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Bridging knowledge gaps in liquid- and vapor-fed CO2 electrolysis through active electrode area

Permalink https://escholarship.org/uc/item/3vp8c573

Journal Chem Catalysis, 2(11)

ISSN

2667-1093

Authors

Corral, Daniel Lee, Dong Un Ehlinger, Victoria M et al.

Publication Date

2022-11-01

DOI

10.1016/j.checat.2022.09.017

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Peer reviewed

1 Bridging knowledge gaps in liquid- and vapor-fed CO₂ electrolysis using catalyst

2 surface area

- 3 Daniel Corral^{+1,2}, Dong Un Lee⁺¹, Victoria M. Ehlinger³, Stephanie Nitopi¹, Jaime E. Avilés Acosta¹, Lei
- 4 Wang¹, Alex J. King⁴, Jeremy T. Feaster⁵, Yi-Rung Lin¹, Adam Z. Weber⁴, Sarah E. Baker⁵, Eric B. Duoss²,
- 5 Victor A. Beck^{*3}, Christopher Hahn^{*5}, and Thomas F. Jaramillo^{*1,6}
- 6 + These authors contributed equally to this work
- 7 *Correspondence should be addressed to <u>beck33@llnl.gov</u>, <u>hahn31@llnl.gov</u> and
- 8 jaramillo@stanford.edu
- 9

10 Affiliations:

- 11 1. SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford
- 12 University, Stanford, CA 94305, USA. E-mail: jaramillo@stanford.edu
- 13 2. Materials Engineering Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA.
- S. Computational Engineering Division, Lawrence Livermore National Laboratory, Livermore, CA 94550,
 USA. E-mail: <u>beck33@llnl.gov</u>
- 4. Energy Conversion Group and Liquid-Sunlight Alliance, Lawrence Berkeley National Laboratory,
 Berkeley, CA 94720, USA.
- 18 5. Materials Science Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA. E mail: <u>hahn31@llnl.gov</u>
- 20 6. SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park,
- 21 CA 94025, USA.



TOC Figure

- We achieve a ~700-fold and ~10-fold increase in multi-carbon product formation by designing roughened catalysts for both foil- and gas diffusion-type electrodes, respectively. We showcase catalyst surface area as a key descriptor for understanding the interplay between the electrode structure and local reaction environment on activity and selectivity. Both experimental and computational modeling determine heightened reaction rates towards CO₂R at lower
- 32 overpotentials, which uncover a clear dependence on electrode roughness.
- 33

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35 Highlights

- 36
- Distinct catalyst morphologies are translated between electrode types
- Reaction rate toward CO₂R and C₂₊ products is enhanced at lower overpotentials
- Increase in J_{geo} up to ~735x and ~10x are observed with foil and GDEs, respectively
- 40 Experiments and model show Tafel-like description of roughness and potential shift

41 Summary

Increased use of gas-diffusion electrodes for CO₂ electroreduction widens the 42 43 experimental phase space (i.e., increased reaction rate and mass transport) that was previously 44 inaccessible using foil electrodes. This raises fundamental questions over the impacts of key 45 variables that translate between liquid- and vapor-fed CO₂ electrolysis systems, warranting 46 comparisons to aid our understanding of the underlying processes that control performance. In 47 this work, we studied the interplay of current-potential profiles and electrode roughness on 48 product activity and selectivity for both liquid- and vapor-fed CO₂ reduction. We implement a Cu 49 nanoflower morphology on both electrode architectures, allowing us to tune the 50 electrochemically active surface area (ECSA) and thus overpotential. This results in decreased 51 overpotentials as high as 460 and 174 mV for foil and gas diffusion electrodes, respectively, while 52 maintaining or improving multi-carbon product current density. We further investigate these 53 overpotential shifts and product activities by normalizing the current density by ECSA, uncovering 54 current-potential relationships akin to those of the Tafel description. A continuum, 1D steady-55 state model rationalized the shifts, demonstrating that Tafel-like kinetics are useful for describing 56 the roughness dependence for both liquid- and vapor-fed systems. This analysis establishes a 57 holistic approach for establishing key catalyst design criterion that guide the development of 58 improved materials and devices for CO₂ electrolysis technologies.

60 The bigger picture

CO₂ electrolysis is an attractive method for producing industrially relevant chemicals 61 62 while reducing emissions coupled with renewable energy sources. Recent advancements have 63 focused on evolving the electrode architecture from metal foils to porous gas diffusion electrodes for improving the reaction rate. However, the contributions from surface kinetics and local 64 65 reaction environment are convoluted and vary when translating from liquid- to vapor-fed 66 systems. Herein, we draw connections between these systems by evaluating identical catalyst 67 structures of varying roughness for both electrode types. Our experimental and modeling approaches provide better understanding of the interplay between electrode structure and 68 69 reaction environment on the activity and selectivity. We observe nominal changes in the intrinsic activity of Cu with significant overpotential savings corresponding to the roughness factors across 70 electrode types. 71

72 **1. Introduction**

73 Increased accessibility and rapidly declining costs of renewable technologies have incentivized gradual decarbonization in the global energy landscape.^{1,2} However, other energy 74 75 services essential to modern civilization cause emissions that will be more difficult to eliminate 76 fully, such as aviation, long-distance transportation and shipping, and production of carbon 77 intensive structural materials.³ To address these and other remaining emissions, methods of 78 carbon capture and sequestration are being developed to remove CO₂ from air and point sources of emissions, requiring further development and cooperative policy for economic viability.^{4,5} 79 Thus, there is great motivation to utilize CO₂ after it has been captured to make valuable 80 81 products.⁶ Electrochemical CO₂ reduction (CO₂R) has risen as a promising candidate in that regard 82 based on two criteria, including: (1) the ability to address emissions while producing essential carbon-based fuels and chemicals,⁷ and (2) CO₂R can be coupled with intermittent renewable 83 technologies such as wind and solar power, to convert electricity to more versatile forms of 84 85 chemical energy for storage and transportation.⁸

86 Knowledge gained from liquid-fed systems has provided a strong foundation for vapor-87 fed devices using gas-diffusion electrodes (GDEs) as the field focuses on industrial implementation. For both systems - which use aqueous electrolytes - complicated surface 88 89 kinetics and competing homogeneous and hydrogen-evolution reactions (HER) limit performance.^{9–11} More recently, the concept of the microenvironment (i.e. local reaction 90 91 environment) in cooperation with polarization and surface effects has helped frame our 92 understanding of device performance.¹² For foil electrodes in liquid-fed devices, roughening likely 93 does not increase the intrinsic activity of Cu towards CO₂R^{,9,13} yet, it does influence product selectivity due to nano- and meso-scale effects.^{14–17} Differences in selectivity have been 94 attributed to varying coordination number,¹⁸⁻²³ pore size and shape,^{24,25} and subsurface 95 96 oxygen.²⁶ Ren et al. demonstrated changing selectivity based on the potential window²⁷ and De Luna et al. have correlated C₂H₄ activity with suppressed CH₄ formation,²⁸ both achieved via 97 nanostructuring. This also changes the local pH^{14,15,29}, which can suppress the HER rate and 98 promote C_{2+} selectivity.^{28,30–32} Naturally, the strategy for operating at low overpotential in 99

alkaline electrolytes has resulted in nearly full selectivity towards multi-carbon products from CO reduction.³³ By extension, these criteria have been employed for enhanced CO₂R performance in vapor-fed systems; GDEs permit highly active CO₂R in alkaline electrolytes (e.g. KOH) while minimizing species diffusion lengths in thin catalyst layers.^{31,34} Such systems have been able to target multi-carbon production at lower overpotentials by controlling the microenvironment; which there are likely many more when using GDEs compared to foil electrodes.^{12,31,34–36} Yet, it is unclear what effects translate between environments by nanostructuring the catalyst layer.

107 In this work, we utilize catalyst surface area to provide insight and bridge knowledge gaps 108 between two different systems; liquid- and vapor-fed CO₂R electrolyzers that utilize foil 109 electrodes and GDEs, respectively (Figure S1). We observe the complex interplay between 110 overarching potential-dependent trends, microenvironment, and electrodes of varying design 111 and roughness factor (RF). We propose that the CO₂R selectivity trends and catalyst design 112 strategies for tuning product formation in liquid-fed CO₂ electrolysis extend to the vapor-fed 113 systems (Figure 1). That is, (1) at a constant overpotential, the geometric current density will 114 increase with increasing RF and (2) at constant geometric current density, the overpotential will 115 decrease with increasing RF, both of which can affect product selectivity. By utilizing Cu 116 nanoflower (NF) catalysts with intermediate RFs (e.g. ~185), we observe enhancements in multi-117 carbon (C₂₊) production at lower overpotentials. Activity and selectivity trends are further 118 explored by comparing the formation of products accounting for electrode RF. More importantly, 119 the overpotential savings are proportional to the ratio of RFs between electrodes at similar 120 geometric current densities, regardless of the electrode architecture. We corroborate and 121 explain these findings via computational Multiphysics modeling of kinetics with local species 122 transport to estimate differences in microenvironment. Tafel parameters derived from the foil 123 electrodes are used to predict the current densities for GDEs of varying RF, showcasing RF 124 dependence. In this way, a more generalized catalyst-design criterion is established; namely, the 125 surface area should be targeted to specific current-potential regimes that enhance product 126 selectivity or increase energy efficiency.



$$\propto \frac{1}{RF}$$
 at constant current density

- 128 Figure 1. CO₂R electrode development strategy using RF
- 129 Effect of electrode roughness on geometric current density, electrochemical potential, and
- 130 major CO₂R product selectivity for liquid- and vapor-fed CO₂ reduction. Product groups are
- 131 defined as $2e^{-}$ single-carbon ($2e^{-}C_{1}$), > $2e^{-}$ single-carbon (> $2e^{-}C_{1}$), multi-carbon hydrocarbon (C_{2+}
- HC), and multi-carbon oxygenate (C_{2+} OXY). η and CO₂R Current Density represent overpotential
- 133 and geometric current density, respectively. Relationships of potential and current density (x-
- and y-axes, respectively) with respect to RF are depicted.

135 **2. Results and Discussions**

Planar Nanoflower Foil Electrodes A 1 µm С **Gas Diffusion Electrodes** Ε 240 G 14x NF 92x - NF 200 **Roughness Factor** 160 120 80 3x 40 РV́D PVD pc 0 Foil GDE-275 GDE-1000 Sample

136 **2.1.** Synthesis and characterization of electrode morphology

- 138 Figure 2. Nanoflower catalyst design and physical characterization
- 139 (A-D) top view SEM images of (A) foil polycrystalline copper, (B) foil nanoflower copper, (C) PVD
- 140 GDE, and (D) nanoflower GDE.
- 141 (E and F) Cross-section view SEM images of (E) PVD GDE, and (F) nanoflower GDE.
- 142 (G) Roughness factor comparisons of foil and GDE samples before and after nanoflower
- 143 formation.

144 To modulate the surface area of the active catalyst layer readily, we employed a facile 145 etching technique based on a previously reported procedure,³³ where $(NH_4)_2S_2O_8$ oxidatively etches the surface of polycrystalline copper foil³⁷ (foil-pc) to form 3-dimensional self-assembled 146 147 nanoflower structures (foil-NF) (Figure S2). The surface conversion from foil-pc (Figure 2A) to foil-148 NF (Figure 2B) was characterized by a scanning electron microscope (SEM), revealing significant 149 reconstruction from a smooth surface to a roughened porous flower-like network. For GDEs, we 150 formed electrodes containing Cu on porous expanded polytetrafluoroethylene (ePTFE) 151 substrates via physical vapor deposition (PVD) (Figure 2C), denoted as either GDE-275 or GDE-152 1000 depending on the deposited Cu thickness in nm. NF formation was translated to a GDE by employing the same procedure used on electrodes (referred to as GDE-275-NF and GDE-1000-153 154 NF), as exposure time and solution composition can modulate the electrode nanostructure and surface area.³³ Both top (Figure 2D) and cross-section (Figure 2F) SEM images of these electrodes 155 156 further show that the dense Cu layer formed by PVD (Figure 2E) results in a nanoflower structure, 157 similar in feature and pore size (~100-200 nm) as foil-NF (Figure 2B and S3). Additionally, we 158 validated the stability of this structure by conducting SEM after electrochemical testing, which 159 showed some sintering while the major morphological features are maintained (Figure S4). The 160 X-ray photoelectron spectroscopy (XPS) spectra of the Cu 2p region for the NF electrodes exhibited a broad peak at ~933.5 eV and satellite features in the range of 940-945 eV, both 161 corresponding to the Cu²⁺ oxidation state (Figure S5). Similarly, the corresponding X-ray 162 diffraction (XRD) patterns reveal the presence of CuO in agreement with Cu²⁺ observed via XPS 163 164 (Figure S6).

165 To estimate the ECSA of each electrode, we performed cyclic voltammetry to measure 166 the double-layer capacitance in a non-Faradaic potential window (Figure S7). The RF, defined as 167 the ratio of ECSA to geometric area of the electrode, resulted in values of 2 and 185 for foil-pc 168 and foil-NF, respectively (Figure 2G). This substantial increase of 92x in ECSA is likely due to large 169 amounts of Cu available within the foil-pc electrode that converted to NF. In comparison, GDE-170 275 and GDE-1000 resulted in comparable RFs of 11 and 13 before NF formation, respectively, 171 despite their difference in the catalyst-layer thickness; as bulk Cu atoms are shielded from the 172 electrolyte, they do not affect the ECSA measurements nor participate in CO_2R . After NF

formation the average RFs scaled with the PVD Cu thickness, with values of 33 (GDE-275-NF) and 185 (GDE-1000-NF). We found that nanostructuring an initial PVD layer of 1000 nm thickness (GDE-1000) led to a near identical roughness as that of the foil-NF. It is noted that while the wet etching process increases the ECSA, it does so by simultaneously altering both catalyst thickness and porosity (Figure 2E-F). The resulting increase in the ECSA for GDEs (3x and 14x as rough) is notably less relative to the foil electrodes due to higher ECSA of non-nanostructured GDE-275 and GDE-1000 samples (Table S7).



182

Figure 3. Potential shifts and fractional selectivity towards C₂₊ and C₁ products from CO₂ reduction

185 (A and B) CO₂R (A) and C₂₊ (B) partial current densities for foil electrodes (foil-pc and foil-NF)

and GDEs (GDE-1000 and GDE-1000-NF) at various operating potentials.

187 (C-F) Fraction of C₂₊ products (C) and C₁ products (D) for foil and GDEs with planar morphology.

188 Fraction of C₂₊ products (E) and C₁ products (F) for foil and GDEs with nanoflower morphology.

189 C_{2+} products divided into multi-carbon oxygenate (C_{2+} OXY) and multi-carbon hydrocarbon (C_{2+}

HC). C₁ products divided into two electron single carbon ($2e^{-}C_{1}$) and CH₄. Foil-pc data adapted

191 from previous work.²⁷

To understand the changes in the electrocatalytic activity and selectivity with changing electrode structure, we tested CO₂R performance under both liquid- and vapor-fed conditions using the same corresponding electrochemical reactor and underlying substrate. These comparisons are done by plotting the applied potential with respect to the standard hydrogen electrode (V_{SHE}), which allows for the assessment of trends based on an absolute potential reference and thus circumventing variable pH corrections and differences in electrolyte concentration. It is important to note that the GDEs can operate at much greater geometric current densities (J_{geo}) for CO₂R than the foils due to substantially increased diffusivity and smaller diffusion lengths of CO₂ in vapor- and aqueous phase, respectively.³⁹ Thus, any improvements in applied potential or J_{geo} will be conservative compared to those on the RHE scale (denoted as V_{RHE}), as the GDEs will result in a higher shift due to increased pH from higher J_{geo} . When comparing electrodes of the same architecture, we use V_{RHE} where appropriate (see SI). Additionally, the results shown at each current density were repeated three times to establish statistical significance, which exhibited reasonable standard deviations of the data (Table S1-S6).

206 Between the foils and GDEs, we observe a >310 mV potential difference between foil-pc 207 and GDE-PVD at a CO₂R J_{geo} of 10 mA cm⁻², highlighting the impact of increased CO₂ mass transport and higher ECSA within the GDEs.^{39,40} Within the same electrode architecture, there is 208 209 a positive shift in the operating potential window with the higher RF (NF morphology) electrodes (Figure 3A and B), alluding to the activation overpotential dependence on RF. At a CO₂R J_{geo} of 210 ~0.8 mA cm⁻², the foil electrodes resulted in a maximum potential shift of 460 mV. The GDEs 211 212 resulted in a smaller shift of 176 mV, as the RF ratio is smaller than that of the foil. For the thinner 213 GDE-275, there was an even smaller shift of 62 mV at the same CO₂R J_{geo} of 57 mA cm⁻² (Figure 214 S10). At a constant potential, the CO₂R J_{geo} increases by up to 16x with the foil-NF electrodes, 215 whereas up to 9.5x is achieved with the GDEs. In terms of $C_{2+} J_{geo}$, the shift in the potential range 216 for the foil electrodes is reduced to 320 mV, whereas the GDEs have largely maintained the 217 potential shift of 174 mV. Thus, the degree of overpotential shift can vary depending on the electrode type and operating potential window. We infer that the greater difference (460 – 320 218 219 mV) between the foil electrodes is due to CO, HCOO⁻, and CH_3COO^- being formed at lower 220 overpotentials due to an increased ECSA (Figure S11). Overall, this indicates that the increased 221 catalyst surface area helps to decrease the overpotentials in the predominantly activation-222 controlled regime, and thus increase energy efficiency, while maintaining the rate at which CO₂R 223 products are generated for both GDEs and foil electrodes.

The foil-NF electrode is highly selective towards two-electron single-carbon ($2e^{-}C_{1}$) products starting at $-0.49 V_{RHE}$ ($-0.89 V_{SHE}$) (Figure S8). Peak selectivity towards CO (72.2%) and HCOO⁻ (31.8%) are observed along with a modest 8.5% FE toward H₂; formation of these $2e^{-}$ products is due to the low overpotential similar to other reported high RF systems operating in

228 similar to more positive potentials.^{18,22,22,41–43} With increasing overpotentials (<-0.58 V_{RHE} or -229 0.98 V_{SHE}), higher selectivity towards C₂₊ products including C₂H₄, C₂H₅OH, C₃H₇OH, CH₃COO⁻, and 230 small quantities of C₂H₆ are measured. Furthermore, an oxygenate-to-hydrocarbon ratio of up to 231 11.8 is measured on the foil-NF at lower overpotentials (Figure S17). Previously, we observed this 232 enhanced C_{2+} oxygenate formation for CO_2R and CO reduction correlating with increased ECSA and low overpotentials.^{18,33} Additionally, the combination and increased quantity of oxide-233 derived active sites present in foil-NF may promote selectivity towards oxygenates.^{26,44,45} For GDE 234 235 samples, C₂H₄ formation on the NF samples exceeds that of both PVD samples at 71 mA cm⁻², 236 with lower selectivity towards C_2H_5OH and H_2 (Figure S9). Effects due to internal diffusion within 237 the pores such as trapping⁴⁶ and local pH changes may aid in the formation of further-reduced products at low J_{geo}.^{33,47} Our modeling analysis shows that sufficient CO₂ concentration (>21 mM) 238 239 and less alkaline pH are expected throughout the rougher, more porous catalyst layers, 240 supporting the aforementioned effects (Figures S38-39). However, the effects of decreasing pH 241 and CO₂ concentration are more pronounced at the higher current densities of 143 and 214 mA 242 cm⁻², resulting in the NF samples exhibiting lower selectivity towards C₂₊ products compared to 243 the thinner PVD catalyst layers.

244 To better understand the distribution of CO₂R products, the fractional selectivity for both 245 the foil and GDE is given in Figure 3C-F. The GDE-PVD demonstrates significantly greater C₂₊/CO₂R 246 ratio compared to that of the foil-pc electrode at similar applied potentials (Figure 3C). 247 Remarkably, C_{2+} oxygenates are observed at potentials as positive as $-1.26 V_{SHE}$ with the GDE, whereas only C₂₊ hydrocarbons are found in the case of the foil. This earlier onset corresponds 248 249 to higher oxygenate-to-hydrocarbon ratios on the GDE-PVD than the foil (Figures S17-18). 250 Additionally, the GDE shows a lower preference for C_1 formation compared to the foil (Figure 3D). 251 We posit this is due to enhanced C-C coupling with higher average CO₂ concentration throughout 252 GDEs (Figures S35 and S38) and a local pH effect caused by increased current density.²⁹ 253 Comparing foil electrodes, CH₄ is not observed on the foil-NF due to the overpotential shift being 254 in the positive direction while activation-controlled. For the foil-pc, CH₄ increases at potentials <-1.28 V_{SHE}, becoming the majority CO₂R product due to limited solubility of CO₂.³⁷ Despite these 255

256 differences, exclusive formation towards $2e^{-}$ products for both foil and GDE is observed at 257 potentials >-1.28 V_{SHE}, which is again attributed to the low overpotential.

258 Unlike the planar Cu morphology, greater C₂₊/CO₂R fractions are obtained with the foil-259 NF electrode under liquid-fed aqueous conditions compared to those of the GDE-1000-NF in a 260 similar potential window (-1.20 to -1.32 V_{SHE}) (Figure 3E). Relative to the foil, we see greater 261 fractions towards 2e⁻ product formation at higher overpotentials on the GDE due to *CO desorption when higher concentrations of CO₂ are present (Figure 3F).⁴⁸ However, this is 262 opposite for the NF morphology, which results in a higher oxygenate-to-hydrocarbon ratio for 263 264 the foil compared to the GDE (Figures S17-18). Because both electrodes exhibit similar 265 morphology, porosity (Figures 2F and S2), and RF (~185), we deduce that the increased oxygenate fraction on the foil-NF is likely influenced by differences in the microenvironment.¹² The 266 267 concentration and residence times of adsorbates can vary between electrode architectures at 268 lower current densities. For example, the GDE architecture may result in more effective removal 269 of hydroxide than the foil setup due to flowing electrolyte and CO₂ being fed on the GDL side, 270 which reduces local oxygen concentration and the propensity for oxygenate production. We 271 observe a clear preference towards C_{2+} production for all NF electrodes at potentials >-0.95 V_{RHE} (Figures S14-S16), with up to 10x enhancement in C_{2+}/CO_2R for the foil NF at ~-0.9 V_{RHE} (-1.3 V_{SHE}). 272 273 Thus, the influence from the combination of both electrode RF and microenvironment lead to 274 the observed enhancements in C₂₊ formation, not just the potential. Furthermore, the increase 275 of the C_{2+}/CO_2R ratios associated with the GDE-NF samples are not observed at potentials <-0.95 276 V_{RHE} (<-1.41 V_{SHE}) (Figures S14-16). The effects of ECSA on the current density-potential behavior 277 and product selectivity are more prominent in liquid-fed systems as compared to vapor-fed 278 systems at potentials more positive than $-0.95 V_{RHE}$, which may suggest decreasing influence 279 from local reaction environments in GDEs.

280





- 284 (A-C) ECSA-normalized partial current density towards (A) CO₂R products, (B) C₂₊ products, and
- 285 (C) C_1 products as a function of potential (V vs SHE) for foil and GDE samples. Blue oval in (A)
- 286 indicates J-V slopes towards CO₂R appear similar while activation-controlled.

287 Due to the importance of the local microenvironment and conditions on CO_2R selectivity, 288 we examine the data in terms of the local current density (i.e., ECSA-normalized) or average turnover frequency per active site for each electrode.⁴⁹ There is an increase in the ECSA-289 290 normalized current density (J_{ECSA}) towards CO₂R for the GDEs compared to foil electrodes (Figure 291 4A).⁴⁰ We identify the slopes for CO₂R activity to be similar for all the samples in this study prior 292 to mixed-control (shaded blue). Furthermore, the J_{ECSA} towards CO₂R for all GDE samples collapse onto a single curve, validating the observed potential shift associated with Jgeo under activation-293 294 control. Thus, we observe little to no enhancement in the intrinsic activity of Cu towards CO₂R 295 with increasing ECSA in the form of a GDE, similar to what is observed in liquid-fed systems using 296 foil electrodes.^{9,13}

297 To assess changes in product activity, we provide results for the individual products (Figures S19-S26), and C₂₊ (Figure 4B) and C₁ (Figure 4C) product groupings. The current-voltage 298 299 (J-V) slopes for C_2H_4 , C_2H_5OH , and C_3H_7OH appear consistent across all samples while in the 300 activation-controlled regime, suggesting the rate-limiting step plausibly remains unaffected 301 (Figure S22-S24).⁵⁰ The changing slope for CH_3COO^- compared to other C_{2+} products (Figure S25) 302 reinforces the hypotheses regarding ECSA and pH effects resulting in divergent reaction mechanisms for these products.^{51,52} However, the activities towards C₂₊ products show light 303 304 promotion ascribed to the NF GDEs. While the foil-NF sample appears to suppress both CO₂R and 305 HER (Figure S26) when compared to foil-pc, it promotes C_{2+} product formation by an order of 306 magnitude (~10x at -1.15 V vs SHE). The average number of electrons per molecule reaffirms 307 that the formation of C₂₊ products is achieved with the rougher NF samples at lower 308 overpotentials (Figure S28). We infer the contribution on C_{2+} product activity from changing ECSA 309 and morphology may be larger for liquid-fed CO₂R on foil electrodes than vapor-fed CO₂R on 310 GDEs. Additionally, the discernable asymptotic and/or decreasing J_{ECSA} indicates the samples may 311 be entering a mixed-control regime at varying potentials.

The enhancements in C_{2+} products suggest a corresponding suppression of C_1 product formation with all NF electrodes (Figure 4C). The NF samples show poor activity towards HCOO⁻ compared to the planar counterparts (Figure S20). The suppression of this terminal reaction pathway leads to the formation of *CO, the common intermediate for all other CO₂R products.⁹

316 The overall product distribution supports the preference for *CO dimerization, as CO formation 317 is also suppressed on the NFs like HCOO⁻ (Figure S19). Additionally, little to no formation of CH₄ 318 on the NFs leads to a combined lower J_{ECSA} towards C₁ products (Figure S20). Interestingly, the 319 GDE-1000-NF has a lower fraction of products going through the COR pathway compared to foil-320 NF (Figure S29); we posit the effects of concentration overpotential and lower residence times 321 of adsorbed intermediates on the NF GDEs may allow for more facile *CO desorption. 322 Additionally, this may be related to the quantity of hydrogen evolving; the activity towards 323 hydrogen results in similar J-V slopes for all NF electrodes, whereas asymptotic regions are 324 present on the foil-pc and PVD electrodes where CO_2R is dominant (Figure S26). Based on this 325 analysis, we provide insight onto the varying contributions of microenvironment and morphology 326 on product activity and selectivity.

327 2.4. Investigating RF influence on overpotential shift via analytical and modeling 328 approaches







(A) Potential (V vs. SHE) resulting from various applied current densities obtained with the four

333 GDEs from experiment (scatter), and the predicted relationship from the model using an 334 average of $6e^{-}$ per CO₂ (solid and dashed lines).

(B) Potential shift resulting from six possible combinations of RF ratios from the four GDE

samples (scatter) and the model prediction using the Tafel parameters extracted from Figure 5A(line).

338

To probe further the relationship between RF and overpotential shift, we simulate the effects using a 1D, steady-state GDE catalyst-layer model for CO₂R and HER reactions (complete description in Section S3). We account for CO₂R and HER by using single electrochemical reactions with the average electrons passed per product; two electrons for HER and 5-6 electrons per CO₂ molecule reduced. This is based on the observation that the majority species are two-carbon products within the potential range that was tested as shown in the experimental data (Figure S28)):

346
$$CO_2 + H_2O + 6e^- \rightarrow \text{products} + 6 \text{ OH}^-, \quad U^0 = 0.02 \text{ V vs RHE}$$

347
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-, \qquad U^0 = 0.00 V \text{ vs } RHE$$

348 This reaction kinetics are modeled using the Tafel expressions,

$$j_{CO_2R} = j_{CO_2R,0} \left(\frac{c_{CO_2}}{c_{CO_2^{ref}}} \right) \exp\left(\frac{\alpha_{CO_2R}F}{RT} \left(\phi_s - \phi_l - \left(U_{CO_2R}^0 - \frac{2.303RT}{F} \, \text{pH} \right) \right) \right)$$
(1)

$$j_{\rm HER} = j_{\rm HER,0} \exp\left(\frac{\alpha_{\rm HER}F}{RT} \left(\phi_s - \phi_l - \left(U_{\rm HER}^0 - \frac{2.303RT}{F}\,{\rm pH}\,\right)\right)\right).$$
(2)

The Tafel parameters (α_{CO_2R} , α_{HER} , $j_{CO_2R,0}$ and $j_{HER,0}$) are determined using a pHcorrected foil electrode model (complete description in Section S3.1). Piecewise-linear and linear fits accurately describe the foil data from the foil-pc and foil-NF samples, respectively (Figure S35). The electrochemical reaction rate for species *i* is calculated as

$$R_i = \sum_h \frac{a_v v_{i,h} j_h}{n_h F} \tag{3}$$

where $v_{i,h}$ is the stoichiometric coefficient for species *i* in electrochemical reaction *h*, n_h is the number of electrons in electrochemical reaction *h*. The specific surface area is calculated using the dimensions and measured ECSA of each catalyst layer, which is normalized by the roughness factor of the foil electrode data that was used to fit the kinetics,

$$a_{\nu} = \frac{RF_{\rm GDE}}{RF_{\rm foil}} \cdot \frac{1}{L_{CL}} \cdot S \tag{4}$$

357 where S is the saturation. The saturation accounts for the fraction of the catalyst layer surface 358 that is not wetted by the electrolyte and a value of 0.64 is assumed for an ideally-wetted catalyst 359 layer.⁵³ Dividing the RF of the GDE by the RF of the foil-NF electrode normalizes the exchange 360 current densities to the ECSA at which the kinetic parameters were extracted. By incorporating CO₂ and ion-transport effects, electrode parameters, and bulk electrolyte reactions (as described 361 by Weng et al.),⁵³ we predict the J-V relationships for the four GDEs labeled by their RFs (Figure 362 363 5A). The results show that the Tafel fit to the foil-NF data, when scaled by ECSA, give an accurate 364 prediction of the J-V relationships for all GDE samples. Additionally, there was little sensitivity to 365 the average number of electrons between five and six (Figure S41). This suggests that our 366 utilization of ECSA in the modified Tafel description is a valid method for estimating the trend of 367 decreasing overpotential with increasing RF for the GDEs.

368 We then determined six RF ratios (dividing any two electrode RFs) from combinations of 369 the four GDE samples (Figure S31A). Further comparison of the modeling results provided a semi370 logarithmic relationship between the ratio of RFs and the difference in applied potentials at 71 371 and 143 mA cm⁻² (Figure 5B). The computational model predicts similar shifts in potential for the 372 various RF ratios, further corroborating the use of the number of electrons per CO_2 molecule as 373 an effective approach towards understanding activity relationships between HER and CO₂R. 374 Furthermore, these results suggest some proportional dependence of overpotential shift on the 375 ratio of RFs (Figure S31), despite the complex reaction networks on the catalytic surface. These differences are exacerbated at a J_{geo} of 214 mA cm⁻², where a notable deviation from linearity is 376 377 observed along with increased deviations between sample potentials (Figure S32). The surface 378 CO₂ concentration from the model indicates a drastic decrease with thicker electrodes and a 379 commensurate increase in the local pH at high current densities (Figures S38-39). Additionally, 380 we posit observations including increased overpotential (due to low CO₂ concentration) and 381 hydrogen evolution are indicative of entering a mixed-control regime.

The resulting slopes of 151 mV dec⁻¹ (at 71 mA cm⁻²) and 128 mV dec⁻¹ (at 143 mA cm⁻²) 382 383 vary due to the differences in catalyst-layer thickness, morphology, and product selectivity within 384 each combination of electrodes. Additionally, the contributions from surface faceting cannot be 385 ignored and are also tied to the applied potential.²⁸ We extend this analysis by measuring the 386 current-potential slopes from the J_{ECSA} of the total and CO₂R reactions showing 123 and 116 mV 387 dec⁻¹, respectively (Figure S30). This is in agreement with the slopes of potential shift vs RF ratio, 388 which are in fact both b according to the definition of the Tafel expression (full the derivation in 389 the SI). Specifically, the slopes obtained using potential shifts at a total J_{geo} of 143 mA cm⁻² from 390 both the experiment (128 mV dec⁻¹), and the model (123 mV dec⁻¹) are comparable. This is likely 391 due to the majority of total current being comprised of CO₂R current, thereby the slope derived 392 from J_{CO2R} results in a similar value of 116 mV dec⁻¹. We observe that the above trends in potential 393 shift and RF ratio apply across all electrodes in this work, regardless of electrode architecture 394 (Figure S33). At any near-equivalent value of J_{geo} for total and CO₂R reactions, the range of 395 potential shifts increases with RF. These results signify RF/ECSA as an important descriptor for 396 developing computational models that deepen our understanding of current-potential 397 relationships. A more robust model including microkinetic parameters for various intermediates 398 and mechanisms can further elucidate the dependence on RF.

399 **3. Conclusion**

400 In this work, we identify and bridge knowledge gaps between liquid- and vapor-fed CO_2 401 reduction systems, using active surface area as a descriptor to understand the effects of changing 402 local environments and resultant activity and selectivity trends. For the liquid-fed CO₂R system, 403 the Cu foil-NF electrode demonstrates up to 735x increase in geometric current density towards 404 CO_2R (-0.75 V vs RHE) and an overpotential shift up to 460 mV compared to the foil-planar. A 405 preference towards multi-carbon products (>95% of CO_2R is C_{2+}) is observed as compared to the 406 foil-pc from previous work. Within vapor-fed devices, rougher GDEs provide similar overpotential 407 shifts (170 mV) and geometric current-density enhancements (10x towards CO₂R). Such 408 overpotential shifts can lead to increased energy efficiency while maintaining a desired current 409 density, however, selectivity trends do not necessarily extend between electrode architectures. 410 Additionally, the NF morphology prefers multi-carbon product formation on an activity basis, 411 even though the J-V slopes from the ECSA-normalized current densities from different electrodes 412 are similar. With a 1D computational model using a simplified Tafel-description, the observed 413 potential shifts are strongly suggested to be related to the RF ratios of electrodes when 414 activation-controlled. Through this comparative investigation, we demonstrate a general 415 strategy that utilizes electrode engineering efforts to translate foil electrodes from liquid-fed to 416 GDEs for more industrially relevant operating conditions. Our approach towards understanding 417 the interplay of current-potential relationships, electrode formulation, and local reaction 418 environment can be applied to a variety of systems and reactions for improved design and 419 performance.

420

421 **4. Methods**

422 4.1. Electrode Preparation and Characterization

423 A cleaned and polished copper foil was immersed in an aqueous solution containing 0.25 424 M sodium hydroxide and 62.5 mM ammonium persulfate at 60 °C for one hour to form cupric 425 oxide nanoflowers (See SI for full preparation procedure). The same procedure was used to make 426 the nanostructured GDE samples from a layer of copper deposited via e-beam physical vapor 427 deposition on the expanded polytetrafluoroethylene (ePTFE) gas-diffusion-layer (GDL) substrate. 428 The as-prepared electrodes were characterized by scanning electron microscopy (SEM) to 429 confirm nanoflower morphology, and focused ion-beam (FIB) SEM was used to measure 430 electrode thicknesses. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) were 431 used to confirm the oxidation and crystal structure of the copper catalyst, respectively. The 432 electrodes were electrochemically pre-reduced prior to performing CO₂ reduction at a potential 433 of -0.75 V vs Ag|AgCl, the electrochemically active surface area (ECSA) was determined by 434 performing double-layer capacitance measurements via cyclic voltammetry (CV).

435 **4.2. Elect**

4.2. Electrochemical Evaluation

436 For the liquid-fed system, a CO₂-saturated 0.1 M KHCO₃ electrolyte was fed with 437 humidified CO₂ at the flow rate of 20 sccm. For the vapor-fed system, CO₂ gas at 10 sccm is 438 directly introduced to the backside of the GDE in addition to the CO₂-saturated 1 M KHCO₃ 439 electrolyte at the front of the GDE. For the liquid-fed system, chronoamperometry was used for 440 1 hour, while chronopotentiometry was used for vapor-fed analyses. IR-compensation was 441 performed by an average of measured resistances (taken every three minutes) over the 442 electrolysis period. The entire protocol was repeated three times to confirm reproducibility for 443 each condition.

444 **4.3. Reactor and System Set Up**

445 A custom polycarbonate electrochemical cell and advanced manufactured 446 electrochemical cell was used for liquid-fed and vapor-fed CO₂R experiments, respectively.^{33,38}

Both cells formed a three-electrode system: (1) foil and gas diffusion electrodes were used as working electrodes and exposed to the electrolyte; (2) a platinum foil (Alfa Aesar; 99.99% trace metals basis) and IrO₂ (Dioxide Materials) were used as counter electrodes for liquid-fed and vapor-fed systems, respectively; (3) an Ag/AgCl electrode was used as the reference electrode through a Luggin capillary. Anion-exchange membranes comprised of (Selemion AMV, AGC Inc.) and Fumasep were used in between the working and counter electrode compartments for liquid-453 and vapor-fed systems, respectively.

454 4.4. Product Analysis

455 Product identification and quantification were conducted according to protocols described in detail in our previous work.^{29,37,38} For each tested operating condition, 1 mL of 456 457 reactor exhaust gas was injected multiple times into a GC (SRI Instruments; Multiple Gas #3, 458 8610C) during the electrolysis period to analyze the concentration of products in the gas phase. 459 After CA/CP measurements, the electrolyte was collected, and then the liquid-phase products 460 were analyzed by using water suppression ¹H NMR (600 MHz, Varian Inova and 500 MHz, Avance 461 III HD Bruker with Prodigy cryoprobe). The anolyte was also analyzed in the same way to account 462 for acetate and formate species that crossed over the membrane due to their anionic character.

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610 6. Acknowledgements

611 This work was performed at both the Department of Chemical Engineering at Stanford University 612 and Lawrence Livermore National Laboratory, funded by a cooperative research and 613 development agreement with TOTAL American Services, Inc. (affiliate of TOTAL SE) under 614 agreement number TC2307. This work was performed under the auspices of the U.S. Department 615 of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and 616 was supported by Laboratory Directed Research and Development funding under project 19-SI-617 005. Project conceptualization and liquid-fed CO_2 reduction experiments was performed by 618 Daniel Corral, Stephanie Nitopi, and Lei Wang with the Joint Center for Artificial Photosynthesis, 619 a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department 620 of Energy under Award Number DE-SC0004993. Alex King was supported by a NSF Graduate 621 Fellowship (DGE 1752814) and along with Adam Weber acknowledge support from the Liquid 622 Sunlight Alliance, which is supported by the U.S. Department of Energy, Office of Science, Office 623 of Basic Energy Sciences, Fuels from Sunlight Hub under Award Number DE-SC0021266. Daniel 624 Corral thanks the Stanford Graduate Fellowship, as well as the GEM Fellowship at Stanford 625 University and Lawrence Livermore National Laboratory. The authors thank and appreciate 626 guidance and discussions from colleagues including Julie Hamilton, Dr. Alan Landers, David Koshy, 627 Kabir Abiose, Dr. McKenzie Hubert, Kyra Yap, Prof. Carlos Morales-Guio, Prof. Andrew Wong, 628 Prof. Drew Higgins, Dr. Shaffiq Jaffer, and Dr. Amitava Sarkar. The authors thank Alex King and 629 Dr. Adam Weber for modeling guidance and helpful discussions. The authors thank the Nuclear 630 Magnetic Resonance Spectroscopy Facilities, and part of this work was performed at the Stanford 631 Nano Shared Facilities (SNSF), supported by the National Science Foundation under award ECCS-632 2026822. The authors thank Maryann C. Tung for collecting SEM images using FIB. The authors 633 thank the Nuclear Magnetic Resonance Spectroscopy and Cleanroom Facilities at Lawrence 634 Livermore National Laboratory.

636 **7. Author contributions**

- 637 D.C. and D.L. contributed significantly and equally to this work. Writing original draft: D.C.,
- 638 D.L., V.M.E., S.N., and J.E.A.; Writing Review & Editing: D.C., D.L., V.M.E., S.N., J.E.A., L.W.,
- A.J.K., J.T.F., Y.L., A.Z.W., S.E.B., E.B.D., V.A.B., C.H., and T.F.J.; Conceptualization: D.C., D.L., S.N.,
- and L.W.; Investigation: D.C., D.L., V.M.E., S.N., J.E.A., L.W., and A.J.K.; Methodology: D.C., D.L.,
- 641 V.M.E., J.E.A., A.J.K., and V.A.B.; Formal Analysis: D.C., J.E.A., V.M.E., A.J.K., A.Z.W., and V.A.B.;
- 642 Software: V.M.E., A.J.K., A.Z.W., and V.A.B.; Validation: D.C., D.L., S.N., V.M.E., J.E.A., L.W., J.T.F.,
- 643 Y.L., and V.A.B.; Project Administration: D.C., D.L., S.E.B., E.B.D., V.A.B., C.H., and T.F.J.; Funding
- 644 Acquisition: D.C., A.J.K., A.Z.W., S.E.B., E.B.D., V.A.B., C.H., and T.F.J.

646 8. Author Information

647	Daniel Corral	0000-0003-0778-4832
648	Dong Un Lee	0000-0001-7591-5350
649	Victoria M. Ehlinger	0000-0001-7333-1271
650	Stephanie Nitopi	0000-0001-6815-0628
651	Jaime E. Avilés Acosta	0000-0002-2259-1935
652	Lei Wang	0000-0002-1931-7767
653	Alex J. King	0000-0002-3156-1607
654	Jeremy T. Feaster	0000-0003-0729-9650
655	Yi-Rung Lin	0000-0003-0331-3822
656	Adam Z. Weber	0000-0002-7749-1624
657	Sarah E. Baker	0000-0003-4695-3918
658	Eric B. Duoss	0000-0002-5473-2528
659	Victor A. Beck	0000-0002-0625-9545
660	Christopher Hahn	0000-0002-2772-6341
661	Thomas F. Jaramillo	0000-0001-9900-0622