Electrocatalysts derived from copper complexes transform CO into C2+ products effectively in a flow cell

Shaoxuan Ren

University of British Columbia

Zishuai Zhang

University of British Columbia

Eric Lees

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

Arthur Fink

University of British Columbia

Luke Melo

University of British Columbia

Camden Hunt

University of British Columbia

David Dvorak

University of British Columbia

Wen Yu Wu

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

Edward Grant

University of British Columbia

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

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

Research Article

Keywords: Electrocatalysis, Carbon-neutral Chemicals and Fuels, electrochemical CO reduction

Posted Date: October 6th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-83176/v2>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Chemistry – A European Journal on March 28th, 2022. See the published version at <https://doi.org/10.1002/chem.202200340>.

Electrocatalysts derived from copper complexes transform CO into C₂₊ products effectively in a flow cell

Shaoxuan Ren,¹ Zishuai Zhang,¹ Eric W. Lees,² Arthur G. Fink,¹ Luke Melo,¹ Camden Hunt,³ David J. Dvorak,³ Wenyu Wu,² Edward R. Grant,¹ 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

Electrochemical reactors that electrolytically convert CO_2 into higher-value chemicals and fuels often pass a concentrated hydroxide electrolyte across the cathode. The challenge is that this strongly alkaline medium converts the majority of CO_2 into unreactive HCO_3^- and CO_3^{2-} byproducts rather than into CO_2 reduction reaction (CO₂RR) products. The electrolysis of CO (instead of CO_2) does not suffer from this undesirable reaction chemistry because CO does not react with OH^- . Moreover, CO can be more readily reduced into products containing two or more carbon atoms (i.e., C_{2+} products) than CO_2 . We demonstrate here that an electrocatalyst layer derived from copper phthalocyanine (**CuPc**) mediates this conversion effectively in a flow cell. This catalyst achieved a 25% higher selectivity for acetate formation at 200 mA/cm² than known state-of-art solid-state catalysts. A gas diffusion electrode coated with **CuPc** electrolyzed CO into C_{2+} products at high rates of product formation (i.e., current densities $\geq 200 \text{ mA/cm}^2$), and at high Faradaic efficiencies for C_{2+} production ($FE_{\text{C}_{2+}}$; $>70\%$ at 200 mA/cm²). While *operando* Raman spectroscopy did not reveal evidence of structural changes of the copper molecular complex, X-ray photoelectron spectroscopy points to the catalyst undergoing a conversion to a metallic copper species during catalysis. Notwithstanding, the ligand environment about the metal still impacts catalysis, which we demonstrated through the study of a homologous CuPc bearing ethoxy substituents. These findings reveal new strategies for using metal complexes for the formation of carbon-neutral chemicals and fuels at industrially relevant conditions.

Introduction

Using renewable electricity to drive the CO₂ reduction reaction (CO₂RR) is an appealing way to synthesize carbon-neutral chemicals and fuels.¹ Driving electrolytic CO₂RR at a high rate of product formation requires the continuous feed of reactants to the respective electrodes in a flow cell (or “electrolyzer”).^{1,2} A microfluidic flow cell is a type of flow cell proven to be particularly effective for mediating CO₂RR electrolysis at high current densities ($J > 500 \text{ mA/cm}^2$).^{3,4} The highest performance microfluidic CO₂RR flow cells reported to date pass a highly alkaline aqueous solution (e.g., 7 M KOH) between an anion exchange membrane (AEM) and cathodic gas diffusion electrode (GDE).⁵ This high pH serves to promote CO₂RR by suppressing the competing hydrogen evolution reaction (HER); however, these strongly alkaline conditions convert up to 70% of reacted CO₂ into unreactive (bi)carbonates (Eq. 1–2).^{6,7} This formation of (bi)carbonates not only impacts the energy efficiency of the reactor, it also induces solid salt formation that compromises flow cell operation.^{8,9}

The use of CO as a reagent (instead of CO₂) can produce the same carbon-containing products as CO₂RR electrolysis while bypassing the formation of (bi)carbonates that reduce both the efficiency and durability of a flow cell.^{10–12} An additional advantage of CO reduction reaction (CORR) electrolysis is that the process saturates the electrocatalyst surface with adsorbed CO (*CO),^{13,14} which increases the probability of carbon-carbon coupling to form multi-carbon (C₂₊) products.^{15,16} This ability to favor carbon-carbon bond formation reaction chemistry is appealing because C₂₊ products are generally more economically valuable than the C₁ products (e.g., CO, HCOOH) that are more readily produced by CO₂RR electrolysis.¹⁷

The challenge to date is that solid-state copper is the only electrocatalyst known to mediate high rates of CORR (i.e., $J > 100 \text{ mA/cm}^2$).^{18–23} This electrocatalyst produces a range of C_{2+} products (e.g., acetate, ethylene, and alcohols), but not selectively. A CORR electrocatalyst that can favour the formation of a single C_{2+} product is needed, yet the highest reported CORR selectivity is merely 48% (for the formation of acetate).^{19,20,24,25} While there are a number of ways to modify solid-state electrocatalysts, our program is intrigued by the use of molecular electrocatalysts to control reaction selectivity in flow cells because of the acute synthetic control over the electronic environment of the active site as well as the primary coordination and secondary coordination spheres.^{3,26–30} We showed previously that a cobalt phthalocyanine complex can operate at high current densities in a CO₂RR flow cell for the selective conversion of CO₂ into CO (i.e., FE_{CO} of 95% at 150 mA/cm^2),³¹ but the use of molecular electrocatalysts that reduce CO at high current densities in a flow cell has not yet been documented.³²

We report here that coating a gas diffusion electrode with copper phthalocyanine (**CuPc**, Supplementary Fig. 1) is effective at reducing CO into C_{2+} products at a Faradaic efficiency ($FE_{\text{C}_{2+}}$) $> 70\%$ at current densities up to 200 mA/cm^2 in a flow cell. Cognizant that molecular catalysts are known to degrade under such conditions,³³ we performed a series of control experiments to confirm the molecular structure of the catalysts does undergo a transformation into a metallic species during electrolysis. This molecule-derived catalyst layer yields partial current densities for C_{2+} formation of $\sim 150 \text{ mA/cm}^2$.

Results and Discussion

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. 1). This “flow-through” configuration forces convective transport of gaseous reactants through the porous electrode, differing from the traditional “flow-by” configuration whereby gas reactants reach the electrocatalyst only by diffusion (see Supplementary Fig. 2 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 CO_(g) at 10 standard cubic centimeters per minute (sccm) from the back side and through the carbon black immobilized **CuPc** coated GDE that is fixed on the cathode current collector with a titanium 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 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 CO₂RR products and hydrogen gas from the hydrogen evolution reaction (HER)s 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 nuclear magnetic resonance (NMR) spectroscopy using methylsulfonylmethane (MSM) and potassium hydrogen phthalate (KHP) as internal standards with corresponding calibration curves.

Fig. 1| Exploded view of the microfluidic flow cell architecture used in this study. The graphic shows the positioning of the components, the feeds going into the inlet, and the products (C_{2+} includes C_2H_4 , AcO^- , C_2H_6O , C_3H_8O , C_3H_6O) exiting the outlet, as well as the electrodes that are physically connected to the external power supply. **inset**, photograph of the microfluidic flow cell.

We first immobilized **CuPc** 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 supported on carbon nanotubes (**OD-Cu**) were prepared for control experiments according to a previously reported procedure.²¹ These two electrocatalyst ink solutions were spray-coated separately onto the microporous layer (MPL) of hydrophobic gas diffusion layers (GDLs; $2 \times 2 \text{ cm}^2$; Sigracet 39BB) to form GDEs with catalysts (**CuPc** and **OD-Cu**) loadings of $\sim 0.6 \text{ mg/cm}^2$. The **OD-Cu** coated GDEs were subjected to a preconditioning step where a constant cathodic current of 15 mA/cm^2 was applied for 800 s.

To test the competency of **CuPc** as a CORR electrocatalyst, we performed chronopotentiometry experiments at constant current densities of 50, 100, 150, and 200 mA/cm². Each current density was tested in triplicate with a freshly prepared GDE and electrolyte. GC analysis of the gaseous products and ¹H NMR analysis of liquid products were completed after 20 min of electrolysis. The GC analyses were used to quantify all gaseous products detected: C₂H₄, H₂, and CH₄. ¹H NMR analyses of the anolyte and catholyte reservoirs were used to quantify all liquid products detected acetate (AcO⁻), ethanol (C₂H₆O), propanol (C₃H₈O), and allyl alcohol (C₃H₆O) (Fig. 2). The chemical shifts of these products were consistent with the literature values.³⁵ Standard solutions were prepared and analyzed using ¹H NMR to obtain calibration curves for each liquid product (Supplementary Fig. 3). AcO⁻ was found to be the predominant liquid species. The FE_{AcO^-} of 36% at 200 mA/cm² corresponds to a turnover frequency (TOF) of 4.11 min⁻¹ for each copper site (see Methods for details). The predominant gaseous product was C₂H₄ with a $FE_{C_2H_4}$ of ~20% at all applied current densities that were tested. The highest partial current density for C₂₊ formation (J_{C_2+}) was measured to be 147 ± 6 mA/cm², and was achieved at a high single-pass conversion of 32%. A high single-pass conversion reduces the need to separate unreacted CO₂ from the product mixture stream. The electrolysis of CO in a batch-type “H-cell”, in which CO mass transport is much lower, yields a far lower J_{C_2+} (16 mA/cm² *cf.* 147 mA/cm²) at the same potential and pH (Supplementary Fig. 4).²¹

Fig. 2 | CO electroreduction performance of a GDE coated with CuPc. **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 C_{2+} as a function of applied potentials for CO electroreduction on **CuPc**. Alcohols include ethanol, propanol, and allyl alcohol.

We tested the state-of-the-art electrocatalyst **OD-Cu** under the same operating conditions (i.e., electrolyte composition, current density, etc.) as those used for experiments with the **CuPc** immobilized carbon black GDE. Our electrolysis experiments with **OD-Cu** yielded a product distribution of ethylene, oxygenates, and hydrogen that matched literature reports (Supplementary Fig. 5).²¹ The relative amounts of C_{2+} produced matched those 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 then tested how robust the GDE was in the flow cell by measuring the *FE* of the different products over 20 h of electrolysis at 100 mA/cm² periodically replenishing the KOH catholyte to ensure the concentrations of liquid products remained within the calibration ranges for ¹H NMR analyses (Supplementary Fig. 6). A high $FE_{C_{2+}}$ of >60% was maintained throughout the 20 h of electrolysis. We did observe a 10% decrease in $FE_{C_{2+}}$ over this period, but this decline in performance compares favorably to solid-state Cu electrocatalysts operated at the same current densities in microfluidic cells.²⁰ Our system is likely more stable than these previous reports because of the cell design: We operated the microfluidic flow cell in a “flow-through” configuration rather than a “flow-by” configuration (i.e., we do not claim that **CuPc** is more stable than a solid-state catalyst). The flow-through configuration pushes gaseous CO through the GDE to mitigate “flooding”, a common flow cell failure mode due to excessive electrolyte percolation into the GDE.³⁶

Fig. 3 | X-ray Photoelectron Spectra measurements of CuPc before and after electrolysis. **a**, Cu 2p and **b**, N 1s of CuPc before the electrolysis. **c**, Cu 2p and **d**, N 1s after the electrolysis for 4 h at 200 mA/cm². Post electrolysis samples were stored under N₂ before the analysis.

The durability of the GDE with the electrocatalyst layer was tested by analyzing the gas diffusion electrodes before, during and after electrolysis using a variety of techniques. SEM imaging of the GDEs and powder XRD diffractograms before and after electrolysis did not detect any structural changes for the copper molecular complex (Supplementary Fig. 7–9). *Operando* Raman spectroscopy also did not reveal any changes in the molecular complexes (Supplementary Fig. 10). However, X-ray photoelectron spectroscopy (XPS) did indicate chemical changes of **CuPc** at the GDE surface after 4 h of continuous electrolysis at 200 mA/cm². The deconvoluted Cu 2p spectra indicate the reduction of Cu^{2+} (935.4 eV) to a combination of Cu^+ (934.1 eV) and Cu^0 (933.1 eV) species (Fig. 3a, 3c). The high-resolution N 1s spectrum of **CuPc** catalyst also showed the emergence of a new peak at 400.3 eV

after electrolysis (Fig. 3b, 3d). This peak has been previously ascribed to pyrrolic nitrogen (N-H) of non-metallated H₂Pc (Supplementary Fig. 11). These results preclude our ability to claim that the molecular species remains intact during catalysis.

Fig. 4 | Quantitative X-ray Photoelectron elemental measurements of CuPc coated electrodes before and after electrolysis. Green, element analysis of the GDE before the electrolysis; red, element analysis of the GDE after the electrolysis at 200 mA/cm² for 4 h; grey, analysis of GDE after the electrolysis and air exposure for three days.

Previous studies have claimed that **CuPc** can undergo reversible ligation during electrolysis experiments tested in an H-cell.^{33,37} This reversible ligation is unlikely to be occurring in our experiments recorded in a flow cell: Quantitative XPS element analyses showed a 4-fold reduction in the relative atomic amount of N to Cu present in the GDE following electrolysis (Fig. 4). This experiment is consistent with the ligands being liberated from the metal and removed from the flow cell, and the formation of a metallic copper species during electrolysis.

We note that *in-situ* generated metallic copper clusters are air-sensitive and can be easily reoxidized, which can complicate the XPS analysis of the copper oxidation states. For example, air exposure of the post-electrolysis sample for three days resulted in a significant increase of Cu²⁺ component, yet no change in N:Cu ratio was observed (Fig. 4, Supplementary Fig. 12). From this

experience, the quantitative elemental analysis of N:Cu ratio should be performed to monitor the molecular integrity of **CuPc**.

While the reduced form of the electrocatalyst is difficult to define at this stage, the nature of the ligand still clearly plays a role during catalysis. We prepared an analogous catalyst bearing ethoxy substituents about the ligand that we refer to here as “**CuPc-OEt**”. Compared with the unmodified CuPc, these ethoxy group-functionalized CuPc-OEt catalysts exhibit a 38% higher $FE_{C_{2+}}$ at 300 mA/cm² (Supplementary Fig. 13). This finding points to the ligand environment affecting the nature of the catalytically active species, a subject that will be the focus of future investigations.³³

Conclusion

We show in this study how a copper complex, **CuPc**, coated on a carbon-based GDE can mediate the electrolytic conversion of CO into C_{2+} products in a microfluidic flow cell at current densities of ~ 150 mA/cm². The molecular species does not remain intact during electrolysis, but the electrocatalyst does behave as an effective electrocatalyst layer. These findings present the opportunity to use the rich library of metal-complexes catalysts available in the literature, as well as new derivatives, for effective CO electrolysis at industrially-relevant rates of product formation. We contend that further investigations into metal complexes electrocatalysts in flow reactors will broaden the scope of energy-dense products that can be produced efficiently from CO.

Methods

Materials. Copper phthalocyanine (**CuPc**, dye content >99%), potassium hydroxide (KOH), methylsulfonylmethane (MSM), copper nanoparticle (TEM 25 nm), and potassium hydrogen phthalate (KHP) were purchased from Sigma-Aldrich. The gas diffusion electrode (GDE) (Sigracet 39 BB) and carbon powder (Vulcan XC-72R) were both purchased from Fuel Cell Store. All chemicals were used as received without further purification. Anionic exchange membrane (AEM) Sustainion® X37-50 Grade RT membrane was purchased from Dioxide Materials and activated in 1.0 M KOH before use. Nickel foam was purchased from MTI corporate. N₂ (99%), CO (99%), and Ar (99.999%) gasses were obtained from Praxair Canada Inc.

Syntheses of chemicals and catalysts

3,6-Diethoxyphthalonitrile. 3,6-Diethoxyphthalonitrile was synthesized using a modified literature procedure.⁵⁰ A mixture of 2,3-dicyanohydroquinone (10 g, 62.5 mmol, 1 equiv.) and K₂CO₃ (17.26 g, 124 mmol, 2 equiv.) in 125 mL of wet acetone was sparged with Ar for 30 minutes then heated to reflux. Ethyl iodide (29 g, 186 mmol, 3 equiv.) was then added dropwise to the mixture. The yellow slurry was stirred under reflux for 24 h. After cooling, the yellow solid was filtered and washed successively with 500 mL of DI water, 150 mL of EtOH, and 150 mL of Et₂O. The product was collected and dried under reduced pressure for 24 h, affording a white powder. Yield: 5.34 g (45.8%). ¹H NMR (400 MHz, CDCl₃, see Supplementary Fig. 14)

Lithium 1,4,8,11,15,18,22,25-Octaethoxyphthalocyanine (HLiPc-OEt). This precursor was synthesized using the same procedure.⁵⁰ A mixture of 5.28 g (0.025 mol, 1 equiv) of 3,6-diethoxyphthalonitrile in 75 mL of EtOH was heated to reflux and sparged with Ar for 10 min. Li metal (2.43 g, 0.347 mol, 12.5 equiv) were added over the course of 10 min. After addition of the Li pellets, another 75 mL of EtOH was added then refluxed for a week. After cooling, 100 mL of EtOH and 100 mL of DI water was added, and the green solid was filtered off and washed with 100 mL of DI water, 100 mL of EtOH, and

100 mL of Et₂O. The resulting green powder was dried under high vacuum overnight. Yield: 4.86 g (98%). ¹H NMR (400 MHz, CDCl₃, see Supplementary Fig. 15)

CuPc-OEt. This compound was synthesized using a modified literature procedure.⁵¹ EtOPcHLi (0.414 g, 0.48 mmol, 1 equiv.), CuCl₂ (0.322 g, 2.40 mmol, 5 equiv.), and NaHCO₃ (0.214 g, 2.54 mmol, 5.3 equiv.) were combined in a round-bottom flask with 20 mL of DMF, and the resulting mixture was heated to 165 °C for 3 days. 160 mL of DI water was then added and the solution was stirred for 30 min, and subsequently filtered out, leaving a dark green solid. The solid was washed with 600 mL of DI water and 40 mL of EtOH and subsequently collected and dried under reduced pressure. Yield: 0.16 g (36.4%). ¹H NMR (400 MHz, CDCl₃, see Supplementary Fig. 16): δ 4.58 (bs, 16H), δ 1.61 (bs, 24H). MS (MALDI-TOF, see Supplementary Fig. 17): calculated 927.29 (M⁺) found 927.50 (M⁺).

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

preconditioned via *in-situ* electrochemical reduction at a constant current density of 15 mA/cm² for 800 s.

Electrode Characterization. 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. XPS Samples were stored in a glove box under nitrogen atmosphere. These samples were removed from the glove box 30 minutes before they were loaded into the XPS chamber. Samples were cut into ~1 mm x 1 mm pieces. Samples were handled with tweezers, and only the perimeter of the samples were touched.

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 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 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. 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, CH₄, and C₂H₄ 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, CH₄, H₂, C₂H₄, C₂H₆, CO₂, and C₃H₈. 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 cm^2). The ink-uncoated area of GDE was taped by Kapton tape and covered with an 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 experiment³⁸:

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

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 (example for AcO^-).

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

Eq. 6

$$\% \text{ CO conversion to AcO}^- = 100 \times \frac{\text{mL min}^{-1} \text{ CO consumed for AcO}^-}{10 \text{ mL min}^{-1} \text{ CO flow rate}} \quad \text{Eq. 7}$$

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

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. S.R., E.W.L., and C.P.B. wrote the manuscript.

Acknowledgements

The authors are grateful to the Canadian Natural Science and Engineering Research Council (RGPIN-2018-06748), Canadian Foundation for Innovation (229288), Canadian Institute for Advanced Research (BSE-BERL-162173), Carbon Engineering Ltd., National Research Council of Canada's

Materials for Clean Fuels Challenge Program (MCF-107), and Canada Research Chairs for financial support. This work made use of the 4D LABS shared facilities supported by the Canada Foundation for Innovation (CFI), British Columbia Knowledge Development Fund (BCKDF), Western Economic Diversification Canada (WD), and Simon Fraser University (SFU). This research was undertaken thanks in part to funding from the Canada First Research Excellence Fund, Quantum Materials and Future Technologies Program.

References

1. Weekes, D. M., Salvatore, D. A., Reyes, A., Huang, A. & Berlinguette, C. P. Electrolytic CO₂ Reduction in a Flow Cell. *Acc. Chem. Res.* **51**, 910–918 (2018).
2. Xia, C. *et al.* Continuous production of pure liquid fuel solutions via electrocatalytic CO₂ reduction using solid-electrolyte devices. *Nature Energy* **4**, 776–785 (2019).
3. Wang, M. *et al.* CO₂ electrochemical catalytic reduction with a highly active cobalt phthalocyanine. *Nature Communications* vol. 10 (2019).
4. Verma, S., Lu, S. & Kenis, P. J. A. Co-electrolysis of CO₂ and glycerol as a pathway to carbon chemicals with improved technoeconomics due to low electricity consumption. *Nature Energy* **4**, 466 (2019).
5. Arquer, F. P. G. de *et al.* CO₂ electrolysis to multicarbon products at activities greater than 1 A cm⁻². *Science* vol. 367 661–666 (2020).
6. Ma, M. *et al.* Insights into the carbon balance for CO₂ electroreduction on Cu using gas diffusion electrode reactor designs. *Energy Environ. Sci.* **13**, 977–985 (2020).
7. Larrazábal, G. O. *et al.* Analysis of Mass Flows and Membrane Cross-over in CO₂ Reduction at High Current Densities in an MEA-Type Electrolyzer. *ACS Appl. Mater. Interfaces* **11**, 41281–41288 (2019).
8. Ma, M. *et al.* Insights into the carbon balance for CO₂ electroreduction on Cu using gas diffusion electrode reactor designs. *Energy Environ. Sci.* **13**, 977–985 (2020).
9. Burdyny, T. & Smith, W. A. CO₂ reduction on gas-diffusion electrodes and why catalytic performance must be assessed at commercially-relevant conditions. *Energy & Environmental Science* vol. 12 1442–1453

(2019).

10. Jouny, M., Hutchings, G. S. & Jiao, F. Carbon monoxide electroreduction as an emerging platform for carbon utilization. *Nature Catalysis* **2**, 1062–1070 (2019).
11. Ozden, A. *et al.* Cascade CO₂ electroreduction enables efficient carbonate-free production of ethylene. *Joule* (2021) doi:10.1016/j.joule.2021.01.007.
12. Overa, S., Feric, T. G., Park, A.-H. A. & Jiao, F. Tandem and Hybrid Processes for Carbon Dioxide Utilization. *Joule* **5**, 8–13 (2021).
13. Liu, X. *et al.* pH effects on the electrochemical reduction of CO(2) towards C₂ products on stepped copper. *Nat. Commun.* **10**, 32 (2019).
14. Nitopi, S. *et al.* Progress and Perspectives of Electrochemical CO₂ Reduction on Copper in Aqueous Electrolyte. *Chem. Rev.* **119**, 7610–7672 (2019).
15. Hori, Y., Wakebe, H., Tsukamoto, T. & Koga, O. Electrocatalytic process of CO selectivity in electrochemical reduction of CO₂ at metal electrodes in aqueous media. *Electrochim. Acta* **39**, 1833–1839 (1994).
16. Kortlever, R., Shen, J. & Schouten, K. J. P. Catalysts and reaction pathways for the electrochemical reduction of carbon dioxide. *The journal of* (2015).
17. Jouny, M., Luc, W. & Jiao, F. General Techno-Economic Analysis of CO₂ Electrolysis Systems. *Ind. Eng. Chem. Res.* **57**, 2165–2177 (2018).
18. Li, J. *et al.* Constraining CO coverage on copper promotes high-efficiency ethylene electroproduction. *Nature Catalysis* **2**, 1124–1131 (2019).
19. Ripatti, D. S., Veltman, T. R. & Kanan, M. W. Carbon Monoxide Gas Diffusion Electrolysis that Produces Concentrated C₂ Products with High Single-Pass Conversion. *Joule* **3**, 240–256 (2019).
20. Luc, W. *et al.* Two-dimensional copper nanosheets for electrochemical reduction of carbon monoxide to acetate. *Nature Catalysis* **2**, 423–430 (2019).
21. Jouny, M., Luc, W. & Jiao, F. High-rate electroreduction of carbon monoxide to multi-carbon products. *Nature Catalysis* **1**, 748–755 (2018).
22. Zhuang, T.-T. *et al.* Copper nanocavities confine intermediates for efficient electrosynthesis of C₃ alcohol

- fuels from carbon monoxide. *Nature Catalysis* **1**, 946–951 (2018).
23. Li, C. W., Ciston, J. & Kanan, M. W. Electroreduction of carbon monoxide to liquid fuel on oxide-derived nanocrystalline copper. *Nature* **508**, 504–507 (2014).
 24. Zhu, P. *et al.* Direct and continuous generation of pure acetic acid solutions via electrocatalytic carbon monoxide reduction. *Proc. Natl. Acad. Sci. U. S. A.* **118**, (2021).
 25. Zhu, Q. *et al.* Carbon dioxide electroreduction to C₂ products over copper-cuprous oxide derived from electrosynthesized copper complex. *Nat. Commun.* **10**, 3851 (2019).
 26. Torbensen, K. *et al.* Molecular Catalysts Boost the Rate of Electrolytic CO₂ Reduction. *ACS Energy Lett.* **5**, 1512–1518 (2020).
 27. Zhang, X. *et al.* Molecular engineering of dispersed nickel phthalocyanines on carbon nanotubes for selective CO₂ reduction. *Nature Energy* **5**, 684–692 (2020).
 28. Proppe, A. H. *et al.* Bioinspiration in light harvesting and catalysis. *Nature Reviews Materials* 1–19 (2020).
 29. Zhang, S., Fan, Q., Xia, R. & Meyer, T. J. CO₂ Reduction: From Homogeneous to Heterogeneous Electrocatalysis. *Acc. Chem. Res.* **53**, 255–264 (2020).
 30. Nichols, E. M. & Chang, C. J. Urea-Based Multipoint Hydrogen-Bond Donor Additive Promotes Electrochemical CO₂ Reduction Catalyzed by Nickel Cyclam. *Organometallics* **38**, 1213–1218 (2019).
 31. Ren, S. *et al.* Molecular electrocatalysts can mediate fast, selective CO₂ reduction in a flow cell. *Science* **365**, 367–369 (2019).
 32. Wu, Y., Jiang, Z., Lu, X., Liang, Y. & Wang, H. Domino electroreduction of CO₂ to methanol on a molecular catalyst. *Nature* vol. 575 639–642 (2019).
 33. Weng, Z. *et al.* Active sites of copper-complex catalytic materials for electrochemical carbon dioxide reduction. *Nat. Commun.* **9**, 415 (2018).
 34. Han, L., Zhou, W. & Xiang, C. High-Rate Electrochemical Reduction of Carbon Monoxide to Ethylene Using Cu-Nanoparticle-Based Gas Diffusion Electrodes. *ACS Energy Lett.* **3**, 855–860 (2018).
 35. Ren, D., Wong, N. T., Handoko, A. D., Huang, Y. & Yeo, B. S. Mechanistic Insights into the Enhanced Activity and Stability of Agglomerated Cu Nanocrystals for the Electrochemical Reduction of Carbon Dioxide to n-Propanol. *J. Phys. Chem. Lett.* **7**, 20–24 (2016).

36. Hernandez-Aldave, S. & Andreoli, E. Fundamentals of Gas Diffusion Electrodes and Electrolysers for Carbon Dioxide Utilisation: Challenges and Opportunities. *Catalysts* **10**, 713 (2020).
37. Weng, Z. *et al.* Electrochemical CO₂ Reduction to Hydrocarbons on a Heterogeneous Molecular Cu Catalyst in Aqueous Solution. *J. Am. Chem. Soc.* **138**, 8076–8079 (2016).
38. Lin, S. *et al.* Covalent organic frameworks comprising cobalt porphyrins for catalytic CO₂ reduction in water. *Science* **349**, 1208–1213 (2015).

Figures

Figure 1

Exploded view of the microfluidic flow cell architecture used in this study. The graphic shows the positioning of the components, the feeds going into the inlet, and the products (C₂₊ includes C₂H₄, AcO⁻, C₂H₆O, C₃H₈O, C₃H₆O) exiting the outlet, as well as the electrodes that are physically connected to the external power supply. inset, photograph of the microfluidic flow cell.

Figure 2

CO electroreduction performance of a GDE coated with CuPc. 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 C_{2+} as a function of applied potentials for CO electroreduction on CuPc. Alcohols include ethanol, propanol, and allyl alcohol.

Figure 3

X-ray Photoelectron Spectra measurements of CuPc before and after electrolysis. a, Cu 2p and b, N 1s of CuPc before the electrolysis. c, Cu 2p and d, N 1s after the electrolysis for 4 h at 200 mA/cm². Post electrolysis samples were stored under N₂ before the analysis.

Figure 4

Quantitative X-ray Photoelectron elemental measurements of CuPc coated electrodes before and after electrolysis. Green, element analysis of the GDE before the electrolysis; red, element analysis of the GDE after the electrolysis at 200 mA/cm² for 4 h; grey, analysis of GDE after the electrolysis and air exposure for three days.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SRCuPcCORRSINC3rdforupload1.pdf](#)