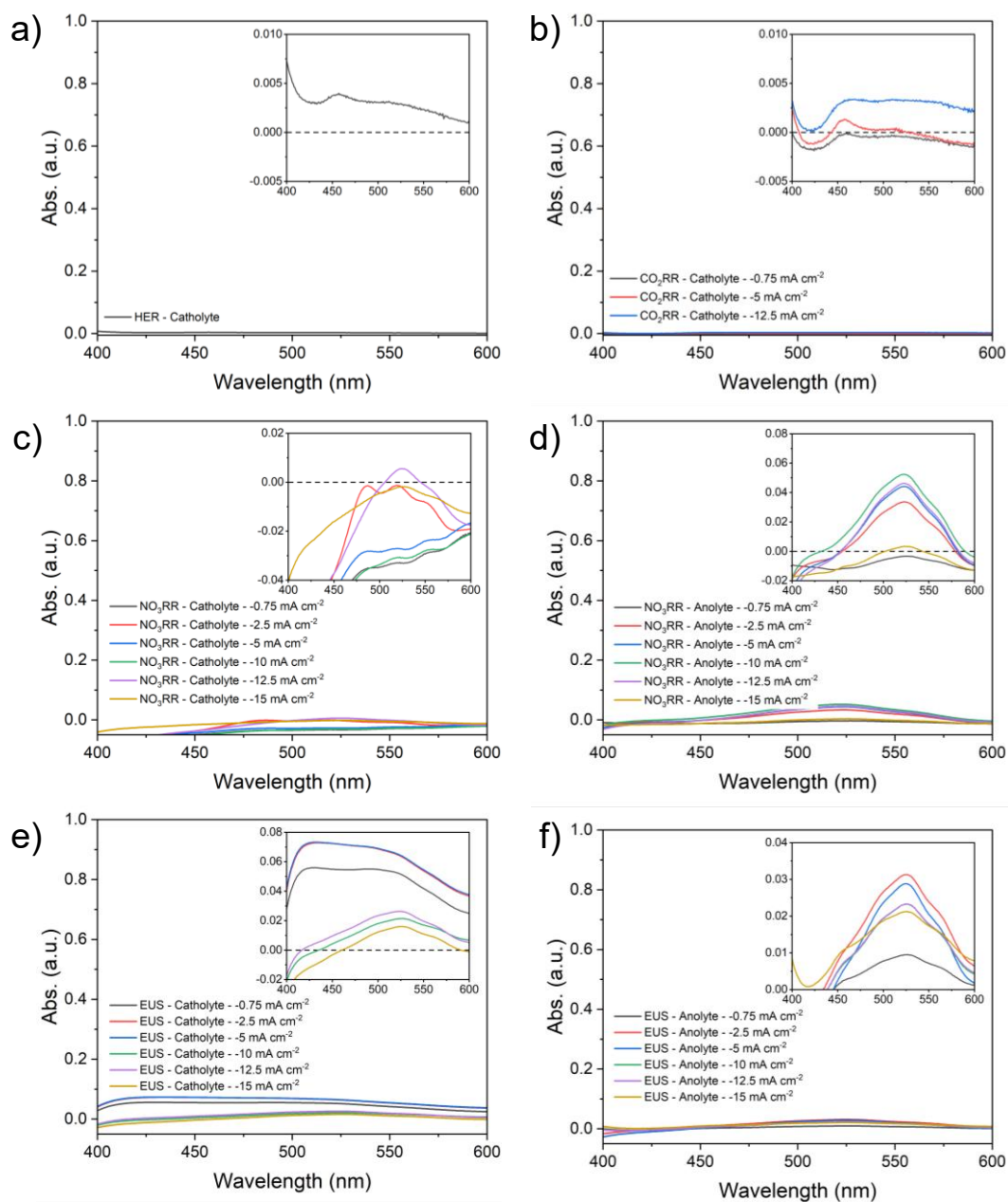


Figure 38 Tentative detection of urea by the classic DAMO-TSC method in post-electrolysis H-cell samples. a) HER catholytes; b) CO₂RR catholytes; c) NO₃RR catholytes; d) NO₃RR anolytes; e) EUS catholytes; f) EUS anolytes.

High nitrite concentrations in the catholyte under EUS conditions produced low-absorbance false positives (Figure 38e), whereas even stronger false signals were detected in the anolyte, further confirming the unreliability of the method. This effect stems from the use of an anion exchange membrane (AEM), which permits

partial crossover of nitrite ions, leading to their accumulation and interference in both compartments. Such crossover generates subtle yet significant false positives, even in the absence of one reactant (*e.g.*, under pure NO_3RR conditions; Figure 38c,d).

When the same post-electrolysis samples were analyzed using the M-DAMO-TSC method (Figure 39), all spectral features in the 500-550 nm region disappeared, indicating that the previously observed peaks originated exclusively from nitrite interference and confirming the absence of urea in the analyzed solutions.

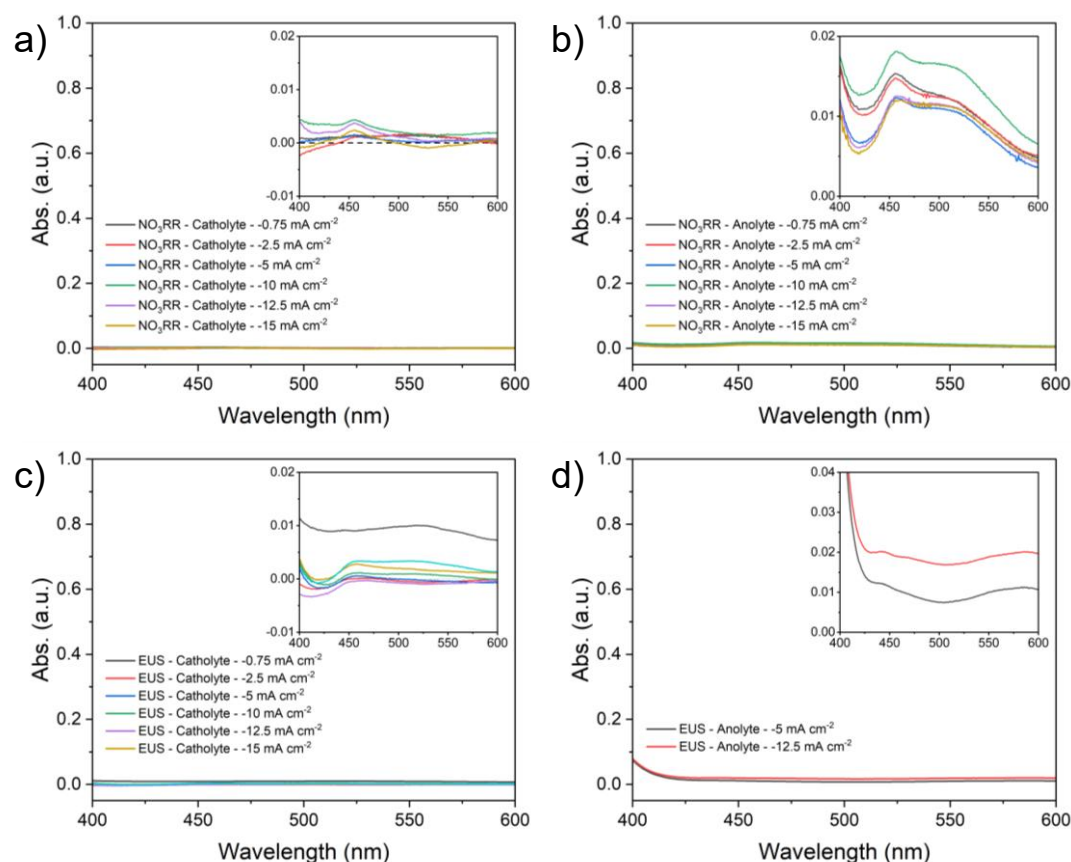


Figure 39 Tentative detection of urea by the modified M-DAMO-TSC method in post-electrolysis H-cell samples. a) NO_3RR catholytes; b) NO_3RR anolytes; c) EUS catholytes; d) EUS anolytes.

In the 17-hours long tests, nitrate ions convert completely to ammonia (Figure 40b) leading to the disappearance of nitrite ions in the catholyte (Figure 40a). Consequently, the UV-Vis spectra of catholyte samples treated with both the DAMO-TSC and M-DAMO-TSC methods (Figure 40c,d, red curves) were essentially flat, confirming the absence of urea and nitrite-related interferences. In contrast, the corresponding anolyte spectra (Figure 40c,d, gray curves) exhibited an

elevated yet featureless baseline, the origin of which remains uncertain and is difficult to interpret.

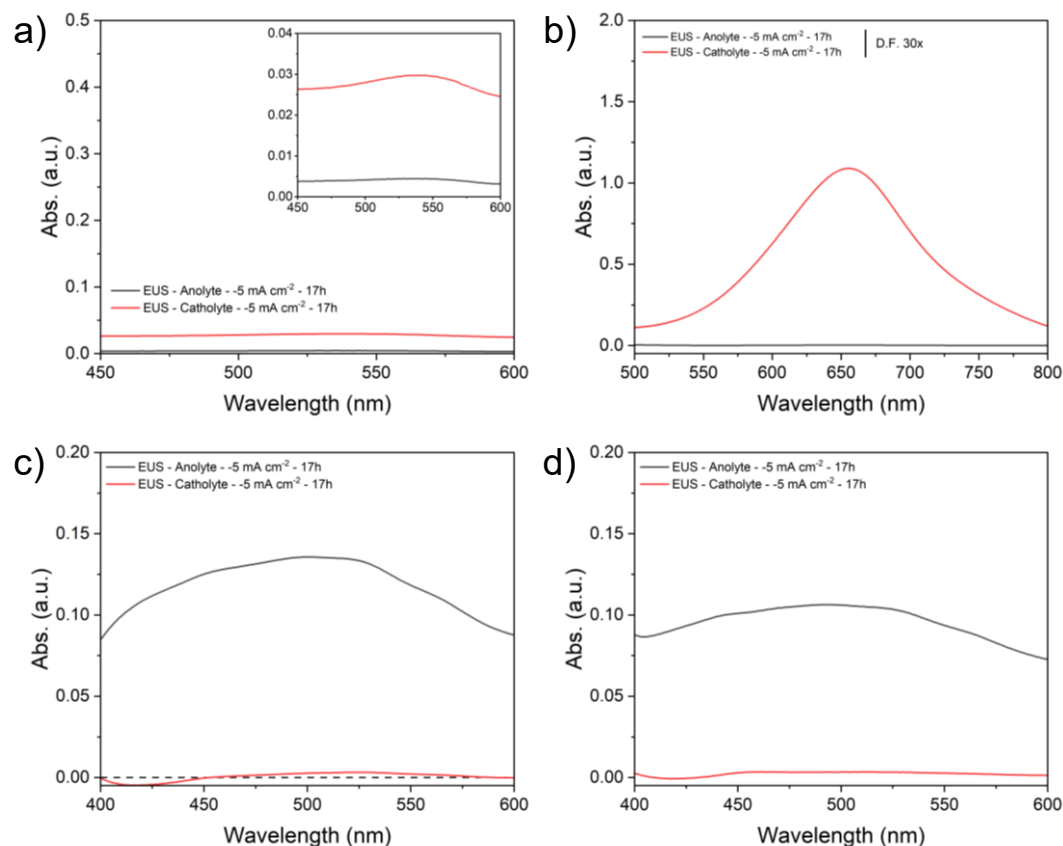


Figure 40 Spectrophotometric test conducted on post-electrolysis samples, 17-hours long CP at -5 mA cm^{-2} , EUS conditions. a) Griess test showing the absence of nitrite ions due to the complete conversion of nitrate ions to b) ammonia, detected by the indophenol blue method (D.F. stands for dilution factor). c) DAMO-TSC and d) M-DAMO-TSC tests, demonstrating the absence of either urea or nitrite-based false positives.

High-performance liquid chromatography (HPLC) analyses of the same post-electrolysis samples confirmed the absence of urea. The chromatograms revealed a recurring peak at approximately 4.3 minutes, which, based on previous observations, can be attributed to one of the following species: nitrite ions, formamide, or acetamide. Comparison of the chromatographic peak areas (Figure 41, left) with the corresponding absorbance signals obtained via the Griess method (Figure 41, right) shows a consistent trend across all samples, allowing the peak at 4.3 minutes to be confidently assigned to nitrite ions. In agreement with this interpretation, the disappearance of the peak at 4.3 minute after the 17-hour CP experiment at -5 mA cm^{-2} corresponds to the complete consumption of nitrite species. Likewise, the full conversion of nitrate ions, predicted by the calculated

reactant balance, is corroborated by the absence of the chromatographic peak at approximately 9 minutes.

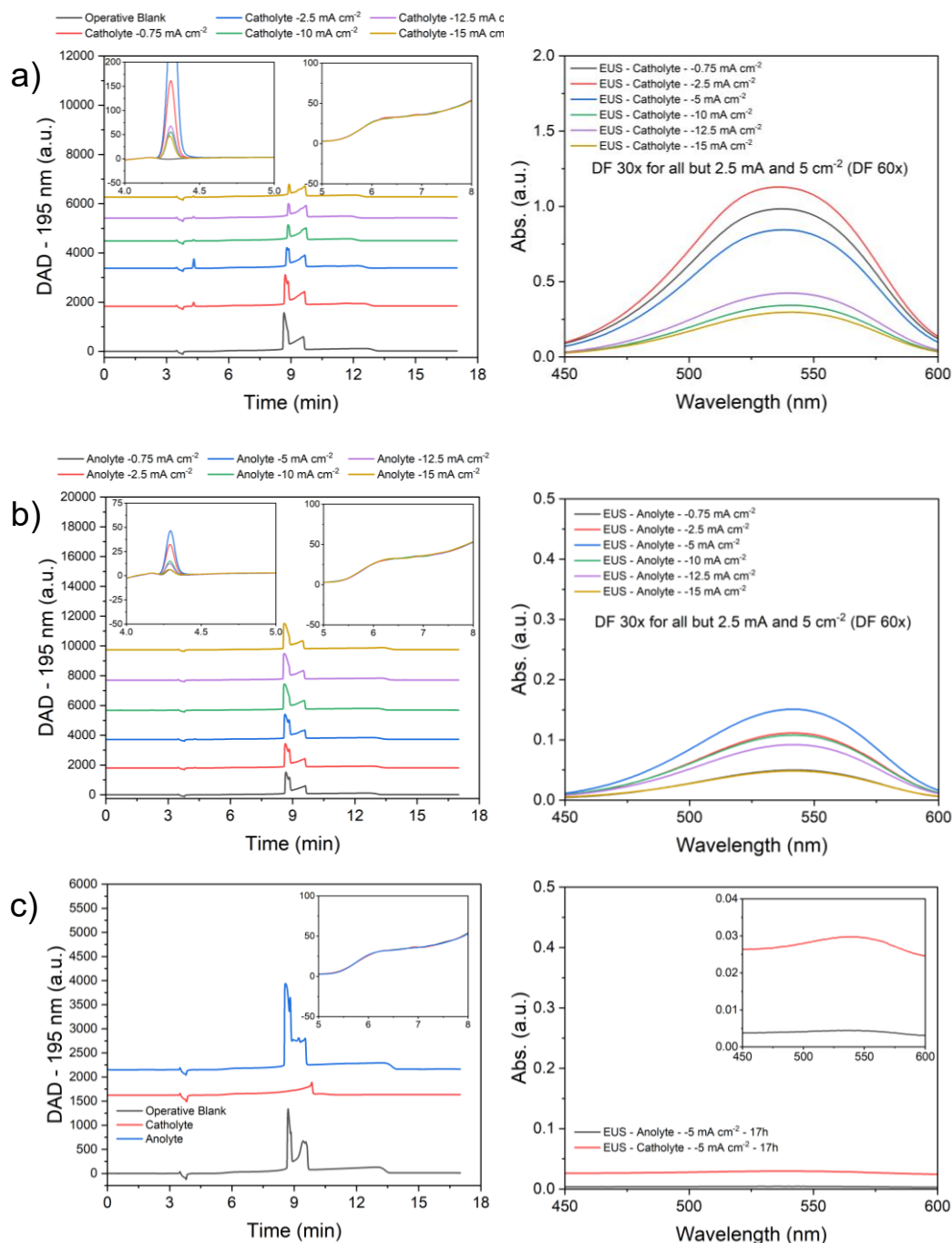


Figure 41 HPLC chromatographs (left side) and corresponding colorimetric tests according to the Griess method (right). a) Catholytes and b) anolytes collected after 1-hour long CP scans at different current densities under EUS conditions. The acronym DF in right figures stands for Dilution Factor. c) Catholyte and anolyte collected after a 17-hours long CP scan at -5 mA cm⁻² under EUS conditions.

3.2.6. Urea migration and diffusion through the AEM and/or degradation under operative conditions

Since the use of anion exchange membranes (AEMs) in urea electrosynthesis has not been previously reported, it was considered essential to verify the absence of urea crossover through the membrane. Such crossover could result in the oxidation of urea at the anode *via* the urea oxidation reaction (UOR), thereby consuming the desired product and potentially leading to false-negative results.

Furthermore, given that the 17-hour electrolysis tests demonstrated complete depletion of nitrate ions from the electrolyte (Figure 38c), it was also necessary to assess whether urea undergoes degradation under operational conditions once one of the co-reduction pathways ceases to sustain its formation.

To address both questions, two dedicated experiments were performed; “urea migration” test, in which the cell was operated at a constant current density of -25 mA cm^{-2} using a 0.2 M KHCO_3 electrolyte containing 100 ppm urea as the catholyte (with CO_2 feed) and 0.2 M KHCO_3 as the anolyte, and “urea diffusion” test, in which the system was left at OCP for one hour under otherwise identical conditions. After each experiment, samples from both compartments were analyzed by HPLC (Figure 42).

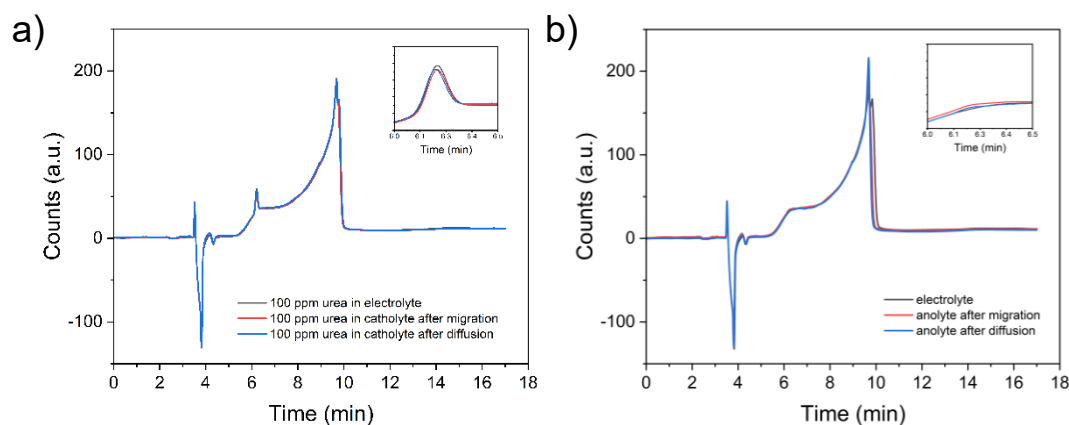


Figure 42 HPLC chromatograms of (a) catholytes and (b) anolytes before and after the urea migration (red traces) and diffusion (blue traces) experiments. Insets magnify the region in which the urea peak is expected.

The chromatograms revealed that the urea concentration in the catholyte remained constant regardless of the experimental condition. Consistently, no urea-related peaks were detected in the anolyte, confirming the absence of urea crossover through the membrane.

3.2.7. pH variations upon electrolysis

During direct electrolysis experiments (*e.g.*, CP scans), the cathode consumes protons while the anode generates them. Consequently, when small electrolyte volumes are continuously recirculated in a closed-loop configuration, progressive catholyte alkalization and anolyte acidification can occur. This effect is particularly pronounced in low-concentration electrolytes with limited buffering capacity.

Our results clearly reflect these trends: catholyte alkalization is observed during both HER and NO₃RR (gray and blue symbols in Figure 43a), whereas under CO₂RR and EUS conditions (red and green symbols, respectively), the pH remains nearly constant. This stability can be attributed to the continuous dissolution of CO₂, which generates carbonic acid and thereby counterbalances local proton consumption. Conversely, all anolytes exhibit progressive acidification, irrespective of the reaction environment (Figure 43b).

These pH variations, spanning several units even under relatively mild current densities and short test durations, pose a serious challenge to the accurate determination and reporting of electrochemical potentials in EUS-related studies. Indeed, as illustrated in Figures 40c and 40d, using either the initial or final pH value for the IR-corrected potential under HER and NO₃RR conditions can introduce discrepancies approaching 100 mV. As detailed in Section 3.1.3.1. “*Potential corrections*”, all potentials in this work were corrected using the final pH values measured after electrolysis.

Overall, these findings highlight yet another limitation of low-concentration, near-neutral bicarbonate electrolytes for EUS studies. While pH fluctuations could be mitigated by increasing the electrolyte volume or adopting a single-pass flow configuration, such strategies would inevitably lead to excessive product dilution, thereby hindering urea detection and quantification (30).

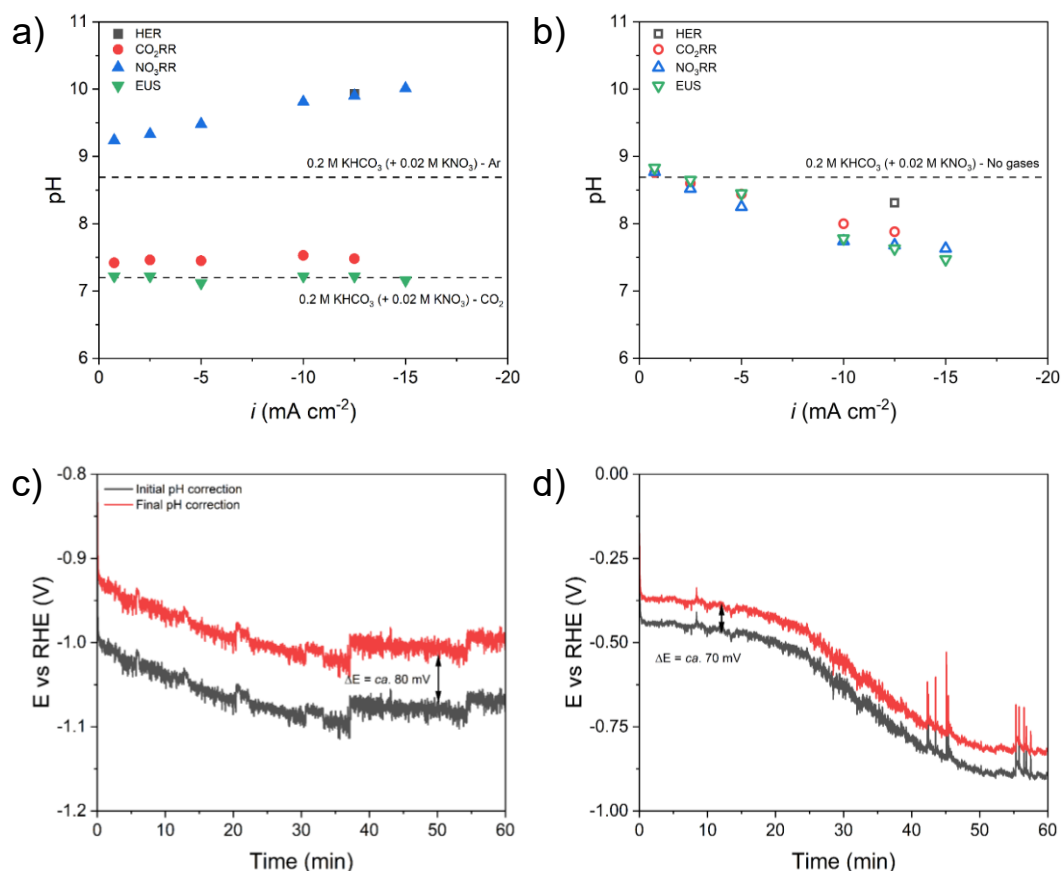


Figure 43 pH variations of the a) catholytes and b) anolytes during CP scans in different environments and at different current densities. 1-hour long CP traces collected under individual c) HER and d) NO₃RR conditions and corrected by the initial (gray trace or final (red traces) pH values.

3.2.8. Cu foil electrode characterization

A basic characterization of the Cu foil used as the WE in H-cell tests confirmed its polycrystalline nature and the absence of preferential dissolution or exposure of specific crystallographic facets, both after electropolishing in concentrated H₃PO₄ and following EUS operation (Figure 44a). Although mechanical polishing was not feasible due to the limited thickness of the foils, the micrometric surface roughness observed on the as-received material (Figure 44b) was effectively removed through the electropolishing procedure. This treatment, however, induced mild pitting corrosion, likely associated with the highly anodic potentials and the use of concentrated phosphoric acid (Figure 44c).

Post-electrolysis samples preserved the smooth morphology imparted by electropolishing, exhibiting only nanoscale surface features on the order of a few

hundred nanometers (Figure 44d). ICP-OES analyses further confirmed the absence of impurities on both the surface and in the bulk of the copper foils.

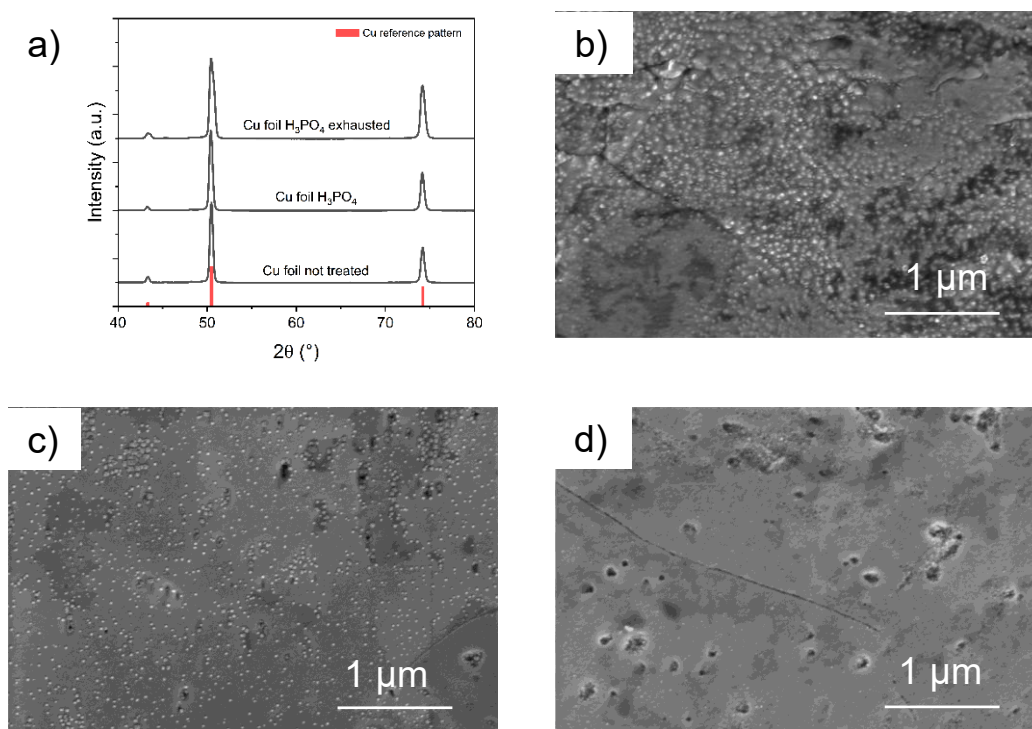


Figure 44 Basic characterization of Cu foils electrodes used for H-cell testing. a) XRD patterns collected on pristine, electropolished, and post-electrolysis (EUS conditions) WEs. SEM images of b) pristine, c) electropolished, and d) post-electrolysis Cu foils.

3.2.9. Conclusions

Overall, the outcomes of the H-cell experiments underscore two main conclusions: (i) the intrinsic limitations of this cell configuration for EUS testing, and (ii) the inadequacy of the standard DAMO-TSC colorimetric method for quantitative urea detection. Furthermore, the interpretability of EUS experiments is hindered by the use of low-concentration, near-neutral bicarbonate electrolytes such as those adopted in this study (30). The limited buffering capacity of these media, combined with the small electrolyte volume typical of H-cells, results in substantial pH variations during operation, which in turn complicate potential referencing and data reproducibility.

3.3. Flow-cell testing

Given the limitations identified in H-cell testing, the investigation was extended to a GDE-based configuration (Figure 30), employing a polycrystalline Cu/PTFE electrode as the cathode. Despite minor differences in design and operation (see Section 3.1.5. “*Extended Rationale of the Study*” for details), this configuration allows for a more accurate reproduction of the early reports of urea electrosynthesis by CO_2 and NO_3^- co-reduction (16), while leveraging modern analytical tools for reliable product quantification.

3.3.1. Calibration of RE

In analogy with the H-cell setup, Figure 45 reports a representative calibration of the RE employed in flow-cell tests. Due to the small diameter of the RE port drilled into the cathodic compartment, a 2 mm outer diameter Ag/AgCl (3 M KCl, eDAQ leakless) electrode was used. The standard potential (E^0) measured prior to electrochemical testing (gray trace) closely matched the theoretical value of approximately 222.5 mV vs RHE.

However, a gradual upward drift in the experimental E^0 was observed when the RE was recalibrated immediately after prolonged electrochemical operation, particularly following extended CP scans under EUS conditions (red trace). This drift appeared to correlate with the occurrence of NO_3RR within the cell, suggesting a transient poisoning of the reference electrode, plausibly caused by adsorption or diffusion of ammonia/ammonium species produced during electrolysis.

Importantly, this effect proved reversible: during recalibration against the RHE, the potential of the RE progressively shifted back toward lower values (red trace, inset) and fully recovered its nominal E^0 after overnight equilibration in clean 3 M KCl solution.

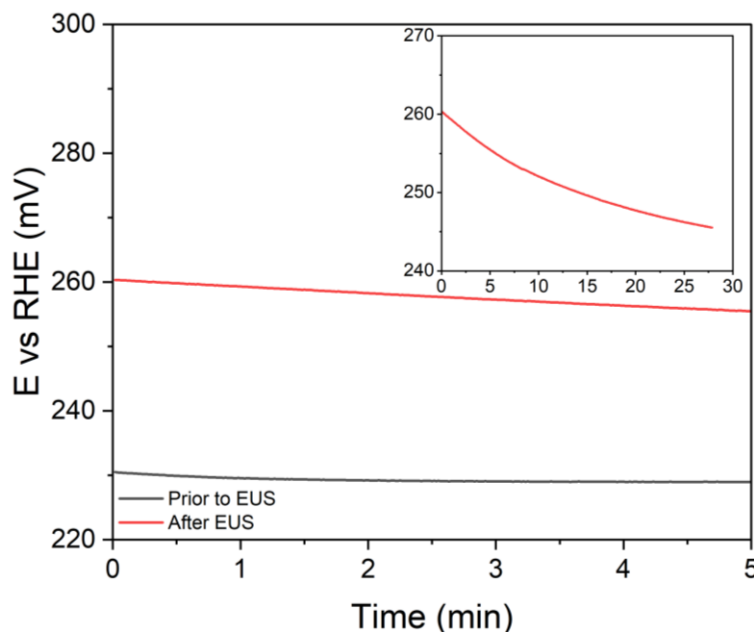


Figure 45 Sample calibration of the RE (3 M KCl Ag/AgCl, eDAQ leakless), obtained measuring its OCP in 0.5 M H₂SO₄ (pH 0) versus an RHE. Inset: downward drift of the RE potential when the calibration time is lengthened.

3.3.2. HER, CO₂RR, NO₃RR and EUS assessment

Following the same analytical approach used for H-cell testing, the comparison of CVs collected under different reaction environments provides an initial assessment of EUS feasibility in the flow-cell setup.

The overall electrochemical trends observed for the individual reactions in the H-cell are largely retained in the flow-cell configuration (Figures 46-49), with one key distinction. Due to the enhanced CO₂ deployment at the cathode surface (34, 36), the CO₂RR competes more effectively with the HER across a relatively wide potential range, from approximately -0.65 to -0.85 V vs RHE, although the near-neutral electrolyte still thermodynamically favors hydrogen evolution (37).

Figures 46-49 compile the cyclic voltammetry (CV, panels a) and galvanostatic electrochemical impedance spectroscopy (GEIS, panels b) data collected for each individual reaction. Since the general electrochemical behavior, such as the presence of characteristic peaks, plateaus, and overall trends, closely resembles that observed in the corresponding H-cell studies, see those sections for detailed discussion. The main distinction between the two configurations lies in the markedly improved CO₂RR performance relative to the parasitic HER, a direct consequence of implementing a gas diffusion electrode (GDE).

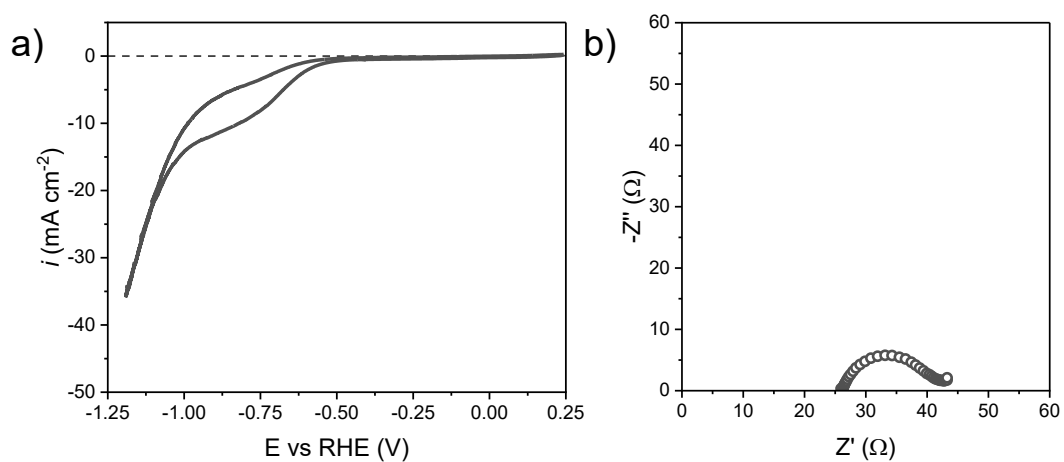


Figure 47 Cu/PTFE electrochemical testing under HER conditions (i.e., 0.2 M KHCO_3 , Ar) in flow cell configuration. a) CV curve (5th scan, scan rate 100 mV s^{-1}), b) GEIS (collected at -5.65 mA, 1.4 mA amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.5 Hz).

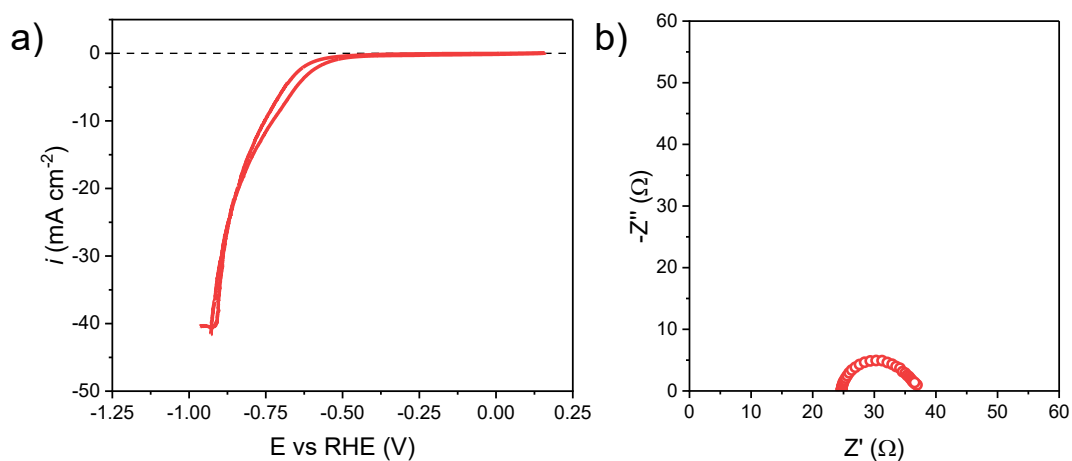


Figure 46 Cu/PTFE electrochemical testing under CO_2RR conditions (i.e., 0.2 M KHCO_3 , CO_2) in flow cell configuration. a) CV curve (5th scan, scan rate 100 mV s^{-1}), b) GEIS (collected at -5.65 mA, 1.4 mA amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.5 Hz).

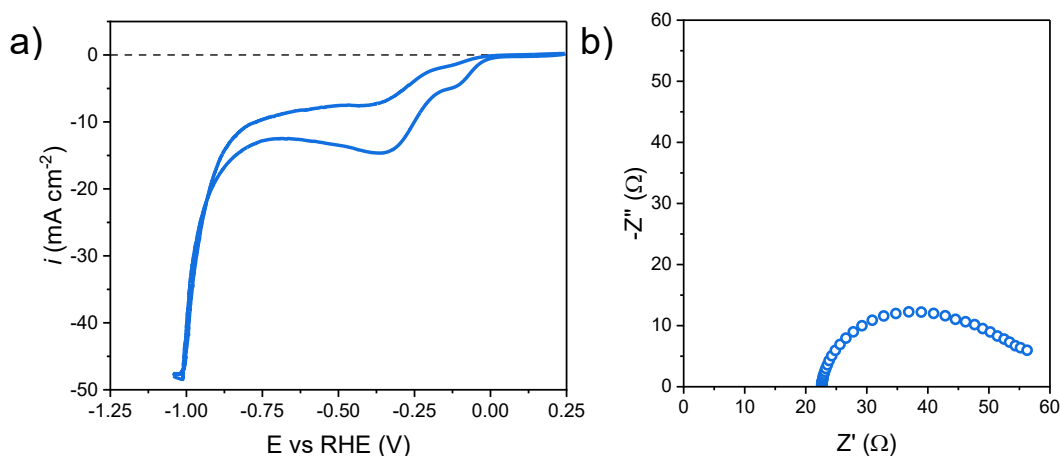


Figure 48 Cu/PTFE electrochemical testing under NO_3RR conditions (i.e., $0.2 \text{ M KHCO}_3 + 0.02 \text{ M KNO}_3$, Ar) in flow cell configuration. a) CV curve (5^{th} scan, scan rate 100 mV s^{-1}), b) GEIS (collected at -5.65 mA , 1.4 mA amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.5 Hz).

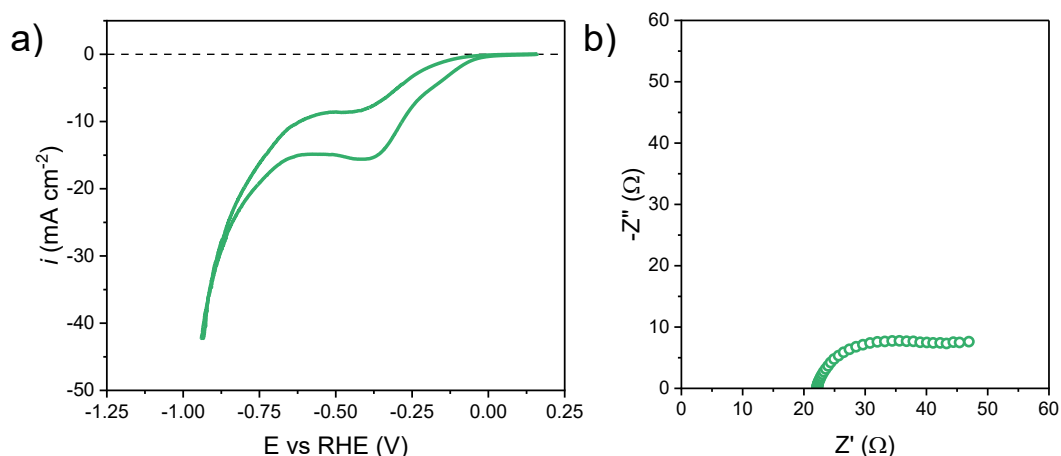


Figure 49 Cu/PTFE electrochemical testing under EUS conditions (i.e., $0.2 \text{ M KHCO}_3 + 0.02 \text{ M KNO}_3$, Ar) in flow cell configuration. a) CV curve (5^{th} scan, scan rate 100 mV s^{-1}), b) GEIS (collected at -5.65 mA , 1.4 mA amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.5 Hz).

Under EUS conditions, the voltammetric profile again appears as a complex hybrid of CO_2RR and NO_3RR features, making straightforward interpretation difficult. In an oversimplified interpretation, the potential window between roughly -0.35 and -0.8 V vs RHE exhibits higher current densities than either individual reaction alone, suggesting the possible occurrence of CO_2 and NO_3 co-reduction.

Regarding the GEIS measurements, noticeable differences arise in both the equivalent circuit representation and the absolute values of certain parameters, particularly the uncompensated resistance (R_u). For the flow-cell experiments, the

impedance spectra are best described by a simplified $R_1(R_2Q_1)$ circuit, where R_1 corresponds to R_u . The recorded Nyquist plots exhibit slightly flattened, asymmetric semicircles, a feature tentatively attributed to the high porosity of the Cu/PTFE WEs.

Interestingly, the measured R_u values are unusually high. While the low conductivity of the near-neutral electrolyte could partly account for this, the close proximity of the RE to the WE, directly immersed in the catholyte chamber, would typically yield uncompensated resistances of ohms, as observed in the H-cell setup. The elevated R_u may therefore stem from a combination of gas bubbles generation at the cathode and the vertical positioning of the RE, located directly in the path of rising bubbles.

Regardless of its origin, the experimentally determined R_u values were used for accurate iR correction of the applied potentials, as described in the Section 3.1.3.1 “*Potential correction*”. Although a lower system resistance would be preferable, the primary objective of these measurements was to identify potential electrochemical windows conducive to EUS and to enable precise urea detection, rather than to optimize cell performance.

3.3.3. Chronopotentiometric scans & related electrolyte pH and product distribution

Long CP scans (16 hours-last) were conducted in the flow-cell setup under EUS conditions (Figure 50) at three representative current densities encompassing the potential windows of interest for EUS.

At the current density of -1 mA cm^{-2} (gray trace, Figure 50), the potential exhibits a continuous downward drift throughout the test, most likely resulting from the progressive depletion of nitrate ions, since NO_3RR is the only active cathodic process at this potential, combined with catholyte alkalization (see Figure 51 and related discussion). Similar trends are observed for the CPs collected at -10 and -30 mA cm^{-2} (red and blue traces, respectively), although in these cases the potential stabilizes after a certain period.

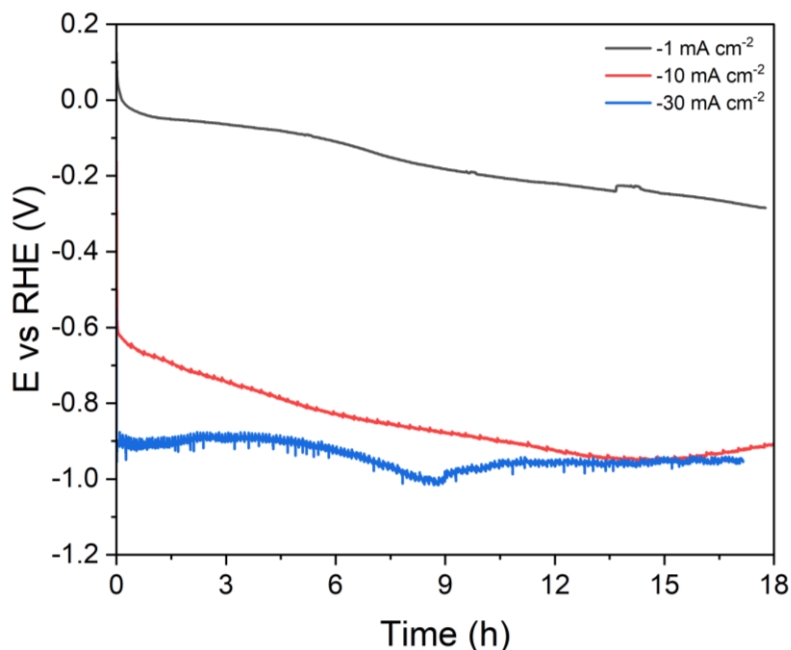


Figure 50 Long CP scans, collected in flow cell configuration, EUS conditions, at different current densities.

An interesting feature arises at longer electrolysis times ($t_{\text{CP}} \geq ca. 10 \text{ h}$), where the -10 and -30 mA cm^{-2} traces intersect and subsequently overlap. This behavior is interpreted as an artifact originating from pH fluctuations during electrolysis (Figure 51), compounded by the use of the final pH value for potential correction, a procedure consistent with that adopted for the H-cell measurements (see related section).

Importantly, the potential ranges explored at -10 and -30 mA cm^{-2} fall within the broad window identified as favorable for EUS. Consistent with this, traces of urea were detected in the corresponding post-electrolysis catholytes using the M-DAMO-TSC method (inset of Figure 54).

Consistent with the observations discussed in “pH Variations upon Electrolysis”, significant pH changes occur during electrolysis in the flow-cell configuration. The catholytes exhibit pronounced alkalization, with ΔpH values ranging from approximately 1.5 to nearly 3 units (solid triangles in Figure 51), whereas the anolytes undergo the expected acidification (hollow triangles in Figure 51). Once again, the substantial pH increase observed in the catholyte highlights the inherent challenges associated with accurate potential correction in EUS experiments.

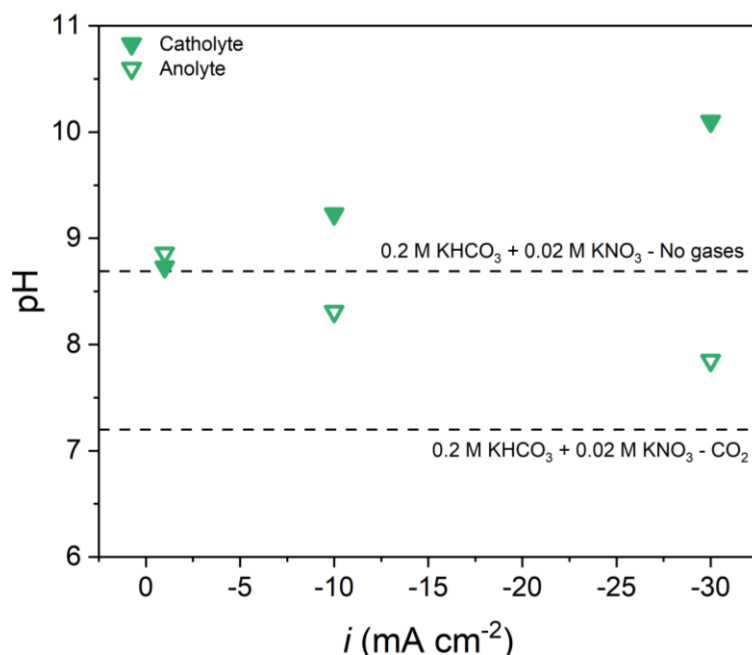


Figure 51 Final pH measured in post-electrolysis catholytes (full triangles) and anolytes (hollow triangles). Dashed lines represent the initial pH values measured in for catholytes (CO_2 feed, bottom) and anolytes (no gas feed, top).

HPLC analyses of the post-electrolysis electrolytes provide valuable insight into the reaction outcomes. Most notably, no urea-related peaks were detected in any of the catholyte samples (Figure 52a, right inset). To verify that this absence was not due to analytical limitations, a spiking test was performed by adding a few microliters of a urea solution (prepared in 0.2 M KHCO_3 + 0.02 M KNO_3 fresh electrolyte) to the catholyte obtained after electrolysis at -10 mA cm^{-2} . The resulting chromatogram (purple trace, Figure 52a) clearly displays the urea peak, confirming the method's suitability for urea detection in the actual sample matrix.

As expected, the large nitrate signal observed in the fresh electrolyte significantly decreases, or even disappears, after electrolysis, consistent with the full consumption of nitrate ions. A distinct peak assignable to nitrite ions (Figure 52a, left inset) was detected only in the sample obtained at -1 mA cm^{-2} , aligning with the electrochemical potentials recorded during CP scans and with the results of the colorimetric analyses.

The composition of the anolytes is likewise consistent with expectations. All anolyte samples appeared free of detectable products, with the exception of the one corresponding to the -1 mA cm^{-2} test, in which a small amount of nitrite ions was

observed (Figure 52b). This finding supports the hypothesis of limited nitrite crossover through the membrane under these specific conditions.

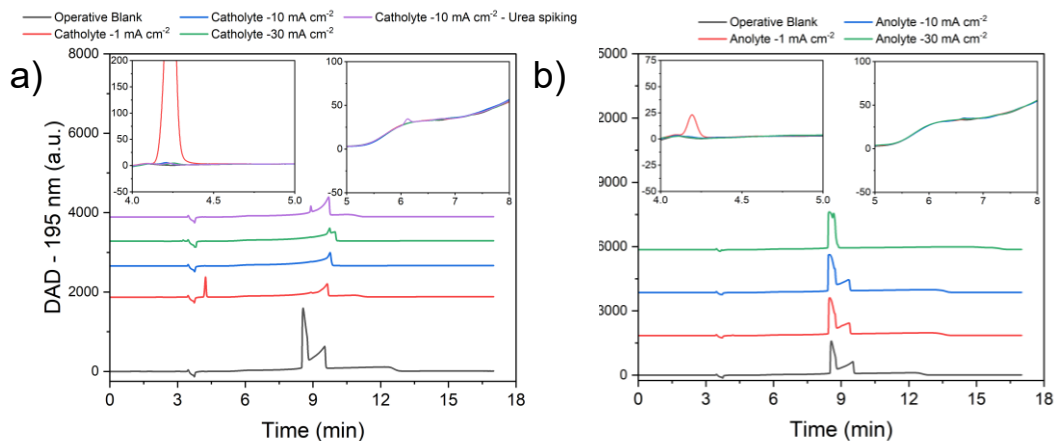


Figure 52 HPLC chromatograms collected according to the developed HILIC method on post-electrolysis flow cell samples. a) Catholytes analyses and b) anolyte analysis, with insets magnifying the region of nitrite (left) and urea (right) peaks.

Although not central to the scope of this study, it is noteworthy that the bicarbonate signal is absent in the anolyte obtained after electrolysis at -30 mA cm^{-2} (green trace, Figure 52b). This observation is likely attributable to the acidic environment developed during electrolysis (Figure 51). Specifically, the substantial proton generation associated with the anodic oxygen evolution reaction (OER) is expected to promote the complete depletion of bicarbonate ions *via* carbonic acid formation and subsequent CO_2 evolution.

Further discussion could be devoted to the potential crossover of (bi)carbonate species through the AEM, which may partially replenish the anolyte's bicarbonate content, as well as to the possible competition between (bi)carbonates and other anionic species (*e.g.*, nitrate ions) during membrane transport. However, the investigation of these phenomena requires a dedicated study and falls beyond the scope of the present work.

The overall product distribution obtained from the flow-cell CPs was not quantitatively determined, primarily due to fluctuations in catalyst selectivity during operation due to progressive changes in electrolyte pH and composition throughout electrolysis. In these experiments, the catholyte and anolyte were analyzed only at the end of each CP run, whereas gas-phase products were monitored *in situ* every four hours using the inline GC.

As shown in Figure 53a, the GC peak areas of the gaseous products, and consequently their calculated FE, vary significantly over the course of the experiment, reflecting dynamic shifts in reaction selectivity. A similar behavior is likely to occur for liquid-phase products; however, since their concentrations were determined only post-electrolysis, the data provide a snapshot of the final electrolyte composition (Figures 53b-53d).

Although these oscillations prevent an accurate quantitative assessment of product distribution, valuable qualitative insights can still be extracted. In the CP conducted at -1 mA cm^{-2} (gray traces), only NO_3RR products, namely ammonia and nitrite ions, were detected (Figures 53c,d), confirming that nitrate reduction was the sole operative process within the potential range recorded for this test. The high nitrite content observed in the corresponding anolyte (Figure 53d, right panel) is attributed to ion crossover through the anion exchange membrane (AEM).

In contrast, CPs carried out at -10 and -30 mA cm^{-2} (red and blue traces) reveal the simultaneous presence of products from all individual reactions (HER, CO_2RR and NO_3RR) consistent with the voltammetric features previously discussed. This coexistence of reduction pathways indicates that these conditions fall within the potential window in which EUS may occur.

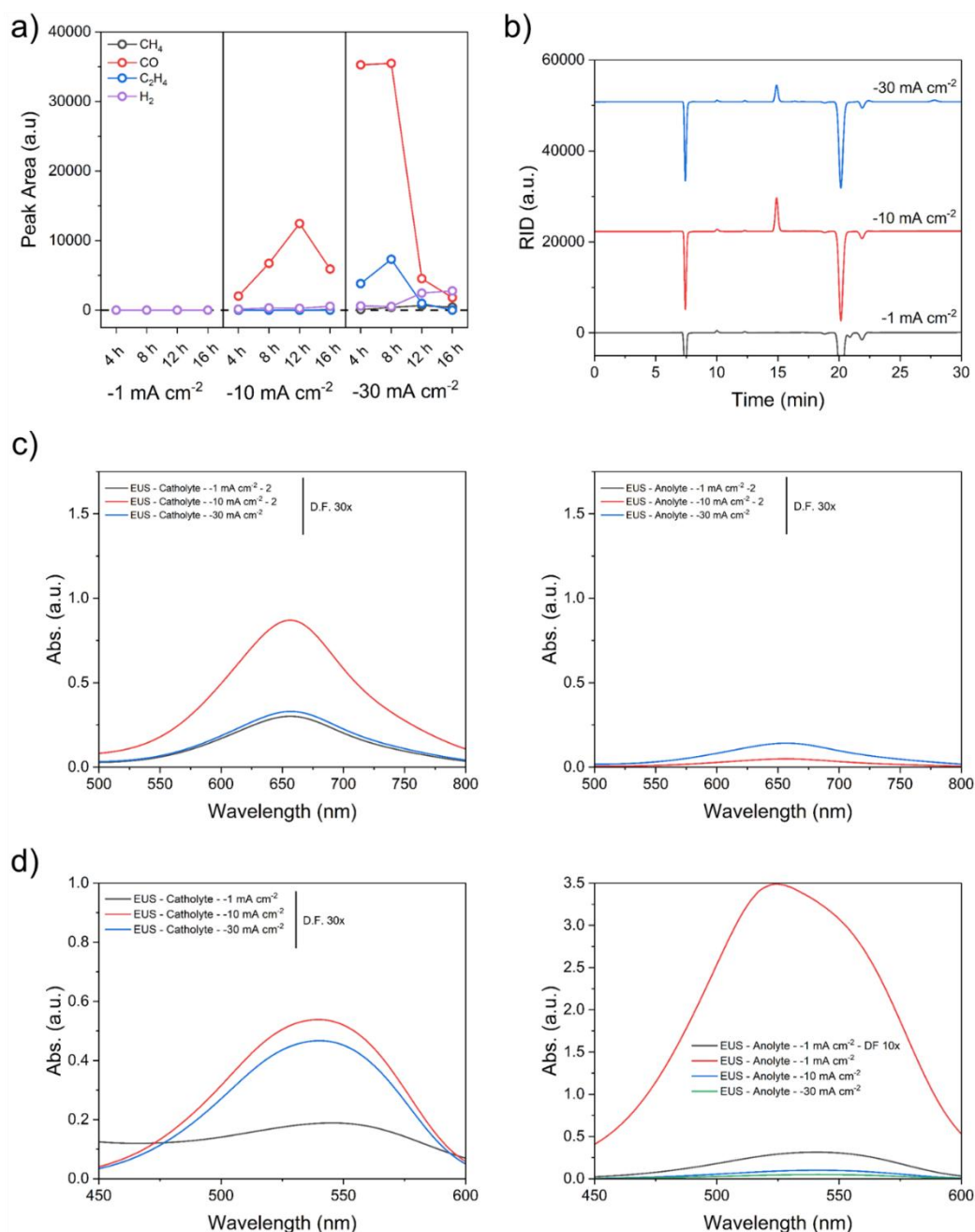


Figure 53 GC, HPLC, and colorimetric analyses carried out on the post-electrolysis electrolytes collected after long CP scans in flow-cell configuration, EUS conditions. a) Peak area of the detected products at different times and at different current densities, evidencing the fluctuations in the production rates. b) HPLC analyses (HiPlex method, for CO_2RR products detection) of catholytes, evidencing the presence of (mainly) formate ions. Colorimetric tests for the detection and quantification of c) ammonia and d) nitrites. D.F. stands for dilution factor.

Despite the absence of urea signals in the HPLC analyses (Figure 53), the same post-electrolysis catholytes were further examined using the colorimetric M-DAMO-TSC method. The conventional DAMO-TSC protocol was intentionally excluded due to the confirmed presence of nitrite ions, as determined by the Griess assay (Figure 53d), which are known to generate false-positive responses.

The resulting spectra (Figure 54) exhibit slightly higher baselines within the analyzed wavelength region; however, upon magnification (inset of Figure 54), a weak but discernible absorption feature can be confidently attributed to urea. Given the very low absorbance intensity, clearly outside the calibration range established in Figure 17, no FE_{Urea} was calculated.

Overall, these findings suggest that the amount of urea produced under the investigated conditions is significantly lower than the values reported in previous literature but is nonetheless detectable, conversely to what observed under H-cell conditions. These findings underscore a critical need to establish new performance benchmarks to drive progress in electrochemical urea synthesis.

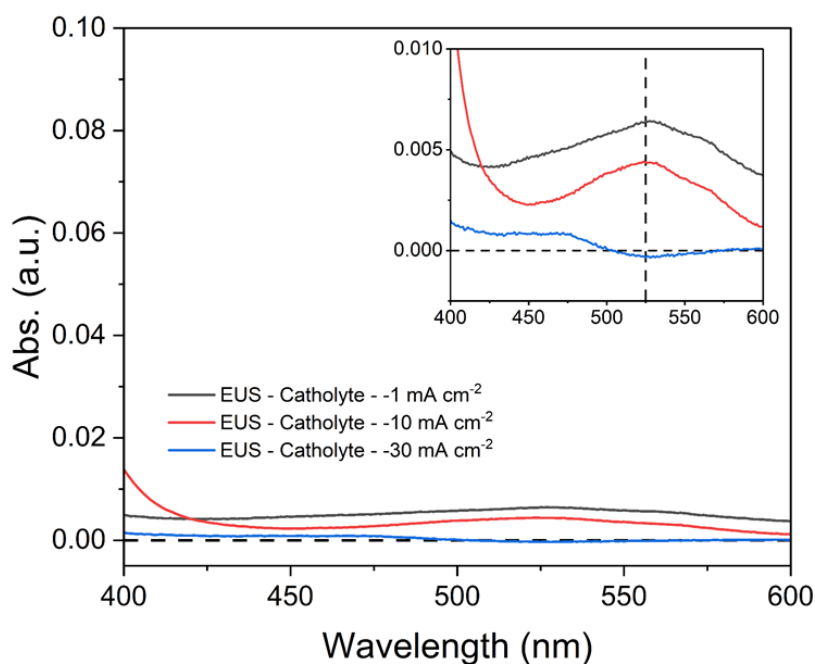


Figure 54 Spectra collected on the post-electrolysis catholytes obtained from flow-cell testing. The detection/quantification method applied was the M-DAMO-TSC one.

3.3.4. Cu/PTFE electrode characterization

X-ray diffraction (XRD) analysis of the Cu/PTFE electrodes confirmed the polycrystalline nature of the thin metallic copper (Cu^0) film deposited on the gas diffusion layer, as well as the preservation of this crystallographic structure after electrolysis (Figure 55a). Complementary scanning electron microscopy (SEM) and X-ray fluorescence (XRF) analyses performed on the pristine Cu/PTFE samples (Figures 55b and 55c) demonstrate the uniformity and chemical purity of the deposited Cu^0 layer.

Post-electrolysis samples (Figure 55d) display partial mechanical damage, primarily associated with the assembly and disassembly of the cell, specifically, localized delamination of the Cu^0 layer upon removal of the copper contact tape. Nevertheless, the XRF spectra confirm the continued chemical integrity of the electrode, with no detectable contamination except for a minor potassium signal, likely attributable to residual K-based carbonate species trapped within the pores or deposited on the surface of the electrode.

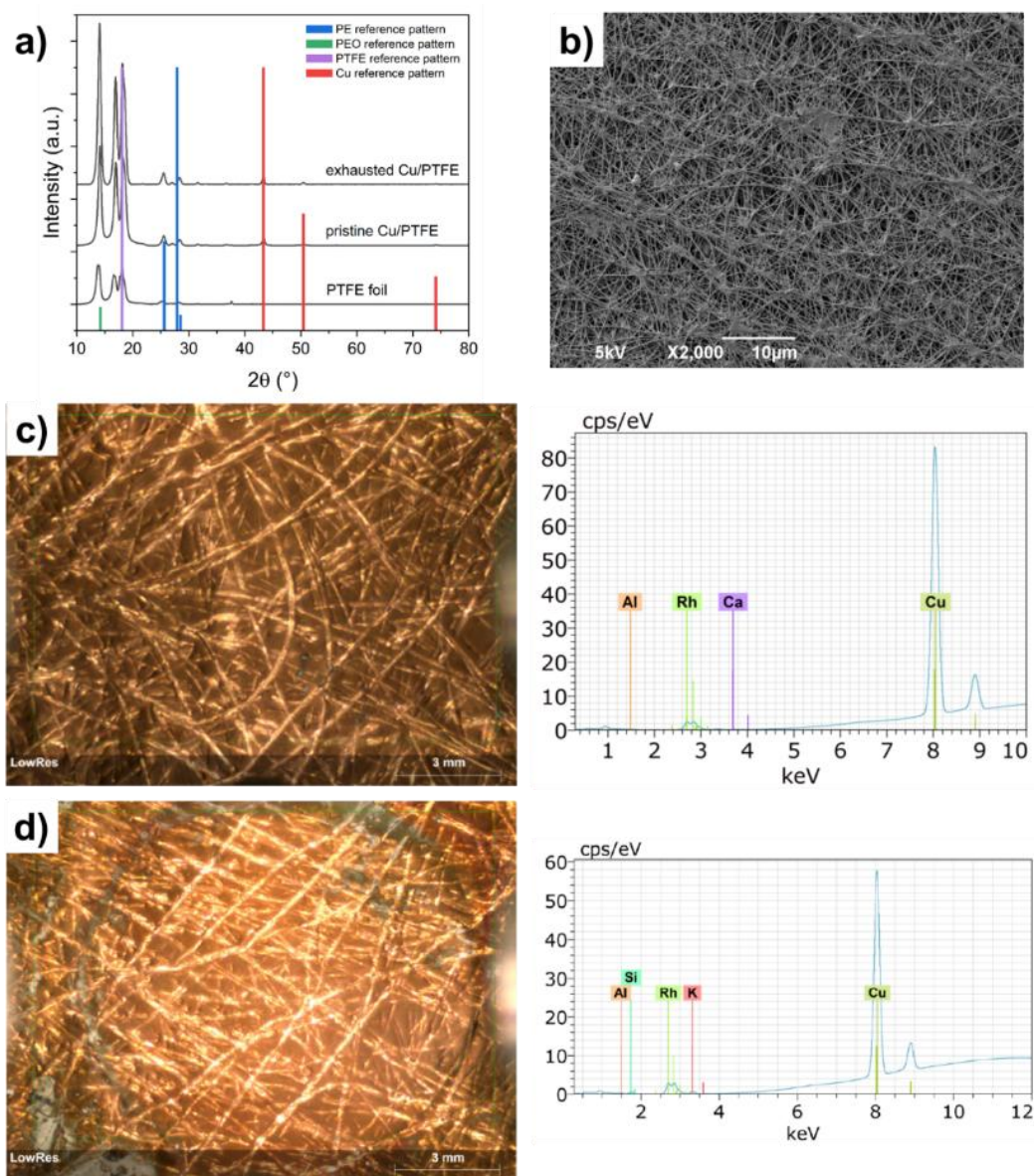


Figure 55 Basic characterization of the Cu/PTFE electrodes used for flow-cell testing. a) XRD patterns collected on the bare support (PTFE) and on the pristine and post-electrolysis electrode. PE and PEO stand for polyethylene and polyethylene oxide, constituents of the backing layer of the PTFE membrane. Pristine Cu/PTFE b) SEM image and c) XRF analysis. (d) XRF analysis of the used Cu/PTFE.

3.3.5. Conclusions

In summary, the flow-cell tests demonstrate that, despite the intrinsic advantages of this configuration, such as enhanced mass transport and continuous CO₂ deployment *via* GDEs, only traces of urea were detected under CO₂ and NO₃⁻ co-reduction conditions. These results indicate that urea electrosynthesis remains primarily limited by kinetic and interfacial factors, allegedly the stabilization and coupling of *CO and *NH₂ intermediates, rather than by reactant availability. Despite the minimal productivity/selectivity obtained in these experiments, the flow-cell platform holds promise for future optimization.

3.4. References

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Chapter 4

EUS assessment in alkaline electrolyte

Building on the proof-of-concept that the co-reduction of CO₂ and nitrate ions in flow-cell configuration under near-neutral pH conditions enables the electrochemical synthesis of urea, though only in trace amounts, alternative operating conditions, aimed at enhancing the efficiency of the process, were investigated. In previous experiments (Chapter 3), the near-neutral pH and low concentration electrolyte was identified as a potential limiting factor for EUS efficiency, as its use not only results in poor ionic conductivity, posing significant challenge for the industrial scalability of EUS (1), but also favors parasitic HER, reducing selectivity toward urea. To address these bottlenecks, EUS feasibility was investigated in a flow-cell configuration employing a concentrated alkaline electrolyte (*i.e.*, 1 M KOH + 0.1 M KNO₃). Such condition is expected to substantially increase ionic conductivity while simultaneously suppressing HER, thereby providing more favorable reaction pathways for CO₂ and nitrate ions co-reduction for electrochemical urea synthesis. GDEs composed of Me/PTFE (where Me is Ag, Cu or Au), which have been reported by Shibata as the most efficient transition metals for electrochemical urea synthesis under his investigated conditions (2), were employed to systematically assess catalytic performance under these modified conditions. Although Cu, Au, and Ag are known to be active for CO₂RR (3), Cu uniquely exhibits a CO binding energy within the optimal range that allow subsequent C-N coupling reaction for urea synthesis (4).

4.1. Materials and methods

The following sections detail the methodologies for electrode preparation and characterization, electrochemical testing, and quantitative analysis of reaction products.

4.1.1. Electrode preparation and characterization

4.1.1.1. Me/PTFE electrode

Me/PTFE electrodes were prepared, as previously discussed in Section 3.1.1.2. “*Cu/PTFE electrode (flow-cell)*”, by depositing Cu, Ag or Au onto PTFE membranes (Sterlitech® Aspire QL822, 0.45 μm pore size) using electron-beam evaporation (Kenosistec KE500ET combined e-beam/thermal evaporator) at a deposition rate of 50 $\text{\AA s}^{-1}$. The resulting Cu, Ag and Au films, with a final thickness of approximately 300 nm, provided uniform coverage of the PTFE substrate and ensured sufficient electrical conductivity for subsequent catalytic applications.

4.1.1.2. Reference electrodes calibration

Prior to use in flow-cell configuration, the reference electrode was calibrated by measuring their Open Circuit Potential (OCP) in electrolyte solution employed for the electrochemical tests against a Reference Hydrogen Electrode (RHE, HydroFlex®, Gaskatel).

4.1.1.3. X-Ray Diffraction (XRD) Analysis

XRD measurements were carried out under ambient conditions and at room temperature, with Me/PTFE electrode supported on a zero-diffraction single-crystal substrate. Data acquisition was performed using a PANalytical Empyrean diffractometer equipped with a 1.8 kW Cu K α ceramic X-ray tube and a PIXcel3D 2×2 area detector, operating at 45 kV and 40 mA. The diffraction patterns were processed and analyzed using HighScore Plus version 4.1 (PANalytical).

4.1.1.4. Scanning Electron Microscopy (SEM)

Electron micrographs were acquired using a FEI Helios NanoLab DualBeam 650 system operated at a landing voltage of 5 kV and a probe current of 50 pA.

4.1.2. Electrochemical testing

Experiments were conducted in a three-compartment flow cell, as previously described in Section 3.1.2.2. “*Flow cell-setup*” The cell employed a Me/PTFE as WE (GDE; exposed geometric area: 1.13 cm^2). The RE was an Hg/HgO (1 M KOH, Latech, model R0501) with an outer diameter of 5-5.5 mm. The same CE and ion-exchange membrane utilized in Section 3.1.2.2 were employed here as well.

All operational parameters were maintained identical to those adopted in Chapter 3, with both anolyte and catholyte flow rates set to 7.5 mL min^{-1} and gas flow rate set to 18 mL/min .

The Me/PTFE electrodes were electrochemically characterized under four distinct conditions, alternating between individual and combined reactant feeds (Table 3). As previously discussed, this approach enabled the assessment of catalyst activity and selectivity for the individual reactions (*i.e.*, HER, CO₂RR and NO₃RR), as well as under co-reduction conditions (*i.e.*, CO₂RR + NO₃RR). CP measurements were conducted exclusively under EUS testing conditions using a 1 M KOH + 0.1 M KNO₃ electrolyte and a CO₂ gas feed with the objective of evaluating urea formation.

Table 3 Electrolytes and gas feeds used to investigate individual and co-reduction processes. The initial electrolyte pH is intended after saturation with the gas of choice.

<i>Expected reaction</i>	<i>Electrolyte</i>	<i>Gas feed</i>	<i>Initial electrolyte pH</i>
HER	1 M KOH	Ar	13.98
CO ₂ RR (+ parasitic HER)	1 M KOH	CO ₂	13.97
NO ₃ RR (+ parasitic HER)	1 M KOH + 0.1 M KNO ₃	Ar	14.00
EUS (CO ₂ RR + NO ₃ RR) (+ parasitic HER)	1 M KOH + 0.1 M KNO ₃	CO ₂	13.99

4.1.3. Urea quantification

Given that the primary objective of this testing campaign was to identify the optimal operating conditions for electrochemical urea synthesis, the catholytes obtained from CP@-70 mA cm⁻² under EUS conditions for each three Me/PTFE electrodes were subsequently analyzed *via* HPLC (method described in Section 2.1 “*Optimization of the HPLC/UV-Vis method for urea detection/quantification*”) to specifically detect and quantify urea. An additional urea quantification was performed on catholytes obtained from chronopotentiometric measurements carried out at different current densities under EUS conditions *via* the DAMO-TSC method to underscore, once more, the fallacies of this method. The DAMO-TSC method was performed as detailed in Section 3.1.4.4 “*Colorimetric methods*”, using

standard analyte solutions in 1 M KOH + 1 M KNO₃ to construct calibration curves in the electrolyte of interest (Figure 56).

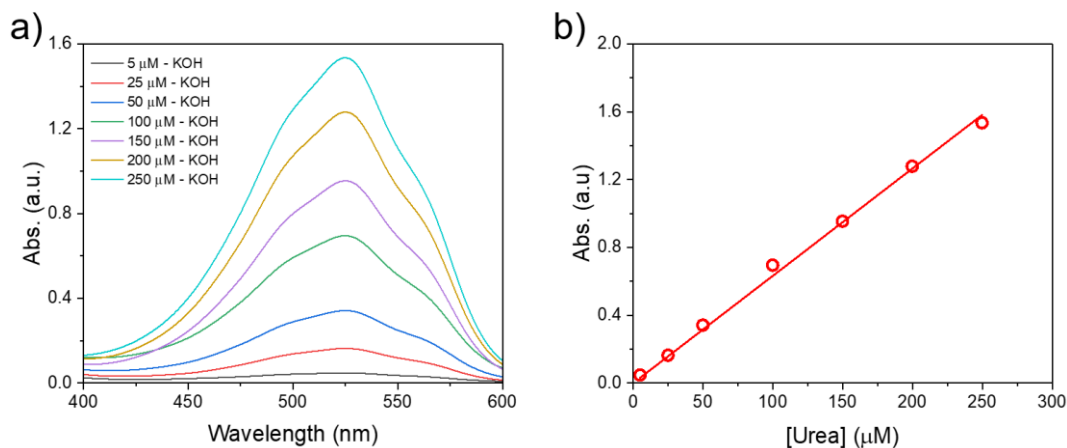


Figure 56 (a) Absorption spectra collected upon the application of the DAMO-TSC method on standard urea samples in KOH + KNO₃ based electrolyte and (b) the resulting calibration line, regressed according to the Lambert-Beer equation.

4.2. HER, CO₂RR, NO₃RR and EUS assessment

4.2.1. Cu GDE

4.2.1.1. Open Circuit Potential (OCP)

The Open Circuit Potential of the WE was monitored under different reaction environments (Figure 57). The observed potential profiles indicate a thermodynamic tendency of the copper surface toward corrosion, as the measured values exceeded the standard reduction potential of the Cu²⁺/Cu⁰ couple ($E^0_{\text{Cu}^{2+}/\text{Cu}^0} = 340 \text{ mV vs RHE}$) (8).

Notably, the introduction of nitrate ions into the electrolyte (blue trace) lowers the measured OCP, suggesting a partial protective effect that mitigates copper oxidation. Conversely, the presence of CO₂ (red traces) results in higher OCP values. Despite the use of a GDE configuration, a portion of the supplied CO₂ undergoes spontaneous chemical reaction with the alkaline electrolyte, generating carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) species that can precipitate or adsorb on the electrode surface, promoting the formation of mixed carbonate/oxide films and altering the interfacial electrochemical behavior. Indeed, under EUS conditions

(green trace), where both CO_2 and NO_3^- are simultaneously present, their combined influence results in a further increase of the potential, contrary to expectations.

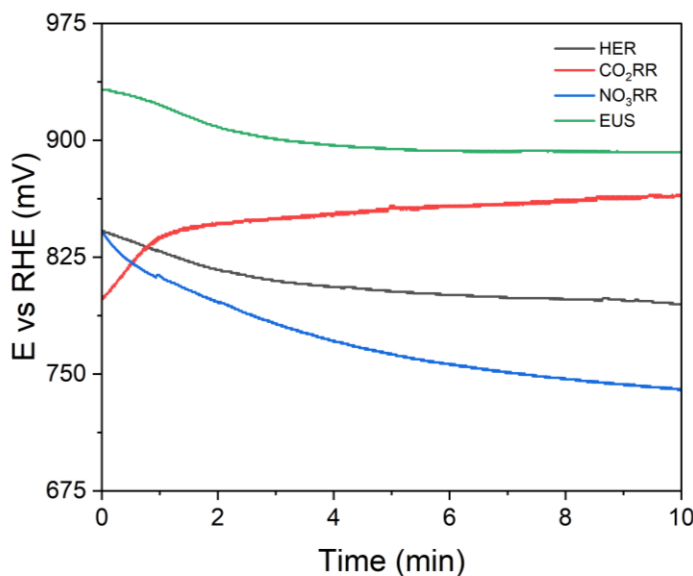


Figure 57 Open Circuit Potential (OCP) traces collected on the Cu/PTFE WE under different reaction environments (*i.e.*, with different electrolytes and gas feeds, details in Table 3).

4.2.1.2. Cyclic Voltammetry (CV) and Galvanostatic Electrochemical Impedance Spectroscopy (GEIS)

To investigate the fundamental electrochemical behavior and selectivity of the individual reactions contributing to the EUS process (*i.e.*, HER, CO_2RR and NO_3RR), voltammetric measurements were carried out (Figure 58a).

Under HER conditions (black trace), the CV scan of Cu/PTFE electrode displays an onset potential at *ca.* -0.4 V vs RHE, consistently with HER on metallic Cu in alkaline media (5).

Under CO_2RR conditions (red trace), the enhanced deployment of CO_2 at the cathode surface (6, 7) enables CO_2RR to effectively compete with HER, resulting in a less cathodic onset potential (*ca.* -0.25 V vs RHE).

As previously discussed in Chapter 3, the introduction of NO_3^- ions (blue trace) leads to a more complex CV profile characterized by multiple peaks and diffusion-limited plateaus, which can be attributed to the distinct activity of the different crystallographic facets of the WE (5).

Finally, the EUS condition (green trace), involving the simultaneous presence of CO_2 and NO_3^- , displays features combining those observed for the individual CO_2RR and NO_3RR conditions. This synergistic response suggests concurrent activation of CO_2 and nitrate species at the Cu surface, consistent with the hypothesized cooperative mechanism leading to C-N bond formation for urea synthesis.

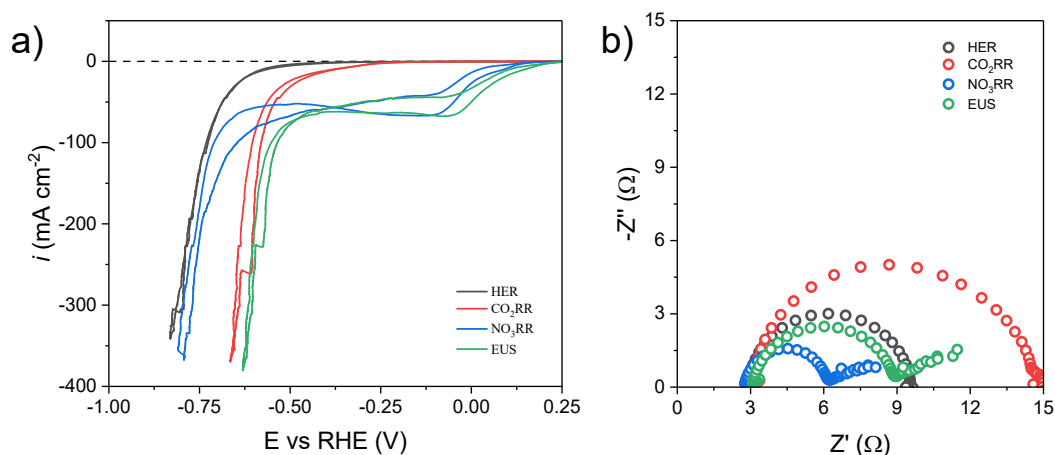


Figure 58 Cu/PTFE electrochemical testing under various conditions. a) CV curve (5th scan, scan rate 100 mV s^{-1}), b) GEIS (collected at -10 mA cm^{-2} , 2.8 mA cm^{-2} amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz).

As discussed in the Section 3.1.3.2. “Uncompensated resistance determination”, the uncompensated system resistance (R_u) was evaluated to enable accurate ohmic drop correction. The GEIS spectra collected under various reaction environments (Figure 58b) exhibit typical Nyquist plots with a single semicircle, where the high-frequency intercept corresponds to R_u . Under NO_3RR and EUS conditions, the presence of nitrate introduces an additional diffusional contribution visible in the low-frequency region. Overall, the system’s behavior across all environments can be qualitatively described by an equivalent circuit of the type $R_1(R_2Q_1)$. No model-based fitting was applied and the R_u was directly extracted as the real component (Z') measured at high frequency (50 kHz).

4.2.1.3. Product Quantification

CP measurements were performed under EUS conditions for 30 minutes at different current densities, selected according to the voltammetric trends within the potential window where urea formation is hypothesized to take place (Figure 59a). Post-electrolysis catholytes were analyzed for urea using the DAMO-TSC method. No detectable signal was observed (Figure 59b), with the only exception being a weak

response from the catholyte obtained from CP@-70 mA cm⁻² that was also analyzed using the developed HPLC method (Figure 66, brown line).

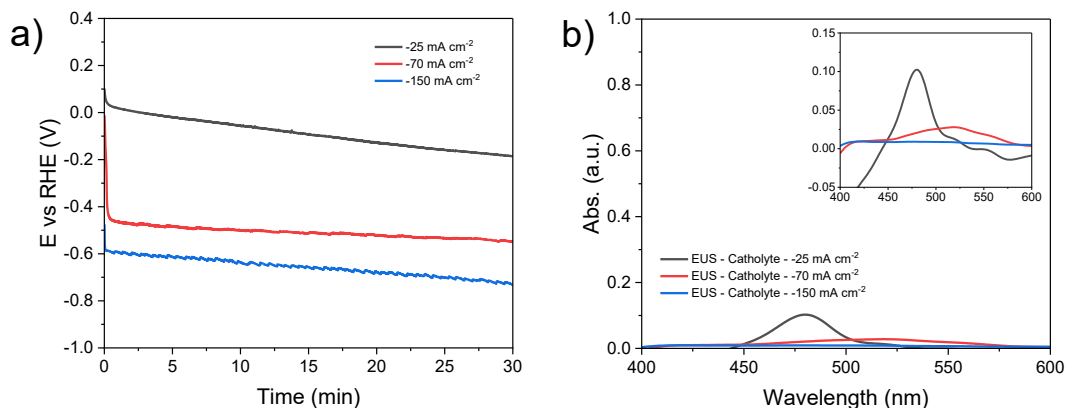


Figure 59 a) CP scans under EUS conditions at different current density, b) Tentative detection of urea by the classic DAMO-TSC method in post-electrolysis samples and c) HPLC chromatogram collected according to the developed HILIC method on post-electrolysis catholyte.

4.2.2. Ag GDE

4.2.2.1. Open Circuit Potential (OCP)

The Open Circuit Potential of the WE was monitored under different reaction environments (Figure 60), providing valuable insight into the interfacial electronic state of silver under catalytic conditions. The potential behavior observed for the Ag/PTFE WE indicates a spontaneous thermodynamic tendency toward surface oxidation, with measured potentials exceeding the standard reduction potential of the Ag⁺/Ag⁰ couple ($E^0_{\text{Ag}^+/\text{Ag}^0} = 0.80 \text{ V vs RHE}$) (8).

Interestingly, the introduction of either nitrate ions or CO₂ into the electrolyte (red and blue traces, respectively) does not significantly alter the measured OCP, suggesting minimal individual influence on the equilibrium surface state. In contrast, under EUS conditions (green trace), where both CO₂ and NO₃⁻ are simultaneously present, the potential shifts unexpectedly to more anodic values. This particular behavior was not further investigated.

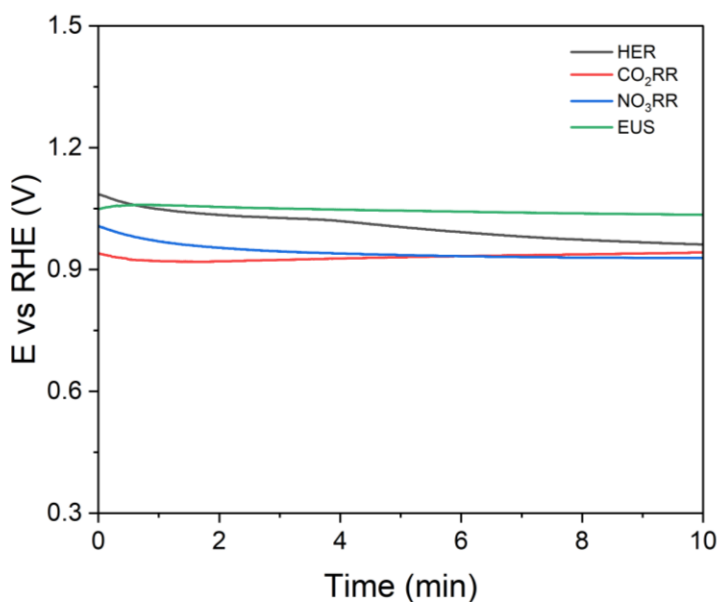


Figure 60 Open Circuit Potential (OCP) traces collected on the Ag/PTFE WE under different reaction environments (*i.e.*, with different electrolytes and gas feeds, details in Table 3).

4.2.2.2. Cyclic Voltammetry (CV) and Galvanostatic Electrochemical Impedance Spectroscopy (GEIS)

To investigate the fundamental electrochemical behavior and selectivity of the individual reactions contributing to the EUS process (*i.e.*, HER, CO₂RR and NO₃RR), voltammetric measurements were carried out on Ag/PTFE electrode (Figure 61a). The overall electrochemical trends observed for Cu/PTFE electrode are largely retained in the Ag/PTFE electrode.

Under HER conditions (black trace), the CV scan of Ag/PTFE electrode displays an onset potential at *ca.* -0.5 V vs RHE, consistent with the hydrogen evolution reaction (HER) on metallic Ag.

Under CO₂RR conditions (red trace), the enhanced deployment of CO₂ at the cathode surface enables CO₂RR to effectively compete with HER, resulting in a less cathodic onset potential (*ca.* -0.36 V vs RHE).

The introduction of NO₃⁻ ions (blue trace) leads to a more complex CV profile characterized by multiple peaks and diffusion-limited plateaus, which can be attributed to the distinct activity of the different crystallographic facets of the WE.

Finally, the EUS condition (green trace), involving the simultaneous presence of CO_2 and NO_3^- , displays features more closely resembling those observed for the individual CO_2RR condition rather than a combination of the behaviors associated with the individual CO_2RR and NO_3RR conditions.

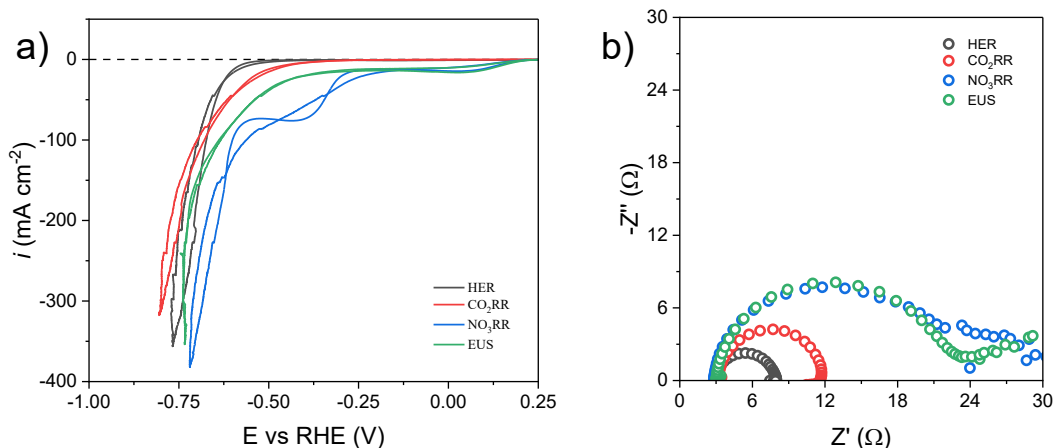


Figure 61 Ag/PTFE electrochemical testing under various conditions. a) CV curve (5th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -10 mA cm⁻², 2.8 mA cm⁻² amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz)

As for the Cu/PTFE electrode, the uncompensated system resistance (R_u) was evaluated to enable accurate ohmic drop correction when Ag/PTFE is the WE. The GEIS spectra collected under various reaction environments (Figure 61b) exhibit typical Nyquist plots with a single semicircle, where the high-frequency intercept corresponds to R_u . Under NO₃RR and EUS conditions, the presence of nitrate introduces an additional diffusional contribution visible in the low-frequency region. Overall, the system's behavior across all environments can be qualitatively described by an equivalent circuit of the type $R_1(R_2Q_1)$. No model-based fitting was applied and the R_u was directly extracted as the real component (Z') measured at high frequency (50 kHz).

4.2.2.3. Product Quantification

CP measurements were performed under EUS conditions for 30 minutes at different current densities, selected according to the voltammetric trends within the potential window where urea formation is hypothesized to take place (Figure 62a). Post-electrolysis catholytes were analyzed for urea using the DAMO-TSC method. Scarce signals were observed for all the catholytes (Figure 62b). The catholyte obtained from CP@-70 mA cm⁻² that was also analyzed using the developed HPLC method (Figure 66, grey line).

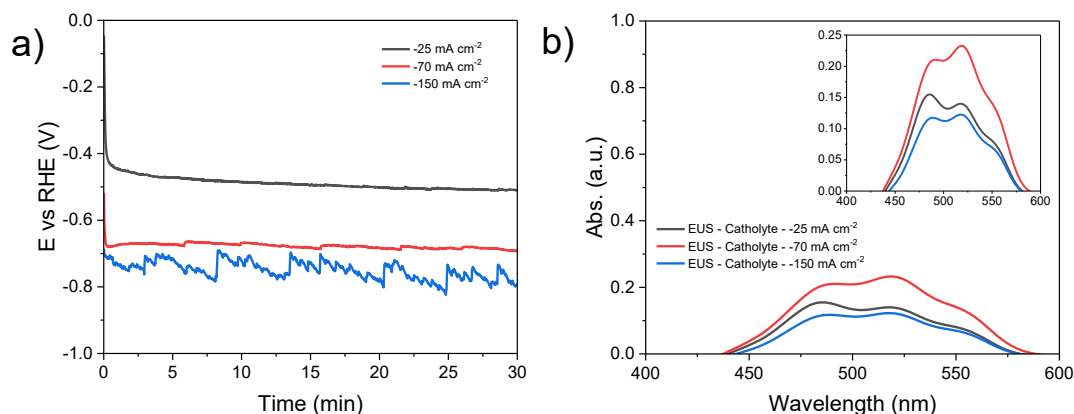


Figure 62 CP scans under EUS conditions at different current density and b) Tentative detection of urea by the classic DAMO-TSC method in post-electrolysis samples.

4.2.3. Au GDE

4.2.3.1. Open Circuit Potential (OCP)

The Open Circuit Potential of the Au/PTFE WE was monitored under different reaction environments (Figure 63) resulting lower than the standard reduction potential of the Au^{3+}/Au couple ($E^0_{\text{Au}(\text{OH})_2/\text{Au}0} = 1.50 \text{ V vs RHE}$) (8).

Notably, the introduction of either nitrate ions or CO_2 or both into the electrolyte (red, blue and green traces, respectively) alter the measured OCP, suggesting partial surface passivation. This behavior points to a synergistic effect, likely arising from the concurrent adsorption of carbonate and nitrate species, which collectively destabilize the metallic gold surface and promote partial oxidation.

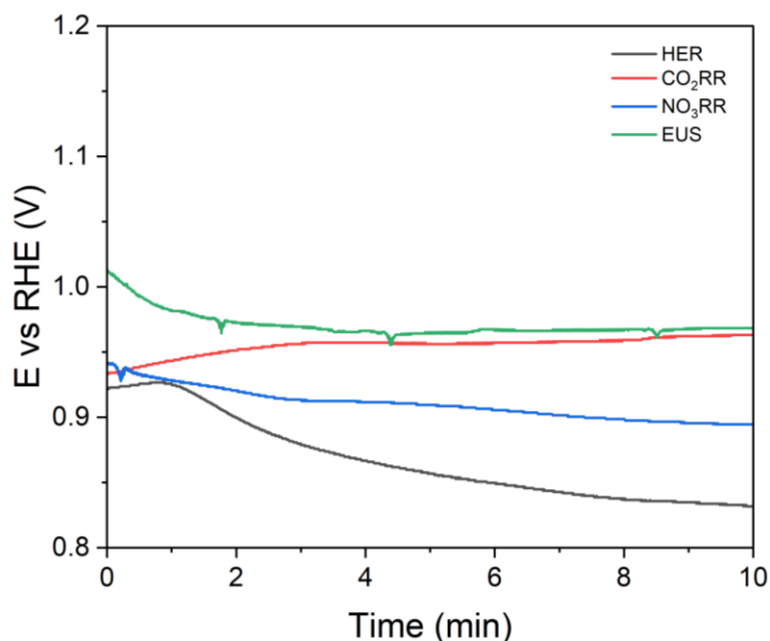


Figure 63 Open Circuit Potential (OCP) traces collected on the Au/PTFE WE under different reaction environments (*i.e.*, with different electrolytes and gas feeds, details in Table 3).

4.2.3.2. Cyclic Voltammetry (CV) and Galvanostatic Electrochemical Impedance Spectroscopy (GEIS)

To elucidate the intrinsic electrochemical behavior and selectivity of the individual reactions contributing to the EUS process (*i.e.*, HER, CO₂RR and NO₃RR), voltammetric measurements were carried out on Au/PTFE electrode (Figure 64a). The overall electrochemical trends observed for Cu/PTFE and Ag/PTFE electrodes are largely preserved on Au electrode, with subtle differences. HER and CO₂RR processes remain clearly decoupled, whereas NO₃RR appears more competitive with CO₂RR. Additionally, the onset potential for NO₃RR on Au electrode is associated with lower current densities compared to those recorded on Ag and Cu electrodes, likely reflecting a more sluggish charge-transfer kinetics on the gold surface.

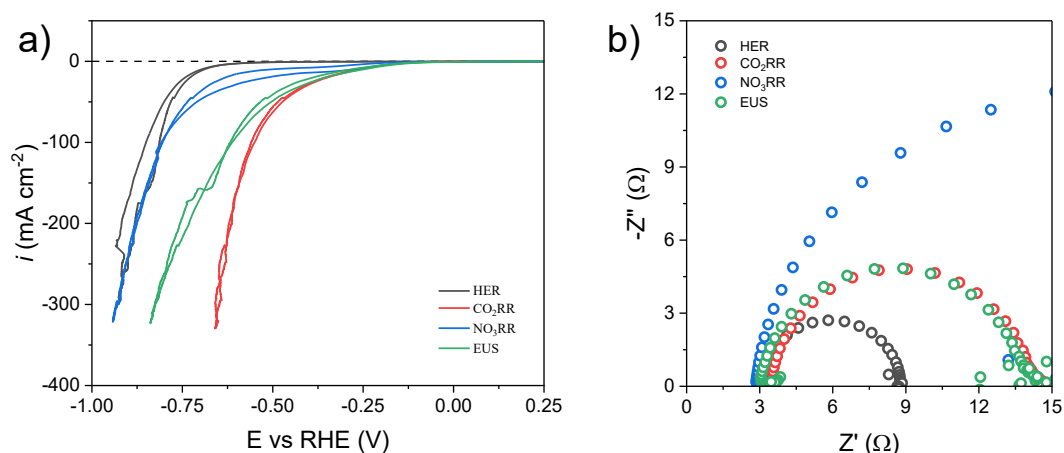


Figure 64 Au/PTFE electrochemical testing under various conditions. a) CV curve (5th scan, scan rate 100 mV s⁻¹), b) GEIS (collected at -10 mA cm⁻², 2.8 mA cm⁻² amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz).

4.2.3.3. Product Quantification

CP measurements were performed under EUS conditions for 30 minutes at different current densities, selected according to the voltammetric trends within the potential window where urea formation is hypothesized to take place (Figure 65a). Post-electrolysis catholytes were analyzed for urea using the DAMO-TSC method. Scarce signals were observed for all the catholytes (Figure 65b). Also in the case of Au/PTFE WE, the catholyte obtained from CP@-70 mA cm⁻² that was also analyzed using the developed HPLC method (Figure 66, yellow line).

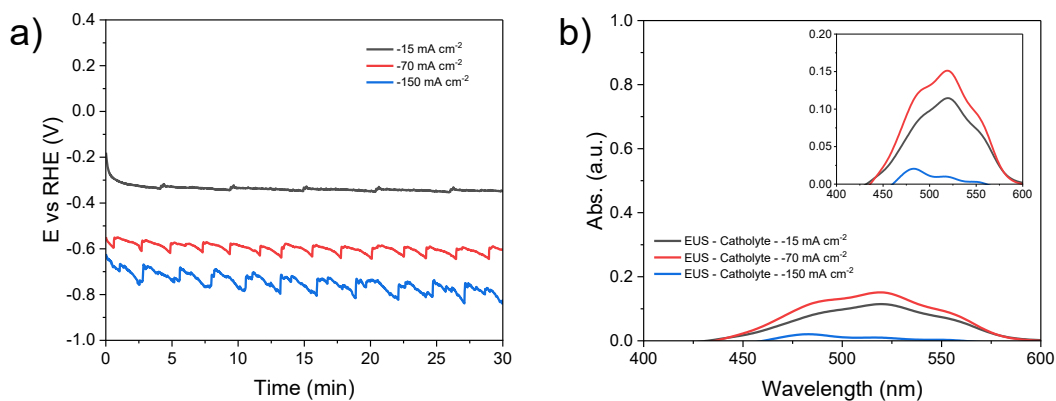


Figure 65 CP scans under EUS conditions at different current density and b) Tentative detection of urea by the classic DAMO-TSC method in post-electrolysis samples.

4.3. Consideration o product analysis

The catholytes collected after the chronopotentiometric scans at -70 mA cm^{-2} for each Me/PTFE electrode were analyzed using the developed HPLC method (Figure 66).

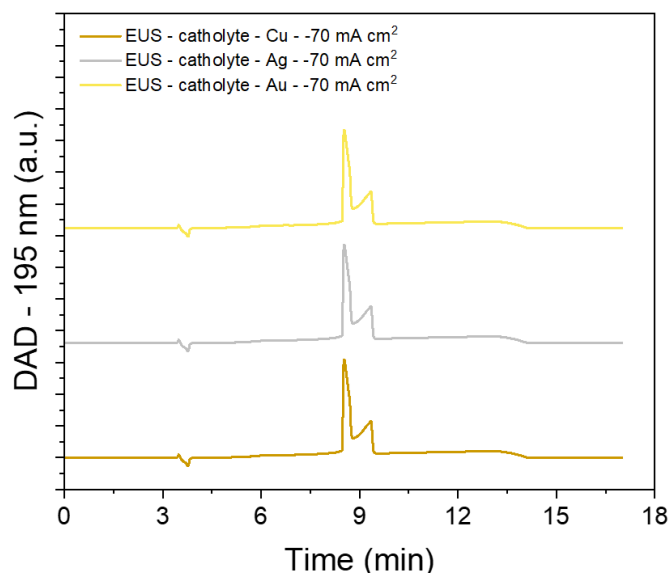


Figure 66 HPLC chromatograms collected according to the developed HILIC method on post-electrolysis flow cell catholytes under EUS conditions.

No urea was detected. However, peaks corresponding to bicarbonate (formed through the dissolution and reaction of CO_2 in solution) and to nitrates present in the starting electrolyte were observed.

An additional urea detection was performed using the classic DAMO-TSC method to highlight the limitations of the colorimetric method. The absorption spectra obtained (Figure 67a) appear similar in shape to those obtained by applying the method to standard urea solutions. However, the λ_{max} is shifted to 519 nm instead of 525 nm, and the absorption curve shapes exhibit features characteristic of those obtained standard nitrite ion solutions (Figure 67b).

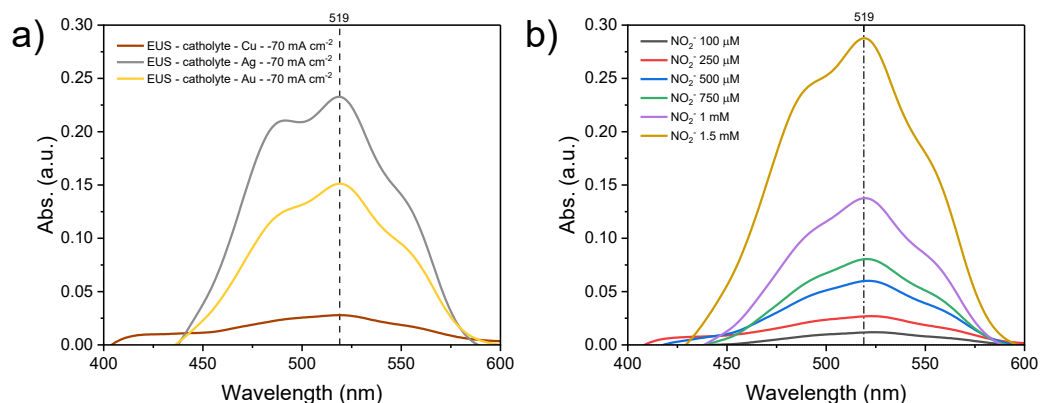


Figure 67 Absorption spectra obtained applying DAMO-TSC method on a) catholytes obtained from CP scans under EUS conditions for each metal electrode and b) standard nitrite samples.

4.4. Me/PTFE electrode characterization

X-ray diffraction (XRD) analysis of the Me/PTFE electrodes confirmed the polycrystalline nature of the thin metallic copper (Cu⁰), silver (Ag⁰) and gold (Au⁰) films deposited on the gas diffusion layer, as well as the preservation of this crystallographic structure after electrolysis (Figure 68a-b-c).

Complementary scanning electron microscopy (SEM) analyses performed on the pristine Me/PTFE samples (Figures 68) demonstrate the uniformity and chemical purity of the deposited Cu⁰, Ag⁰ and Au⁰ layer.

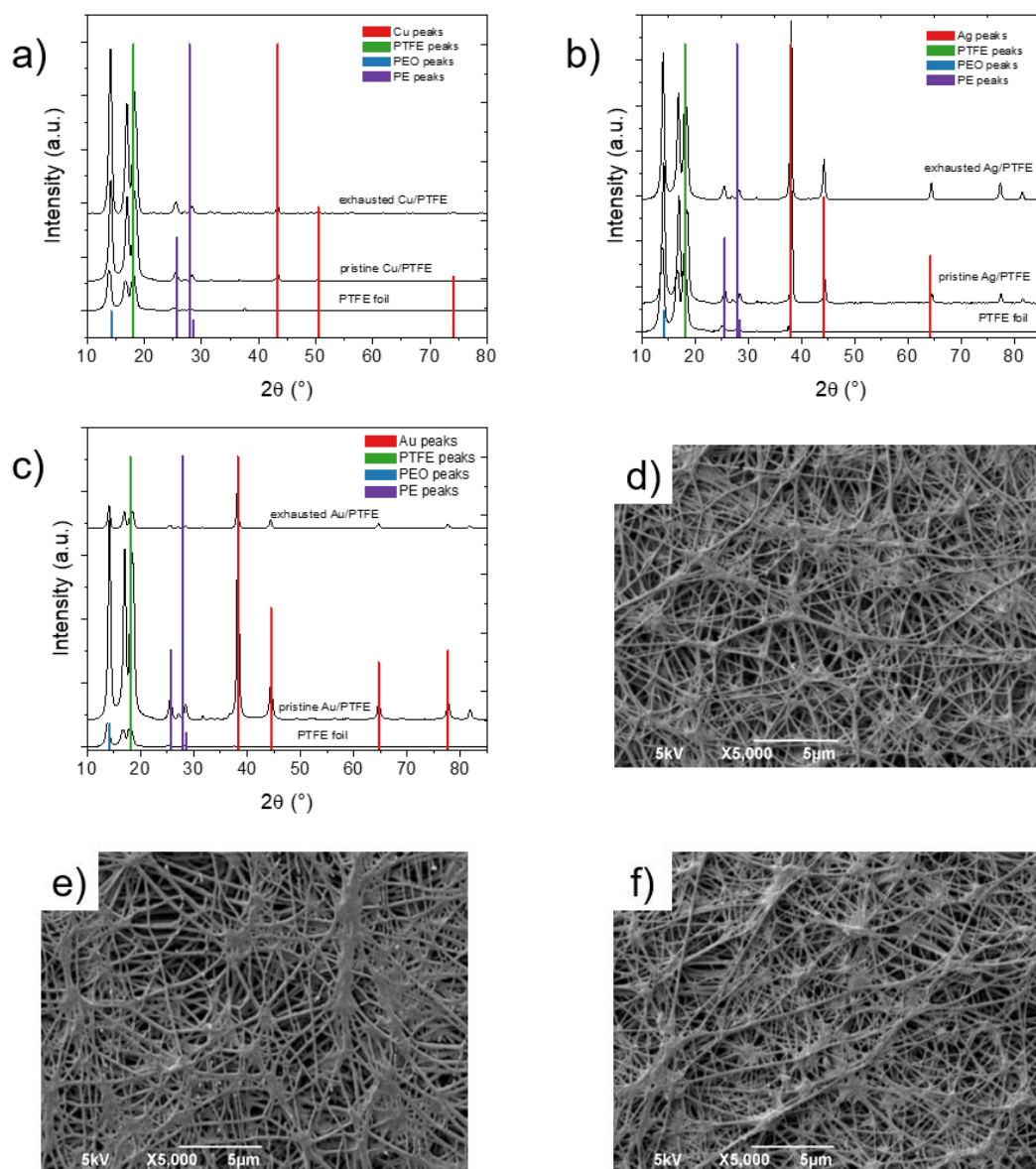


Figure 68 Basic characterization of the Me/PTFE electrodes used for flow-cell testing. XRD patterns collected on the bare support (PTFE) and on the pristine and post-electrolysis a) Cu/PTFE, b) Ag/PTFE and c) Au/PTFE electrodes. SEM image of c) Cu/PTFE, d) Ag/PTFE and e) Au/PTFE electrodes.

4.5. Conclusions

The experimental campaign performed in a flow-cell using 1 M KOH + 0.1 M KNO₃ as the electrolyte and Me/PTFE gas diffusion electrodes (Me = Cu, Au, Ag) confirmed that an alkaline electrolyte effectively suppresses the HER while enhancing ionic conductivity, as evidenced by the high current densities achieved. Nonetheless, such alkaline conditions, together with the tested electrodes, do not constitute suitable conditions for the electrochemical synthesis of urea.

4.5. References

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Chapter 5

EUS assessment through NH₃ oxidation

The results obtained from the cathodic co-reduction of CO₂ and NO₃⁻ highlighted the intrinsic complexity of driving selective C-N bond formation under reductive conditions. Despite extensive efforts in both H-cell and flow-cell configurations, and the evaluation of different Me/PTFE catalysts (Au, Cu, Ag), only urea traces were detected. These findings underscored the kinetic and selectivity limitations of the cathodic approach, mainly due to competing reduction reactions such as HER and the difficulty of coordinating multi-electron transfer steps involving carbon and nitrogen species.

Building on this outcome, the next stage of the project explored an anodic (*i.e.*, oxidative) pathway as an alternative route toward urea synthesis. This direction is motivated by the prospect that urea production may proceed through a multi-step tandem process, and that, in the near future, both CO and NH₃ will be widely available from green, electrochemical synthesis. In this approach, the C-N coupling is envisioned to occur via the oxidation of ammonia in the presence of a carbon monoxide stream. This inversion of electrochemical polarity offers a distinct mechanistic environment, one in which ammonia can be activated to reactive nitrogen intermediates under controlled anodic potentials, while CO serves as the carbon source for subsequent coupling.

The motivation for adopting this anodic approach arises from recent advances in understanding the ammonia oxidation reaction (AOR), recognized as a cornerstone for sustainable hydrogen production and efficient nitrogen valorisation (1). As reported by Babar and Botte, ammonia electrolysis operates at a remarkably low thermodynamic potential (0.059 V), coupling ammonia oxidation at the anode with hydrogen evolution at the cathode (2). Mechanistic studies indicate that AOR follows the Gerischer-Mauerer (G-M) pathway, involving sequential dehydrogenation of NH₃ to NH_x intermediates and surface recombination to form N₂ (1-3). Among all catalysts, platinum remains the benchmark for AOR, offering

optimal N-adsorption energy, favorable kinetics, and resistance to poisoning (4, 5). Building on these well-established insights, this work investigated the extension of ammonia oxidation chemistry toward oxidative C-N coupling between NH_3 and CO.

The reaction is hypothesized to proceed through an anodic electrochemical step, generating cyanate ions (OCN^-), followed by a thermal chemical step, where OCN^- reacts with excess ammonia at moderate temperature (approximately 50 °C) to form urea via the classical Wöhler reaction. The conversion of ammonium cyanate into urea is known to proceed through ionic or molecular mechanism (6). In the ionic mechanism, the reaction proceeds directly between the ammonium (NH_4^+) and cyanate ions (OCN^-), following second-order kinetics proportional to their ionic concentrations. Assuming this ionic pathway, the reaction is expected to occur efficiently within a pH range between 3.7 and 9.2, which corresponds respectively to the pKa of HNCO/OCN^- and of $\text{NH}_4^+/\text{NH}_3$. Within this interval, both ionic species can coexist in solution, providing the necessary conditions for the reaction to proceed through ionic coupling.

Based on these considerations, the oxidative coupling of ammonia and carbon monoxide was investigated using a Pt coil as the electrocatalyst in a conventional H-cell configuration.

5.1 Materials and Methods

5.1.1. Electrochemical testing

Given the preliminary stage of this study, the experimental work was designed primarily to assess the feasibility of electrochemical urea synthesis via oxidative coupling of ammonia and carbon monoxide. For this reason, the experimental campaign was intentionally kept limited in scope, serving as a proof-of-concept exploration to validate the plausibility of the anodic route for urea synthesis.

The experiment was carried out in a conventional H-cell configuration in 8 M NH_3 + 0.5 M $(\text{NH}_4)_2\text{SO}_4$ + 0.05 M K_2SO_4 . A Pt coil (Pine Research Instrumentation - RRP249PT, area *ca.* 4.7 cm²) was employed as the working electrode, a Ni mesh as the counter electrode and a Ag coil as the reference one, due to the high corrosive environment. Both compartments were filled with 15 mL of electrolyte and separated by Fumasep FAB-PK-130 Anion Exchange Membrane. The gas inlet was supplied with high-purity CO at a flow rate of 20 sccm. Prior to the test, the

electrolyte was purged with the gas for a minimum of 15 minutes to ensure saturation and removal of dissolved air.

5.1.2. Quantification of products

Given that the primary objective of this testing campaign was to evaluate electrochemical urea synthesis under oxidative coupling conditions, the anolytes obtained from chronopotentiometric measurements under EUS conditions were subsequently analyzed via the DAMO-TSC method to quantify urea formation. The DAMO-TSC method was performed as detailed in Section 3.1.4.4. “*Colorimetric methods*”.

It should be noted that, under the conditions considered in this study, the classical DAMO-TSC method is regarded as reliable, as the formation of nitrite ions, which could otherwise interfere with the accurate quantification of urea, is excluded.

5.2. Discussion

To establish a mechanistic basis for the anodic approach, fundamental electrochemical characterizations were performed; monitoring of the OCP of the WE, electrode conditioning by cyclic voltammetry, determination of the uncompensated resistance (R_u) via Galvanostatic Electrochemical Impedance Spectroscopy (GEIS), and 1-hour long chronopotentiometric scans at various current densities to evaluate urea formation. Each CP experiment was conducted using freshly prepared electrolyte and catholytes were analyzed using the classic DAMO-TSC method.

The OCP (Figure 69a) remained relatively stable over 10 minutes, fluctuating around +0.33 V vs Ag coil. This behavior indicates that the electrode rapidly reached a steady-state potential in the NH_3/CO electrolyte, suggesting the absence of significant spontaneous oxidation processes or surface instabilities.

The CV profile (Figure 69b) shows the onset of anodic current around 1.0 - 1.1 V vs Ag coil, which is consistent with the characteristic potential range for ammonia electro-oxidation on Pt (0.6 - 0.8 V vs RHE (2)). The absence of pronounced redox peaks at less anodic potentials confirms that CO does not undergo oxidation under these conditions and that the observed response originates primarily from NH_3 oxidation.

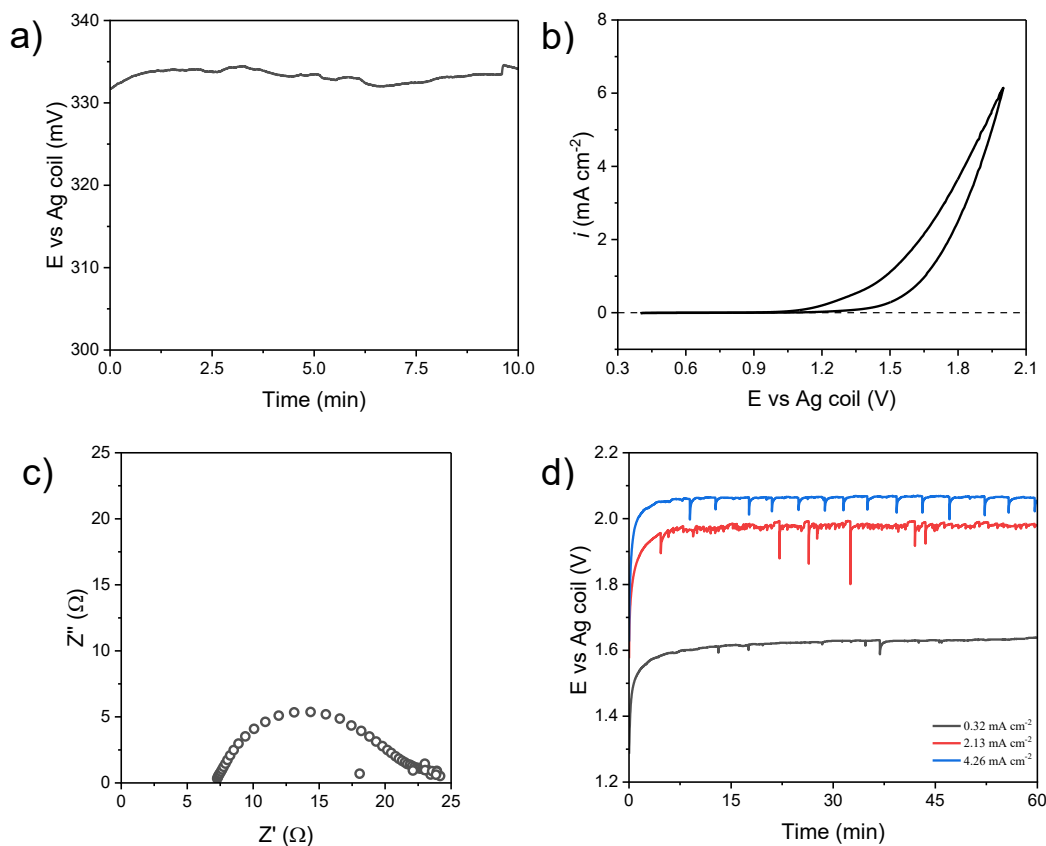


Figure 69 a) Open Circuit Potential (OCP) traces collected on Pt coil WE under oxidative EUS condition. b) CV curve (10^{th} scan, scan rate 100 mV s^{-1}), c) GEIS (collected at 10 mA cm^{-2} , 2 mA cm^{-2} amplitude, acquisition period 5 seconds, 55 frequencies per decade, 50 kHz to 0.05 Hz), d) CP scans at different current densities

The Nyquist plot displays a single semicircle, indicative of a charge-transfer controlled process (Figure 69c). The impedance spectra are best described by a simplified $R_1(R_2Q_1)$ circuit, where R_1 corresponds to R_u .

Chronopotentiometric scans recorded at 0.32 , 2.13 and 4.26 mA cm^{-2} display the typical potential stabilization behavior of AOR. The potential initially rises sharply, then stabilizes within a few minutes, reflecting the establishment of a steady-state coverage of reactive intermediates on the Pt surface.

The catholytes obtained from the chronopotentiometric measurements at different current densities were analyzed using the classical DAMO-TSC method, as nitrite ions are absent and therefore do not interfere with the accurate quantification of urea, in the days following the electrochemical test, as shown in Figure 70, revealing a progressive increase in absorbance, indicative of the formation of

cyanate ions that gradually react with the excess ammonium present in the electrolyte, forming urea.

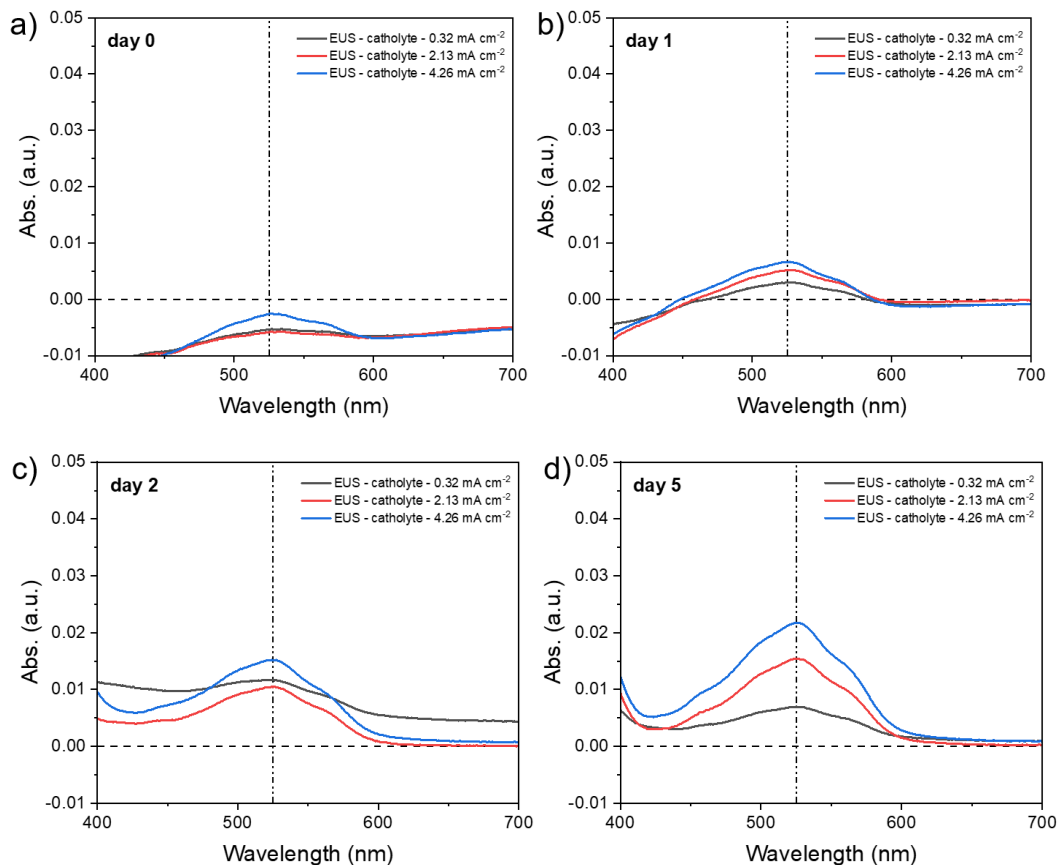


Figure 70 Absorption spectra obtained applying DAMO-TSC method on catholytes obtained from CP scans at various current densities in the days following the electrochemical test.

The same analytical procedure was applied to samples heated at 50 °C for 1 hour (Figure 71), which exhibited a marked increase in absorbance, confirming an enhanced conversion of ammonium cyanate into urea. These results highlight the effectiveness of the thermal step and further support the feasibility of the electrochemical-chemical pathway proposed for urea formation.

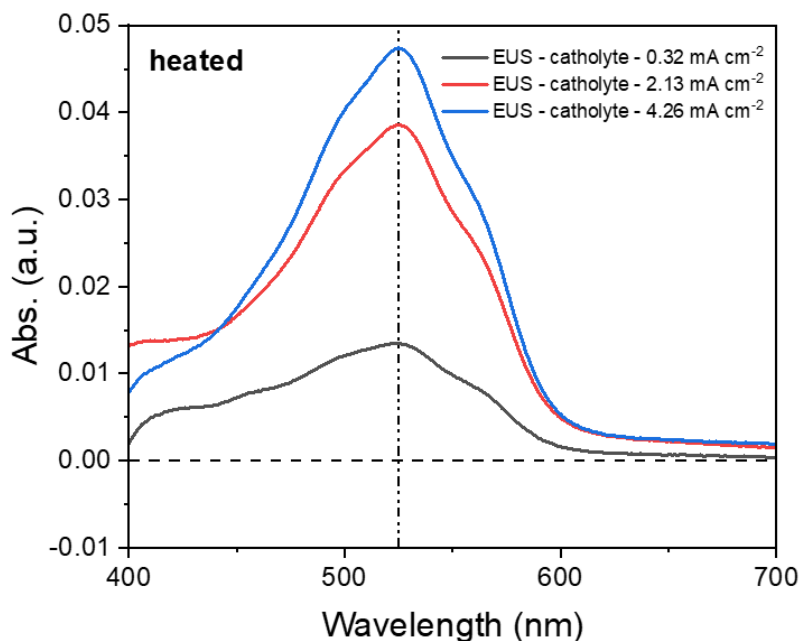


Figure 71 Absorption spectra obtained applying DAMO-TSC method on catholytes obtained from CP scans at various current densities after heating at 50 °C for 1 hour.

5.3. Conclusions

This preliminary study demonstrated the feasibility of electrochemical urea synthesis via oxidative coupling of ammonia and carbon monoxide, employing a platinum coil electrode in a conventional H-cell configuration with an electrolyte composed of 8 M NH_3 + 0.5 M $(\text{NH}_4)_2\text{SO}_4$ + 0.05 M K_2SO_4 . While the system was not optimized, the results established a proof-of-concept for urea formation under oxidative conditions, confirming that ammonia oxidation in the presence of CO can effectively yield cyanate ions, which subsequently undergo conversion to urea, through the Wohler reaction. We acknowledge that, while this work was being carried out, Xiong et al. (7) published a study reporting comparable results under similar operating conditions. Their independent validation of urea production via oxidative coupling of CO and NH_3 further supports the mechanistic interpretation proposed here and reinforces the relevance of this approach as a viable alternative pathway for electrochemical urea synthesis. On going studies focus on translating the process to a flow-cell configuration, where improved mass transport and gas-liquid interface control may enhance reaction rates and selectivity, and defining better operative conditions for this process.

5.4. References

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Conclusions

This doctoral research successfully established a robust analytical procedure, based on liquid chromatography (HPLC) separation, enabling a reliable assessment of electrochemical urea synthesis (EUS) *via* both CO₂ and NO₃⁻ co-reduction and the oxidative coupling of ammonia and CO.

The development of this optimized analytical protocol, specifically designed for accurate detection and quantification of urea in complex electrochemical environments, was motivated by a detailed examination of existing literature methods, which revealed significant reliability issues.

Electrochemical urea synthesis was investigated *via* CO₂ and NO₃⁻ co-reduction in both near-neutral and alkaline electrolytes. Although the use of an alkaline electrolytes, compared to a near-neutral pH one, suppress parasitic HER and provides higher ionic conductivity, tests were also performed in 0.2 M KHCO₃ + 0.02 M KNO₃ not only to maintain consistency with the first report demonstrating the feasibility of electrochemical urea synthesis, but also to investigate the influence of cell configuration on process efficiency. Indeed, flow-cell experiments revealed the formation of trace amounts of urea, highlighting how flow-cells enable enhanced mass transport and a continuous supply of CO₂ to the electrode surface compared to H-cells. Conversely, the use of an alkaline electrolyte, which was expected to enhance the efficiency of the process, did not lead to any detectable urea formation.

Ultimately a novel anodic (oxidative) route for urea synthesis, based on C-N coupling through ammonia oxidation in the presence of CO, was investigated. This innovative inversion of electrochemical polarity introduces a promising mechanistic framework in which ammonia can be selectively activated into reactive nitrogen intermediates under anodic potentials, while CO acts as the carbon source for subsequent coupling.

One promising strategy is the deliberate decoupling of carbon and nitrogen activation steps, rather than their simultaneous electrochemical co-reduction. As recently demonstrated in cascade-based approaches, the use of pre-activated liquid carbon carriers and oxidized nitrogen species can alleviate gas-liquid mass transport limitations and reduce the energetic penalty associated with direct CO₂ activation. Building on these concepts, future research should evaluate oxidative or hybrid

electrosynthetic schemes in which nitrogen-containing intermediates are generated and stabilized upstream, prior to C-N coupling. At the same time, catalyst design should focus on multifunctional or spatially separated active sites capable of selectively activating carbon- and nitrogen-based intermediates while minimizing competitive side reactions. Finally, system-level integration, including modular reactor design and energy-efficient coupling of plasma, electrochemical, and separation units, will be critical to assess whether such oxidative cascade strategies can offer a realistic pathway toward scalable and low-carbon urea synthesis.

Appendix

Chapter 2

Analyte		t _{Retention}	Slope	Slope Std. Err	Adj. R-Square
-		-	<i>a.u.</i>		-
H ₂	Peak 1*	2.0	1297.99	4.15	0.99984
	Peak 2	3.2	1145.57	2.69	0.99992
N ₂	Peak 1*	8.8	106.08	0.15	0.99997
	Peak 2	9.1	127.13	0.53	0.99976
CH ₄	Peak 1	4.7	55240.65	392.11	0.99960
CO	Peak 1	6.5	53388.93	356.22	0.99964
C ₂ H ₄	Peak 1	13.9	109851.76	733.13	0.99964
C ₂ H ₆	Peak 1	15.8	108893.34	788.74	0.99958

*Table 4 Response factors (i.e., slope) and related statistics regressed from GC calibration data. * Indicates the peaks selected for the quantification of products. The choice was based on the statistical parameters and the easiness of integration (i.e., quality of the local baseline).*