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Shaoxuan Ren

University of British Columbia

Arthur Fink

University of British Columbia

Eric Lees

University of British Columbia <https://orcid.org/0000-0002-0524-3816>

Zishuai Zhang

University of British Columbia

Wen Yu Wu

University of British Columbia <https://orcid.org/0000-0002-1528-7257>

David Dvorak

University of British Columbia

Curtis Berlinguette (✉ cberling@chem.ubc.ca)

University of British Columbia <https://orcid.org/0000-0001-6875-849X>

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Molecular electrocatalysts transform CO into C₂+ products effectively in a flow cell

Shaoxuan Ren,¹ Arthur G. Fink,¹ Eric W. Lees,² Zishuai Zhang,¹ Wendie Wu,² David J. Dvorak,³ and
Curtis P. Berlinguette^{1,2,3,4}

¹Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British
Columbia, V6T 1Z1, Canada.

²Department of Chemical and Biological Engineering, The University of British Columbia, 2360 East
Mall, Vancouver, British Columbia, V6T 1Z3, Canada.

³Stewart Blusson Quantum Matter Institute, The University of British Columbia, 2355 East Mall,
Vancouver, British Columbia, V6T 1Z4, Canada.

⁴Canadian Institute for Advanced Research (CIFAR), 661 University Avenue, Toronto, Ontario, M5G
1M1, Canada.

Abstract

The highest performance flow cells capable of electrolytically converting CO₂ into higher value chemicals and fuels pass a concentrated hydroxide electrolyte across the cathode. A major problem for CO₂ electrolysis is that this strongly alkaline medium converts the majority of CO₂ into unreactive HCO₃⁻ and CO₃²⁻ rather than CO₂ reduction reaction (CO₂RR) products. The electrolysis of CO (instead of CO₂) does not suffer from this same problem because CO does not react with hydroxide. Moreover, CO can be more readily converted into products containing two or more carbon atoms (i.e., C₂₊ products). While several solid-state electrocatalysts have proven competent at converting CO into C₂₊ products, we demonstrate here that molecular electrocatalysts are also effective at mediating this transformation in a flow cell. Using a molecular copper phthalocyanine (**CuPc**) electrocatalyst, CO was electrolyzed into C₂₊ products at high rates of product formation (i.e., current densities $J \geq 200$ mA/cm²), and at high Faradaic efficiencies for C₂₊ production ($FE_{C_{2+}}$; 72% at 200 mA/cm²). These findings present a new class of electrocatalysts for making carbon-neutral chemicals and fuels.

1 Introduction

2 Using renewable electricity to drive the CO₂ reduction reaction (CO₂RR) is an appealing way to
3 synthesize carbon-neutral chemicals and fuels.¹ Electrolytic CO₂RR at a high rate of product formation
4 requires the continuous feed of reactants to the respective electrodes in a flow cell (or “electrolyzer”).^{1,2}
5 A microfluidic flow cell is a type of flow cell proven to be particularly effective for mediating CO₂RR
6 electrolysis at high rates of product formation.^{3,4} The highest performing microfluidic CO₂RR flow cells
7 pass an aqueous 7 M KOH solution between an anion exchange membrane (AEM) and cathodic gas
8 diffusion electrode (GDE).⁵ This high pH serves to promote the CO₂RR by suppressing the competing
9 hydrogen evolution reaction (HER). However, these strongly alkaline conditions convert up to 70% of
10 reacted CO₂ into unreactive (bi)carbonates (Eq. 1–2), which also inducing solid salt formation that
11 compromises flow cell operation.^{6,7}

16 The use of CO as a reagent (instead of CO₂) can produce the same carbon-containing products as
17 CO₂RR electrolysis while bypassing the formation of (bi)carbonates that reduce the efficiency and
18 durability of a flow cell.⁸ An additional advantage of the CO reduction reaction (CORR) electrolysis is
19 that it inherently involves saturating the electrocatalyst surface with adsorbed CO (*CO),^{9,10} thereby
20 increasing the probability of carbon-carbon coupling to form multi-carbon (C₂₊) products.^{11,12} This
21 Faradaic efficiency is appealing because C₂₊ products are generally more economically valuable than the
22 C₁ products (e.g., CO, HCOOH, CH₄) that are more readily produced by CO₂RR electrolysis.¹³

23

24 Solid-state copper is the only electrocatalyst reported to mediate high rates of CORR (i.e., $J > 100$
25 mA/cm²).^{14–19} This electrocatalyst produces a range of C₂₊ products (e.g., acetate, ethylene, and alcohols),

1 but not selectively. A major challenge for addressing CORR electrolysis is discovering an electrocatalyst
2 that can selectively produce a single C_{2+} product. The highest reported CORR selectivity is merely 48%
3 (for the formation of acetate).¹⁶ While there are a number of studies exploring ways to modify solid-state
4 electrocatalysts, our program is intrigued by the use of molecular electrocatalysts to control reaction
5 selectivity in flow cells because of the acute synthetic control over the electronic environment of the active
6 site and the primary coordination and secondary coordination spheres.^{3,20–24} While we have shown that
7 molecular electrocatalysts can operate at high current densities in a CO₂RR flow cell for the selective
8 formation of CO (i.e., FE_{CO} of 95% at 150 mA/cm²),²⁵ the use of molecular electrocatalysts that reduce
9 CO at high current densities under flow conditions has not yet been documented.^{26,27}

10 We report here that a copper phthalocyanine (**CuPc**; Fig. 1) molecular electrocatalyst can reduce
11 CO into C_{2+} products at a Faradaic efficiency ($FE_{C_{2+}}$) >70% at current densities up to 200 mA/cm². These
12 performance parameters were realized in a microfluidic flow cell by continuously delivering gaseous CO
13 and 2 M KOH electrolyte to the surface of a GDE. The C_{2+} formation rates we report here [i.e., current
14 density for C_{2+} products ($J_{C_{2+}}$) of ~150 mA/cm²] constitute a marked improvement relative to previous
15 reports of molecular electrocatalysts (i.e., $J_{C_{2+}}$ <10 mA/cm² in prior art; Fig. 1). Moreover, we show that
16 **CuPc** maintains stable C_{2+} formation at 100 mA/cm² for >20 h without significant declines in
17 electrocatalyst activity (i.e., <10% decrease in $FE_{C_{2+}}$). These results are not only commensurate with state-
18 of-the-art solid-state electrocatalysts,^{15,16} but the performance metrics also establish molecular
19 electrocatalysts as a new research domain for CO reduction electrocatalysts relevant to flow cell reactors.

20

Fig. 1 | CuPc molecular electrocatalyst competes with state-of-the-art solid-state copper electrocatalysts. Faradaic efficiencies towards C_{2+} ($FE_{C_{2+}}$) production as a function of current density (J) for high-performing molecular electrocatalysts^{28–33} (blue; details in Supplementary Table 1) and the state-of-the-art solid-state Cu electrocatalysts.^{5,14–18} (gray) are presented. The data for **CuPc** featured in this study is indicated in orange.

Results and Discussions

All electrochemical experiments in this study were performed in a commercial three-compartment flow cell reactor (Micro Flow Cell®) operating in a “flow-through” configuration (Fig. 2). This “flow-through” configuration forces gaseous reactants to penetrate through the electrocatalyst on the electrode, differing from the traditional “flow-by” configuration whereby gas reactants reach the electrocatalyst only by diffusion (see Supplementary Fig. 1 for details).³⁴ The electrochemical reactor consisted of two PTFE housing pieces, a Pt/Ni anode current collector, a Ti cathode current collector, three polytetrafluoroethylene (PTFE) flow frames containing expanded PTFE meshes for turbulence, and rubber gaskets. The first flow frame delivered $\text{CO}_{(\text{g})}$ at 10 standard cubic centimeters per minute (sccm) from the back side and through the **CuPc**-coated gas diffusion electrode (GDE) that is fixed on the cathode current collector with a Ti frame. The unreacted CO and product mixture is delivered into the second flow

frame carrying 2 M KOH catholyte solution at a flow rate of 6 mL/min between the anion exchange membrane (AEM, Sustainion®) and the electrocatalyst side of the GDE. A leak-free Ag/AgCl reference electrode was inserted into the second flow frame to measure the cathodic potential. On the opposing side of the AEM, 2 M KOH anolyte was circulated at 6 mL/min through a third flow frame between the AEM and the nickel foam fixed on the anode current collector. The outlet catholyte was recycled to a reservoir that was continuously purged through the headspace with N_{2(g)} at 44 sccm to carry CO and gaseous product to the in line gas chromatograph (GC) for analysis. The flow rate of the gas mixture was measured by a flow meter before the gas entered into the GC. Liquid products collected from both the catholyte and anolyte were quantified by ¹H NMR spectroscopy using methylsulfonylmethane (MSM) and potassium hydrogen phthalate (KHP) as internal standards with corresponding calibration curves.

Fig. 2| Illustration of the microfluidic flow cell architecture. **a**, Exploded view of the microfluidic cell used in this study. **b**, Scheme of the flow of species at the cathode electrocatalyst. Reactant CO gas flows through the gas diffusion electrode (GDE) for its reduction to various products. KOH catholyte furnishes an alkaline environment at the cathode and transports gaseous and liquid products to the reservoir for analysis by GC or ¹H NMR, respectively. The flow of CO and KOH catholyte are indicated in black dash line. The molecular structure of CO, C₂H₄ and AcO⁻ are shown. (red, oxygen; grey, carbon; white, hydrogen)

CuPc was immobilized on carbon black by sonication in ethanol for 1 h. Nafion® ionomer was then added to the solution and sonicated for another hour. Oxide-derived copper electrocatalysts (**OD-Cu**)

1 were synthesized for control experiments according to a previously reported procedure.¹⁷ These two
2 electrocatalyst ink solutions were spray-coated separately onto the microporous layer (MPL) of
3 hydrophobic gas diffusion layers (GDLs; $2 \times 2 \text{ cm}^2$; Sigracet 39BB) to form GDEs. Each batch of GDE
4 furnished an average **CuPc** loading of $\sim 0.6 \text{ mg/cm}^2$. The loading of **OD-Cu** was measured to be ~ 0.6
5 mg/cm^2 . The **OD-Cu** coated GDEs were subjected to a preconditioning step where a constant cathodic
6 current of 15 mA/cm^2 was applied for 800 s.

7
8 To test the competency of **CuPc** as an electrocatalyst, we performed chronopotentiometry
9 experiments at constant current densities of 50, 100, 150, and 200 mA/cm^2 . Each current density was
10 tested in triplicate with a freshly prepared GDE and electrolyte. GC analysis of the gaseous products and
11 ^1H NMR analysis of liquid products were completed after 20 min of electrolysis. The GC analyses were
12 used to quantify all gaseous products detected: C_2H_4 , H_2 , and CH_4 . ^1H NMR analyses of the anolyte and
13 catholyte reservoirs was used to quantify all liquid products detected acetate (AcO^-), ethanol ($\text{C}_2\text{H}_5\text{O}$),
14 propanol ($\text{C}_3\text{H}_7\text{O}$), allyl alcohol ($\text{C}_3\text{H}_6\text{O}$), and trace amounts of formate (HCOO^-) (Fig. 3a). The chemical
15 shifts of these products were consistent with the literature values.³⁵ Standard solutions were prepared and
16 analyzed using ^1H NMR to obtain calibration curves for each liquid product (Supplementary Fig. 8). AcO^-
17 was found to be the predominant liquid species. The FE_{AcO^-} of 36% at 200 mA/cm^2 corresponds to a
18 turnover frequency (TOF) of 4.11 min^{-1} for each molecular electrocatalyst site (see Methods for details).
19 The predominant gaseous product was C_2H_4 with a $FE_{\text{C}_2\text{H}_4}$ of $\sim 20\%$ at all applied current densities that
20 were tested. The highest partial current density for C_{2+} formation ($J_{\text{C}_{2+}}$) was measured to be 147 ± 6
21 mA/cm^2 , and was achieved at a cathode potential of -1.61 V (vs. RHE, without iR correction). This
22 performance corresponds to a high single pass conversion of 32%. These metrics of electroreduction with
23 a molecular electrocatalyst at practical rates show a significant improvement relative to state-of-the-art
24 molecular electrocatalysts ($J_{\text{C}_{2+}} < 10 \text{ mA/cm}^2$). We attribute this increased performance to the efficient
25 delivery of CO to the electrocatalyst in our flow cell.^{34,36,37}

Fig. 3 | CO electroreduction performance of the CuPc and OD-Cu. **a**, Cumulative *FE* as a function of applied current density for CO electroreduction by CuPc. Error bars represent standard deviation from at least three independent measurements. **b**, Partial current densities of C₂⁺ as a function of applied potentials of -0.77, -1.07, -1.31, and -1.61 V vs RHE for CO electroreduction on CuPc. Alcohols include ethanol, propanol, and allyl alcohol. **c**, Product distribution of C₂⁺ for CO electroreduction on CuPc and OD-Cu at a current density of 200 mA/cm². See Supplementary Fig. 2 for *FE* of each electrolysis product. **d**, *FE*_{C₂⁺} (y axis, left) and cathodic potential (y axis, right) as a function of time over a span of 20 h of electrolysis with CuPc at current density of 100 mA/cm². See Supplementary Fig. 3 for *FE* of each electrolysis product. The value of *FE*_{C₂⁺} is obtained by the summation of *FE*_{C₂H₄}, *FE*_{AcO⁻}, *FE*_{C₂H₆O}, *FE*_{C₃H₈O}, and *FE*_{C₃H₆O}.

As a control experiment, we then tested the state-of-the-art electrocatalyst OD-Cu under the same operating conditions as those used for the CuPc electrocatalyst (i.e., electrolyte composition, current density, etc.). These electrolysis experiments with OD-Cu yielded a similar product distribution of ethylene, oxygenates, and hydrogen that matched literature reports (Fig. 3c).¹⁷ The relative amounts of

C₂₊ produced matched that observed with **CuPc**, yet **CuPc** was 25% more selective towards AcO⁻ production than **OD-Cu**, while **OD-Cu** was 12 % more selective for alcohols (e.g., ethanol and propanol).

We tested the stability of **CuPc** in a flow cell by measuring the *FE* of the different products over 20 h of electrolysis at 100 mA/cm² (Fig. 3d). During this stability test, the KOH catholyte was periodically replenished to ensure the concentrations of liquid products remained within the calibration ranges for ¹H NMR analyses. A high *FE*_{C₂₊} of ≥64% was maintained throughout the 20 h period of electrolysis. While a 10% decrease in *FE*_{C₂₊} was observed over this period, this value compares remarkably favorably to solid-state Cu electrocatalysts that lasted merely 3 h at the same current densities.^{16,17} One reason our system may be more stable than previous reports is because we operated the microfluidic flow cell in a flow-through configuration. This flow-through configuration pushes gaseous CO through the GDE and helps to mitigate “flooding” which is a common flow cell failure mode due to excessive electrolyte percolation into the GDE.³⁸

We analyzed the morphologies of the electrocatalyst layers on the carbon GDEs before and after 2 h of electrolysis at 150 mA/cm² using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. We observed similar porous morphologies and evenly distributed elemental signals in the SEM and EDX images, respectively, but there was evidence of some electrocatalyst aggregation (Supplementary Figs. 4–5). X-ray diffraction (XRD) spectroscopy measurements showed an identical crystallinity pattern before and after the electrolysis (Supplementary Fig. 6). X-ray photoelectron spectroscopy (XPS) measurements of **CuPc** before and after 20 h of electrolysis at 100 mA/cm² showed no changes in Cu²⁺ signals (~935.3 eV and ~955.2 eV; Supplementary Fig. 7). Collectively, these XRD and XPS measurements confirm **CuPc** remains largely intact after electrolysis (i.e., no solid-state copper was detected).

Conclusion

We show in this study how a molecular electrocatalyst, **CuPc**, coated on a carbon-based GDE can mediate the electrolytic conversion of CO into C₂₊ products in a microfluidic flow cell at high rates of C₂₊ formation (i.e., J_{C_2+} of 147 ± 6 mA/cm²). This conversion rate exceeds all previous reports of molecular electrocatalysts. These findings present the opportunity to explore the rich library of molecular catalysts available in the literature, as well as new derivatives, for effective CO electrolysis at industrially-relevant rates of product formation. Moreover, the well-defined structure of molecular electrocatalysts can be used to elucidate reaction mechanisms pertinent to the rate-limiting carbon-carbon formation step that is relevant to both CO₂RR and CORR. We contend that further investigations into molecular electrocatalysts in flow reactors will broaden the scope of energy-dense products that can be produced efficiently from CO.

1 **Methods**

2 **Materials.** Copper phthalocyanine (**CuPc**, dye content >99%), potassium hydroxide (KOH),
3 methylsulfonylmethane (MSM), and potassium hydrogen phthalate (KHP) were purchased from Sigma-
4 Aldrich. The gas diffusion electrode (GDE) (Sigracet 39 BB) and carbon powder (Vulcan XC-72R) were
5 both purchased from Fuel Cell Store. All chemicals were used as received without further purification.
6 Anionic exchange membrane (AEM) Sustainion® X37-50 Grade RT membrane was purchased from
7 Dioxide Materials and activated in 1.0 M KOH before use. Nickel foam was purchased from MTI
8 corporate. N₂ (99%), CO (99%), and Ar (99.999%) gasses were obtained from Praxair Canada Inc.

9
10 **Electrode preparation.** The catalyst inks were prepared by sonicating 80 mg of **CuPc** with 80 mg carbon
11 black in 50 mL EtOH solution for 1 h. Nafion® 117 solution (5 wt% in a mixture of lower aliphatic alcohols
12 and water) was added and then sonicated for another 1 h. These catalyst inks were deposited onto carbon
13 GDLs covered by a metal plate with 4-cm² windows using a SonoTek ExactaCoat spray-coater operating
14 at nozzle power of 1 W and flow rate of 0.6 mL min⁻¹. The hotplate below the GDEs was heated to 30 °C
15 to accelerate solvent evaporation during ultrasonic spray-coating. The carbon paper was cleaned by air
16 plasma prior to ultrasonic spray-coat deposition. The nickel foam was cleaned by sonication in acetone
17 and then in deionized water. To synthesize oxide-derived Cu (**OD-Cu**), copper nanoparticles were
18 annealed at 500 °C for 3 h and cooled to room temperature. 100 mg of the resulting powder was then
19 sonicated together with 568 µL Nafion® 117 solution, 0.5 mL tetrahydrofuran containing 0.5 mg mL⁻¹ of
20 multiwall carbon nanotubes (>98% carbon basis, O.D.×L 6–13nm×2.5–20µm; Sigma-Aldrich), and 12
21 mL isopropanol. The catalyst ink was manually spray-coated onto carbon paper covered by a metal plate
22 with 4-cm² windows and dried under a heat lamp. The **OD-Cu** electrode was preconditioned via in situ
23 electrochemical reduction at a constant current density of 15 mA cm⁻² for 800 s.

24

Electrode Characterization. X-ray Diffraction (XRD) experiments were operated by Bruker D8-Advance X-ray diffractometer with a Bragg-Brentano configuration. The radiation source is Copper $K_{\alpha 1}$ & $K_{\alpha 2}$ with a nickel filter to remove K_{β} . The detector is LynxEye silicon strip and the slits are 1 mm divergent, 8 mm anti-scatter, and 2.5° soller. A FEI Helios NanoLab 650 scanning electron microscope (SEM) was utilized to obtain micrographs of the GDE surface morphology. Energy dispersive X-ray (EDX) maps of size 256×200 pixels were collected at 25 kX magnification using an accelerating voltage of 5 kV and beam current of 1.6 nA. X-ray photoelectron spectra (XPS) were collected with Kratos Analytical Axis Ultra DLD XPS system. The XPS spectra was calibrated with the C1s binding energy of 284.8 eV.

Electrolysis and product analysis. The electrolysis experiments were performed in a flow cell purchased from Electrocell®. A pre-calibrated leak-free Ag/AgCl reference electrode was used to record the cathodic potential. The CO flow rate to the cathode was set to 10 standard cubic centimeters per minute (sccm) by a flow controller (AALBORG); 2 M KOH was recirculated through the anolyte flow frame and catholyte flow frame at a flow rate of 6 mL min^{-1} using a peristaltic pump (McMaster-Carr; 43205K11). During the electrolysis, the outlet of CO was blocked by a syringe to force CO flow through the GDE. The KOH electrolyte outlet was introduced into a catholyte reservoir where gas and liquid are separated. $\text{N}_{2(g)}$ was supplied at 44 sccm to carry the gaseous product to the gas-sampling loop of the gas chromatograph (GC; SRI-8610C; Mandel). A mass flow meter was used to measure the actual flow rate before the gas mixture entered into the GC. The GC was equipped with a packed MolSieve 5 A column and a packed HaySep D column. Argon (Praxair, 99.999%) was used as the carrier gas. A flame ionization detector with a methanizer was used to quantify CO, CH_4 , and C_2H_4 while a thermal conductivity detector (TCD) was used to quantify hydrogen. The GC was calibrated by injecting different calibration gas mixes from NorLAB from 100 to 50000 ppm containing CO, CH_4 , H_2 , C_2H_4 , C_2H_6 , CO_2 , and C_3H_8 . Aliquots were taken from both liquid anolyte and catholyte to quantify the liquid products by ^1H NMR. ^1H NMR spectra were collected on a Bruker Avance 400 dir instrument at ambient temperatures, operating at 400 MHz for

¹H nuclei under water suppression mode. Each product was quantified by the corresponding linear calibration curve made by various amounts of pure chemicals and methylsulfonylmethane and potassium hydrogen phthalate as internal standards. Electrochemical measurements were conducted at room temperature and pressure by means of a potentiostat (CH instruments 660D with a 680C Amp Booster) through three-electrode cell measurements. Current density is expressed as the total current divided by the geometric catalyst area of the electrodes (4 cm²). The ink-uncoated area of GDE was taped by Kapton tape and covered with a EPDM gasket. The Faradaic efficiency (FE) of a gaseous product k was determined in accordance with equation 3.

$$FE = \frac{q_k F x_k F_m}{I} \quad \text{Eq. 3}$$

Where q_k is the number of electrons exchanged, F is Faraday's constant ($F = 96,485 \text{ C mol}^{-1}$), x_k is the mole fraction of the gas k in the gaseous mixture analyzed, F_m is the molar flow rate in mol/s, and I is the total current in A. The molar flow rate is derived from the volume flow rate F_v by the relation $F_m = pF_v/RT$, with p being the atmospheric pressure in Pa, R the ideal gas constant of $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, and T the temperature in K. The FE of a liquid product j was determined by equation 4.

$$FE = \frac{q_j F n_j}{It} \quad \text{Eq. 4}$$

Where q_j is the number of electrons exchanged, F is Faraday's constant ($F = 96,485 \text{ C mol}^{-1}$), n_j is the moles of product j , I is the applied current, t is the electrolysis time. Turnover frequency (TOF) was calculated using equation 5 for each experiment³⁹:

$$TOF = \frac{I \times FE}{q \times F \times n_{cat}} \quad \text{Eq. 5}$$

Where q is the number of electrons exchanged, F is Faraday's constant ($F = 96,485 \text{ C mol}^{-1}$), n_{cat} is the moles of catalyst deposited on the gas diffusion electrode, I is the applied current, FE is Faraday efficiency. The consumption of CO (in mL/min) was obtained by equation 6. Then, the single pass conversion was calculated using equation 7 (exemple for AcO^-).

$$\left(\frac{\text{mC}}{\text{s cm}^2}\right)\left(\frac{1 \text{ C}}{1000 \text{ mC}}\right)\left(\frac{\text{mol } e^-}{96485 \text{ C}}\right)\left(\frac{1 \text{ mol } \text{AcO}^{--}}{4 \text{ mol } e^-}\right)\left(\frac{2 \text{ mol } \text{CO}}{1 \text{ mol } \text{AcO}^{--}}\right)\left(\frac{22.4 \text{ L}}{1 \text{ mol } \text{CO}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)\left(\frac{60 \text{ s}}{1 \text{ min}}\right)(4 \text{ cm}^2 \text{ geometric})$$

Eq. 6

$$\% \text{ CO conversion to } \text{AcO}^- = 100 \times \frac{\text{mL min}^{-1} \text{ CO consumed for } \text{AcO}^-}{10 \text{ mL min}^{-1} \text{ CO flow rate}}$$

Eq. 7

The total single pass conversion was calculated by dividing the sum of CO consumed (in mL min^{-1}) for each product by the inlet CO flow rate of 10 mL min^{-1} .

Author contributions

C.P.B. supervised the project. S.R. and C.P.B. conceived the study. S.R. and W.W. generated the figures. S.R. and Z.Z. designed the experiments. S.R., A.G.F., and W.W. performed the flow cell experiments. D.J.D. performed the SEM/EDX characterization of the GDEs. S.R. and E.W.L. wrote the first manuscript draft. All authors contributed to manuscript writing.

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Figures

Figure 1

CuPc molecular electrocatalyst competes with state-of-the-art solid-state copper electrocatalysts. Faradaic efficiencies towards C_{2+} ($FE_{C_{2+}}$) production as a function of current density (J) for high-performing molecular electrocatalysts^{28–33} (blue; details in Supplementary Table 1) and the state-of-the-art solid-state Cu electrocatalysts^{5,14–18} (gray) are presented. The data for CuPc featured in this study is indicated in orange.

Figure 2

Illustration of the microfluidic flow cell architecture. a, Exploded view of the microfluidic cell used in this study. b, Scheme of the flow of species at the cathode electrocatalyst. Reactant CO gas flows through the gas diffusion electrode (GDE) for its reduction to various products. KOH catholyte furnishes an alkaline environment at the cathode and transports gaseous and liquid products to the reservoir for analysis by GC or 1H NMR, respectively. The flow of CO and KOH catholyte are indicated in black dash line. The molecular structure of CO, C_2H_4 and AcO^- are shown. (red, oxygen; grey, carbon; white, hydrogen)

Figure 3

CO electroreduction performance of the CuPc and OD-Cu. a, Cumulative FE as a function of applied current density for CO electroreduction by CuPc. Error bars represent standard deviation from at least three independent measurements. b, Partial current densities of C₂⁺ as a function of applied potentials of -0.77, -1.07, -1.31, and -1.61 V vs RHE for CO electroreduction on CuPc. Alcohols include ethanol, propanol, and allyl alcohol. c, Product distribution of C₂⁺ for CO electroreduction on CuPc and OD-Cu at a current density of 200 mA/cm². See Supplementary Fig. 2 for FE of each electrolysis product. d, FEC₂⁺ (y axis, left) and cathodic potential (y axis, right) as a function of time over a span of 20 h of electrolysis with CuPc at current density of 100 mA/cm². See Supplementary Fig. 3 for FE of each electrolysis product. The value of FEC₂⁺ is obtained by the summation of FEC₂H₄, FEAcO⁻, FEC₂H₆O, FEC₃H₈O, and FEC₃H₆O.

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