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Yet Another UREAlity Check: Compliant Analytical Tools, Electrochemical Insights, and Cell Configuration Effects in Urea Electrosynthesis on Polycrystalline Cu Electrodes

Original
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VIEWPOINT

Yet Another UREAlity Check: Compliant Analytical Tools, Electrochemical Insights, and Cell Configuration Effects in Urea Electrosynthesis on Polycrystalline Cu Electrodes

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The chemical industry classifies as a hard-to-abate sector as it relies on fossil fuels as both feedstock and energy input for the synthesis of the main commodity and specialty chemicals.[1] Electrochemical processes, ideally fed by renewable electricity and alternative feedstock (e.g., water, CO_2), provide an effective and scalable means to the decarbonization of chemical manufacturing.[2−4] With electrochemical water splitting and electrochemical CO_2 reduction (CO_2RR) having reached and approaching the industrial scale, fundamental research has begun to explore the electrochemical generation of carbon−heteroatom bonds.[5,6] Currently, the attention of researchers is focused on the electrochemical bonding of carbon and nitrogen (C−N),[7,8] with urea as the main target product. The reasons behind the interest in electrifying urea synthesis are multiple: the current reliance on fossil fuel energy input and derived feedstock for its production, large market share as fertilizer, and fundamental societal impact on food production. An extended overview of the topic can be found in recent literature.[1,9−12]

In a recent Viewpoint,[12] our group reported on the most common pitfalls in the nascent field of Electrochemical Urea Synthesis (EUS). Despite the nature of the feedstock (e.g., CO_2 or CO as the C source, N_2 or nitrate/nitrites as the N source) and of the chosen electrosynthetic approach (usually, coreduction of reactants[5]), today's research lacks rigorous experimental protocols, with urea detection and quantification being the crux of the matter. Other significant downsides, specific to the pursuit of EUS by the most common coreduction approach (the combination of CO_2RR and nitrate reduction reaction, NO_3RR), are represented by improper cell design[12−14] and the lack of reliable catalytic benchmarks.[12]

Following up on our previous work, we have developed a robust, interference-free and time-effective chromatographic method for the quantification of urea in postreaction EUS electrolytes. Coupled with electrochemical testing, this analytical tool has been used to screen the EUS activity of polycrystalline copper, the first EUS-active catalyst reported by Shibata et al. in 1995.[15] EUS has been investigated under near-neutral pH (i.e., $KHCO_3$ + KNO_3 aqueous electrolyte) in both static H-cell and three-compartment flow cell setups (Figures S1 and S2). Overall, the present study aims at reporting a simple and robust HPLC/UV−vis method for urea quantification while spotlighting the common electrochemical and analytical pitfalls in EUS testing and urea detection/quantification. As some of the choices at the basis of the present investigation might appear to conflict with previous viewpoints expressed by the literature[12,14] an extended rationale is reported in the Supporting Information ("*Choice of catalyst and reaction conditions*").

Urea quantification in EUS is hindered by poor accuracy and reproducibility (urease method[16−18]), and susceptibility to interferers (diacetyl monoxime-thiosemicarbazide method, DAMO-TSC[19−21]), or by slow, detection-limited techniques (^{1}H NMR[14,18,22]). HPLC, when properly configured, offers a faster, more reliable, and interference-free alternative.[12,18] Despite their growing adoption,[23,24] the inconsistent use of columns and detectors (UV−vis, MS) and lack of methodological detail limit the development of standardized protocols.

In our laboratories, we have developed a method based on the separation principles of the Hydrophilic Interaction LIquid Chromatography (HILIC), a technique expressly designed for the retention and separation of small polar analytes in reversed-phase mode.[25] Urea detection and quantification is instead carried out by UV−vis spectroscopy (λ = 195 nm). After a stepwise optimization in which we have screened the effect of several parameters, from flow rate to eluent composition and gradient ("*Optimization of the HPLC/UV-Vis method for urea detection/quantification*", Supporting Information), we have successfully separated urea from typical EUS electrolytes (e.g., 0.2 M $KHCO_3$ + 0.02 M KNO_3). The

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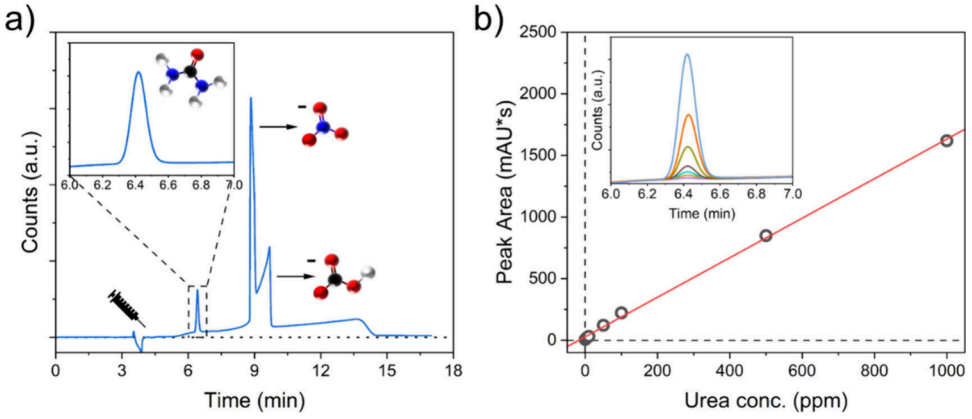

Figure 1. (a) Sample chromatogram, obtained by injection of a urea standard (100 ppm in 0.2 M $KHCO_3$ + 0.02 M KNO_3) and related (b) urea calibration curve (inset displays the actual urea peaks obtained by standard injections). Column: Poroshell 120 HILIC-Z. Mobile phase A = 10 mM formic acid in H_2O. Mobile phase B = 10 mM formic acid in ACN (see "Materials and methods" for the preparation procedure of mobile phase B). Flow: 0.500 mL min^{-1}. Gradient: from 5/95 to 50/50 in 9 min (linear gradient), then isocratic 50/50 for 8 min. Re-equilibration: 10 min at the initial 5/95 eluent composition. Injection: 2.5 μL. Column temperature: 30 °C. Detection: UV, 195 nm, 20 Hz. Figure S9 in the Supporting Information features complete calibration data.

method, thoroughly described in the Supporting Information ("*Materials and methods*" and "*Optimization of the HPLC/UV-Vis method for urea detection/quantification*", Figures S3−S11), employs a zwitterionic HILIC phase column and a gradient elution in formic acid-buffered water/acetonitrile. In our separations, urea elutes at *ca.* 6.4 min (Figure 1a) in a chromatographic run lasting 27 min (including column re-equilibration). Moreover, in virtue of their scarce detectability at the selected wavelength and the optimization of the separation conditions, the most common CO_2RR and NO_3RR products and other C−N containing molecules (e.g., formamide, acetamide) do not interfere with urea quantification (Figure S8). The urea calibration curve (Figure 1b and S9) shows linearity up to a concentration of *ca.* 1000 ppm (*ca.* 16.6 mM). Statistics (Supporting Information and SI Excel file) set the limits of detection (LOD) and quantification (LOQ) at 5 ppm (*ca.* 83 μM) and 20 ppm (*ca.* 330 μM), respectively. A simple calculation (SI Excel file) demonstrates that such limits meet the requirement of EUS, assuming that FE_{Urea} are compliant with those previously reported for polycrystalline copper[15,26] and provided that electrolysis time and current densities are carefully chosen. Further details on the method development and urea detectability are available in the Supporting Information.

Complementary to this HPLC-based method, we have also explored the suitability of the modified colorimetric method proposed by Chen et al. (M-DAMO-TSC),[27] which application has been endorsed by several authors.[12,14,20] This method incorporates a nitrite suppression step into the standard DAMO-TSC colorimetric method by reacting the postreaction electrolyte with sulfamic acid under acidic conditions. Our results ("*Modified DAMO-TSC method (M-DAMO-TSC)*", Supporting Information) confirm its efficacy in removing the typical nitrite interference on the DAMO-TSC method; the M-DAMO-TSC method is thus used in combination with the HPLC-based one, extending our urea quantification range. However, it must be stressed that nitrite ions are not the only source of errors in urea quantification by DAMO-TSC. As thoroughly detailed by Tiange et al.,[18] even minimal sunlight exposure and/or the presence of other C−N containing molecules (e.g., cyanates) might impair color development, making M-DAMO-TSC still liable of urea quantification errors.

Finally, although not strictly relevant to the objective of the present study, the good practices in electrocatalysis impose to detect and quantify all the byproducts of the reaction(s) under study. Therefore, the calibration curves for all the most common products of CO_2RR, NO_3RR and the parasitic Hydrogen Evolution Reaction (HER) have been collected and are reported in the Supporting Information with the related procedures ("*Calibration of most common EUS by-products*", Figures S12−S22).

With urea (and byproducts) analytics in place, we proceeded to investigate the EUS activity/selectivity of polycrystalline Cu under H-cell configuration. Experimental details on the cell configuration and the overall setting of these experiments can be found in the Supporting Information ("*Electrochemical testing*" section, Figure S1). Ancillary experiments and measurements have also been carried out and are discussed in the Supporting Information (Figures S23 and S24 and related discussion).

In an effort to understand the basic electrochemistry and selectivity of the individual processes (i.e., the parasitic HER and the desired CO_2RR and NO_3RR) taking place during EUS (i.e., CO_2RR + NO_3RR coreduction), we have collected voltammetric curves and analyzed the product distribution obtained in 1 h-long chronopotentiometric scans in the presence/absence of each reactant (Figure 2). The main results are commented in the following, while additional discussion on both electrochemical data and product detection can be found in the Supporting Information (Figures S25−S28).

The cathodic branches of the cyclic voltammetries (CV) under individual HER, CO_2RR and NO_3RR conditions (Figure 2a, gray, red, and blue curves), and the product distributions obtained at different current densities (Figures S25−S28) are helpful to preliminarily evaluate the feasibility of EUS under these catalytic conditions.

When HER is the only cathodic process (0.2 M $KHCO_3$, Ar feed), the high onset potential and the sole H_2 production are consistent with literature[28,29] and expectations (Figure S25). Moving on to CO_2RR conditions (0.2 M $KHCO_3$, CO_2 feed),

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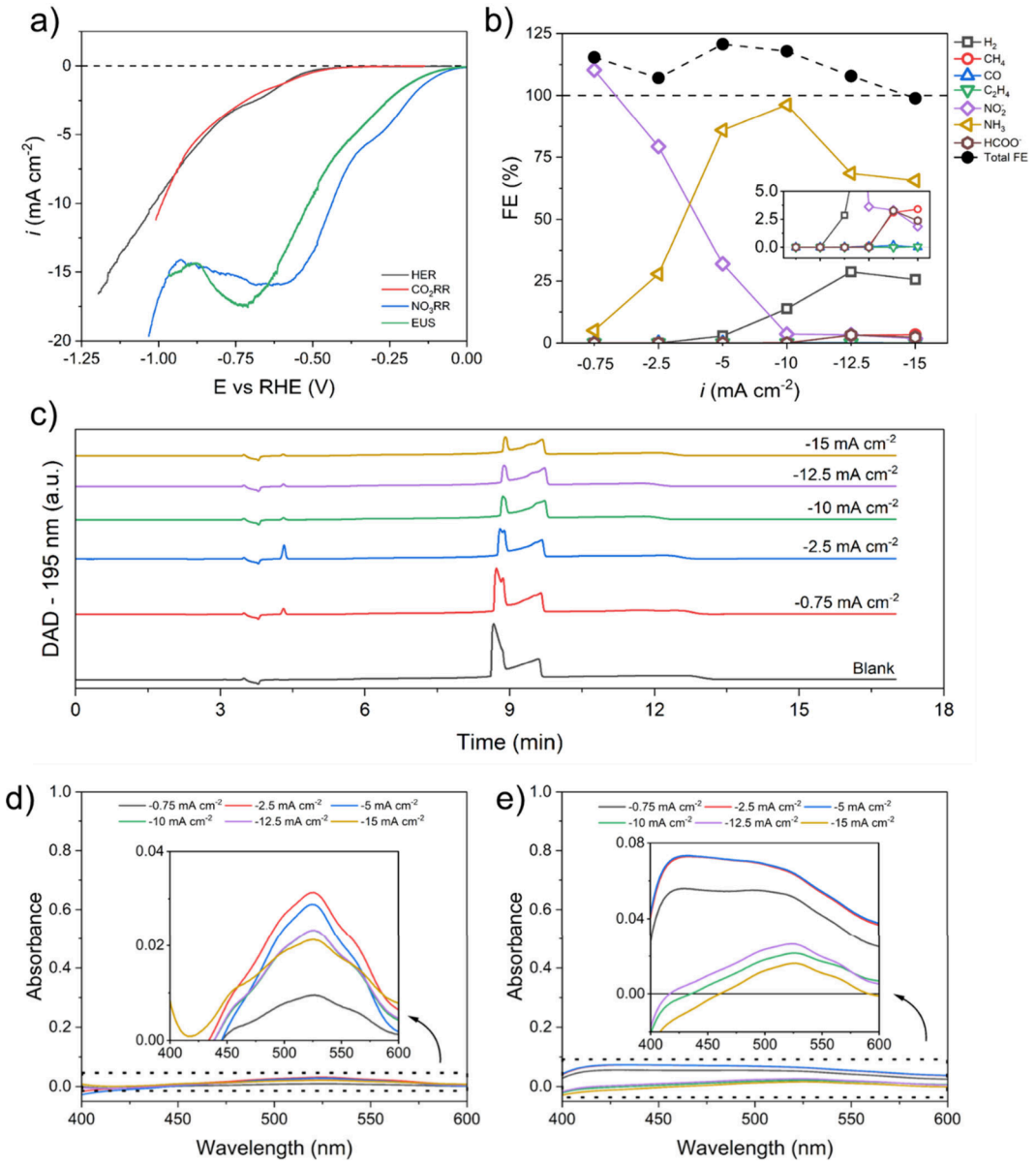

Figure 2. H-cell testing. (a) Cathodic branches of the cyclic voltammetries under individual HER (black), CO_2RR (red), NO_3RR (blue), and EUS (green) conditions. (b) Product distribution obtained at various current densities under EUS condition. (c) Chromatograms collected on the postelectrolysis catholytes, showing no urea peaks. Tentative detection of urea by the colorimetric DAMO-TSC method in (d) catholytes and (e) anolytes. Complete electrochemical and product distribution data for each individual and combined reaction are available in Figures S25−S28.

the limitations posed by the H-cell configuration (i.e., gas feed through CO_2 solubilization in the electrolyte[13,30]) are evident: the competition between the processes results in almost superimposed voltammetric curves (black and red curves in Figure 2a). The product distribution is consistent with the major contribution from the parasitic HER (Figure S26). Overall, the massive presence of hydrogen and the scattered CO_2RR selectivity are in agreement with the extensive literature on Cu-based catalysts in bicarbonate-based electrolytes and H-cell configuration.[29] When NO_3RR is the reaction under study (0.2 M $KHCO_3$ + 0.02 M KNO_3, Ar feed), a complex voltammetric trace is obtained. The presence of multiple wave/peak and plateau-like features is consistent with the behavior reported by Pérez-Gallent et al. on Cu single crystals (100 and 111 facets) in both alkaline and acidic media.[31] The actual product distribution appears to be dependent on the applied potential/current density, with NO_3RR selectivity shifting from nitrite ions to ammonia under increasingly cathodic bias. Concomitantly, parasitic HER is more relevant as the potential becomes more negative (Figure S27).

According to these premises, the voltammetric features obtained under coreduction conditions (0.2 M $KHCO_3$ + 0.02 M KNO_3, CO_2 feed) can be interpreted as a combination of those observed in the individual reactions (Figure 2a, green trace). Identifying a region where CO_2RR and NO_3RR are simultaneously occurring in the absence of the parasitic HER is challenging due to both the complexity of the traces and the competition between HER and CO_2RR. Under the assumption that urea formation takes place upon interaction of C- and N-based intermediates on the catalyst surface, such behavior highlights the unsuitability of H-cells (and in general of all the

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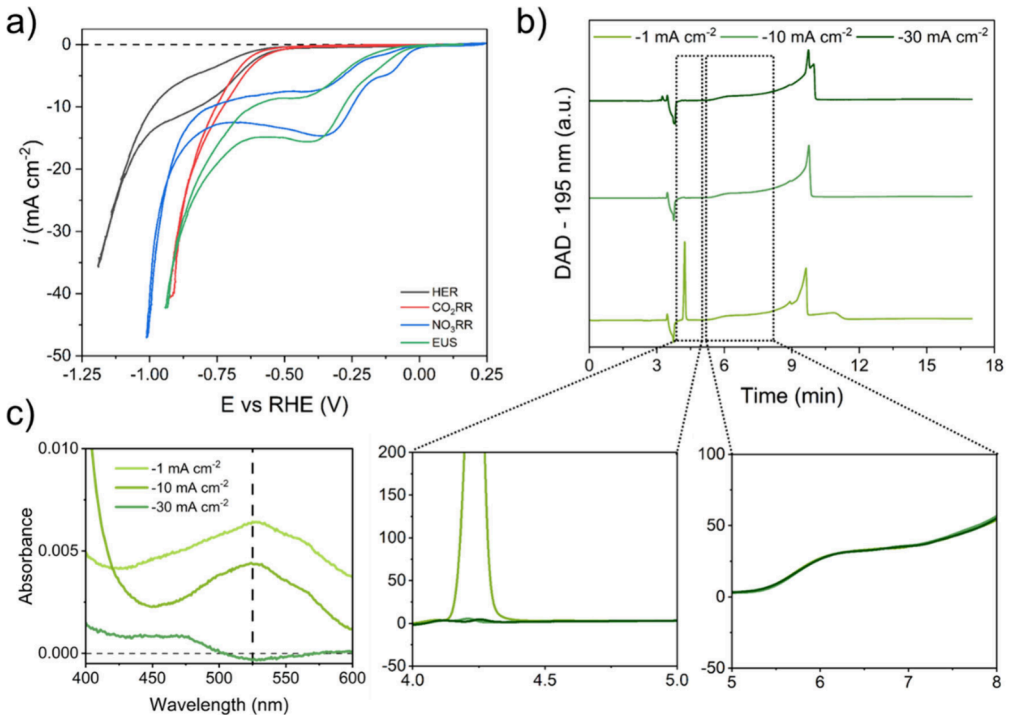

Figure 3. Flow cell testing. (a) Cyclic voltammetries collected under individual HER (black), CO_2RR (red), NO_3RR (blue), and EUS (green) conditions. (b) Chromatograms obtained from EUS catholytes, with magnification of the nitrite (bottom, left) and urea (bottom, right) regions. (c) Spectra obtained on the same catholytes of (b) upon the application of the M-DAMO-TSC colorimetric method.

systems in which CO_2 is fed through bubbling in the electrolyte) for EUS testing.[12,14] Despite this, the CO_2RR and NO_3RR product distribution in the range between −5 and −15 mA cm^{-2} presents relevant percentages of $*CO_{(ads)}$-derived products (e.g., CO, methane, ethylene[32]) and ammonia, respectively. According to the correlation inferred by Shibata and Furuya[15,26,33−36] and recent DFT calculations,[37,38] EUS might nonetheless take place.

A broad screening of EUS under different current densities (Figure S28) evidenced a product distribution that is dominated by NO_3RR products (Figure 2b), as expected from the earlier onset potential of the latter reaction in respect with CO_2RR and HER (Figure 2a). No urea was detected by either the HPLC/UV−vis or M-DAMO-TSC methods, even during 17 h CP scans (CP trace reported in Figure S28c, analytical data in Figures S29−S32). The fallacies of the standard DAMO-TSC method, of which some sample spectra are collected in Figure 2d,e, are evident: the relatively high concentrations of nitrite ions in EUS catholytes yield low-absorbance false positives (Figure S29e) while even higher absorbance values are obtained by analyzing EUS anolytes, further proving the unsuitability of the method. Such phenomenon is due to the use, in our setup, of an Anion-Exchange Membrane (AEM), for which the membrane crossover by nitrite ions results in lower and more interfering concentrations, leading to relevant and subtle false positives even in the absence of one of the reactants (i.e., under NO_3RR conditions, Figure S29c,d). Control tests have ascertained the impossibility of urea membrane crossover, thus ruling out the possibility of false EUS negatives dictated by the urea oxidation at the anode (Figure S33 and related discussion). Overall, the outcomes of our H-cell testing emphasize the major limitations of this cell configuration and, incidentally, the inadequacy of the standard DAMO-TSC method for urea quantification. It is also noteworthy that the overall understanding of EUS is hindered by the use of typical low-concentration bicarbonate-based electrolytes, such as the one used in this study.[12] The limited buffering ability of the electrolyte, together with the typical small volume of H-cells, causes indeed non-negligible pH variations in several tests, posing threats to the correct reporting of potentials (Figure S34). Finally, a trivial although necessary pre- and postelectrolysis characterization of the polycrystalline Cu electrode (Figure S35) demonstrates the absence of electrode contaminations and/or modifications upon testing.

Despite the issues encountered in H-cell testing, we have moved our attention to a GDE-based setup (Figure S2) implementing a polycrystalline Cu/PTFE electrode as cathode. Apart from some slight differences in the cell/process design (see "*Electrochemical testing*" and "*Extended Rational of the Study*" for more details), said setup can be confidently used for reproducing the first experiments reporting urea electrosynthesis by CO_2RR + NO_3RR coreduction[15] with the support of modern analytics.

Following the same approach adopted for H-cell testing, the overlay of the voltammetric curves collected under different conditions (Figure 3a) allows for a first evaluation of EUS feasibility.

The general trends observed for individual reactions in the H-cell also apply to flow cell data (Figures S37−S40), but with a significant difference. In virtue of the improved deployment of CO_2 at the cathode surface,[13,30] CO_2RR displays a winning competition against HER in a fairly large potential window (from *ca.* −0.65 to *ca.* −0.85 V vs RHE), although the near-neutral pH of the electrolyte still favors hydrogen evolution.[39] On the other hand, the EUS trace is once again a CO_2RR + NO_3RR hybrid of difficult interpretation. In a simple (and oversimplified) interpretation, the potential window from

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approximately −0.35 to −0.8 V vs RHE shows higher current densities than those of the individual reactions, suggesting possible coreduction of species.

CP scans (≥16 h long, Figure S41) at three selected current densities, covering the whole potential window deemed useful for EUS, yielded interesting results in terms of electrolyte pH variation (namely, alkalization of the catholyte, Figure S42), reactants depletion (i.e., complete nitrate conversion, Figure S43) and product distribution in the gas and liquid phases (Figure S44), all covered in the Supporting Information for the sake of conciseness. Briefly, at the lowest current density under investigation (−1 mA cm^{-2}, delivered in the range comprised between *ca.* 0.1 and −0.2 V vs RHE), only NO_3RR occurred. Instead, when higher current densities (−10 and −30 mA cm^{-2}, delivered in the −0.5 to −0.8 V vs RHE potential window) are explored, all the individual reactions occur (Figure S44). Their detailed product distribution is further discussed in the Supporting Information.

No urea has been detected by HPLC/UV−vis analyses (Figure 3b and S43a). Nonetheless, the more sensitive M-DAMO-TSC method detected traces of urea in the catholytes of the tests conducted at −10 and −30 mA cm^{-2} (Figures 3c and S45). However, even if the presence of urea traces at these specific currents/potentials is consistent with our (simplistic) interpretation based on coreduction potential windows, it is not compliant with the FE_{Urea} reported by Shibata et al.[15] on Cu-based catalysts. It is however worth considering that the same authors investigated a large number of different catalyst (from zerovalent metals[15,26,33,34] to borides[35] and metal-lophthalocyanines[36]), not necessarily based on Cu, whose EUS activity may be confirmed regardless of the present results. Finally, as for the WE used in the H-cell testing, Figure S46 confirms the structural/morphological stability of the used catalyst.

In conclusion, this work consistently endorses previous reviews, viewpoints and perspectives[12,14,16−18,16−18,20−22] that recommend to use advanced, accurate and reproducible analytical techniques for urea detection and quantification. It also provides several insights on the pitfalls of EUS testing in H-cells and using low-concentration electrolytes with limited buffering ability/capacity. Our experimental results demonstrate that reproducing the data collected in pioneering[15,26,33−36] and recent works is an essential stepping stone for the EUS community. Implementing adequate analytical and electrochemical protocols while tailoring setups/electrolytes to the actual needs of the reaction will allow for the proper mapping of EUS activity/selectivity of catalysts.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.5c01652.

Experimental section (PDF)
Excel file (XLSX)

■ AUTHOR INFORMATION

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Author Contributions

M.R. carried out all the electrochemical experiments and helped in the related data analysis. M. Ferrera and J.S.P.C. optimized, characterized and fabricated the Cu/PTFE. S.M.B. helped in developing the chromatographic methods and analyzing the related data. A.G. carried out the XRD measurements and helped in the overall characterization of the catalysts. L.G. worked on the ^1H NMR detection of urea and supported the overall analytical efforts. I.K. and L.M. provided guidance and supervised the whole project. M.F. conceptualized the work, supervised the experiments, and analyzed the electrochemical data. M.R. and M.F. wrote the first draft of the paper. All the authors contributed to the editing of the final manuscript.

Notes

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS.

The authors declare the following competing financial interest(s): M.F. and L.M. declare that they are the founders of Antares Electrolysis S.r.l., an IIT startup dedicated to designing and manufacturing stacks for electrolyzers. They currently serve as Chief Scientific Officer and Scientific Advisor, respectively.

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