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Jun Li[1,2†], Ziyun Wang[2†], Christopher McCallum[1†], Yi Xu[1], Fengwang Li[2], Yuhang Wang[2],

Christine Gabardo[1], Cao-Thang Dinh[2], Tao-Tao Zhuang[2], Liang Wang[3], Jane Y. Howe[4], Yang

Ren[3], Edward H. Sargent[2]* & David Sinton[1]*

[1]Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College
Road, Toronto, Ontario, M5S 3G8, Canada.

[2]Department of Electrical and Computer Engineering, University of Toronto, 10 King's College
Road, Toronto, Ontario, M5S 3G4, Canada.

[3]Advanced Photon Source, Argonne National Laboratory, Lemont, Illinois, 60439, United States

[4]Hitachi High Technologies America, Inc., 22610 Gateway Center Drive, Suite 100, Clarksburg,
Maryland 20871, USA

[†]These authors contributed equally: Jun Li, Ziyun Wang and Christopher McCallum.

*Corresponding email: ted.sargent@utoronto.ca; sinton@mie.utoronto.ca

The availability of inexpensive industrial CO gas streams motivates efficient electrocatalytic upgrading to higher-value feedstocks such as ethylene. However, the electrosynthesis of ethylene via the CO reduction reaction (CORR) has suffered from low selectivity and energy efficiency. Here we find that the recent strategy, so effective in CO_2RR, of increasing performance through the use of highly alkali electrolyte, fails in CORR anddrives the reaction to acetate. We then observe that ethylene selectivity increases when we constrain (decrease) CO availability. Using density functional theory, we show how CO coverage on Cu influences the reaction pathways of ethylene versus oxygenate: lower CO coverage stabilizes the ethylene-relevant intermediates while higher CO coverage favours oxygenate formation. We then control local CO availability experimentally by tuning the CO concentration and reaction rate; we achieve ethylene Faradaic efficiencies of 72% and partial current density > 800 mA cm^{-2}. The overall system provides a half-cell energy efficiency of 44% for ethylene production.

29

30   The electrochemical upgrading of CO_2 into carbon-based chemicals and fuels provides a

31   means to close the anthropogenic carbon cycle and store excess renewable electricity[1-3]. Much

32   effort has been dedicated to the production of valuable two-carbon (C_2) products via direct CO_2

33   electrolysis[4-7]. Ethylene is an electrolysis product of particular interest in view of high demand

34   for it, as a chemical feedstock.

35   Starting from CO, instead of CO_2, as feedstock, avoids carbonate formation in alkaline CO_2

36   electrolyzers, and thus overcomes issues in feedstock utilization and stability[8,9]. Additionally,

37   CO gas feedstock streams are available industrially at a range of purities. Abundant and

38   inexpensive manufactured gases such as syngas, coal gas and producer gas, and also effluent

39   streams from steel manufacturing, have CO concentrations in the range of 10% to 60%[10-14]. Gas

40   purification from these streams is costly, as indicated by the sale price of high purity CO which

41   is over ten times that of commercial CO streams having low purities (e.g. syngas)[15]. These costs

42   will be avoided once available dilute CO gas streams – whether they be manufactured or effluent

43   – are upgraded to ethylene with a high efficiency.

44   Recent advances in the CO reduction reaction (CORR) for ethylene production have focused

45   on increasing the reaction rate and selectivity[8,9,16-19]. CO-to-ethylene at moderate current

46   densities (~ 100 mA cm^{-2}) has been demonstrated on nanostructured copper catalysts employing

47   gas diffusion electrodes that overcome mass transfer limitations[9,16-18]. Increasing the alkalinity of

48   the electrolyte has increased activity and selectivity for ethylene in both CO_2RR[4] and CORR[9].

49   However, even with concentrated KOH electrolytes and pure CO reactant gas, the highest

50   reported CO-to-ethylene Faradaic efficiency (FE) remains ~40% with a cathodic energy

51   efficiency of ~20%[9].

52   Here we present high-efficiency ethylene electroproduction from CO on Cu at current densities

53   above 100 mA/cm^2. The system performs well across a wide range of CO input concentrations.

54   We find that increased ethylene selectivity is obtained when we decrease the CO availability up

55   to the CO mass transport limit by operating at high current densities. This finding motivates us to

56   investigate the link between local CO availability and ethylene selectivity. Using density

57   functional theory (DFT) calculations, we first assess – as a function of CO coverage – the

58   activation energies and enthalpy changes of the key elementary steps branching the ethylene

59   versus the oxygenate pathways. We find that lowering CO coverage on copper benefits the

60   ethylene pathway both thermodynamically and kinetically. In experiments, we constrain the local

61   CO concentration at the catalyst:electrolyte interface by tuning the combination of CO supply

62   concentration and reaction rate (e.g. applying high reaction rates for high input CO

63   concentrations). Implementing this strategy, we achieve an ethylene partial current density >

64   800 mA cm^{-2} and an ethylene Faradaic efficiency over 70% across a wide range of CO

65   concentrations (5 – 100%). Combining high selectivity with low overpotential we achieve a

66   44% half-cell energy efficiency for ethylene production.

67   **Results**

68   **Effect of KOH concentration**

69   Hydroxide ions have – in the context of CO_2 reduction – been shown to play a crucial role in

70   promoting both selectivity and activity in ethylene production. They do so when they bring the

71   onset of ethylene production closer to that of CO[4]. A subsequent CORR flow cell study with

72   increasing KOH concentration from 0.1 M to 1 M further demonstrated increased ethylene

73   production via the suppression of hydrogen generation[9].

74   To assess the effect of electrolyte alkalinity on ethylene production from CORR, we varied the

75   KOH concentration from 1 M to 5 M and carried out CORR in highly alkaline conditions in a

76   flow cell electrolyzer (**Supplementary Fig. 1**)[4-6,20]. Copper oxide pre-catalysts (see *Methods*)

77   were deposited and then reduced to active Cu catalysts via CORR.

78   We found that increasing the alkalinity of the electrolyte above 1 M decreased ethylene

79   electroproduction (**Fig. 1a**) and increased acetate formation (**Supplementary Fig. 2**). The

80   increase of $FE_{acetate}$ with elevated KOH concentration can be attributed to the reaction of

81   concentrated hydroxide ions with CORR intermediates relevant to ethylene, ethanol and 1-

82   propanol[8,9,21]. This interaction of hydroxide ions and intermediates is not significant in the case

83   of alkaline CO_2 electroreduction due to the pH-moderating influence of dissolved CO_2[4], in which

84   the concentration of hydroxide ions under CO_2 reduction is more than one order of magnitude

85   lower than under CORR at similar current and bulk electrolyte conditions[9].

86   Under the electrolyte concentrations tested, $FE_{ethylene}$ increased with applied potential/current

87   (**Fig. 1a**), and peaked just prior to a sharp increase in hydrogen production (**Supplementary**

88   **Fig. 3**). Specifically, increasing the potential from -0.2 to -0.6 V versus a reversible hydrogen

89   electrode (vs. RHE) in 5 M KOH resulted in a linear increase of $FE_{ethylene}$ (0.8 to 58%) and an

90   exponential increase of ethylene partial current density (0.06 to 728 mA cm^{-2}) (**Fig. 1b**).

91   Carrying out a reaction-diffusion model analysis, we found a dramatic decrease of local CO

92   concentration at the catalyst layer due to increased reaction kinetics and thereby a buildup of

93   hydroxide ions, i.e. an increase in local pH. A further increase of overpotential leads to severe

94   depletion of local CO availability from rapid ethylene formation, a sharp increase of hydrogen

95   binding and evolution (**Supplementary Fig. 4**), and thereby a reduction of $FE_{ethylene}$. The shift to

96   hydrogen signals the onset of CO mass transport limits, and represents the lower limit of CO

97   availability for efficient ethylene production.

98   We then determined the cathodic energy efficiency for ethylene production from the measured

99   overpotential and ethylene selectivity (**Supplementary Fig. 5** and **Supplementary Note 1**). The

100   highest ethylene cathodic energy efficiency of 35% is achieved when we used 1 M KOH.

101   Improving this energy efficiency further would require increased ethylene selectivity at lower

102   overpotential. Results here (**Fig. 1**) indicate that increasing electrolyte alkalinity will not increase

103   ethylene selectivity further; however, reaction-rate driven changes in local CO availability can

104   influence ethylene selectivity. We therefore hypothesized that independently controlling local

105   CO concentration at the catalyst surface could offer a route to advance ethylene production

106   efficiency.

107   **Density functional theory calculations**

108   We sought to understand, with the aid of DFT, the connection between local CO concentration

109   and the ethylene versus oxygenate formation pathways. Previous reports correlate

110   ethylene/oxygenate production from CO reduction with the hydrogenation of oxygen-containing

111   intermediates[22-24], indicating that once all the oxygen-containing groups are removed by

112   hydrogenation to form water, the intermediate state is likely to proceed towards ethylene.

113   Specifically, *CHCOH (denoted IM, **Fig. 2a**) has been identified as the key intermediate for

114   hydrogenation into both ethylene and oxygenates[23], in which the hydroxyl group can be

115   deoxidized forming *CCH (IM-C), leading to ethylene. The intermediate can instead be

116   hydrogenated into *CHCHOH (IM-O), favouring the production of oxygenates. We wondered

117   whether controlling the IM reduction step to encourage the C-pathway (IM-C) instead of the O-

118   pathway (IM-O) could promote ethylene production.

119   Using DFT calculations, we predicted the geometries of IM, IM-C, and IM-O on Cu(100) (**Fig.**

120   **2a**). We note that the main difference between the IM-O and IM-C intermediate state is the

121   degree of unsaturation (**Supplementary Note 2**), namely 2.5 for IM-C and 1.5 for IM-O. Thus

122   IM-C requires more surface bonding ability in order to be stabilized. As the adsorption of

123   intermediates is affected by the surface coverage of CO due to adsorbate-adsorbate interactions[25],

124   tuning the surface bonding ability of IM-C by controlling the coverage of adsorbed *CO could

125   influence the relative stability of ethylene-forming IM-C vs. IM-O.

126   We first calculated the reaction energies of the C-pathway and O-pathway (**Fig. 2b**). The

127   reaction energies for these pathways are similar at zero CO coverage, and the O-pathway

128   becomes more favorable at higher CO coverages. Noting the key role of kinetics in these

129   reactions[22], we used an explicit water model to calculate the energies of the three intermediate

130   states (IM, IM-C, IM-O) and associated transition states (TS-C and TS-O) with coverage of *CO

131   ranging from 0 to 3/9 (**Supplementary Fig. 6-15**)[26]. A coverage of 3/9 was selected based on a

132   kinetic modelling prediction of ~0.3 ML CO coverage on Cu surfaces[27]. We found the barriers to

133   both the C-pathway and the O-pathway increase with increasing CO coverage (**Fig. 2c**). At low

134   CO coverage the C-pathway is kinetically favoured over the O-pathway, and the O-pathway

135   becomes more favourable at 3/9 ML. These models do not indicate the species expected: acetate,

136   ethanol and 1-propanol. However, both the reaction energy and enthalpy calculations indicate

137   that an oxygenate-forming O-pathway is favoured at higher CO coverages.

138   We also calculated the effects of CO coverage on the CO dimerization barriers and enthalpy

139   changes (**Supplementary Fig. 16-22**). Both show decreased values as CO coverage increases,

140   indicating that high CO coverage favors CO dimerization. The barrier to CO dimerization at 2/9

141   ML, with two CO reactants and no other adsorbed CO, is calculated to be 0.66 eV, which is

142   lower than the threshold (0.75 eV) for fast kinetics[28], and suggests that dimerization is not

143   limiting under these conditions. We further assessed the barriers of the C-pathway and O-

144   pathway with applied potentials (**Supplementary Fig. 23**)[27,29]. These barriers are lower than

145   those associated with CO dimerization at similar CO coverages, suggesting that CO dimerization

146   is the rate-determing step, consistent with previous findings[28,30].

147   These DFT simulations predict that limiting the surface coverage of CO would favour ethylene

148   production. In practice, CO coverage can be limited by increasing the reaction rate, but not

149   without higher overpotentials and reduced efficiency. An independent means of controlling CO

150   coverage is via the local CO concentration ($[CO]$) or CO pressure (P_{CO}), where $[CO]$ correlates

151   with P_{CO} via Henry's law. At equilibrium, the surface coverage of CO (θ_{CO}) is directly

152   proportional to the local CO partial pressure, as given by equation[31,32]:

153    $$\theta_{CO} = \theta_* \, P_{CO} \, e^{-\frac{E_{CO}}{RT}} \qquad (1)$$

154   where θ_* is the coverage of free surface sites. E_{CO} is the CO adsorption energy on the surface.

155   R and T are the ideal gas constant and temperature, respectively. Therefore, to achieve low

156   coverage of CO favoring ethylene production, decreasing the partial pressure of CO at catalysts

157   layer is a promising approach.

158   **Materials characterization**

159   To explore experimentally the implications of the DFT results, we pursued CORR with a wide

160   range of CO supply gas concentrations via dilution with N_2, beginning with in situ catalyst

161   derivation (**Fig. 3a**). Cu catalysts derived from oxide precatalysts (**Supplementary Fig. 24**) at

162   CO concentration of 100% (**Fig. 3b**) and 2.5% (**Fig. 3c**) show similar morphology of aggregated

163   nanoparticle structures. Operando X-ray absorption spectra at the Cu K-edge exhibit pure

8

164   metallic Cu features from catalysts derived at all tested CO concentrations (**Fig. 3d** and

165   **Supplementary Fig. 25**). High-resolution operando X-ray diffraction analysis[33] further confirms

166   that a stable metallic Cu structure remains the active catalyst during CORR operation under these

167   conditions (**Fig. 3e** and **Supplementary Fig. 26**).

168   **Influence of CO gas concentration**

169   We evaluated CORR performance as a function of input CO gas concentration in 1 M KOH

170   with a range of applied potentials. When we varied the incoming CO concentration from 2.5 to

171   100% (within an inert N_2 carrier gas), we observed an overall increase of both total current

172   density (**Supplementary Fig. 27**) and CORR partial current density (**Fig. 4a** and **4b**). The

173   enhancement of current density follows an exponential increase within the potential window of –

174   0.32 V to –0.52 V vs. RHE at CO concentrations of 2.5%, 5% and 10%. The exponential trend

175   extends further to potentials of -0.66V and -0.72 V vs. RHE at the highest CO concentrations of

176   50% and 100%, respectively. These trends indicate abundant mass transport (no mass transport

177   limitation) over these potential ranges[9]. At higher overpotential, the current density trend is

178   curbed due to CO mass transport limitation (**Fig. 4a, 4b** and **Supplementary Fig. 27**)[8], with a

179   characteristic increase in hydrogen production (**Supplementary Fig. 28**).

180   Ethylene FE increases with applied potential to a peak value corresponding to the onset of

181   mass transport limitation observed in the current output (**Fig. 4c** and **4d**). The result is a similar

182   ethylene partial current density when operating at different CO concentrations without CO mass

183   transport limitation (**Supplementary Fig. 29**), in agreement with a previous report[34]. With 2.5%

184   CO, a peak FE of 51% is reached, commensurate with a 32% FE of hydrogen at -0.53 vs. RHE

185   (**Supplementary Fig. 28**). For cases of CORR performed at 5% and 10% CO conditions, we

186   achieve 72% $FE_{ethylene}$ at -0.52 V vs. RHE with a significant decrease of hydrogen production

187   (**Supplementary Fig. 28**). Further increasing the CO concentration to 50% and 100% results in

188   peak ethylene production of ~70% at higher potentials of -0.66 V and -0.72 V vs. RHE, with

189   ethylene partial current densities of 509 mA cm^{-2} and 808 mA cm^{-2}, respectively. By levering the

190   dependence of overpotential and ethylene selectivity on input CO concentration, we achieved 44%

191   cathodic energy efficiency for ethylene production, as did so using 5% CO (**Supplementary**

192   **Note 1**). These results surpass the best reported CORR $FE_{ethylene}$ (~40%) achieved at a potential

193   of –0.72 V vs. RHE (equivalent to a ~24% increase in cathodic energy efficiency)[9] by a factor of

194   1.6 in ethylene selectivity; and by a factor of 1.8 in cathodic energy efficiency. It represents the

195   most efficient electrocatalytic CO-to-ethylene conversion reported to date (**Supplementary**

196   **Table 1**). To assess further ethylene formation among only carbon-based products, we

197   normalized ethylene selectivity by excluding the H_2 contribution. The normalized $FE_{ethylene}$ first

198   increases and then reaches a plateau at a value of ~75% (**Supplementary Fig. 30**), which further

199   supports the view that limiting CO availability on Cu stabilizes intermediates favourable for

200   ethylene.

201   To gain further insight into this ethylene formation strategy, we performed CORR in 1 M

202   KOH at various CO concentrations and a fixed potential of -0.44 V vs. RHE. With pure CO

203   (100%), we observed a wide distribution of FEs for various products (**Fig. 4e**), in agreement with

204   a recent CORR report[9]. Ethylene was the dominant product with an FE of ~30%. When we

205   decreased the CO concentration from 100 to 5%, $FE_{ethylene}$ increased to ~50% at the expense of

206    $FE_{1-propanol}$, and with little impact on $FE_{acetate}$, $FE_{ethanol}$ and FE_{H2}, confirming that an avenue to

207   increase $FE_{ethylene}$ is to constrain CO. We noted a slight decrease of current densities at reduced

208   CO concentrations, a feature we attributed to the lack of CO reactant and thus sluggish CORR

209   kinetics at these conditions (**Supplementary Fig. 31**).

210   With a further decrease of CO concentration from 5 to 2.5%, the lack of CO reactant manifests

211   in significant hydrogen production. This ethylene selectivity decrease highlights the fact that low

212   CO availability promotes ethylene production only up to the mass transport limit. When the CO

213   availability is decreased beyond the mass transport limit, either by increasing the reaction

214   rate/potential at a fixed CO concentration (**Fig. 4a-d**) or lowering the input CO concentration at a

215   fixed reaction rate/potential (**Fig. 4e** and **Supplementary Fig. 32**), ethylene selectivity reduces,

216   in agreement with previous studies[19,35]. The key to ethylene production from CO is thus to

217   constrain operating conditions such that CO availability is neither too high (promoting

218   oxygenates) nor too low (promoting hydrogen).

219   The normalized $FE_{ethylene}$ (without hydrogen) shows a smooth trend of increased ethylene

220   production with decreasing CO concentration, in all cases (**Fig. 4f**). In terms of carbon products,

221   we produce almost exclusively C_2 at low CO conditions (~70% of ethylene and ~25% of ethanol

222   at a 2.5% CO condition), and we observe a product switching from ethylene to 1-propanol at

223   higher CO concentrations. The development of operando/in-situ techniques capable of tracking

224   key C_{2+} intermediates[36] while operating at conditions relevant to flow cells would further our

225   understanding of the C- and O-pathway branching in these systems.

226   The ethylene production performance measured with Faradaic efficiency, current density and

227   cathodic energy efficiency demonstrates a wide operating zone (**Fig. 4g**). By tuning conditions to

228   constrain local CO availability, we achieve ethylene FEs (65 to 72%), and high cathodic energy

229   efficiencies (35 to 44%), with current densities (120 to 1250 mA cm^{-2}) well above the 100 mA

230   cm^{-2} threshold. We further tested the system by reacting a simulated coke oven gas

231   (**Supplementary Fig. 33**), a by-product of industrial coke production in steel manufacturing,

232   with a gaseous composition of 10% CO, 30% methane and 60% hydrogen[37,38]. We achieved

233   stable CORR with this industrial mixture, producing $FE_{ethylene}$ of ~71% in 1 M KOH at a constant

234   current density of 150 mA cm^{-2}.

235   For the conditions studied, we calculated the local CO concentration using a reaction-diffusion

236   model, and plot it with the potential and Faradaic efficiency values that together determine

237   cathodic energy efficiency (**Fig. 4h**). The highest selectivities for ethylene correspond to low

238   local CO concentrations, and are retained over a wide potential window from -0.5 to -0.8V. The

239   most energy-efficient combination of high selectivity and low overpotential occurs uniquely for

240   low CO input stream concentrations.

241   **Discussion**

242   The findings of prior reports assessing the effect of CO partial pressure on ethylene

243   electroproduction are varied. Schreier and co-workers[34] reported an unaltered ethylene partial

244   current density with varying CO concentration from 100% to 10%, while Li and co-workers[19]

245   showed a decreasing ethylene partial current density at lower CO partial pressures. We found

246   that these findings can be unified on the basis of CO availability. When we start from CO-rich

247   conditions (i.e. not limited by CO mass transport), decreasing CO partial pressure increases

248   ethylene selectivity, but a decrease of total current density (due to sluggish reaction kinetics at

249   low CO concentrations) leads to little change in the ethylene partial current density

250   (**Supplementary Fig. 29**), in agreement with the report by Schreier and co-workers[34]. In

251   contrast, Li and co-workers[19] reduced CO partial pressure from the initial condition of peak

252   ethylene production from 100% CO feed. Under these CO-deficient conditions we also found

253   that any decrease in the local CO concentration decreases ethylene selectivity, current density

254   and ethylene partial current density (**Supplementary Fig. 32**).

255   The CO scarcity effect may play a role in ethylene production from CO_2 reduction[4,39,40].

256   Specifically, a wide potential gap of 200-300 mV for CO and ethylene formation has been

257   observed from CO_2 reduction on Cu catalysts[4,41,42], and the concentration of as-formed *CO

258   intermediates on Cu is low. In CO_2RR, concentrated hydroxide ions accelerate the rate-

259   determining step of CO_2RR (i.e. CO_2 to CO)[4], bridge the potential gap between CO and ethylene,

260   and also serve to limit local CO availability as the high pH electrolyte reduces the available CO_2

261   concentration. In contrast, direct CORR achieves higher local CO concentration on Cu and risks

262   diverting ethylene formation to other products. A high concentration of CO promotes CO

263   dimerization, and leads to a higher density of *C_2 intermediates at the catalysts-electrolyte

264   interface. Within a highly alkaline electrolyte these accumulated *C_2 species react with the

265   abundant hydroxide to form acetate[9]. At more moderate pH the *C_2 can be further reduced to a

266   C_3 product, i.e. 1-propanol, resulting from an intermolecular C-C coupling between *C_2 and

267   adsorbed *CO species[17,18]. Constraining local CO availability at catalyst surfaces in CORR by

268   tuning the incoming gas concentration and reaction rate, provides the route to efficient ethylene

269   production.

270   CO-induced surface restructuring of Cu into nanoclusters has been shown to enhance the

271   catalytic activity of Cu[43-45]. To assess the potential role of Cu nanoclusters in our system, we

272   carried out CO partial pressure dependent tests using commercial polycrystalline Cu as

273   electrocatalysts. In contrast to oxide-derived Cu, polycrystalline Cu does not produce

274   nanoclusters during CORR[38], nor does it exhibit product-specific sites for C_{2+} formations[21,45].

275   The measured ethylene selectivity of polycrystalline Cu, as a function of CO partial pressure

276   (**Supplementary Fig. 34**), was similar to that of oxide-derived Cu (**Fig. 4e**). We conclude that

277   ethylene selectivity is dominated by CO availability, and any surface restructuring in oxide-

278   derived Cu plays a less role.

279   In summary, tuning local CO concentration at the catalyst surface enables efficient ethylene

280   electrosynthesis. Constraining local CO availability on the Cu surface favours ethylene

281   production, a trend seen both in simulations and experiments. We achieved ~70% of $FE_{ethylene}$

282   over a wide range of CO concentrations, and ethylene partial current density of ~808 mA cm^{-2}.

283   With this strategy we combine low overpotential and high selectivity to achieve 44% half-cell

284   ethylene energy efficiency. The performance here demonstrates efficient CO conversion to high-

285   value C_2 chemicals exceeding previous reports in terms of the critical metrics of output purity,

286   energy efficiency and current density. Achieving these performance metrics with a dilute

287   incoming stream presents additional opportunities to convert dilute effluent streams directly into

288   concentrated valued products.

289

290   **Methods**

291   **DFT calculations**

292   In this work, all the DFT calculations were carried out with a periodic slab model using the

293   Vienna *ab initio* simulation program (VASP)[46-49]. The generalized gradient approximation

294   (GGA) was used with the Perdew-Burke-Ernzerhof (PBE)[50] exchange-correlation functional.

295   The projector-augmented wave (PAW) method[51,52] was utilized to describe the electron-ion

296   interactions, and the cut-off energy for the plane-wave basis set was 450 eV. In order to illustrate

297   the long-range dispersion interactions between the adsorbates and catalysts, we employed the D3

298   correction method by Grimme et al.[53] Brillouin zone integration was accomplished using a

299   3×3×1 Monkhorst-Pack k-point mesh. Adsorption geometries were optimized using a force-

300   based conjugate gradient algorithm, while transition states (TSs) were located with a constrained

301 minimisation technique[54-56]. At the intermediate and transition states, one charged layer of water

302 molecules was added to the surface to take the combined field and solvation effects into

303 account[26]. For the modelling of Cu(100), the crystal structure was optimized, and Cu(100) was

304 modelled with a periodic four-layer p(3×3) model with the 2 lower layers fixed and 2 upper

305 layers relaxed. The atomic coordinates of the optimised models, including the structures of initial

306 states and transition states, are provided in **Supplementary Data 1**.

307 **Preparation of electrocatalysts and a gas diffusion electrode**

308 All reagents used in this work were from *Sigma Aldrich* without further purification. Simply put,

309 copper oxide pre-catalysts were synthesized using a method reported earlier[57]. First 4.5 g triblock

310 copolymer Pluronic P123 (MW 5800) was dispersed in 200 mL deionized water under a

311 continuous stirring to form a clear solution. The 20 mL dark blue solution consisting of 0.4 g

312 copper(II) fluoride ($CuF_2.2H_2O$), 3 mL ammonia (~30%) and deionized water was added and

313 stirred to mix well. Last, 0.6 M L-ascorbic acid solution was made and added drop-by-drop into

314 the above solution using a syringe until an orange suspension was formed, indicating the

315 formation of copper oxide nanoparticles. The as-made product was rinsed with ethanol,

316 centrifuged three times, and dried overnight under vacuum at room temperature (~20 ℃). The

317 preparation of a gas diffusion electrode (GDE) was made by air-brushing (N_2 as a carrier gas) a

318 pre-catalyst ink consisting of 30 mg of as-made oxide-precatalysts, 3 mL isopropanol and 120 μL

319 Nafion solution (~5 wt.%), onto a commercial Sigracet gas diffusion layer (GDL, Fuel Cell

320 store) with a size of 4×6 cm^2. The areal loading amount is ~1 mg cm^{-2}. After vacuum drying, a

321 2×2 cm^2 of GDE was cut and assembled into a flow cell electrolyser (**Supplementary Fig. 1**).

322 Active Cu electrocatalysts were then derived under operando CORR condition.

323 **Characterization**

324   Surface morphology was analyzed using a Hitachi SU9000 SEM/STEM at 2 kV. Operando

325   hard X-ray absorption spectroscopy measurements were conducted at beamline 9BM of the

326   Advanced Photon Source (APS, Argonne National Laboratory, Lemont, Illinois). High-

327   resolution operando XRD tests were performed at the beamline 11-ID (λ = 0.4593 Å) of APS

328   using a home-made flow cell (**Supplementary Fig. 26**). Operando measurements were

329   performed at 100 mA cm^{-2} in 1 M KOH.

330   **Electrochemical reduction of carbon monoxide**

331   All CO reduction experiments were performed using a three-electrode flow cell electrolyser

332   (see detailed sketches of flow reactor design in **Supplementary Fig. 1**)[4,58]. As-made GDE,

333   Ag/AgCl (filled with 1 M KCl) and nickel foam (1.6 mm thickness, MTI Corporation) were used

334   as cathode, reference electrode and anode, respectively. Alkaline solutions with various KOH

335   concentrations were used as electrolytes at both cathode and anode sides. An anion exchange

336   membrane (Fumasep FAA-PK-130) was sandwiched between catholyte and anolyte

337   compartments to avoid product crossover. An Autolab PGSTAT204 (Metrohm Autolab) in

338   combination with a BOOSTER10A module (Metrohm Autolab) was used as a power supply.

339   During a CORR experiment, aqueous KOH solution was individually directed into and circulated

340   through the cathode and anode compartments with the assistance of two variable-speed

341   peristaltic tubing pumps (Control Company 3385). A 60 s.c.c.m. continuous flowing CO gas or

342   CO/N$_2$ mixed gas was directed into the gas compartment and reacted at the catalyst-catholyte

343   interface via gas diffusion through the GDL.

344   Applied cathode potentials after iR compensation were converted to the reversible hydrogen

345   electrode (RHE) reference scale using E_{RHE} = $E_{Ag/AgCl}$ + 0.235 V + 0.059 × pH. An iR

346   compensation was performed using the equation:

347   $$E_{iR}=E_{\text{applied}}-0.85*I_{\text{total}}*R \qquad (2)$$

348   where E_{iR} is the iR corrected potential at the cathode, E_{applied} is the applied potential before iR

349   correction, I_{total} is the total current (a negative value at the cathode). R is the cell resistance with a

350   value of 3.31 Ω obtained by performing an electrochemical impedance spectroscopy

351   measurement using an Autolab PGSTAT302N electrochemical workstation coupled with a

352   FRA32M module. A factor of 0.85 is applied in iR compensation during flow cell operation due

353   to a low resistivity of 1 M KOH electrolyte which holds a relatively low voltage drop over the

354   electrolyte.

355   Gas and liquid products were respectively analyzed using a gas chromatograph (GC,

356   PerkinElmer Clarus 680) and a one-dimensional [1]H Nuclear magnetic resonance spectroscopy

357   (^{1}H NMR) coupled with a Agilent DD2 500 spectrometer[4], in which a diluted Dimethyl

358   sulfoxide (DMSO) in D_2O was used as an internal standard for the identification and

359   quantification of liquid products.

360   Faradaic efficiency (FE) of ethylene was calculated using the equation[9]:

361   $$\text{FE (\%)}=\frac{nFxV}{j_{\text{Total}}} \times 100 \qquad (3)$$

362   where n is the number of electrons transferred, F is Faraday's constant, x is the mole fraction

363   of ethylene, V is the total molar flow rate of gas reactant and j_{Total} is the total current applied

364   during CORR.

365

366   **COMSOL modeling**

367   The CO and OH⁻ concentrations were modeled in COMSOL (COMSOL Multiphysics,

368   Stockholm, Se) using a 1D reaction-diffusion model as outlined in **Supplementary Note 3**.

369   **Data availability.** The data that support the findings of this study are available from the

370   corresponding author on reasonable request.

371

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373

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534   **Author contributions**

535   E.H.S and D.S. supervised the project. J.L. designed and carried out all the experiments. Z.Y.W.

536   performed the DFT simulation. C.M. simulated the diffusion-reaction. J.Y.H. conducted the

537   SEM characterization. F.W.L., L.W., and Y.R. assisted the operando XRD measurements and

538   data analysis. Y.X., Y.H.W., C.G., C.T.D. and T.T.Z. contributed in data analysis and manuscript

539   polishing. All authors discussed the results and assisted during manuscript preparation.

540   **Competing interests**

541   The authors declare no competing interests.

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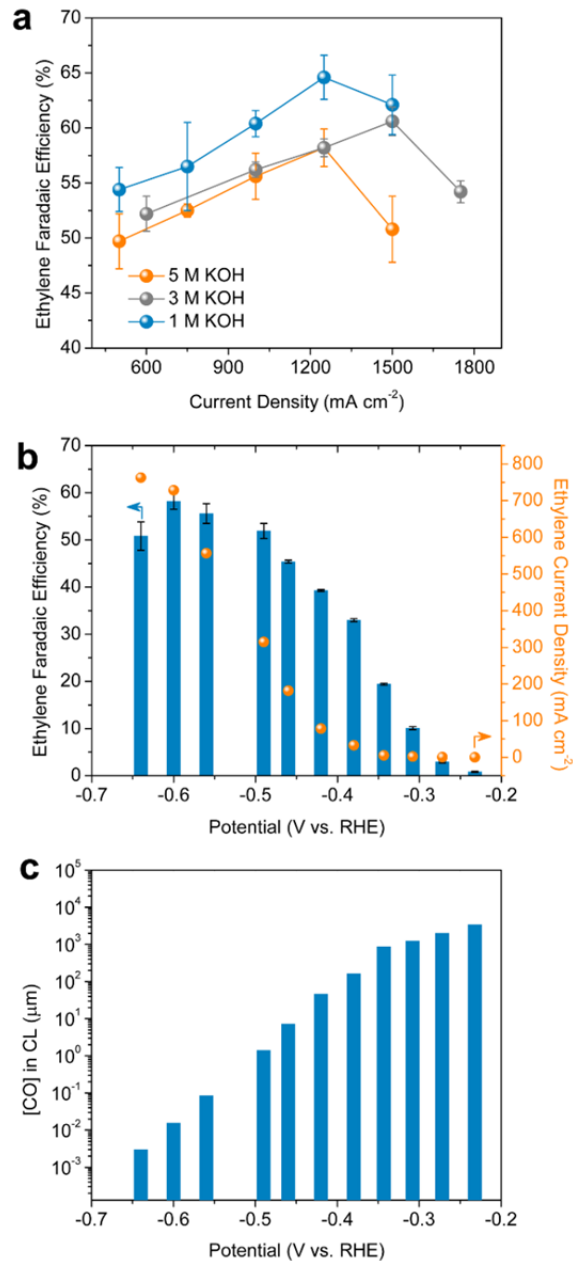
Fig. 1. Influence of KOH concentration on CO reduction. a, A comparison of ethylene Faradaic efficiency at various KOH concentrations as a function of applied current density. **b,** Ethylene Faradaic efficiency and partial current density from CO reduction in 5 M KOH as a function of applied potential. **c,** Simulated local CO concentration [CO] in the catalyst layer (CL) as a function of applied potential in 5 M KOH. Error bars are means ± SD (n = 3 replicates).
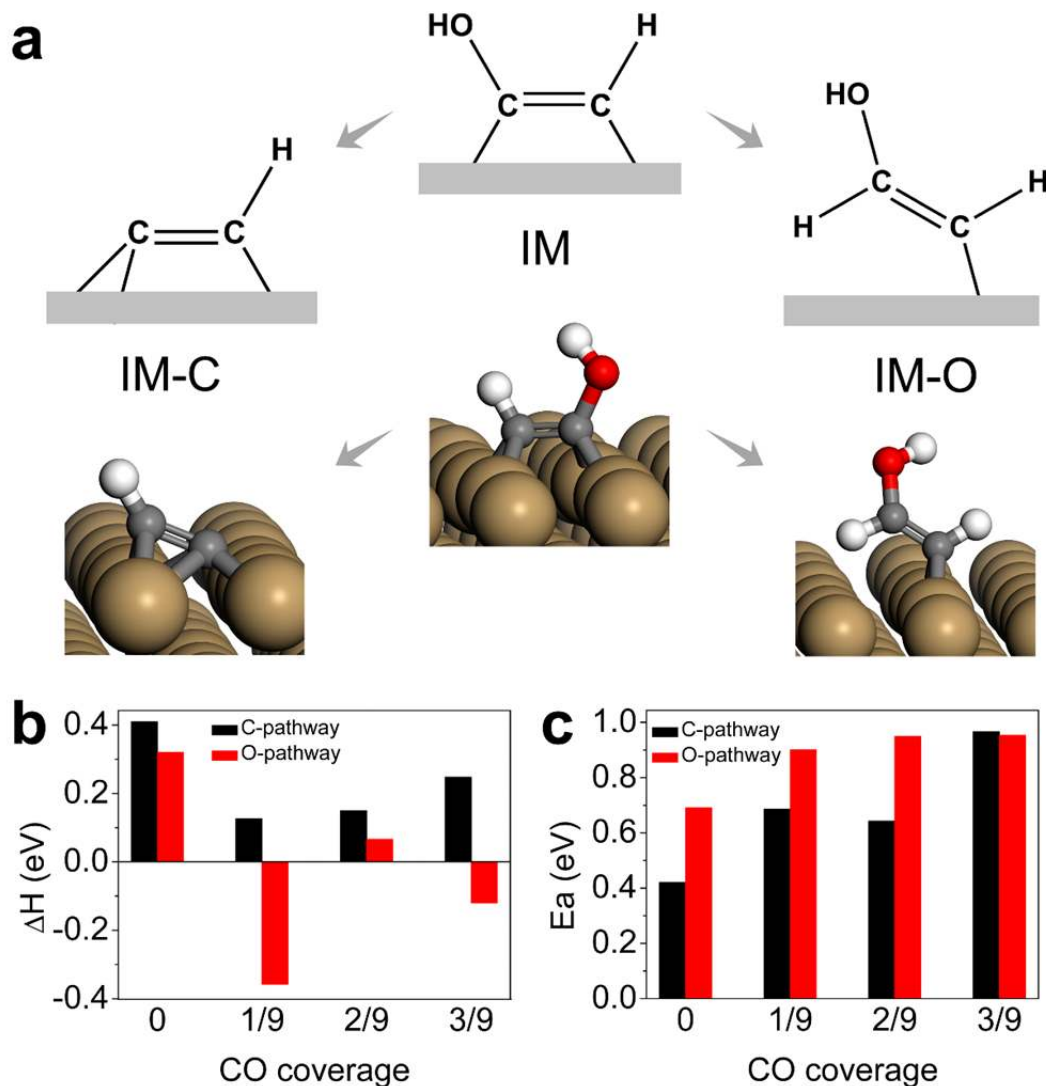
Fig. 2. DFT calculation results on effects of *CO coverage. a, Schematic plot of reaction mechanisms of removing the last oxygen-containing group in *CHCOH (IM) to *CCH (IM-C), and alternative pathway to *CHCHOH (IM-O), as well as the geometries of IM, IM-C and IM-O on Cu(100) surfaces. Yellow, grey, red, and white balls stand for Cu, C, O, and H, respectively. **b,** The enthalpy change for the C- and O-pathways at different levels of CO coverage. **c,** The relation between coverage and activation energy of these two pathways.

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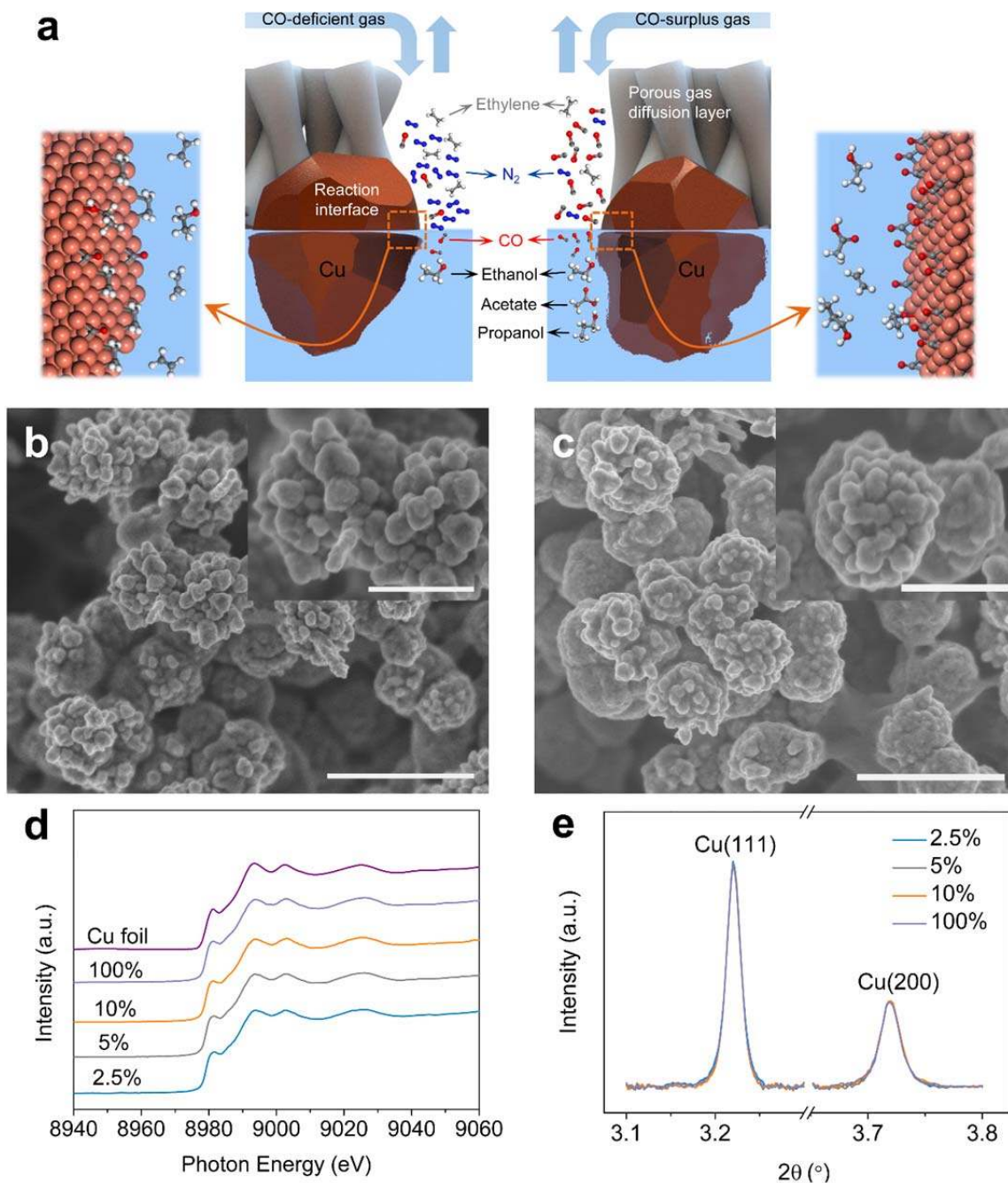
Fig. 3. Characterization of the Cu electrocatalysts. a, Schematic illustration of porous gas

diffusion electrodes with CO reduction at the catalyst-electrolyte interface showing conditions of

CO-deficiency and CO-surplus influencing production. b, c, SEM images of derived Cu catalysts

at CO concentrations of 100% (b) and 2.5% (c); The scale bars are both 500 nm. Insets are

respective high-resolution SEM results with scale bars of 200 nm. d, e, Operando Cu K-edge

564   XAS (**d**) and high-resolution operando XRD (**e**, λ=0.4593 Å) results of derived Cu catalysts at

565   100 mA cm^{-2} in 1 M KOH at various CO concentrations. Ex-situ Cu K-edge XAS of Cu foil is
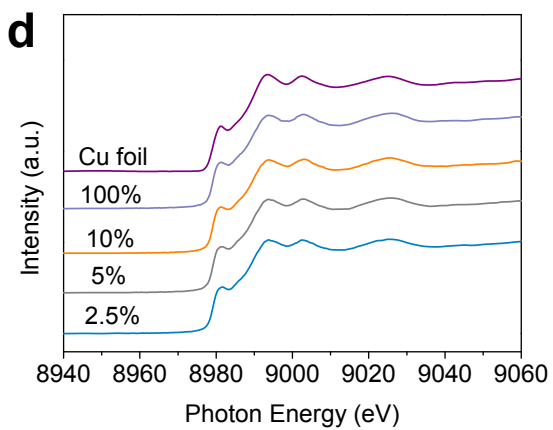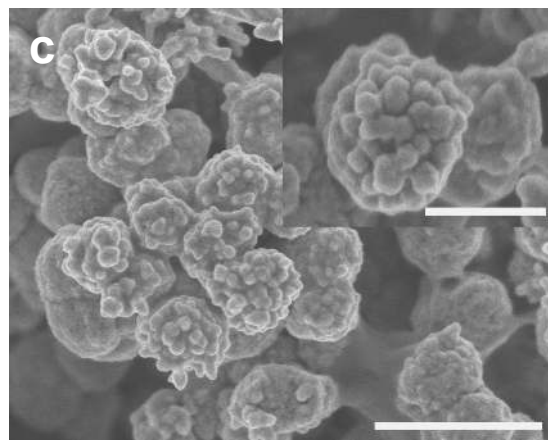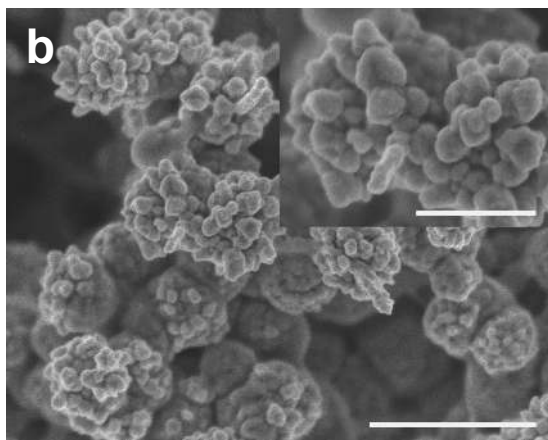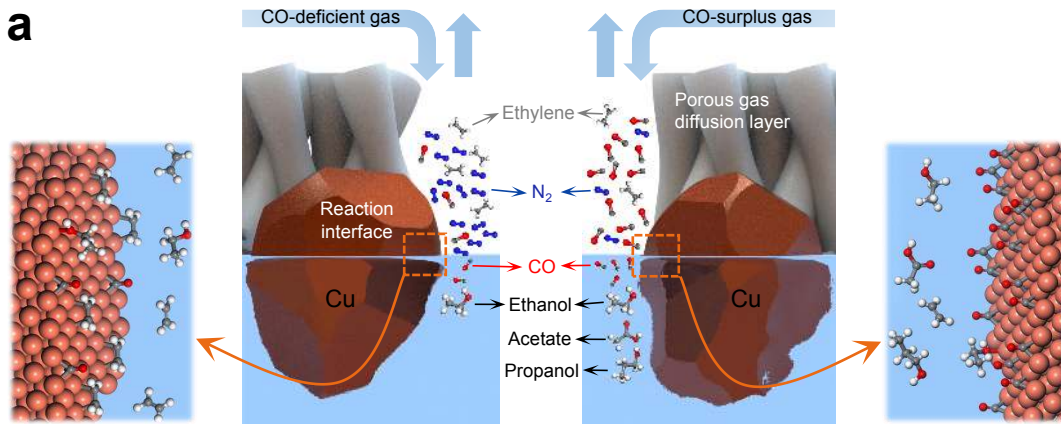
566   included in (**d**) as a reference.

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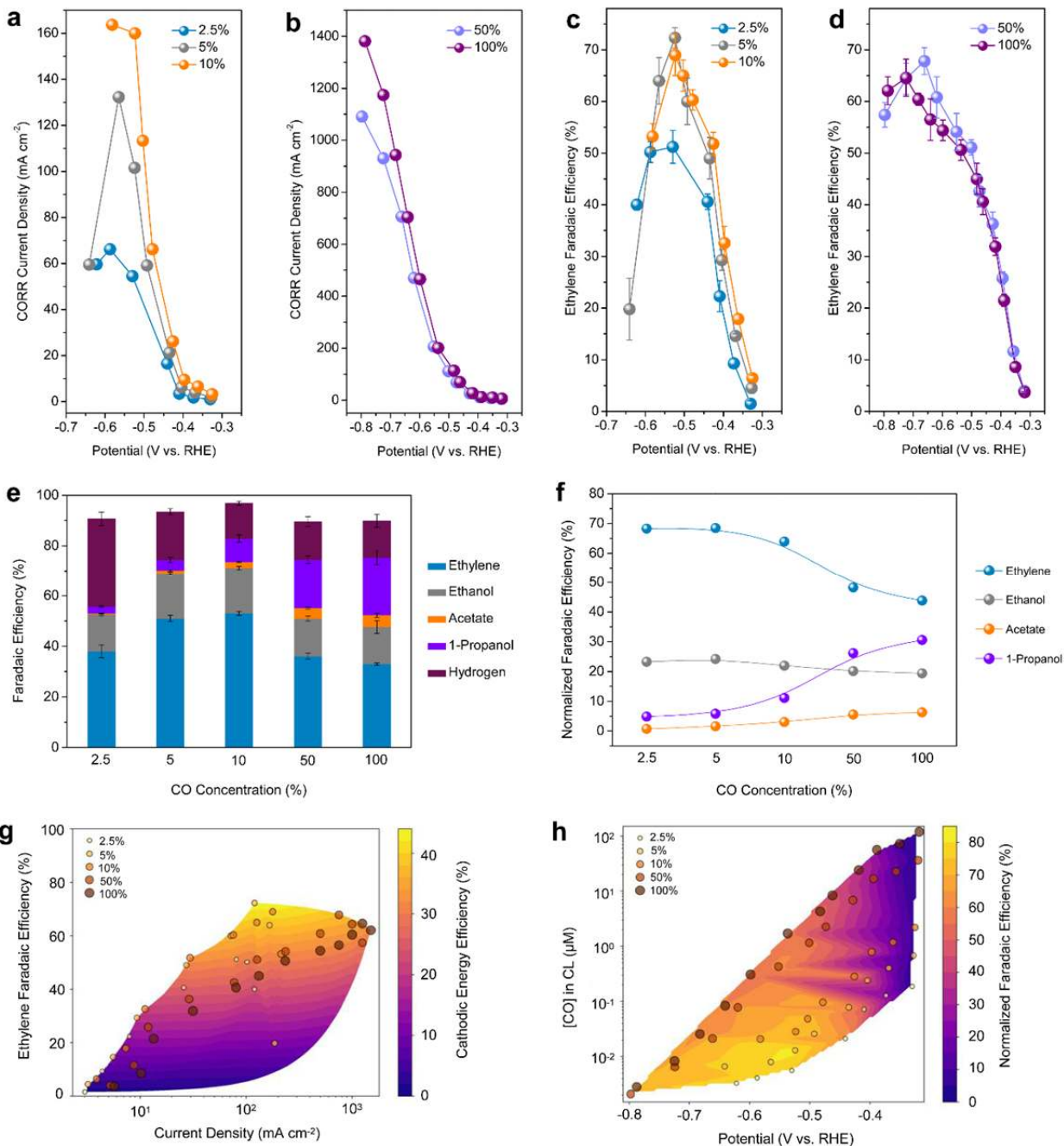
Fig. 4. CORR performance as a function of CO coverage. a-d, CORR partial current densities

(**a, b**) and ethylene Faradaic efficiency (**c, d**) at various CO concentrations as a function of

applied potential in 1 M KOH. **e, f,** Faradaic efficiencies (**e**) and normalized Faradaic efficiencies

(**f**) of CORR products at different CO concentrations at an applied potential of -0.44 V vs. RHE

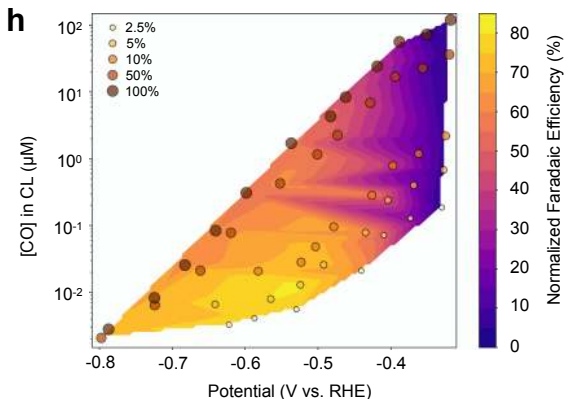in 1 M KOH. **g,** Mapping of the cathodic energy efficiency and ethylene Faradaic efficiency as a
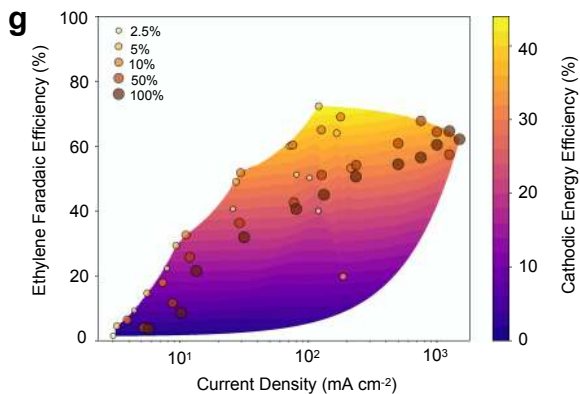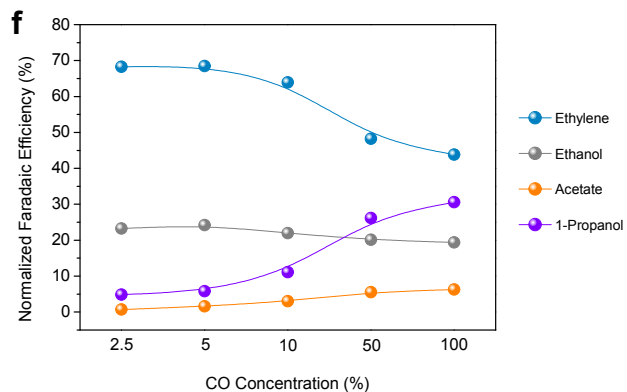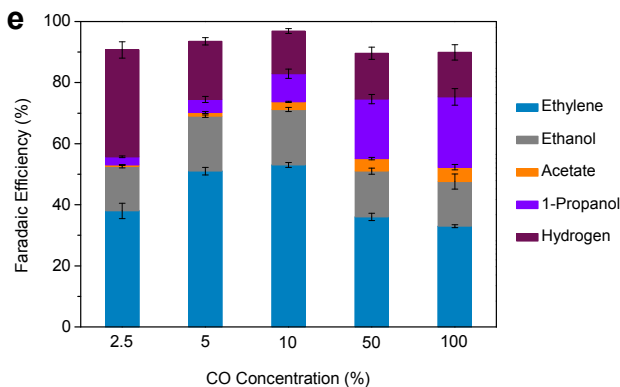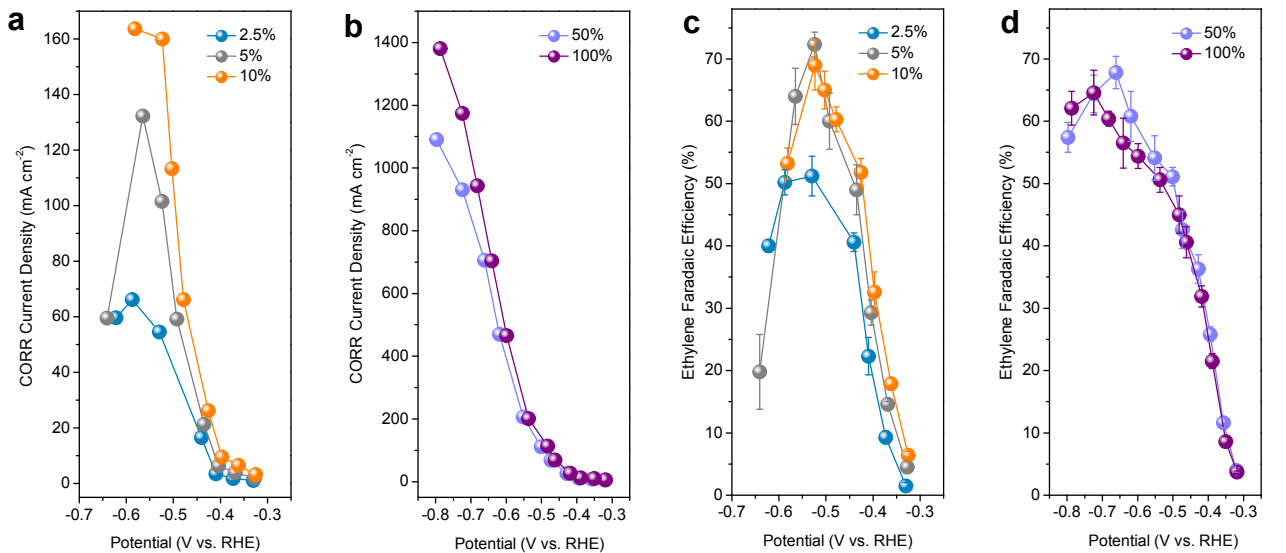
574 function of current density. **h,** Mapping of the normalized ethylene Faradaic efficiency and

575 simulated local CO concentration [CO] in the catalyst layer (CL) as a function of applied

576 potential. Error bars are means ± SD (n = 3 replicates). The heatmap in **g** was generated via

577 linear interpolation using the griddata function of scipy (in *Python 3.6*) to interpolate between

578 points and illustrate the broader relationships between current density, ethylene Faradaic

579 efficiency and cathodic energy efficiency. The heatmap values were interpolated from

580 experimental values. Similarly, the heatmap in **h** was generated via linear interpolation to

581 highlight the effect of simulated local CO concentration and applied potential on the normalized

582 ethylene Faradaic efficiency.

a

IM

IM-C

IM-O

b

- C-pathway
- O-pathway

ΔH (eV)

CO coverage

c

- C-pathway
- O-pathway

Ea (eV)

CO coverage

a

CO-deficient gas

CO-surplus gas

Ethylene

N₂

Porous gas diffusion layer

Reaction interface

Cu

CO

Ethanol

Acetate

Propanol

Cu

b

c

d

Cu foil

100%

10%

5%

2.5%

Intensity (a.u.)

8940 8960 8980 9000 9020 9040 9060

Photon Energy (eV)

e

Cu(111)

Cu(200)

2.5%
5%
10%
100%

Intensity (a.u.)

3.1 3.2 3.7 3.8

2θ (°)

Cu electrocatalysts

CO

N_2

C_2H_4

H_2O