



Local microenvironment tuning induces switching between electrochemical CO₂ reduction pathways

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1 **Local microenvironment tuning induces switching between**
2 **electrochemical CO₂ reduction pathways**

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32

33 Abstract

34 Gas diffusion layers (GDL) have become a critical component in electrochemical CO₂ reduction
35 (CO₂R) systems because they can enable high current densities needed for industrially relevant
36 productivity. Besides this function, it is often assumed that the choice of catalyst and electrolyte
37 play much more important roles than the GDL in influencing the observed product selectivity.
38 Here, we show that tuning of the GDL pore size can be used to control the local microenvironment
39 of the catalyst and hence, effect significant changes in catalytic outcomes. This concept is
40 demonstrated using sputtered Ag films on hydrophobic PTFE substrates with 6 different pore sizes.
41 Although Ag is known to be a predominantly CO generating catalyst, we find that smaller pore
42 sizes favor the generation of formate up to a Faradaic efficiency of 43%. Combined experimental
43 and simulation results show that this is due to the influence of the pore size on CO₂ mass transport,
44 which alters the local pH at the electrode, resulting in reaction pathway switching between CO and
45 formate. Our results highlight the importance of the local microenvironment as an experimental
46 knob that can be rationally tuned for controlling product selectivity: a key consideration in the
47 design of CO₂R systems.

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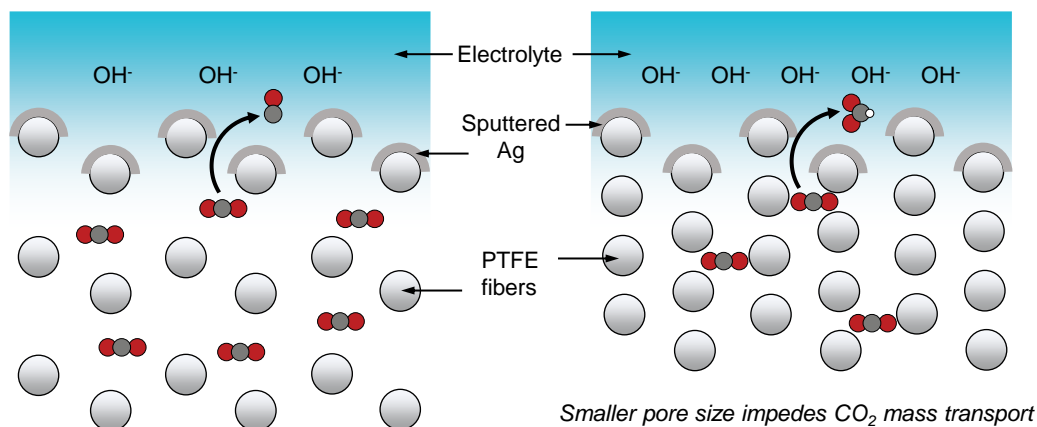
49 **Introduction**

50 Renewable electricity powered electrochemical CO₂ reduction (CO₂R) is a promising strategy for
51 the conversion of carbon dioxide emissions into value-added chemicals and fuels¹⁻¹¹. For this
52 technology to become economically competitive, recent technoeconomic analysis^{12,13} emphasizes
53 the importance of achieving higher current densities, energy efficiency and Faradaic efficiency
54 (FE). As a result, a significant amount of research in this field has been devoted to discovering and
55 designing new catalyst systems for facilitating CO₂R with improved performance¹⁴⁻²¹. The
56 electrolyte is known to be a key factor as well. For example, it was discovered that larger alkali
57 metal cations (Cs⁺) are more beneficial towards promoting CO₂R as compared to when smaller
58 cations (Li⁺) are employed²²⁻²⁵.

59 Furthermore, the reactor system has also been shown to be important. In the majority of early
60 reports in the field, CO₂R was conducted in H-type cells where CO₂ is introduced into the system
61 via continuous bubbling into the electrolyte^{26,27}. However, the low solubility of CO₂ (33 mM)
62 typically results in limiting current densities of only several tens of mA/cm² due to significant
63 mass transport limitations. To raise current densities towards industrially relevant productivity,
64 catalyst particles are deposited onto gas diffusion layers (GDL), allowing CO₂ mass transport
65 limitations to be overcome²⁸⁻³⁴ and enabling current densities of >100 mA/cm². This is due to the
66 hydrophobic and porous nature of the GDL, resulting in the creation of thin layers of electrolyte
67 over the catalyst particles. These thin layers of electrolyte have significantly lower CO₂ transport
68 diffusion lengths, thus facilitating rapid supply of reactants to the catalyst surface. Beyond this
69 role, it is often assumed that the choice of catalyst material and electrolyte play more dominant
70 roles compared to the GDL in controlling the observed product selectivity.

71 Although the mass transport of CO₂ through the GDL should in principle be rapid, it is known
72 that its effective diffusion coefficient is related to the porosity and average pore radius of the
73 porous medium through the Bruggeman relationship³⁵. We therefore reasoned that tuning these
74 parameters could be used to influence the mass transport of CO₂, which directly impacts the
75 catalyst microenvironment (local pH and CO₂ reactant supply). This is because CO₂ molecules can
76 directly react with and hence neutralize electrochemically generated OH⁻ to form bicarbonate and
77 carbonate anions^{27,36}. The altered microenvironment could in turn result in a significant change in
78 catalytic outcomes: an additional experimental knob to control CO₂R selectivity beyond catalyst
79 design and choice of electrolyte.

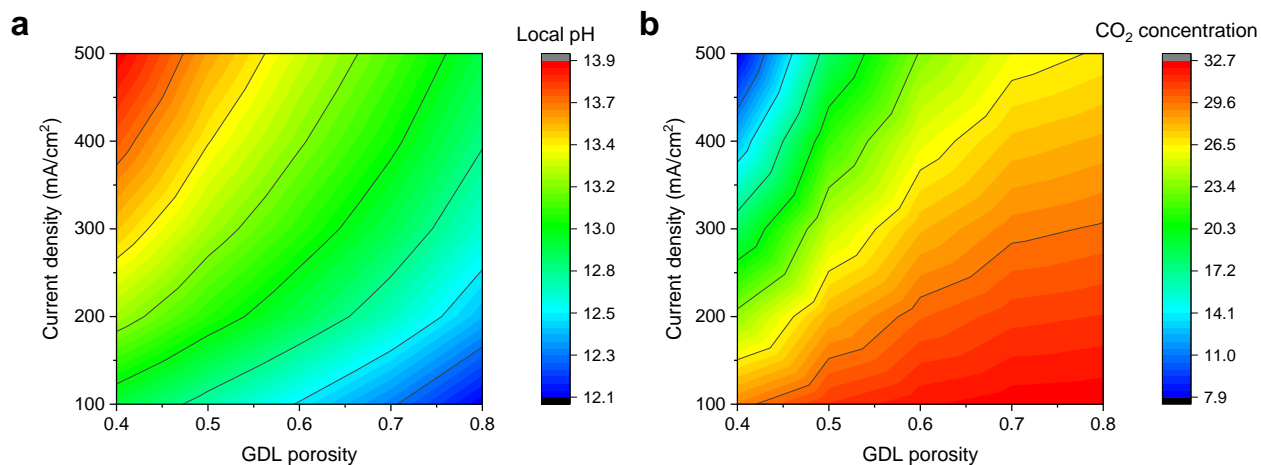
80 In this work, we demonstrate this concept using sputtered Ag films onto hydrophobic PTFE
81 substrates with 6 different pore sizes as the GDL^{37,38} (Schematic 1). Even though Ag is well known
82 to predominantly produce CO³⁹⁻⁴³, we find that smaller PTFE pore sizes favor formate production
83 up to a FE of 43%. Combined experimental and simulation results show that a decrease in GDL
84 pore size slows down CO₂ mass transport, leading to a higher local pH and hence reaction pathway
85 switching from CO to formate. This pH trend was confirmed using a confocal microscopy
86 setup^{44,45} equipped with a custom-built electrochemical cell and a pH sensitive fluorescent dye in
87 the electrolyte. Our results highlight the importance of the properties of the GDL, which can
88 significantly impact the catalyst local microenvironment and should be an important consideration
89 for the design of CO₂R systems.



91 **Schematic 1.** CO₂ mass transport through the gas diffusion layer is slower with a smaller GDL
92 pore size. This results in a higher local pH, which then induces a higher selectivity towards formate.
93 Note: items in the schematic are not drawn to scale.

94 Results and Discussion

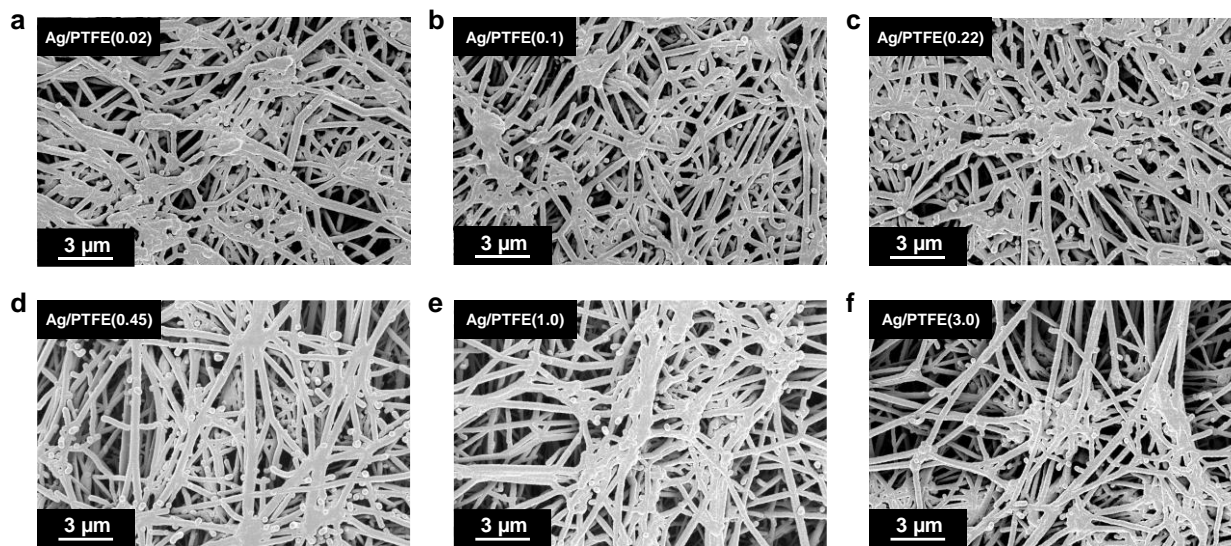
95 To lend support to our hypothesis, we first turned to Multiphysics simulations³⁵ (see methods
96 section in supplementary information) to understand the impact of the GDL porosity on the local
97 pH of the electrode during CO₂R. In our simulations, we varied the porosity values from 0.4 to 0.8
98 and obtained the steady-state results through a series of applied current densities. Fig. 1 shows the
99 simulation results, and we observed a qualitative trend of lower pH and higher CO₂ concentration
100 as the porosity of the diffusion medium increases. This is consistent with the notion that a lower
101 porosity can indeed impede CO₂ mass transport, hence resulting in changes in the reaction
102 microenvironment of the catalyst.



103

104 **Fig 1.** Multiphysics simulation results of varying GDL porosity on the (a) local pH and (b) CO₂
105 concentration at various cathodic current densities of 100, 200, 300, 400 and 500 mA/cm². A lower
106 porosity is observed to result in a higher local pH and lower CO₂ concentration. Detailed results
107 can be found in the Supporting Information (Fig. S1 to S6)

108 Encouraged by these results, we began by sputtering 325 nm thick Ag films onto hydrophobic
109 PTFE^{37,38} substrates with different pore sizes of 0.02, 0.1, 0.22, 0.45, 1.0 and 3.0 μm for use as gas
110 diffusion electrodes (Fig. S7). Each electrode will hence be termed as Ag/PTFE(X), where X is
111 the pore size. Top-down scanning electron microscopy (SEM) images show the structure of these
112 electrodes, with a web-like morphology of interconnected PTFE fibers coated conformally with
113 Ag (Fig. 2). These SEM images reveal the 3D network of macro-scale pores that are inherently
114 formed between the fibers, serving as pathways for reactant and product transport (Fig. S8 to S10).
115 As would be expected, the PTFE substrates with larger pore sizes appear visibly more open and
116 less dense.

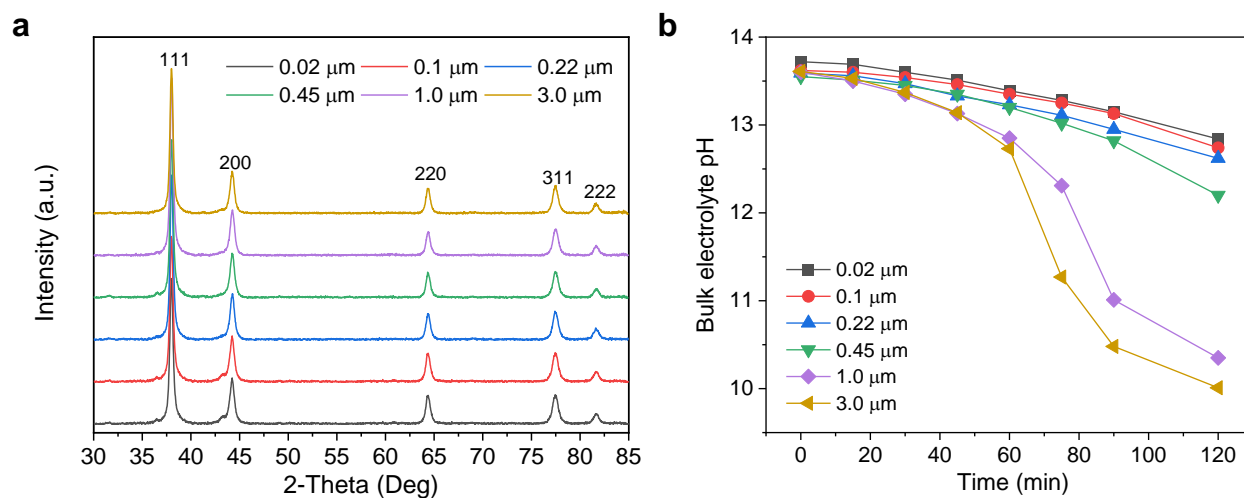


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118 **Fig. 2** SEM images of hydrophobic PTFE substrates of various pore sizes coated with 325 nm of
119 Ag using sputter deposition. The pore sizes are: (a) 0.02 μm, (b) 0.1 μm, (c) 0.22 μm, (d) 0.45 μm,
120 (e) 1.0 μm and (f) 3.0 μm. Digital photographs (Fig. S7) and more SEM images (Fig. S8 to S10)
121 of the samples can be found in the Supporting Information.

122 X-ray diffraction (XRD) characterization of the electrodes was performed (Fig. 3a), with Ag
123 (111) observed as the dominant crystal facet and with no obvious differences between each of the
124 Ag/PTFE with various GDL pore sizes. We also carried out cyclic voltammetry in a potential range
125 where only non-faradaic processes occur to determine the double layer capacitance of each
126 Ag/PTFE electrode (see methods section in Supporting Information). This gives an indication of
127 the electrochemically active surface area (ECSA) since this value is directly proportional to the
128 double layer capacitance⁴⁶. The results (Fig. S11 and S12) show that despite pore size differences,
129 the double layer capacitance and hence ECSA remains approximately within the same order of
130 magnitude.

131 We then designed experiments to obtain a qualitative measure of the CO₂ mass transport for
132 the different pore size Ag/PTFE electrodes. Each electrode was assembled into a gas diffusion
133 flow cell system (Fig. S13), with a similar design to what was previously reported in the
134 literature^{30,37}. 15 ml of 1 M KOH was used as the electrolyte, which was continuously recirculated
135 between the cathode chamber and an external centrifuge tube reservoir using a peristaltic pump.
136 CO₂ was flowed at a rate of 20 sccm, through a gas chamber in contact with the backside of
137 Ag/PTFE. Without applying any current, we monitored the bulk pH of the electrolyte over a 120
138 min period by placing a pH probe into the external centrifuge tube reservoir. The results in Fig. 3b
139 show that the bulk pH decreases significantly with time, as a result of the CO₂ gas continuously
140 diffusing from the backside of the Ag/PTFE and reacting with hydroxide in the electrolyte to form
141 carbonate³⁶. We also observe that the bulk pH decreases more rapidly with increasing PTFE pore
142 size. Importantly, this allows us to experimentally confirm that larger pore sizes do indeed
143 facilitate faster CO₂ mass transport.

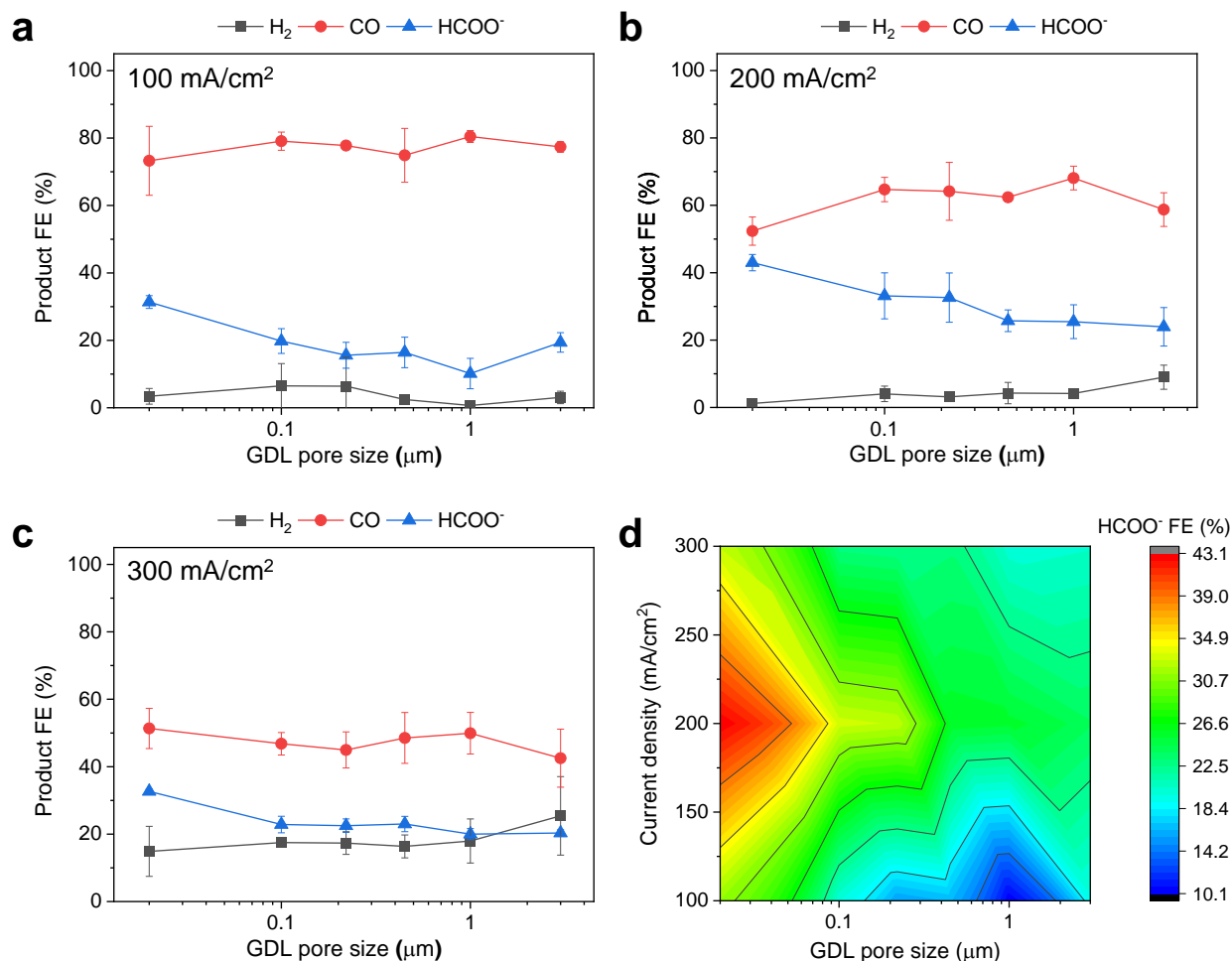


144
145 **Fig. 3** (a) XRD spectrums of Ag sputtered onto PTFE substrates with various pore sizes. (b)
146 Evolution of the bulk electrolyte pH over a 120 min period, with no current applied to the system.

147 15 ml of 1 M KOH was used as the electrolyte and was continuously recirculated through the
148 electrochemical cell using a peristaltic pump.

149 Next, we sought to assess the influence of PTFE pore size on the product selectivity of the
150 Ag/PTFE catalysts. Using the same flow cell system, we evaluated each Ag/PTFE under cathodic
151 current densities of 100, 200 and 300 mA/cm² in 1 M KHCO₃ electrolyte and the FE data are
152 shown in Fig. 4a-c. Based on the results, we observe that the formate FE appears to increase with
153 decreasing pore size, from 24% for Ag/PTFE(3.0) up to a value of 43% for Ag/PTFE(0.02) at 200
154 mA/cm². For better visualization, the formate FE is also presented as a contour plot (Fig. 4d),
155 where the general trend of higher formate FE with smaller pore sizes is observed to hold true for
156 all tested current densities. Also, the hydrogen FE tends to increase with larger pore size. These
157 combined effects result in the CO FE initially increasing with pore size and then decreasing again,
158 with a peak value of around 80% at 100 mA/cm² for Ag/PTFE(1.0).

159 Based on the bulk pH monitoring and simulation results, we hypothesized that this could be
160 due to reduced CO₂ mass transport at the smaller pore sizes, resulting in a higher local pH and,
161 thus, switching selectivity towards formate. This selectivity switching was previously observed by
162 Seifitokaldani et al., where CO₂R was performed with Ag catalysts in KOH electrolyte⁴⁷ with
163 concentrations ranging from 0.1 M to 11 M. It was found that formate was produced with almost
164 60% FE in 11 M KOH, compared to only about 4% in 0.1 M KOH. Using DFT simulations, they
165 concluded that this was due to the activation energy barrier for formate becoming lower than that
166 compared to CO, in the absence of hydronium ions.



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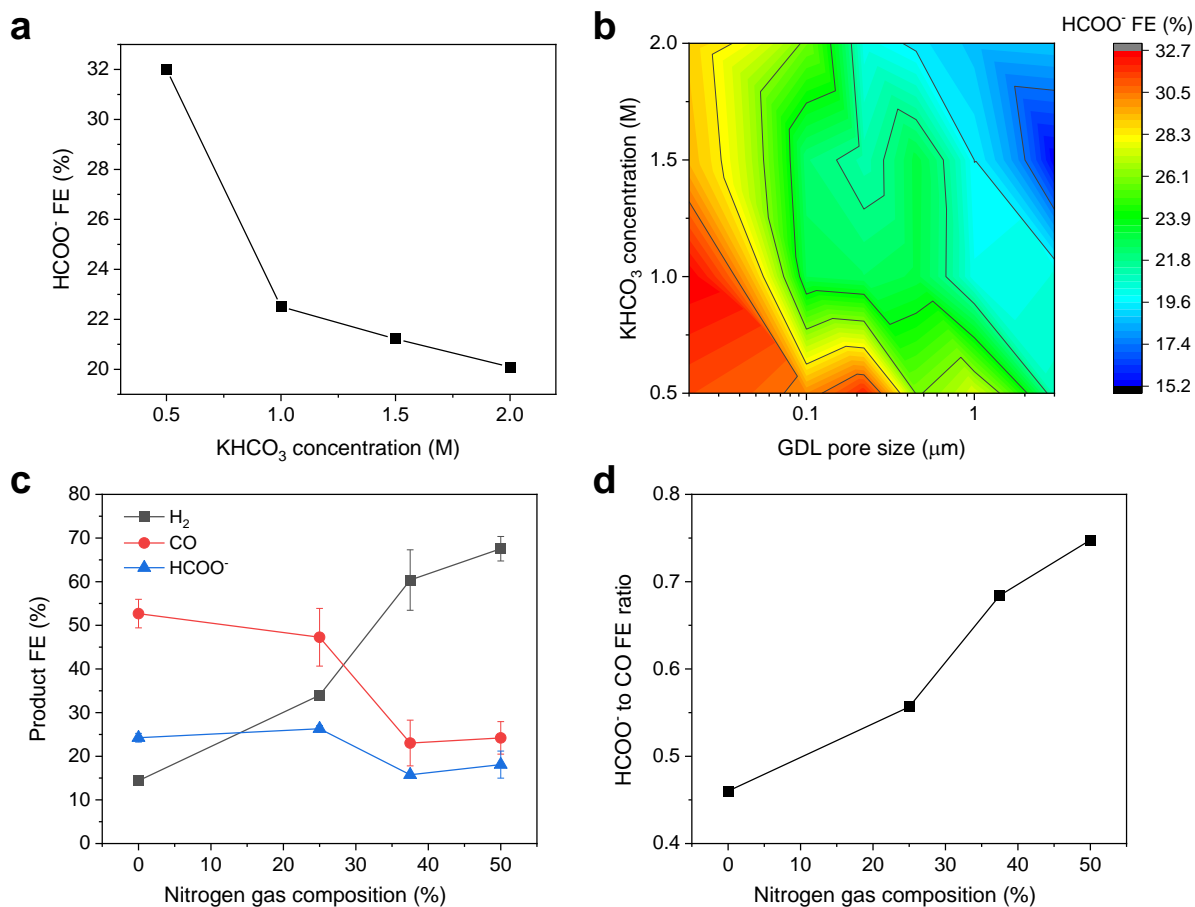
168 **Fig. 4** Electrochemical CO₂ reduction FE results with 1 M KHCO₃ as the electrolyte. (a), (b) and
 169 (c) show the product FE data for Ag/PTFE as a function of GDL pore size under cathodic current
 170 densities of 100, 200 and 300 mA/cm² respectively. (d) is the corresponding color contour map of
 171 the HCOO⁻ FE data for Ag/PTFE as a function of current density and GDL pore size. More data
 172 available in the Supporting Information (Fig. S16).

173 Hence, we employed a suite of experiments to further understand these initial observations
 174 and verify our working hypothesis. Firstly, we tested the Ag/PTFE catalysts in 2 M KHCO₃, which
 175 has a stronger pH buffering ability as compared to 1 M KHCO₃⁴⁸. In this case, we did not observe
 176 any significant differences in the formate FE as a function of GDL pore size (Fig. S14a-b) at

177 cathodic current densities of 100 and 200 mA/cm². This suggests that the stronger buffer results in
178 a similar local pH value for each of these cases, leading to a similar formate FE of around 14%.
179 However, at the higher current density of 300 mA/cm², the trend of higher formate FE with smaller
180 pore size appears again (Fig. S14c), with a FE of 19% for Ag/PTFE(3.0) as compared to a FE of
181 29% for Ag/PTFE(0.02). This results from the expected higher local pH rise with a larger current
182 density and is therefore consistent with the notion that pH effects are indeed influencing the
183 observed FE to formate.

184 To further investigate the effect of buffering, similar CO₂R experiments were carried out with
185 additional buffer conditions of 0.5 M and 1.5 M KHCO₃ at 300 mA/cm² for each pore size
186 condition. The results for Ag/PTFE(0.22) are represented in Fig. 5a, where a trend of higher
187 formate FE with lower buffer concentration is observed. This is because lower buffer
188 concentrations result in a higher local pH⁴⁸, which then promotes the conversion of CO₂ to formate.
189 Formate FE for all Ag/PTFE samples under the different buffer conditions are shown as a colour
190 contour map (Fig. 5b), where the trend of higher formate FE with a lower buffer concentration is
191 observed to hold true for all GDL pore sizes.

192 We also carried out CO₂R electrolysis experiments where the CO₂ feed was diluted with N₂.
193 For a lower CO₂ partial pressure, we expect the local pH to be higher due to fewer available CO₂
194 to react with electrochemically formed OH⁻. For these experiments, Ag/PTFE(0.45) was used as
195 the electrode and a constant current density of 300 mA/cm² was applied. From the results (Fig 5b
196 and 5c), we observe that lower CO₂ partial pressures do indeed result in a higher formate to CO
197 ratio, consistent with our working hypothesis.

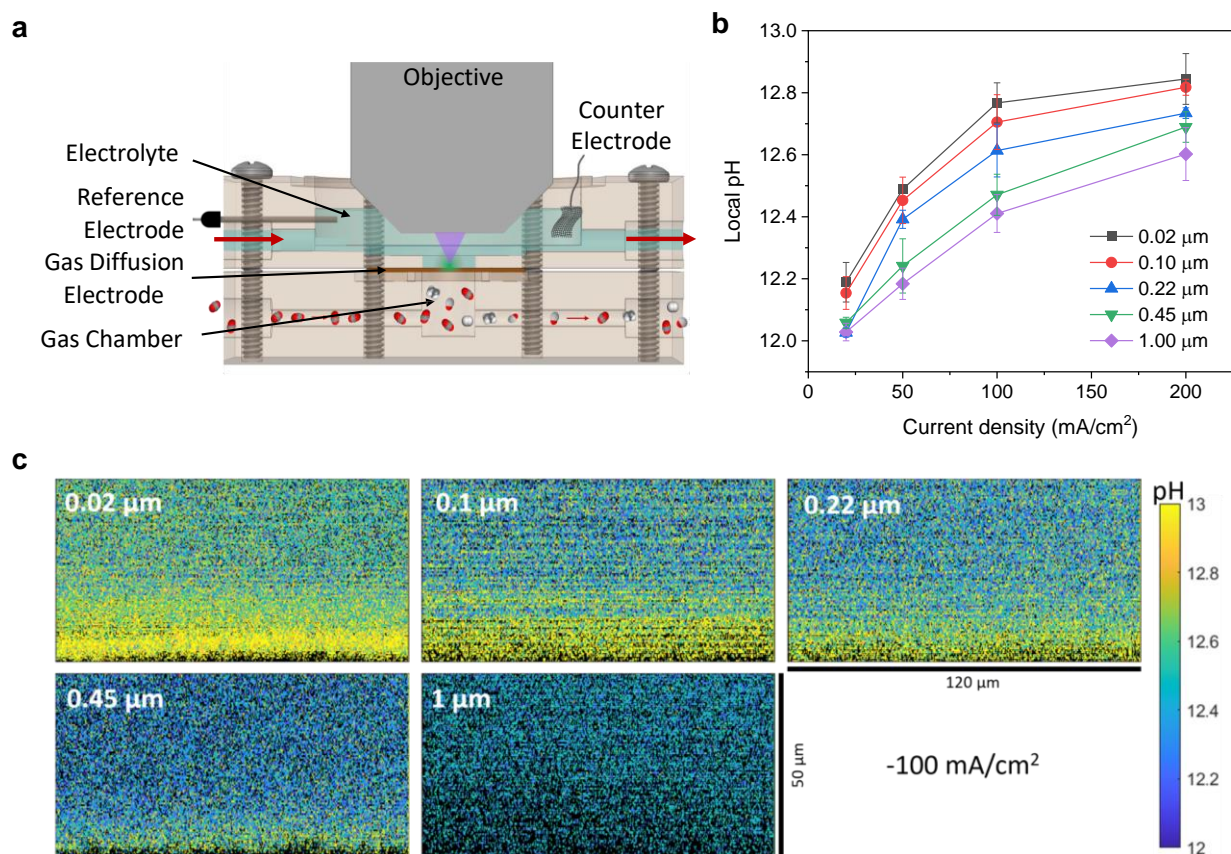


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199 **Fig. 5** (a) HCOO⁻ FE data for Ag/PTFE(0.22) as a function of KHCO₃ concentration. (b) Color
 200 contour map of the HCOO⁻ FE data for Ag/PTFE as a function of KHCO₃ concentration and GDL
 201 pore size. More data for (a) and (b) are available in the Supporting Information (Fig. S15-S17). (c)
 202 Product FE data for the case where the CO₂ feed stream was diluted with various amounts of N₂.
 203 Ag/PTFE(0.45) was used as the cathode and 1 M KHCO₃ was used as the electrolyte at an applied
 204 cathodic current density of 300 mA/cm². (d) Graph showing the formate to CO ratio as a function
 205 of N₂ gas dilution, based on the data shown in (c).

206 Furthermore, we also conducted *in-situ* measurements using confocal microscopy with a pH
 207 sensitive fluorescent dye to provide experimental verification of the local pH trends as a function
 208 of GDL pore size and applied current density. Fluorescent confocal laser scanning microscopy

209 enables imaging of the local pH in three spatial dimensions with a resolution of one micrometer
 210 under operating conditions^{44,45}. Such experiments were carried out using a custom-built
 211 electrochemical cell (Fig 6a and Fig. S18), consisting of a gas chamber for CO₂ flow and an
 212 electrolyte chamber that is stacked above it. The electrolyte chamber is open at the top, which
 213 allows for a water immersion objective to be dipped into the electrolyte, in close proximity to the
 214 electrode surface.



215
 216 **Fig. 6** (a) Cross section of the custom-built electrochemical cell with water immersion objective
 217 for local pH measurements with APTS. (b) Local pH value averaged from zero to forty
 218 micrometers above the electrode surface as a function of current density for different Ag/PTFE
 219 GDLs. (c) Representative pH maps as a cross section through the plane perpendicular to the

220 electrode surface for different Ag/PTFE samples at 100 mA/cm². pH maps for other current
221 densities can be found in Fig. S19.

222 We studied the local pH in the vicinity of the Ag/PTFE electrodes with the ratiometric
223 fluorescent dye 8-aminopyrene-1,3,6-trisulfonic acid trisodium salt (APTS), which is dissolved in
224 the electrolyte. APTS is a direct sensor of the local hydroxide activity and can be used to deduce
225 the local pH (sensitive to values between 11.2 and 14). A more detailed analysis of the sensing
226 mechanism of APTS can be found elsewhere⁴⁵. Measurements for all cases were performed using
227 1 M KHCO₃ electrolyte with 200 μM APTS, which was constantly circulated through the
228 electrochemical cell (more details in the Supporting Information).

229 The pH was mapped for a series of current densities between 20 mA/cm² and 200 mA/cm², in
230 the plane perpendicular to the electrode surface, starting from a few micrometers below the
231 electrode surface. The dimensions of each pH map are 120 μm in the x direction and 50 μm in the
232 z direction (Fig 6c and Fig. S19). From the maps, a pH gradient can be clearly observed for all
233 cases, with the pH being higher at points closer to the electrode surface. We averaged the pH in
234 the area between the electrode surface and 40 micrometers above the electrode surface and plotted
235 this as a function of current density (Fig 6b). As expected, the pH increases as the current density
236 increases since OH⁻ is created as a by-product of CO₂ reduction and hydrogen evolution.

237 Most importantly, for all current densities investigated, there is the clear trend that the local
238 pH decreases with increasing pore size of the GDL. This is consistent with our preceding
239 experimental and simulation results, that a larger GDL pore size can indeed better facilitate CO₂
240 mass transport. This leads to more excess CO₂ molecules that are available at the electrode surface
241 to react with electrochemically generated OH⁻, leading to a lower pH value. These results are
242 therefore strong experimental evidence for our hypothesis that tuning the GDL pore size can indeed

243 directly impact the local pH. This then results in selectivity switching, leading to the observed
244 increased selectivity towards conversion of CO₂ to formate.

245 Finally, we sought to understand if this local microenvironment effect could also affect other
246 catalysts for electrochemical CO₂ reduction. Previous literature reports have indicated that an
247 increased local pH can induce a higher selectivity towards multicarbon (C₂₊) products with Cu
248 based catalysts. Hence to explore this effect, we prepared a series of samples by sputtering 325 nm
249 of Cu onto PTFE substrates of different pore sizes (Fig. S20). These catalysts were then tested at
250 a constant cathodic current density of 200 mA/cm² in 1 M KHCO₃ electrolyte. The results (Fig.
251 S21) show that a smaller pore size does indeed lead to an increase in the FE towards C₂₊ products,
252 as a consequence of the induced higher local pH.

253 However, the C₂₊ FE was observed to drop once the pore size becomes too small. This is
254 because the local CO₂ availability is expected to diminish at the smallest pore sizes, and these
255 conditions are less favorable towards the formation of C₂₊ products. Our findings are consistent
256 with the work by Strasser and co-workers, where they observed different “selectivity zones” within
257 their Cu nanoparticle catalyst coatings on a gas diffusion layer⁴⁹. Zones closer to the gas diffusion
258 layer experience higher local pH and increased CO₂ availability, which enhances the C₂₊
259 selectivity. On the other hand, zones further away from the gas diffusion layer experience CO₂
260 depletion, which reduces C₂₊ product formation. These observations are supported by another
261 report in the literature⁵⁰, which showed that a lowered CO₂ partial pressure suppresses the C₂₊ FE.

262 **Conclusions**

263 In this work, we investigated how the pore size of the gas diffusion layer can be tuned to impact
264 the catalyst local microenvironment and hence, the selectivity for electrochemical CO₂ reduction.

265 We first performed Multiphysics modelling of the reaction system, which showed that smaller
266 GDL porosity can slow down CO₂ mass transport, resulting in a higher local pH at the electrode.
267 Encouraged by these results, we studied this experimentally using sputtered Ag films on
268 hydrophobic PTFE substrates with 6 different pore sizes. Although Ag is known to be a
269 predominantly CO generating catalyst, we find that smaller pore sizes favor the generation of
270 formate up to a Faradaic efficiency of 43%. This is due to the higher local pH, which induces
271 reaction pathway switching towards formate at the expense of CO. These observations are also
272 supported by further investigations with different buffer concentrations and partial pressure
273 experiments. A confocal microscopy setup was further used to map out the electrode local pH
274 using a pH sensitive fluorescent dye. Through this, we experimentally verified that a smaller
275 (larger) pore size does indeed result in a higher (lower) local pH. Overall, our results show how
276 the GDL pore size can be used to impact the catalyst microenvironment and hence serve as an
277 experimental knob that can be rationally controlled to influence product selectivity. These findings
278 will inform and aid the future design of more selective and efficient CO₂R systems.

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287 **Competing interests**

288 The authors declare no competing interests.

289 **Author contributions**

290 Y.L. and H.A.A. supervised the project. Y.L. conceived the idea and designed the experiments.
291 S.B.D. carried out all the experimental work. A.B. performed and analyzed the confocal
292 microscopy experiments. Z.F. and A.J.K. performed the multiphysics simulations. A.Z.W. and
293 E.K. supervised the multiphysics simulations. A.Q.F., A.D.H., W.R.L and X.M contributed to data
294 analysis and manuscript editing. Y.L, A.B. and S.B.D co-wrote the manuscript. All authors
295 discussed the results and assisted during the manuscript preparation.

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