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Thin-film $\text{Cu}_{1-x}\text{N}_x$ catalysts for efficient CO_2 reduction: a scalable magnetron sputtering approach

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Thin-film-based catalysts, fabricated through physical vapor deposition, have attracted significant interest as promising materials for electrochemical CO_2 reduction. In this context, metallic Cu films function as active catalyst layers for the reduction to ethylene and ethanol. However, these films still experience high overpotentials, resulting in low energy efficiencies. In this study, we have fabricated $\text{Cu}_{1-x}\text{N}_x$ films to overcome this issue by incorporating nitrogen into the sputtering process, leading to the formation of an anti- ReO_3 crystal structure of Cu_3N , which contains interstitial vacancies filled with Cu atoms. Under optimal sputtering conditions of $r_{\text{N}_2} = 0.50$, sputter rate = 4 \AA s^{-1} , and pressure = 6 \mu bar , EDX

analysis reveals a sub-stoichiometric thin-film composed of $\text{Cu}_{0.84}\text{N}_{0.16}$. In the electrochemical CO_2 reduction, this film resulted in an increase in energy efficiency from 15.8% to 20% for ethylene compared to pure Cu films, which was attributed to a decrease in the measured potential by $\pm 500 \text{ mV}$, due to the addition of nitrogen in the structure. This key finding suggests that for future applications, $\text{Cu}_{1-x}\text{N}_x$ layers should be employed instead of metallic Cu to reduce the required energy demands while maintaining selectivity.

Broader context

As the field of CO_2 capture and utilization is increasing, many believe that the electrochemical CO_2 reduction holds a future as a large-scale industrial application of efficiently using CO_2 as a feedstock to produce valuable chemicals such as CO, Formic acid, Ethylene, and Ethanol. Driven by renewable electricity, efficient catalysts are needed. In literature, metallic Cu films are widely used to study large-scale operation of CO_2 reduction. However, we note that Cu_3N films, synthesized by adding N_2 to the sputter process, are more efficient catalysts and reduce the energy requirements. Especially since the formation of Ethylene and Ethanol require 12 e^- per mole, the energy demands are quite high. Therefore, reducing overpotentials is a key area that is sometimes overlooked. Herein, we highlight an increase of 25% in energy efficiency and a 20% increase in mass activity by simply changing the cathode material to Cu_3N . Furthermore, initial stability was also improved, due to the strong presence of N^{3-} , which maintains the presence of Cu^+ , and thus reduces catalysts reconstructions that can be detrimental to the operational process. These reasons led us to believe that future research should be conducted with Cu_3N films.

Introduction

Extreme weather events have become the new norm as increasing anthropogenic emissions of CO_2 and other greenhouse gases over the past few decades have contributed to rising global temperatures.¹ In this context, researchers worldwide have focused on the electrochemical CO_2 reduction reaction (eCO_2R), which has emerged as a promising strategy to mitigate the increased CO_2 levels in the atmosphere. This technique can

be powered by sustainable energy sources, and thus has the potential to convert wasteful CO_2 into valuable chemicals such as ethylene, ethanol, CO, and formic acid, which help to close the carbon cycle. An efficient electrocatalyst is required to produce certain products with high faradaic efficiency (FE), low energy input, high stability ($> 10\,000 \text{ h}$), and high production rates to make it commercially viable and competitive with more traditional fossil fuel based routes. Among the wide variety of CO_2 products, C_{2+} products are more desirable than

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C₁ due to their high energy density and commercial value.² However, the reaction to ethylene and ethanol is challenging due to the multiple proton-coupled electron transfers required, resulting in diverse reaction pathways and, thus in most cases, a poor selectivity.^{3–6}

Cu-based catalysts, such as Cu⁷/Cu₂O^{8–10} or Cu–M (M = Ag,^{11–13} Pd,¹⁴ Zn,¹⁵ Bi¹⁶) are known to synthesize C₂₊ products albeit with high energy input, relatively poor stability, and low selectivity towards a single product. Recently, a flow cell design has been reported for the conversion of CO₂ to ethylene, with a FE reaching up to 70%, and a remarkable stability of 150 h, nevertheless this was only achieved with highly corrosive alkaline electrolytes (> 7 M KOH).¹⁷ As a result, tuning Cu-catalysts for more efficient production of a single multi-carbon product at less demanding conditions remains of paramount importance to advance the field. In this regard, Cu₃N catalysts are promising as the limited research into them has shown higher ethylene efficiencies but so far only in H-cell conditions and thus at low current densities. For instance, a study conducted by Yin *et al.*, synthesized Cu₃N nanocubes through wet chemical synthesis as electrocatalysts for CO₂ to ethylene with a reported FE of 60%.¹⁸ Similarly, Wang *et al.* synthesized Cu₃N nanoparticles enclosed with (100) and (111) facets, which operated at a high FE of 61%.¹⁹ Finally, Cu₃N-derived Cu nanowires proposed by Mi *et al.* showed a total C₂₊ of 86% with ethylene being the main product at 66%, and a high stability of 28 h.²⁰ From these results, it is clear that Cu₃N has a catalytic capability towards ethylene, with a more narrow product selectivity than typical Cu/Cu₂O catalysts but they need to be evaluated under the more industrially relevant conditions of a flow cell and high current densities.^{8,9,10,21,22} The main challenge with Cu-based catalysts is the *in situ* reduction of the active Cu⁺ species, which leads to surface reconstructions and subsequent loss of activity.^{2,21} Sargent *et al.* suggested that Cu₃N could prolong the stability of the copper(I) species, which are known to aid in decreasing energy barriers for *CO adsorption and subsequent C–C coupling.²² Moreover, the above mentioned catalyst designs are often complex and require specific chemicals that may be toxic or costly, which also limits their scalability. For this reason, other ways to synthesize these Cu₃N materials are required if they are to replace the typical CuO_x catalysts also in flow electrolyzers.

In this respect, a promising route towards the preparation of stable Cu_{1–x}N_x films on which abundant research has been performed is the physico-chemical fabrication approach including methods such as atomic layer deposition,²³ reactive radio-frequency sputtering,²⁴ and direct current magnetron sputtering,²⁵ resulting in the application of this metastable semiconductor Cu₃N in various fields such as photovoltaics,²⁶ optical storage devices,²³ H₂ gas sensing,²⁷ and tunnel junctions²⁸ but as of yet Cu₃N-based films prepared by this approach have not found their way to eCO₂R. As a non-toxic, and earth-abundant material, it can nevertheless be a viable alternative to other toxic materials. Direct current (DC) sputtering stands out as it provides high scalability, improved homogeneity, controllable thickness and crystallinity.

In this study, we have fabricated Cu-based thin films with reactive sputtering, by adding nitrogen to the argon flow, resulting in the formation of Cu_{1–x}N_x sub stoichiometric layers. By controlling different operational parameters such as N₂/Ar gas fraction (*r*_{N₂}), deposition pressure (P), and sputter rate (Å s^{–1}), we found an optimal sub-stoichiometric layer of Cu_{0.84}N_{0.16} for the eCO₂R to increase the energy efficiency towards ethylene compared to typical metallic Cu thin film. We have thus proven that the implementation of nitrogen in traditional Cu-based thin films can significantly decrease the energy consumption, which is an important discovery, especially for future up scaling research.

Results

Physicochemical results

Cu_{1–x}N_x films were deposited onto carbon-based gas diffusion layers (GDLs), and the influence of operational pressure (P), sputter deposition rate (SR), and nitrogen ratio (*r*_{N₂}) on the total Cu deposition and the performance of the eCO₂R was studied towards C₂₊ products, such as ethylene and ethanol. Various physicochemical characterizations, such as ICP-MS, XRD, SEM, and contact angle, are provided to gain insight in those parameters that have the largest impact on performance. All experimental methods, including the synthesis, characterizations methods, and eCO₂R experiments are explained in detail in the supporting information. Table S1 summarizes the synthesis conditions of all fabricated thin – films, along with the ICP-MS results to determine the Cu loading.

A gradual increase in *r*_{N₂} lowered the total Cu deposition. Because N is a lighter atom than Ar, it has a lower intrinsic kinetic energy, and thus, it yields a slower material transfer rate.^{23,24,29,30} However, during DC magnetron sputtering, the reactive gas (N₂) can be implemented into the subsurface region of the Cu target. Nitrogen can remain as non – reactive ions in the target or form an insulating layer, this results in an increase in power and a decrease of the target erosion rate.³¹ In other words, the bombardment of the Cu target was less effective, resulting in decreased deposition rates.

Next, an increase in sputter pressure also results in reduced deposition, as evidenced by the lower Cu loadings. This was explained as follows in a study by Figueira *et al.*,²⁹ as the atoms in the plasma undergo an increased number of collisions, the mean free path and thus the chances of reaching the target are reduced, along with more target poisoning due to an increase of nitrogen during sputtering, as such decreasing the total deposition.³²

Finally, a higher initial sputtering rate results in more power being applied during operation (see Table S1); and therefore, more localized target heating occurs, which increases the kinetic energy of the Cu atoms, leading to more evaporation.³³ Furthermore, a more efficient cleaning of the target also occurs, which helps in reducing the target poisoning. Ultimately, both results in a higher loading.

To identify the crystalline phases, the XRD patterns of the different films were obtained. A distinct peak in all samples was



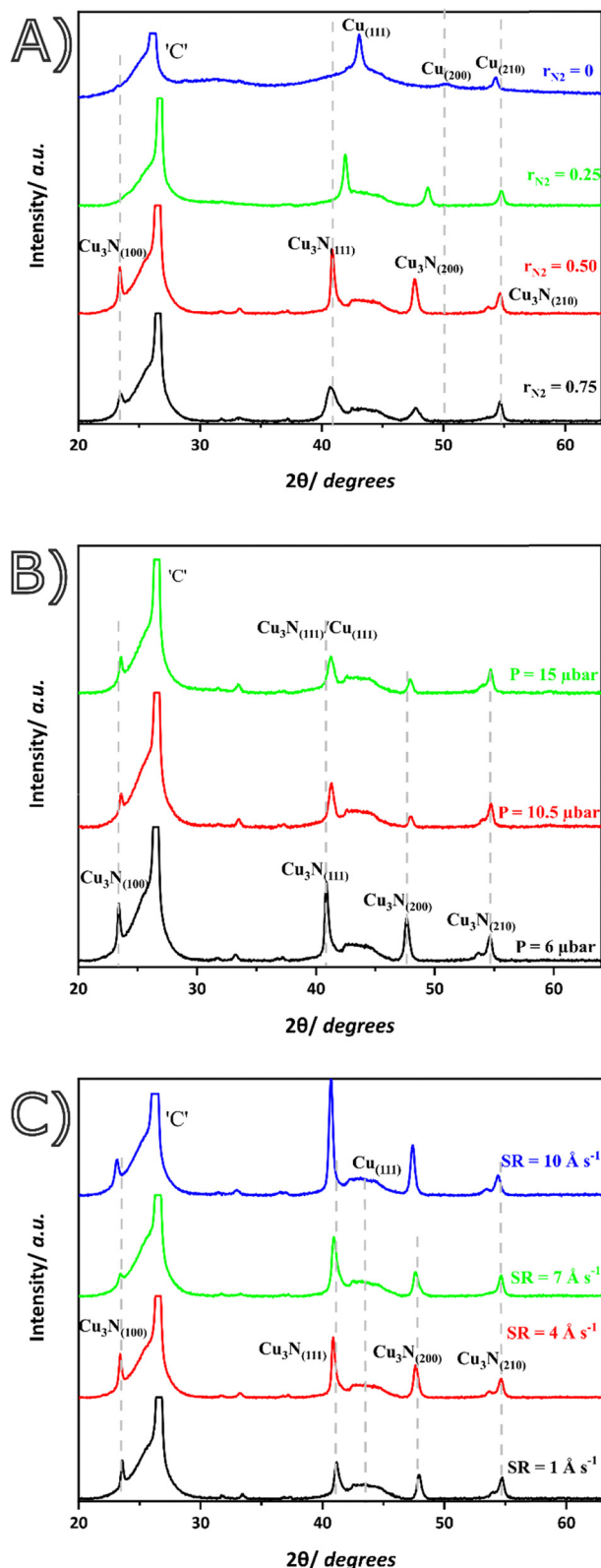


Fig. 1 XRD patterns of the different prepared samples. (A) $\text{Cu}_{1-x}\text{N}_x$ with varying r_{N_2} , constant operational pressure at 6 μbar and sputter rate of 4 \AA s^{-1} . (B) $\text{Cu}_{1-x}\text{N}_x$ with varying pressure, constant $r_{\text{N}_2} = 0.50$, and sputter rate of 4 \AA s^{-1} . (C) $\text{Cu}_{1-x}\text{N}_x$ with varying sputter rate constant $r_{\text{N}_2} = 0.50$, and constant operational pressure at 6 μbar . The phases and indices are labelled.

identified at 28° corresponding to the carbon substrate, which is henceforth labelled 'C'. The peak potential value has been restricted to increase sensitivity of the important peaks. To identify the remaining peaks, reference patterns for Cu_3N (JCPDS File No. 47-1088) and Cu (JCPDS File No. 04-0836) were used. Fig. 1 presents the XRD patterns for all prepared samples. In Fig. 1A, the influence of r_{N_2} is evident. For $r_{\text{N}_2} = 0$, diffraction peaks corresponding to metallic Cu appear at 43° (111), 50° (200), and 53° (210), while no Cu_3N peaks are observed. Upon increasing the r_{N_2} factor, characteristic Cu_3N peaks emerge at 23° (100), 41° (111), 47° (200), and 54° (210). Simultaneously, the Cu peaks gradually shift toward those of Cu_3N , reflecting the growth of Cu_3N domains.^{24,25,30} Nevertheless, residual Cu remain detectable, likely due to the formation of sub-stoichiometric layers in which Cu may exist as interstitial atoms or separate Cu domains. Furthermore, SEM-EDX images (Fig. S2) revealed that an increase in r_{N_2} caused the particles to change from distinct spherical particles to more stacked agglomerated platelets, with sharp edges.²⁴ EDX subsequently determined the percentage of N present in the sample, for increasing r value, this was respectively, 0–13–16–21% (Table S1).

Next, the influence of sputter pressure was investigated in Fig. 1B. The effect of sputter pressure on the crystallinity has been well reported in the literature:^{34–37} a low pressure (<6 μbar) results in grains that grow along the Cu_{111} plane,³⁷ which favors creation of more sub-stoichiometric layers due to a low reactive character of the sputtering process.

A higher operating pressure (15 μbar) will shorten the mean free path, and more atomic collisions will thus occur. As a consequence, the kinetic energy of the Cu species arriving at the substrate will be lower than at lower pressures (6 μbar). The Cu ions with lower energy will be deposited with a more amorphous character, as they lack energy to organize in ordered structures. Upon increasing the pressure, the Cu_3N peaks that are visible at 6 μbar are less intense and shifted towards metallic Cu peaks, evident of a more amorphous layer growth.^{24,32,38} The Cu thus deposits with lower energy on the substrate further inducing defects and yielding a deteriorated crystallinity. SEM images in Fig. S3, show that an increase in deposition pressure results in the particles becoming more stacked and agglomerated, as was observed in previous literature.^{36,38} In this regime, higher diffusion rate and atom mobility result in a more densely stacked surface.

Next, we compared the different sputter rates in Fig. 1C, the crystallinity of the characteristic Cu_3N peaks are similar with varying sputter rate. A higher rate will result in more material deposited on the carbon substrate, as evidenced by the ICP-MS result on Cu loading (Table S1), consequently, the intensity of the Cu_3N peaks increase. Furthermore, SEM images (Fig. S4) reveal an increase in mean average size was detected from 394 nm \pm 47 nm for 1 \AA s^{-1} to 516 nm \pm 35 nm for 10 \AA s^{-1} . This can be attributed to a faster growth rate and less nucleation under the latter conditions.³²

Next, contact angles were measured on the $\text{Cu}_{1-x}\text{N}_x$ coated GDLs for each sample. Table 1 (Fig. S5–S7, for pictures) shows that the contact angle lowers with r_{N_2} , as the nitrogen content



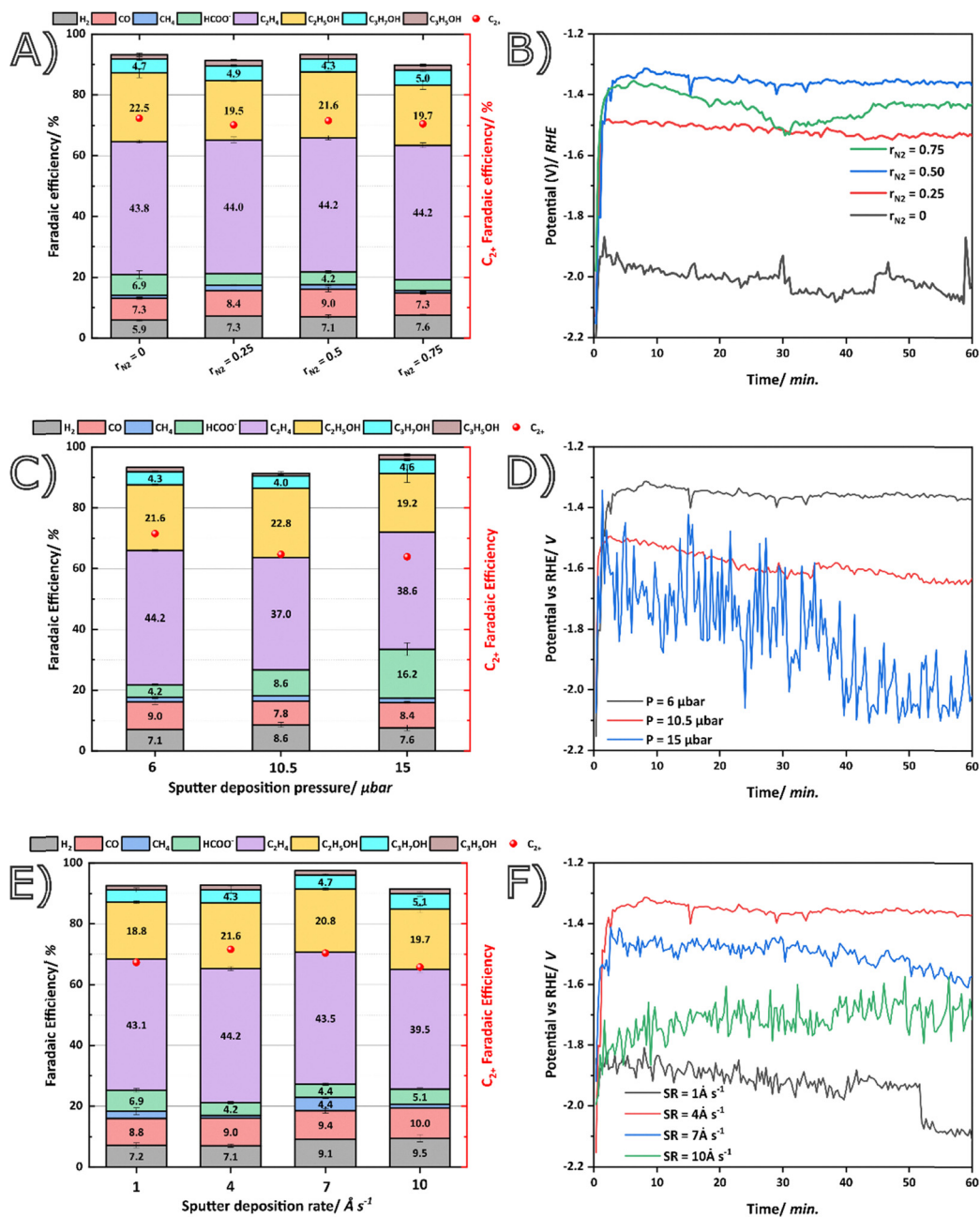


Fig. 2 The product distribution in terms of faradaic efficiency for the different products, and the recorded working electrode potential in RHE are given. Measurements were done in a flow-by configuration with 0.5 M KHCO₃ as catholyte, and 15 sccm of CO₂, chronopotentiometry analysis was done at -150 mA cm^{-2} and repeated three times for reproducibility. The results are presented for the parameters under investigation, (A) and (B) the varying r_{N_2} values, (C) and (D) the different sputter deposition pressures in μ bar, and (E) and (F) for the sputter deposition rates.

other reported studies in terms of EE, however, if iR contribution is applied, a total $EE_{C_2H_4}$ of 28% is found, further showing that our material is better than most previously reported Cu nitride based materials (Table S2). Furthermore, although the FEs might be comparable, emphasis on the high mass activity (due to low Cu loading) for ethylene is highlighted. In most cases, a higher mass activity is observed due to the sputtering fabrication method requiring low Cu loadings ($< 1 \text{ mg cm}^{-2}$). Magnetron sputtering thus allows for facile tuning of properties, whilst providing a rapid, uniform, and scalable fabrication

strategy (up to $\pm 1 \text{ m}^2$) making this an optimal alternative for traditional, and complex synthesis methods even though they sometimes slightly outperform in terms of performance. For instance, Cu₃N-derived Cu nanowires (NWs) exhibit superior performance compared to our sample, achieving an $FE_{C_2H_4}$ of 66% and an $EE_{C_2H_4}$ of 35% albeit at lower current densities in a H-cell.²⁰ Nevertheless, the synthesis procedure entails the production of Cu(OH)₂ NWs, followed by nitridation in a tube furnace, and ultimately, partial electrochemical reduction to Cu NWs. Evidently, this method involves a complex fabrication



process that poses challenges for scaling to quantities relevant for industrial applications.

To conclude, the higher EE with $\text{Cu}_{1-x}\text{N}_x$ as opposed to metallic Cu can be explained as follows. First, the distinct anti- ReO_3 crystal structure that yields interstitial sites filled with Cu (as highlighted by the EDX) and Cu domains, increases the conductivity and stability of Cu^+ due to the presence of residual nitrogen (as supported by *ex situ* XRD analysis). Secondly, the greater interatomic distances ($3.817 > 3.615 \text{ \AA}$)²³ between Cu–Cu atoms can help in stabilizing certain intermediates by reducing the energy barrier and facilitating better adsorption and improved cell potentials. Finally, the significant charge density of N^{3-} contributes in maintaining the more active Cu^+ species, further contributing to the increased cEE.

Finally, we investigated the initial stability of the optimal $\text{Cu}_{1-x}\text{N}_x$ films (for $r_{\text{N}_2} = 0.50$, $\text{SR} = 4 \text{ \AA s}^{-1}$ and $P = 6 \text{ \mu bar}$) and compared it to pure Cu. From Fig. 3A, similar potential trends are seen over the course of the experiment, as before, with $r_{\text{N}_2} = 0.50$ a higher energy efficiency was reached due to a difference of $\pm 600 \text{ mV}$ in the measured working potential. With respect to the ethylene efficiency over time (Fig. 3B), $r_{\text{N}_2} = 0.50$ clearly achieves improved stability as the ethylene is still at 20% after 4 hours, whereas, for pure Cu the ethylene FE has dropped to zero. Therefore, it seems that $\text{Cu}_{0.84}\text{N}_{0.16}$ can retain higher production rates over extended duration and we believe this is due to the more defined crystal structure. During operation, sputtered metallic Cu reorganize into channel-like structures that allow enhanced water penetration.¹³ A similar mechanism occurs with $r_{\text{N}_2} = 0.50$, however, the initial nitrogen

incorporation likely influences activation by stabilizing Cu^+ , similar to the case of oxide-derived Cu.

Chronoamperometry at $-0.5 \text{ V vs. Ag/AgCl}$ (the potential at which Cu^+ reduces) was run until the current reached approximately zero (in $1 \text{ M K}_2\text{SO}_4$). After integrating the resulting curves (Fig. S10), we can calculate the amount of charge (C) required for reduction (when current reaches zero), which is significantly higher for $r_{\text{N}_2} = 0.50$ (at 62.67 mC) than for Cu (38.5 mC), indicating prolonged Cu^+ retention, furthermore, the XRD (Fig. S11) of the spent sample shows some Cu_3N peaks, proving the presence of residual nitrogen which helps in stabilizing the catalyst. Although these initial experiments indicate another advantage of utilizing $\text{Cu}_{0.84}\text{N}_{0.16}$, stability is not solely related to the catalyst, but also to the system. Controlling the differential pressure⁴⁶ to limit flooding effects, operating under pulsations to counteract surface reconstructions,²¹ flow cell setup,⁴⁷ and substrates effects such as a pure PTFE substrate that hinders salt precipitation,⁴⁸ are all determining factors that heavily impact stability, which is not the main aim of this work and also the reason why longer testing was not performed. The main aim is to point out the benefits of utilizing nitrogen during reactive sputtering over pure Cu as electrocatalyst for the CO_2 reduction reaction.

In this study, we have proven that the application of sputtered $\text{Cu}_{1-x}\text{N}_x$ films can be expanded to the field of CO_2 electrolysis, whilst accomplishing similar FEs, the energy input can be significantly improved compared to typical pure Cu films. As previously mentioned, the increase in the mass activity due to relatively low Cu loadings ($< 400 \text{ \mu g cm}^{-2}$) is

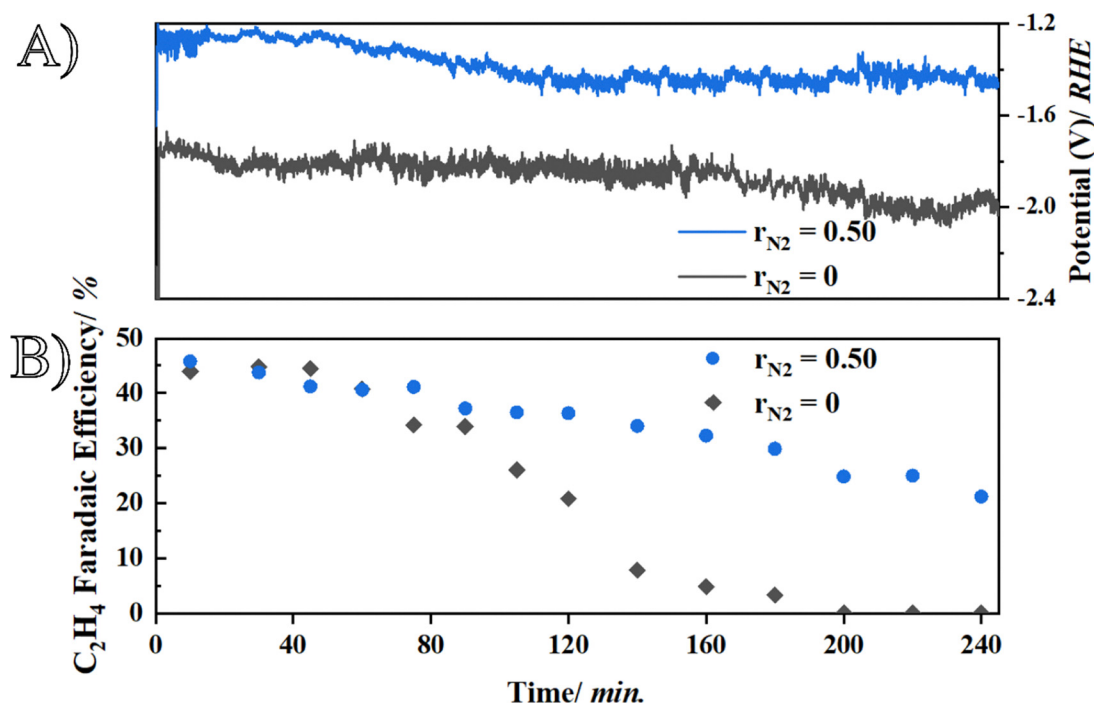


Fig. 3 $\text{Cu}_{1-x}\text{N}_x$ ($r_{\text{N}_2} = 0.50$, $P = 6 \text{ \mu bar}$, $\text{SR} = 4 \text{ \AA s}^{-1}$) and Cu ($r_{\text{N}_2} = 0$, $P = 6 \text{ \mu bar}$, $\text{SR} = 4 \text{ \AA s}^{-1}$) films were subjected to operational stability for 4 hours at -150 mA cm^{-2} . In (A) we plotted the measured working potential vs. RHE/V over time, and subsequently added the (B) ethylene efficiency over time for both samples.



another advantage of this cost – effective and scalable alternative. Therefore, we believe that $\text{Cu}_{1-x}\text{N}_x$ thin films have potential to be used as promising catalysts for the CO_2 reduction reaction, especially given there is still a lot of room for improvement of this system both in terms of efficiency and of stability.

Conclusions

In this study, we employed physical vapor deposition *via* magnetron sputtering to fabricate $\text{Cu}_{1-x}\text{N}_x$ thin films under varying operational parameters, including the r_{N_2} ratio, sputter pressure, and sputter rate, and investigated their structural characteristics. These films were explored, for the first time, as electrocatalysts for the CO_2 reduction to multi-carbon products in a flow-by electrolyzer, and compared with well-studied metallic Cu films. From the results, we determined that $\text{Cu}_{1-x}\text{N}_x$ tends to generate equally remarkable faradaic efficiencies for ethylene (44%) and ethanol (21%) as compared to Cu. Notably, a significant enhancement in energy efficiency – from 15.8% to 20% – was observed for the optimized $\text{Cu}_{1-x}\text{N}_x$ sample ($r_{\text{N}_2} = 0.50$, $\text{SR} = 4 \text{ \AA s}^{-1}$, $P = 6 \text{ \mu bar}$) due to the differences in compositional effects enhancing stabilization of key intermediates and improving initial resistance of the system leading to higher energy efficiencies. Additionally, this straightforward, scalable and cost-effective synthesis allows for effective tuning of properties and has a large industrial relevance. This approach yields higher mass activity due to the reduced Cu loading required for ethylene production. The initial stability of $\text{Cu}_{0.84}\text{N}_{0.16}$ showed improvements compared to metallic Cu, as surface reconstructions are limited due to prolonged Cu^+ presence.

Author contributions

Mathias van der Veer: writing – original draft, conceptualization, investigation. Nick Daems: writing – review & editing, supervision. Pegie Cool: writing – review & editing, project administration, funding acquisition. Tom Breugelmans: writing – review & editing, project administration, funding acquisition.

Conflicts of interest

The authors report no conflict of interest.

Data availability

The (processed) data will be published and made openly and freely available through deposition in the Zenodo repository of the University of Antwerp and Applied Electrochemistry and Catalysis (ELCAT) Research Group. <https://zenodo.org/communities/uantwerp-elcat/>.

Supplementary information: detailed experimental methods; summary of deposition conditions, ICP-MS results, EDX results; literature review of various Cu-based catalysts; view of the flow cell; SEM images of $\text{Cu}_{1-x}\text{N}_x$ films prepared with

different r_{N_2} ratios; SEM images of $\text{Cu}_{1-x}\text{N}_x$ films prepared with different operational sputter pressure; SEM images of $\text{Cu}_{1-x}\text{N}_x$ films prepared with different sputter rates; contact angles of $\text{Cu}_{1-x}\text{N}_x$ films prepared with different r_{N_2} ratios; contact angle of $\text{Cu}_{1-x}\text{N}_x$ films prepared with different operational pressure; contact angle of $\text{Cu}_{1-x}\text{N}_x$ films prepared with different sputter rate; cyclic voltammograms and the resulting linear fit for calculation of EASA data for all used $\text{Cu}_{1-x}\text{N}_x$ films; summary of our results with EE and Cdl; summary of partial mass activity; chronoamperometry with $r_{\text{N}_2} = 0$, and $r_{\text{N}_2} = 0.50$ at $-0.5 \text{ V vs. Ag/AgCl}$; XRD pattern of r_{N_2} sample after electrolysis. See DOI: <https://doi.org/10.1039/d5ey00246j>.

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