

The Sensitivity of Cu for Electrochemical Carbon Dioxide Reduction to Hydrocarbons as Revealed by High Throughput Experiments

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Abstract:

Electrochemical CO₂ reduction to valuable products is a centerpiece of future energy technologies that relies on identification of new catalysts. We present accelerated screening of Cu bimetallic alloys, revealing remarkable sensitivity to alloy concentration that indicates the segregation of alloying elements to critical sites for hydrocarbon formation.

The promise of electrochemical CO₂ reduction to valuable products has prompted substantial research in selective catalysis of the many-electron reduction of CO₂ to products such as light hydrocarbons.¹ However, most metal electrocatalysts have been shown to exclusively form the 2 e⁻ products CO and formate (e.g. Au, Ag, In, and Sn) and/or catalyze the competing hydrogen evolution reaction (HER) (e.g. Fe, Ni, Pt, and Ti).² Cu is the only known elemental catalyst capable of reducing CO₂ to hydrocarbons and alcohols with appreciable Faradaic efficiency (FE) but suffers from poor selectivity to any single product and high overpotentials for generating the highly reduced products.²⁻⁴ The uniqueness of Cu has been understood to be due to its moderate binding energy of CO and other intermediates.^{5,6} Alloying with a secondary metal is a widely-adopted strategy to alter a catalyst's adsorption energetics for reactants and intermediates, and some copper-based bimetallic catalysts have been evaluated for altering the CO₂RR selectivity.⁷ While improved selectivity for 2 e⁻ products has been achieved, success in increasing FE for higher order products has been more limited, as discussed further below.⁸⁻²² Comparison among reported Cu-alloy systems is limited by the variation in catalyst syntheses and morphologies in these studies, motivating the systematic study of different alloying elements and alloying concentrations in the present work.

Exploration of CO₂RR electrocatalysts is hampered by the dearth of accelerated screening systems, which are challenging to realize given the sensitivity of product distribution to the electrochemical environment and the breadth of possible reaction products. The ideal characterization of a given catalyst is quantitative measurement of the activity and product distribution, as a function of time, and for a large range of overpotentials since product distributions vary with aging of the operational catalyst as well as the operating potential. This combination of desired measurement attributes is incompatible with traditional experiments, perhaps most notably due to the duration of quantitative product distribution measurements via chromatography or nuclear magnetic resonance, severely limiting the measurement frequency to observe variations in product distribution as a function of time and/or overpotential. Through principled design of an accelerated screening system, we demonstrate quantitative Faradaic efficiency (FE) measurement of H₂, CH₄, and C₂H₄ during cyclic voltammetry (CV) experiments with a measurement interval of 12 s, enabling rapid screening of arrays of catalyst compositions.

Through exploration of the ASM binary alloy phase diagrams²³ we identified 8 non-precious metals that alloy into fcc-Cu by at least 10 at.% for some temperature below 700 °C. Binary compositionally-graded thin films of each Cu-X system with compositions range from below 3 at.% to above 18 at.% of the alloying element were prepared by combinatorial sputtering and measured at 8 alloy compositions, creating a library of 64 alloys that were each evaluated by a series of 3 CVs using the instrument shown in Fig. 1. The electrolyte flow at 0.16 mL s⁻¹ through a catholyte chamber of ca. 0.32 mL creates a liquid-only electrochemical reactor except during sustained production of products beyond their solubility limit, e.g. prolonged partial current density above ca. 5 mA cm⁻² for gaseous products. The electrolysis effluent flows through a pervaporator cell with poly(tetrafluoroethylene) (PTFE) membrane, which is based on the design of Clark et al.,²⁴ where the vacuum contact promotes evaporation of volatile dissolved species such as H₂, CH₄, and C₂H₄ along with a substantial amount of water. Due to the high H₂O flux from the pervaporator cell, direct connection to the MS system requires substantial differential pumping as well as large background in the mass

spectrometer signal, which prevent hydrocarbon (HC) detection at the desired concentration and acquisition time. This issue is circumvented in the present work with an in-line molecular sieve (mol. sieve) desiccant chamber that sorbs water and alcohols to increase the partial pressure of HCs in the MS inlet by a factor of approximately 100 (Fig. S1). As a result, with 12 s MS measurement intervals, HCs can be detected at partial current densities (J_p) above $30 \mu\text{A cm}^{-2}$. The MS signals at mass-to-charge (m/z) values of 2, 15, and 26 provide quantitative measurement of the partial pressure of H_2 , CH_4 , and C_2H_4 in the post-desiccant vacuum effluent, whose signals are calibrated by saturating the flowing electrolyte with calibration gases with the cell held at open circuit. While other strategies for online product detection have enabled accelerated screening of electrocatalysts,^{22,24–26} we note a unique aspect of the present work is that the rapid flow and decoupling of the reactor and pervaporator ensure that products created from the entire working electrode are detected, as opposed to localized product extraction where spatial variations in mass transport, etc. can cause the measured product stream to poorly represent the electrochemical measurement, creating artifacts in key results such as FE.

Given the excellent partial current density detectability limit, the MS signals can be directly used for identifying catalysts and electrolysis settings that yield HCs. For the present purposes of identifying whether Cu alloys provide higher FE for HCs, especially at lower overpotentials, a CV is the desired electrochemical technique, but appreciable potential scanning rates and/or potential-dependent partial current densities result in the inability of the MS signal to reach steady state. Through modelling of the pervaporation, we find that diffusion through electrolyte in the porous PTFE membrane limits results in an exponential time constant, ca. 7 s for H_2 and 13–14 s for CH_4 and C_2H_4 , for equilibration of the MS signal to the gas concentration in the flowing electrolyte. By calibrating model parameters with toggled flow of calibrants, we established a model for calculating the time-dependent partial current density of each product from the respective measured time-dependent MS signal, as described previously.²⁷ For CVs at 10 mV s^{-1} between un-compensated potentials of -0.4 and -1.3 V vs RHE , we find that J_p is well modelled by assuming that J_p is the same function of applied potential during both the cathodic and anodic voltage sweeps. Furthermore, this function can be approximated by a Gaussian, which represents a peak in J_p when the center potential of the Gaussian is within the CV limits and could also approximate an exponential function when the center potential is beyond the CV limits. Consequently, the series of MS measurements per product and per CV cycle are used to determine the corresponding 3 Gaussian parameters that minimize the loss between the modelled and measured MS signal. Fig. S2–S4 shows the stability of the measurement and of this J_p modelling algorithm through repeated measurements on a series of Cu thin film catalysts, and Fig. 2a illustrates the measurement of 3 MS channels and working electrode current density over 3 CV cycles with 60 s of open circuit potentiometry (OCP) in between to allow MS signals to return to baseline so that each CV can be modelled independently. Fig. 2b shows the J_p resulting from the 3-parameter Gaussian fit using a custom fitting procedure described previously.²⁷ The MS signal corresponding to this fit is also shown in Fig. 2a. It is worth noting that the resulting J_p is quite similar on the second and third cycles, which can differ from that of the first cycle. This variability in the first CV is expected since no electrochemical pretreatment was performed on the sputtered film and is likely related to contaminants from air exposure. As a result, the evolving product distribution during the first cycle exceeds the scope of the Gaussian-based model described above and corresponds to substantial uncertainty in the precise shape of J_p in Fig. 2b. While additional modelling can be used to explore this first cycle, for the purposes of the present work we note that for all alloy catalysts the results of the second and third cycle are consistent, motivating our analysis and reporting of only the third cycle. The measured current is also smoothed with a 129-point cubic Savitsky-Golay filter and then compensated for resistive losses using the measured 60Ω cell resistance. Uncompensated versions of each such figure are included in the SI.

Fig. 3 shows the MS measurements and subsequent modelling for the 8 alloy composition systems along with that of a pure Cu reference. Catalysts exhibiting current densities in excess of 5 mA cm^{-2} for a substantial fraction of each CV cycle typically causing bubble formation that gives rise to the large positive outlier values in the MS measurements. While such data points cause some uncertainty in the resulting J_p , the modelling procedure mitigates sensitivity to the outlier and preferably weights the data points at the onset of product detection.²⁷

Complete datasets for 8 alloy systems elements are provided as Figs. S5–S12, and Fig. 3 includes the compilation of the $\text{Cu}_{0.95}\text{X}_{0.05}$ compositions. A range of potential-dependent FE signals for each product are observed, and the observed differences from the Cu-only catalyst are quite remarkable. The figure also indicates substantial variation in the total current density, which is shown for these compositions in Fig. 4a. To further probe the composition-dependent product distributions, we consider the integral over time of this total current density as well as over each product-specific J_p , yielding electrolysis charge densities for the entire CV. The results shown in Fig. 4b include a dashed line indicating the average over the Cu measurements in Fig. S3.

To unpack this wealth of data we consider alloying elements that behave qualitatively similar and discuss in the context on the Cu alloy literature, which mostly involves higher concentrations of the alloying element. The lack of literature on dilute alloys of fcc-Cu is emblematic of the intuition that small concentrations of alloying elements will have no substantial impact on the catalysis, yet Fig. 4b shows that 2-3 at.% of Sb, In or Sn is sufficient to lower total hydrocarbon production during the CV by a factor of more than 100, a level of sensitivity to an alloying element that to our knowledge has no precedent in electrocatalysis when the contaminant is an alloying element that is itself an electrocatalyst, as opposed to contaminants such as S and Cl that readily poison metal surfaces.^{28,29} It is worth noting that in the CV experiments, high partial current density for non-hydrocarbon products mitigates the ability to form hydrocarbons, not only due to the competitive concentrations of reaction intermediates, but also due to resistive losses as reflected in the range of applied potentials after resistance compensation shown in Fig. 4a.

Sb, In, and Sn alloys exhibit a substantial increase in the current density with the FE for H₂ being relatively unchanged, indicating that the suppression in hydrocarbon formation is the result of a substantially increased activity for other products, perhaps the 2 e⁻ products that these main group catalysts are known to form in the absence of Cu. These results are in agreement with previous reports on Cu-In⁹⁻¹¹ and Cu-Sn¹⁴ catalysts where the weak H adsorption and strong O binding of In and Sn enhances selectivity toward formate and CO. For example, FE of 90% for formate with Cu-Sn and for CO with Cu-In were reported at low potentials, with the present work being the first to explore more dilute alloys of these elements. While further study of the highly active Cu-(Sb,In,Sn) catalysts may be of interest for formation of products other than HCs, their primary scientific importance for CO₂RR is understanding how such a small concentration can so strongly influence product distribution. In the concerted community effort to understand the uniqueness of Cu, these alloys provide a new line of inquiry.

The Cu-Zn alloys share some important similarities and differences compared to the Sb, In, and Sn systems. The hydrocarbon formation is less sensitive to alloy concentration in the 2-6 at.% range. Catalysts with higher Zn concentrations exhibit the highest H₂ production among all the alloys, which not only hampers formation of hydrocarbon but also other CO₂RR products. These results are somewhat surprising given literature precedent of Cu-Zn catalysts. Zn-rich alloy films³⁰ and nanoporous Zn-rich structures¹⁸ have been studied for formate and CO production at low overpotential, which are not directly comparable to the Zn-poor catalysts in Fig. 4 and collectively indicate that product distributions of Cu-Zn catalysts do not vary monotonically with composition. Zn coatings on Cu have been shown to suppress HER and increase CH₄ production,³¹ in stark contrast to the results of Fig. 4, indicating that the surface and near-surface Zn in the alloy catalysts of the present work are critically different from the previously reported application of Zn coatings. Ren et al.³² studied electrodeposited Cu-Zn alloys with Zn concentrations of 9-30 at.% and focused on the increased ethanol production at high Zn concentrations. They also observed increased total current with Cu-Zn alloys compared to Cu at potentials above -0.95 V vs RHE, in agreement with the present work, although the most Cu-rich alloy in that work (9 at.% Zn) exhibited an increase in FE of C₂H₅OH, which is not measured by our study. Feng et al.¹⁷ observed enhanced FE for C₂H₄ on oxide-derived Cu-Zn nanoparticles where Zn concentrations from 12 to 50 at.% were studied, resulting in identification of 20 at.% Zn as optimal for C₂H₄ formation. In this context, the results of Fig. 4 indicate that the morphology and exposed catalyst sites from the oxide-derived synthesis technique is more critical than the presence of Zn, which is commensurate with recent studies³³ on product-specific active sites in oxide-derived Cu catalysts and motivates further inspection of whether Zn directly plays a catalytic role in increasing the FE of C₂H₄ or if it instead stabilizes the hypothesized unique Cu sites generated through electrochemical reduction from the metal oxide.

While the 2 at.% Co alloy enhances hydrocarbon formation by a factor of about 2, Co is otherwise the most innocuous alloying element with no substantial change in the overall current and slightly increasing H₂ and decreasing HC production with increasing alloying concentration. Similar trends of hydrocarbon formation over CuCo was observed by Grote and his coworkers.²² Al is also somewhat innocuous with the primary effect being increase H₂ formation, which is markedly different from the heavier main group elements discussed above.

Other than the overall sensitivity of Cu to small alloying concentrations, perhaps the most intriguing observation is the select cases where the alloying element changes the relative production of CH₄ and C₂H₄, which is shown in Fig. S13. The most Cu-rich alloys with Zn, Al, and Co slightly increase selectivity for CH₄. The 2-5 at.% Sb catalysts are interesting in that they eliminate CH₄ from detectability but not C₂H₄, posing the possibility that improved catalysts could be obtained if this selectivity control could be harnessed without the increased FE in other products. A similar but more gradual trend is observed with Ni and Mn, with both showing a consistent increase in relative C₂H₄ production with increasing alloy concentration. While the total hydrocarbon production of Ni also declines with increasing alloy concentration, the Mn alloys up to 5 at.% show slightly higher total hydrocarbon production, with the 3-4 at.% Mn

increasing the fraction of C₂ hydrocarbons (compared to total hydrocarbons) from the ca. 40 at.% value observed with pure Cu to ca. 60 at.%.

The alloys with 5 at.% CuSn and CuMn were measured with XPS (Fig S14) to assess whether the near-surface concentrations of the alloying elements far exceeded the bulk values, and while enhancements of 1.6× and 2.8×, respectively, were observed, the sensitivity of product distribution to alloy concentration remains remarkable and largely unexplained by present understanding of CO₂RR on Cu-based catalysts. Theoretical characterization of absorption energies for bimetallic alloys³⁴ will help elucidate the composition-selectivity trends, although such data is not presently available in the dilute alloy concentration range and will additionally need to consider elemental surface segregation and reorganization processes. Since it is unlikely that such dilute alloys substantially alter the electronic structure of Cu, the most likely underlying phenomenon is that the hydrocarbon-forming Cu sites have a relatively high surface energy that concomitantly drives surface alloying elements to these same sites, enabling a dilute concentration of these active sites to be contaminated by dilute alloy concentrations. Validating this hypothesis will require further experimentation and/or theoretical investigation, and the notable exceptions to this trend, such as the C₂ product selectivity of Mn, merit further investigation. These results also represent a cautionary tale for development of CO₂RR electrolysis devices as any plating of metal contaminants in the electrolyte can substantially alter product distributions, creating demanding requirements for elimination of trace metal contaminants. A notable precedence for this level of sensitivity to trace metals exists in alkaline oxygen evolution electrocatalysis where trace adventitious Fe from the electrolyte substantially influenced catalytic activity for initially Fe-free catalysts.³⁵ While the activity boost in that situation posed problems for scientific studies but not electrode development, the sensitivity of Cu to metal impurities poses more substantial challenges for electrocatalyst research and development.

Conclusions

We address challenges in CO₂ reduction electrocatalyst discovery through the design of an electrochemical flow cell with online mass spectroscopy-based quantification of the Faradaic efficiency for H₂, CH₄, and C₂H₄ with 12 s measurement intervals and partial current detectability of ca. 0.03 mA cm⁻², enabling high throughput screening of Cu bimetallic alloys with Al, Mn, Co, Ni, Zn, In, Sn, and Sb. The product distribution of Cu-rich catalysts is remarkably sensitive to alloy concentration with 2 at.% of some elements causing tenfold decrease of hydrocarbon formation, indicating that alloying elements segregate to critical sites for hydrocarbon formation, which poses substantial challenges for development and sustainable operation of Cu-based catalysts.

Conflicts of interest

There are no conflicts to declare.

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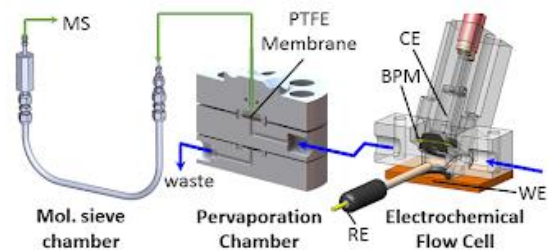


Figure 1: Electrolyte (blue) and in-vacuum product stream (green) flows through the 3 components between the electrolyte reservoir and MS detector. The planar working electrode is pressed against the o-ring at the bottom of the electrochemical cell. The inlet flow tube is directed toward the working electrode (WE), and the outlet flow tube terminates near the membrane at the top of the cell so that any bubbles are readily removed. The reference electrode (RE) is horizontal, terminating near the center of the chamber, ca. 2.8 mm above the WE, and the counter electrode (CE) is separated by the bipolar membrane (BPM). The electrolyte is then injected in the center of a cylindrical pervaporation chamber with volatile species crossing the PTFE membrane, creating a product stream that is differentially pumped by the mol. sieve before continuous injection in the MS for product quantification.

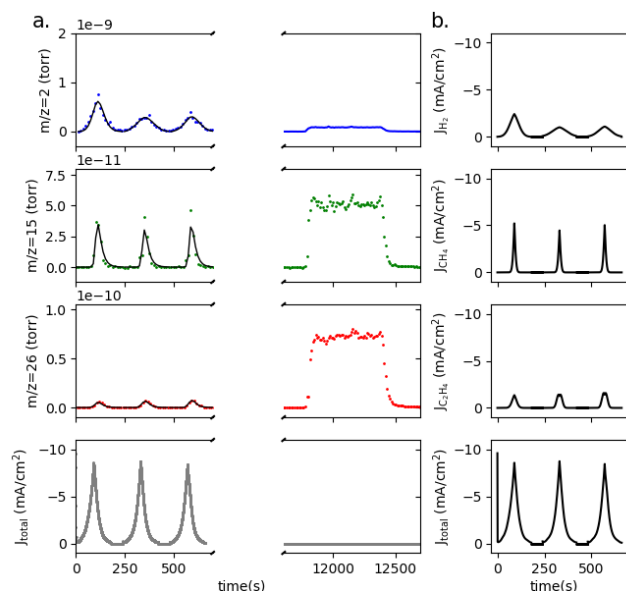


Figure 2. EC-MS demonstration with a thin film Cu electrode. a) Typical experimental process for catalyst screening including 3 CV cycles separated by OCP for enabling MS to return to baseline. After performing such measurements on a series of catalysts, a daily calibration is performed by flowing through electrolyte bubbled with calibration gas containing 0.4% H₂, 0.4% CH₄, and 0.4% C₂H₄ in CO₂. b) Using this calibration and pervaporation model, the modeled partial current density for each species is calculated and compared to the measured total current.

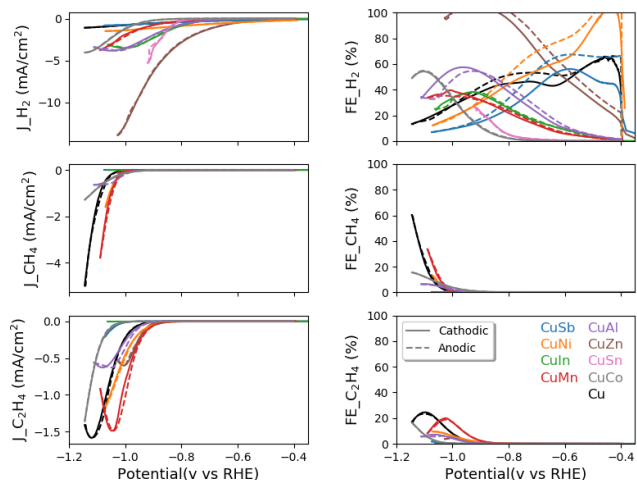


Figure 3. The J_p (left column) and FE (right column) for the third CV cycle is shown for each of the 8 Cu-based bimetallic catalysts with ca. 5% of the alloying metal. The potentials include resistance compensation and legends in bottom-right panel apply to all 6 panels.

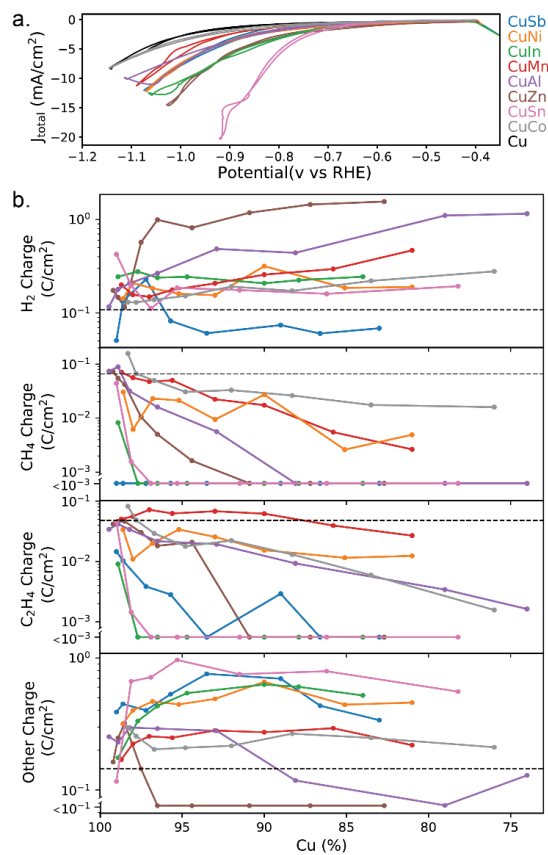


Figure 4. Charge density (integral of J_p over time(s)) for the third CV cycle is shown for each of the 8 alloy elements as a function of alloy concentration. The dashed black line indicates the average charge density for pure Cu. The bottom 3 panels include a broken charge density axis corresponding to product generation near or below the detectability limit.