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Electronic Supplementary Information

Rigorous assessment of CO₂ electroreduction products in a flow cell

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1. Equations for product quantification and analysis

Eqn. S1 Faradaic efficiency for gas products:

$$FE_x (\%) = \frac{Q_x}{Q_{tot}} \times 100\% = \frac{n_x \times C_x \times ut \times F}{I \times t \times V_M} = \frac{n \times C_x \times u \times F}{I \times V_M}$$

 FE_x : Faradaic efficiency for the gas product *x*;

 Q_x : charge transferred for product x formation;

 Q_{tot} : charge passed through the working electrode;

 n_x : electrons transferred for reduction to product x;

 C_x : volume fraction of the product x detected by GC;

u: outlet gas flowrate;

t: CO₂ electrolysis time;

F: Faradaic constant, 96485 $C \mod^{-1}$;

I: total applied current during CO₂ electrolysis;

 V_M : molar volume, 22.4 L mol⁻¹.

Eqn. S2 Overestimation ratio for gas products without considering CO₂ consumption:

$$Overestimation \ ratio = \frac{FE_{uncorrected} - FE_{actual}}{FE_{actual}} \times 100\%$$

 $FE_{uncorrected}$: Faradaic efficiency for gas products without measuring outlet gas flowrate; FE_{actual} : Faradaic efficiency for gas products with measuring outlet gas flowrate.

Eqn. S3 Underestimation ratio for gas products caused by products bubble accumulation:

Underestimation ratio =
$$\frac{FE_{actual} - FE_{uncorrected}}{FE_{actual}} \times 100\%$$

 FE_{actual} : Faradaic efficiency for gas products from the gas and catholyte chamber; $FE_{uncorrected}$: Faradaic efficiency for gas products from the gas chamber.

Eqn. S4 the one-dimensional Nernst–Planck equation:

$$J_{i}(x) = -D_{i} \frac{\partial C_{i}(x)}{\partial x} - \frac{z_{i}F}{RT} D_{i}C_{i} \frac{\partial \phi(x)}{\partial x} + C_{i}u(x)$$

 $J_i(x)$: the flux of component *i* at the distance *x* from the electrode surface;

 D_i : the effective diffusion coefficient of component *i*;

 C_i : the concentration of component *i*;

 z_i : the charge of component *i*;

F : Faradaic constant, 96485 C mol⁻¹;

R: the ideal gas constant;

T: the temperature;

 $\phi(x)$: the potential at the distance x from the electrode surface;

u(x): the flowrate of a volume unit in the solution moving in the x direction.

Solute transport between the catholyte and anolyte in an electrical field can be described with the one-dimensional Nernst–Planck equation. According to the equation, the first term on the right side refers to diffusive transport driven by the concentration gradient. The second term describes electromigration of a charged solute driven by the potential. And the third term describes convective transport, which can be neglected due to the existence of ion exchange membrane between catholyte and anolyte in this study. Note that, the overall penetration rate of liquid products through membrane is much more complicated because of the impact of the IEM and the flowing of catholyte.

Eqn. S5 Faradaic efficiency for liquid products:

$$FE_x = \frac{n_x \times C_x \times V \times F}{I \times t}$$

 FE_x : Faradaic efficiency of the gas product x;

 n_x : electrons transferred for reduction to product x;

 C_x : concentration of the product x detected by NMR;

V : volume of electrolyte;

F : Faradaic constant, 96485 *C* mol⁻¹;

I: total applied current during CO₂ electrolysis;

t : CO₂ electrolysis time.

Eqn. S6 Crossover ratio (underestimation ratio) for liquid products:

$$Crossover \ ratio = \frac{FE_{anolyte}}{FE_{catholyte} + FE_{anolyte}} \times 100\%$$

 $FE_{anolyte}$: Faradaic efficiency for liquid products in anolyte;

 $FE_{catholyte}$: Faradaic efficiency for liquid product in catholyte.

Eqn. S7 Evaporation ratio (underestimation ration) for volatile liquid products:

$$Evaporation \ ratio = \frac{FE_{outlet}}{FE_{catholyte} + FE_{anolyte} + FE_{outlet}} \times 100\%$$

 FE_{outlet} : Faradaic efficiency for liquid products in outlet gas; $FE_{catholyte}$: Faradaic efficiency for liquid products in catholyte.

Eqn. S8 Fick's Law of diffusion:

$$N_i = \frac{D_i}{RTl} (p_A - p_B)$$

 N_i : diffusion rate of the volatile component *i*;

 D_i : the effective diffusion coefficient of component *i*;

R: the ideal gas constant;

T: the temperature;

l : diffusion layer thickness;

 p_A : the equilibrium partial pressure of component i at section A;

 p_B : the equilibrium partial pressure of component i at section B;

Fick's first law relates the diffusive flux to the gradient of the concentration. It postulates that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient.

Eqn. S9 Henry's Law:

$$P_i^* = \frac{C_i}{H}$$

 P_i^* : the partial pressure of component *i* in the gas phase under equilibrium condition;

 C_i : the concentration of component *i* in the aqueous phase;

H: Henry's law solubility constants.

2. Experimental details

Materials

KHCO₃, KOH, isopropanol, D₂O, Ni foam were purchased from Sinopharm Chem. Reagent Co. Ltd. Commercial Cu nanoparticles (\geq 99.9%), DMSO (99.9%) were obtained from Aladdin. Deionized water (DIW, 18.2 M Ω ·cm, Milli-Q) was used for washing and preparation of solutions. Anion exchange membrane (AEM, Fumasep FAB-3-PK-130), cation exchange membrane (NafionTM 117), bipolar membrane (BPM, Fumasep FBM-PK) and gas-diffusion layer (GDL, Sigracet 28 BC) were purchased from Fuel Cell Store. All chemicals and materials were used as received without further purification.

Preparation of Cu GDE

Magnetron sputtered Cu GDE. Cu catalyst layers were deposited on top of microporous layer (MPL) of gas-diffusion layer (Sigracet 28 BC) by direct current magnetron sputtering (20 W) for 12 minutes using a pure Cu target (99.99%) at an argon pressure of 0.8 mPa, resulting a pure and uniform Cu GDE with the size of 6.5×6.5 -cm². The deposition rate (~8 nm min⁻¹) was obtained from the thickness of Cu layer on the planar Si substrate under the same condition.

Airbrushed Cu GDE. Typically, certain amount of commercial Cu nanoparticles was mixed with 2 mL of isopropanol and 40 μ L of Nafion ionomer solution (5 wt.% in lower aliphatic alcohols and water, Sigma-Aldrich), resulting a homogeneous catalyst ink by ultrasonic dispersion. The resulted ink was airbrushed onto 5 × 5-cm² GDL, yielding the Cu GDE with a catalyst loading of ~1.0 or 0.5 mg cm⁻².

Material Characterization

Scanning Electron Microscopy (SEM) measurements were performed by using a Zersss Supra 40. XRD-patterns were collected using a Japan Rigaku DMax- γ A X-ray diffractometer with Cu Ka radiation (λ =1.54178 Å).

Evaluation of the performance for CO₂RR

Electrochemical measurements

All electrochemical measurements were performed in a flow electrolyzer with VSP-300 Potentiostat with a current amplifier (Bio-Logic, France). The reactor was typically composed of two compartments for liquid electrolytes (catholyte and anolyte) and one gas compartment for CO₂ delivery and gas products collection. For CO₂ reduction in the electrolyzer, gaseous CO₂ (99.999%) was passed through

the gas chamber at the back side of the Cu GDE (1×1 -cm²). And the electrolyte (20 ml of 1 M KHCO₃ or KOH) was circulated through both the anode and cathode chambers separated by the ion exchange membrane (IEM) with the exposed area of 1×1 -cm². AEM, CEM or BPM was used depending on experimental needs. A piece of Ni foam and a Ag/AgCl (saturated KCl) electrode was used as counter electrode and reference electrode, respectively. The CO₂ inlet flowrates were ranged from 10 to 50 ml min⁻¹ controlled by a mass flow controller (C100L, Sierra). And the electrolyte flowrate was kept constant at 20 ml min⁻¹ by a peristaltic pump (BT100-2J, Longer Pump). The CO₂ electrolysis was lasted for 30 minutes unless otherwise specified.

Quantification of gas products

Like the test method in previous literatures¹⁻³, the outlet of gas chamber was vented directly into the auto-sampling loop of an on-line gas chromatograph (GC-2014, Shimadzu). The GC analysis was set up to split the gas sample into two aliquots. One aliquot passed a thermal conductivity detector (TCD) to quantify H₂ concentration, and the other was routed through flame ionization detector (FID) with a methanizer to quantitatively analyse the content of CO and hydrocarbon species.

When considering CO_2 consumption, the outlet flowrate was first monitored by a mass flowmeter (AST10-HLC, Asert Instruments) before flowing to GC. For airbrushed Cu GDE, the outlet gas from gas chamber first is passed into the catholyte tank and mixed with the gas products from the cathode chamber before flowing to the on-line GC via a mass flowmeter. The Faradaic efficiency for gas products was calculated by the formula in Eqn. S1.

Quantification of liquid products

To test liquid products, ¹H NMR spectra measured with water suppression using a pre-saturation method was collected on a Bruker 400 MHz spectrometer. Typically, 500 μ l of catholyte and/or anolyte after CO₂ electrolysis was mixed with 100 μ l of D₂O containing 50 ppm (m/m) dimethyl sulphoxide (DMSO) as the internal standard. The same spectral acquisition parameters were used for all measurements to ensure complete relaxation and quantification. The presented data was the accumulated result of 32 scans. To collect the liquid products lost in outlet gas, the outlet gas is passed a scrubber full with DIW (1.5 ml, 80 mm long of bath) to absorb the volatile products. The Faradaic efficiency for liquid products was calculated by the formula in Eqn. S5.

Detailed experimental parameters in each measurement pitfalls:

(1) FEs for gas products with or without considering CO₂ consumption Experimental parameters: catholyte, 20 ml 1 M KHCO₃/KOH (20 ml min⁻¹); anolyte, 20 ml 1 M KHCO₃/KOH (20 ml min⁻¹); CO₂, 10/20/30/40/50 ml min⁻¹; IEM, AEM.

(2) FEs for gas products with or without considering the accumulation of products gas bubbles Experimental parameters: catholyte, 20 ml 1 M KHCO₃ (10/20/40 ml min⁻¹); anolyte, 20 ml 1 M KHCO₃ (20 ml min⁻¹); CO₂, 30 ml min⁻¹; IEM, AEM.

(3) FEs for liquid products with or without considering the crossover issues Experimental parameters: catholyte, 10/20 ml 1 M KHCO₃ (10/20/40 ml min⁻¹); anolyte, 10/20 ml 1 M KHCO₃ (20 ml min⁻¹); CO₂, 30 ml min⁻¹; IEM, AEM/CEM/BPM.

(4) FEs for liquid products with or without considering the evaporation issues Experimental parameters: catholyte, 20 ml 1 M KHCO₃ (20 ml min⁻¹); anolyte, 20 ml 1 M KHCO₃ (20 ml min⁻¹); CO₂, 10/20/30/40/50 ml min⁻¹; IEM, AEM; Scrubbing solution: 1.5 mL DIW.

Detailed experimental parameters in the modified measurement system:

Experimental parameters: catholyte, 20 ml 1 M KHCO₃ (20 ml min⁻¹); anolyte, 20 ml 1 M KHCO₃ (20 ml min⁻¹); CO₂, 30 ml min⁻¹; IEM, BPM;

3. Supplementary experimental results



Fig. S1 A typical flow-cell measurement system for the evaluation of CO₂RR products.



Fig. S2 Schematic illustration (a) and photograph (b) of the flow-cell reactor for CO_2RR in this work. The flow-cell setup in our study consists of two chambers for liquid electrolytes (catholyte and anolyte) and one gas chamber for CO_2 delivery. The size of each chamber is 10 mm × 10 mm × 10 mm. A reference electrode (Ag/AgCl in saturated KCl) is placed in the catholyte chamber. Each chamber has an inlet and outlet connection to flow either electrolyte or gas. The reactor is made of polymethyl methacrylate (PMMA) and the gaskets are made of silicone pad. During CO_2 electrolysis, the cathode and anolyte are circulated between the chamber of the reactor and the liquid storage tank through the silicone tube.



Fig. S3 Characterization of magnetron sputtered Cu GDE. (a) Photo of the Cu GDE with the size of 6.5×6.5 -cm². (b) XRD pattern of Cu GDE. Only a small Cu (111) peak can be found due to strong background signal.



Fig. S4 A sputtered Cu layer was deposited on the polished Si substrate under 25 W for 12 min to obtain the deposition rate of ~ 8.5 nm min⁻¹.



Fig. S5 SEM images of magnetron sputtered Cu GDE. Scale bars: (a) 3µm; (b) 500 nm.



Fig. S6 The cross-sectional backscatter electrons (BsE) and EDX-mapping images of sputtered Cu GDE, suggesting a ~250 nm thickness of the Cu layer.



Fig. S7 Calibration curves for TCD and methanizer-FID detectors in GC, respectively. (a), H_2 and C_2H_4 . (b), CO and CH₄.



Fig. S8 Typical GC spectra of gas products from the electrochemical CO₂ reduction.



Fig. S9 FE for CO_2RR gas products in 1 M KHCO₃. (a) FEs for H₂, CO and CH₄. The CO₂ inlet flowrate was fixed at 30 ml min⁻¹. (b) FE for H₂, CO and CH₄ at various CO₂ inlet flowrates. The applied current density was fixed at 300 mA cm⁻². Columns with dash line show the overestimated FE without considering CO₂ consumption.



Fig. S10 CO₂ consumption in 1M KHCO₃ at 300 mA cm⁻².



Fig. S11 Overestimation of gas products in 1 M KOH. (a) The outlet flowrate as a function of current density at a fixed inlet flowrate of 30 ml min⁻¹. (b) The overestimated FE and overestimation ration for gas products at various current densities. (c) The outlet flowrate as a function of CO_2 inlet flowrates at 300 mA cm⁻². (d) The overestimated FE and overestimation ration for gas products at various inlet flowrates at 300 mA cm⁻². Columns with dash line in (b) and (d) show the overestimated FE without considering CO_2 consumption.



Fig. S12 Physical characterization of airbrushed Cu GDE. (a) XRD pattern of commercial Cu nanoparticles, indicating the presence of oxides due to the surface oxidation. (b) Photo of the airbrushed Cu GDE with a size of 5×5 -cm².



Fig. S13 SEM images of airbrushed Cu GDE with a catalyst loading of ~ 0.5 mg cm⁻². (a) The surface of deposited Cu layer. (b) the cross-sectional backscatter electrons image of deposited Cu layer, showing a thickness of ~ 820 nm.



Fig. S14 Total FE for all main CO_2RR products on airbrushed Cu GDE without considering the bubbles of gas products in the catholyte.



Fig. S15 The photo of CO_2 electrolysis reactor running at 500 mA cm⁻² on airbrushed Cu GDE (~1 mg cm⁻² catalyst loading). It clearly displayed the accumulated product bubbles in catholyte chamber.



Fig. S16 The improved testing procedure for the detection of gas products both in the gas chamber and catholyte chamber. The outlet gas from the gas chamber is passed into a gas-tight catholyte tank and mixed with gas products from the cathode chamber before flowing to the GC though a mass flowmeter.



Fig. S17. Influence of catholyte flowrate on gas products yielded from airbrushed Cu GDE. (a) FEs for gas products at a catholyte flowrate of 10 ml min⁻¹. (b) Underestimated FE and corresponding underestimation ratio. Inset shows the photograph of electrode-electrolyte interface. (b) Catholyte flowrate, 40 ml min⁻¹. (c) FEs for gas products at a catholyte flowrate of 40 ml min⁻¹. (d) Underestimated FE and corresponding underestimation ratio. Inset shows the photograph of electrode-electrolyte interface. Experimental parameters: catholyte, 20 ml 1 M KHCO₃ (10 or 40 ml min⁻¹); anolyte, 20 ml 1 M KHCO₃ (20 ml min⁻¹); CO₂, 30 ml min⁻¹.

Although a slower catholyte flowrate helps to improve the bubble management of the GDE to a certain extent, this strategy will also cause the formation of larger bubbles due to the slow flowrate. These larger gas bubbles will adhere on the GDE surface, thereby preventing the effective contact of the electrode and electrolyte.

We note that solving bubbles accumulation issue requires systematic considerations. In addition to optimizing the structure of GDE, another feasible solution is to add a pressure controller in the reactor downstream to maintain a low pressure, which will facilitate an easy transfer of the gas products from the electrode-electrolyte interface to the effluent gas stream⁴.



Fig. S18 SEM images of airbrushed Cu GDE with a catalyst loading of ~ 0.5 mg cm⁻². (a) The surface of deposited Cu layer. (b) the cross-sectional backscatter electrons image of deposited Cu layer, showing a thickness of ~ 420 nm.



Fig. S19 The FE for gas products on airbrushed Cu GDE (\sim 0.5 mg cm⁻² catalyst loading) with and without collecting gas products from the catholyte chamber.



Fig. S20 Stability test on the airbrushed Cu-GDE (catalyst loading, $\sim 0.5 \text{ mg cm}^{-2}$) at 400 mA cm⁻². (a) FE for gas products. (b) Voltage-time curve. (c) The photograph of the electrode-electrolyte interface during CO₂ electrolysis. (d) The photograph of the back side of the used GDE. (e) Cross-sectional SEM and K EDS-mapping images of Cu GDEs before the stability test. The slight K mapping pixels on as-prepared Cu GDE are derived from instrument noise. (f) Cross-sectional SEM and K EDS-mapping images of Cu GDEs after the stability test.

Data in **Fig. S20a** shows that the Cu-GDE initially showed good selectivity for CO_2RR (FE_{H2} <20%). While the FE for carbon-containing products gradually decreased and H₂ dominated the products progressively after 60 min. In addition, **Fig. S20b** shows a periodically fluctuating voltage curve after 60 min of electrolysis, which was caused by the accumulation and desorption of gas bubbles (see **Fig. S20c**). The accumulation of product bubbles during high-rate CO₂ electrolysis is due to the fact that tremendous gas products carried liquid electrolyte into the gas chamber and led to hydrophobicity degradation of the Cu-GDE, which is the so-called flooding issue. Once the flooding occurs, GDE would lose good gas permeability for CO₂ into and for gas products out of the electrolyte chamber, resulting in the accumulation of bubbles and consequently the performance degradation, as shown in **Fig. S20a-c**.



Fig. S21 The typical ¹H NMR spectrum of the liquid products collected from catholyte and anolyte. Note that both formate and acetate are negatively charged in 1 M KHCO₃ solution (pH, \sim 8.6) because of low pKa values of formic acid and acetic acid (3.77 and 4.76, respectively) The CO₂ electrolysis lasted for 30 min at 300 mA cm⁻².



Fig. S22 Concentrations of main liquid products in the catholyte and anolyte at various current densities, respectively. (a) Formate and acetate. (b) EtOH and n-PrOH.



Fig. S23 Concentrations change of liquid products in the catholyte and anolyte after removing the applied current. The reactor was first operated at 300 mA cm⁻² for 1 h, following by another one hour without applying current. The almost constant concentrations of products indicate that the diffusion transport of products through AEM is minimal.



Fig. S24 Schematic representation of electroosmotic drag in a membrane pore. Electroosmotic drag refers to the movement of water or other electroneutral solvents through a membrane, associated with the movement of ions under the influence of an electric field⁵. In detail, the electric field causes the dissolved ions to experience a net force, and these ions transfer momentum to the solvent molecules through viscous drag, resulting the penetration of electroneutral alcohols through AEM.



Fig. S25 Liquid products oxidation experiment in the anolyte. The reactor was first operated at 300 mA cm⁻² for 30 minutes under CO₂RR conditions to allow the crossover of liquid products. Hereafter, the reactor ran at 300 mA cm⁻² under HER conditions in fresh 1 M KHCO₃. Result shows that formate specie in the anolyte was quickly oxidized while acetate and EtOH were hardly oxidized in a short time, consistent with previous reports^{6, 7}. Ni-based anode catalysts have shown activity for formic acid oxidation; however, these catalysts show lower activity for EtOH and acetate oxidation in neutral electrolyte⁸. Thus there was more formate specie crossing to the anolyte and the crossover issue of the formate in Fig. 3 (Main text) is somewhat underestimated due to the quick oxidation reaction.



Fig. S26 The crossover ratio of main liquid products at various current density. The CO_2 electrolysis ran for 30 min at 300 mA cm⁻². Both the catholyte and anolyte were 10 ml of 1 M KHCO₃.



Fig. S27 The influence of catholyte flowrate on the crossover of liquid products. (a) FEs for main liquid products in catholyte and anolyte at a catholyte flowrate of 10 ml min⁻¹. (b) Corresponding crossover ratio of main liquid products. (c) FEs for main liquid products in catholyte and anolyte at a catholyte flowrate of 40 ml min⁻¹. (d) Corresponding crossover ratio of main liquid products. Experimental parameters: catholyte, 20 ml 1 M KHCO₃ (10 or 40 ml min⁻¹); anolyte, 20 ml 1 M KHCO₃ (20 ml min⁻¹); CO₂, 30 ml min⁻¹; electrolysis time, 30 min.

Data here can be reasonably explained by the one-dimensional Nernst–Planck equation (see **Eqn. S4**), which describes that electromigration rate of species through AEM is proportional to the concentration. Accordingly, reducing the electrolyte flow rate contributes to the electromigration rate of such species by essentially increasing the concentration of the liquid products in the cathode chamber⁹.



Fig. S28 FEs for liquid products in the catholyte (a) and anolyte (b) with the use of AEM, CEM and BPM. Three different ion-selective membranes show comparable catalytic selectivity for CO_2RR , which is primarily due to the similar local reaction environment at the cathode/electrolyte interface via the introduction of a catholyte layer¹⁰. As noted in Fig. S24b, substantial liquid products crossed over from the catholyte to the anolyte via the AEM. In contrast, the CEM and BPM exhibited negligible crossover (FE of products in the anolyte < 0.5% at 500 mA cm⁻²) for both anionic and uncharged products, indicating that both CEM and BPM can inhibit the crossover of liquid products.



Fig. S29 The typical ¹H NMR spectrum of the products collected from catholyte and outlet gas. The CO_2 electrolysis ran for 30 min at 300 mA cm⁻². The catholyte and outlet gas absorbent were 20 ml of 1 M KHCO₃ and 1.5 ml of DIW, respectively.



Fig. S30 Concentrations change of liquid products in the catholyte and outlet gas after removing the applied current. The reactor was first operated at 300 mA cm⁻² for 0.5 h under CO₂ electrolysis conditions, following by another 1 h without applied current. The almost constant concentrations of products in the catholyte and outlet gas indicates that the evaporation mainly occurs at the electrode-electrolyte reaction interface rather than the bulk catholyte.



Fig. S31 Evaporation of trace liquid products. FE (a) and molar fraction (b) for trace liquid products in the catholyte chamber and gas chamber of the flow cell. Other volatile products besides ethanol and propanol, such as methanol, acetone, acetaldehyde and allyl alcohol were also detected in outlet gas. While electroneutral ethylene glycol only exists in the catholyte due to high boiling point (197°C).



Fig. S32 Schematic representation of the evaporation of volatile products from GDEs.

Herein, we use Fick's Law of diffusion (Eqn. S8) to qualitatively analyze the evaporation rate of volatile liquid products at the electrode-electrolyte interface.

$$N_i = \frac{D_i}{RTl} (p_A - p_B) = \frac{D_i}{RT} \times \frac{p_A}{l} \propto \frac{1}{l}$$

 p_A , p_B represents the equilibrium partial pressure of component *i* at section A and section B, respectively. Because of the continuous flow of CO₂ through macroporous support (MPS), the equilibrium partial pressure of component *i* at section B could be regarded as zero, that is, $p_B = 0$. So the evaporation rate is inversely proportional to the diffusion length *l* associated with the CO₂ velocity boundary layer thickness related to the gas flowrate by the following equation¹¹:

$$\delta = 5\sqrt{vx/u}$$

 δ is boundary layer thickness; *v* is the kinematic viscosity of the gas; *x* is the distance downstream from the start of the boundary layer; *u* is CO₂ inlet flowrate. Thus it is easy to find that a low CO₂ inlet flowrate leads to long diffusional path (left), thus low evaporation rate and a high CO₂ inlet flowrate leads to short diffusional path (right), thus fast evaporation rate.

Additionally, according to Henry's Law (Eqn. S9), Eqn. S8 can be further expressed by:

$$N_i = \frac{D_i}{RTl} (p_A - p_B) = \frac{D_i}{HRT} \times \frac{c_{i,A}}{l} \propto c_{i,A}$$

The equation demonstrates that the evaporation rate is proportional to the product concentration at the interface which is related to applied current density and catalytic selectivity.

Overall, qualitative analysis by Fick's Law of diffusion indicates that faster CO₂ inlet flowrate and higher product formation rate at the electrode-electrolyte interface will lead a high evaporation rate by increasing the concentration gradient. Note that, the overall evaporation rate of volatile liquid products is much more complicated because of the complexity of the electrode-electrolyte interface and the structure of porous GDL.



Fig. S33 FE for products in modified measurement system. The electrolysis is performed in 40 ml 1 M KHCO₃ for 30 min at a CO₂ inlet flowrate of 30 ml min⁻¹, showing $100\pm1\%$ FEs for total products at various current densities.



Fig. S34 Schematic illustration of carbon element distribution in a three-compartment flow-cell reactor.

Details for carbon balance analysis:

Fig. S34 illustrates the carbon element distribution for electrochemical CO₂RR in a flow-cell reactor. When CO₂ enters the gas chamber, a part of CO₂ participates in the CO₂RR process, whereas a part of the CO₂ undergoes a neutralization reaction with the electro-generated OH⁻ (see **Eqns. R10-19** below). A large part of unreacted CO₂ flows out from the outlet, which can be circled back for second use.

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	(S10)
$CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^-$	(S11)
$CO_2 + 6H_2O + 8e^- \to CH_4 + 8OH^-$	(S12)
$CO_2 + 8H_2O + 12e^- \rightarrow C_2H_4 + 12OH^-$	(S13)
$CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^-$	(S14)
$2CO_2 + 5H_2O + 8e^- \to CH_3COO^- + 70H^-$	(S15)
$2CO_2 + 9H_2O + 12e^- \to C_2H_5OH + 12OH^-$	(S16)
$3CO_2 + 13H_2O + 18e^- \rightarrow C_3H_7OH + 18OH^-$	(S17)
$CO_2 + OH^- \leftrightarrow H_2O + HCO_3^- (pKa = 6.35)$	(S18)
$HCO_{3}^{-} + OH^{-} \leftrightarrow H_{2}O + CO_{3}^{2-} (pKa = 10.3)$	(S19)

Accordingly, one can calculate the amount of carbon element in products using the FEs of all formed products (**Eqn. S20**). Moreover, the amount of carbon in the CO_2 gas inlet and outlet can be approximately calculated from the Ideal Gas Law (**Eqns. S21-22**).

$$n_{c \ in \ products} = \sum m_i \frac{I \times t \times FE_i}{96485 \times n_i} \tag{S20}$$

$$n_{c \text{ in } CO_2 \text{ input}} = \frac{PV}{RT} = \frac{P \times u_{input} \times t}{RT}$$
(S21)

$$n_{c \text{ in residual } CO_2} = \frac{PV}{RT} = \frac{P \times (u_{outlet} - u_{gas \text{ products}}) \times t}{RT}$$
(S22)

Where P is ambient pressure; u_{inlet} and u_{outlet} is the flowrate of gas inlet and outlet, respectively; R and T are ideal gas constant and absolute temperature; m_i is the number of carbon atom in a certain product molecule *i*; I is the applied current; t is electrolysis time; FE is the Faradaic efficiency for a certain product; 96485 is Faraday constant; n_i is the number of electrons required for producing one product molecule.

However, we stress that it is tricky to directly quantify the magnitudes of carbon element in (bi)carbonates generated from the neutralization reaction. The reasons can be summarized that follow: (1) The (bi)carbonates generated from neutralization reactions (**Eqns. R18-19**) are difficult to distinguish from the KHCO₃ catholyte (1 M) due to the complexity of the multiple equilibria between CO_2 and aqueous catholyte of varying alkalinities. (2) The (bi)carbonates from the neutralization reaction will electromigrate into the anolyte (1 M KHCO₃) during the electrolysis process. Hence, it is quite challenging to quantify the amount of carbon directly based on the (bi)carbonates generated from neutralization reactions.

As shown in **Eqns. S10-17**, we note that the amount of OH^- produced via CO_2RR is the same as the number of reductive electrons that insert into products (as to formate and acetate, OH^- produced from CO_2RR is one less than the reductive electrons). These OH^- groups either transfer through the AEM to the anolyte or equilibrate with CO_2 to form bicarbonate or carbonate. Very recently, Seger and co-workers has experimentally confirmed that almost all OH^- produced will react with CO_2 to form carbonate^{12, 13}. Thus, using **Eqns. S10-19**, we can directly calculate the amount of carbon element entering the electrolyte in the form of carbonate from the amount of OH^- generated from CO_2RR (see **Eqn. S23**).

$$n_{c \ in \ CO_3^{2-}} = \sum_{i=1}^{1 \times t \times FE_i} + \frac{1 \times t \times FE_{formate}}{2 \times 96485} \times \frac{1}{2} + \frac{1 \times t \times FE_{acetate}}{2 \times 96485} \times \frac{7}{8}$$
(S23)

Where i represents the reduction product excluding formate and acetate.

Therefore, the carbon balance can be determined by dividing the total molar quantity of carbon element in products ($n_{c in products}$), carbonates ($n_{c in CO_3^2}$ -) and residual CO₂ ($n_{c in residual CO_2}$) by the molar quantity of carbon element in the CO₂ input ($n_{c in CO_2 input}$):

$$Carbon \ balance(\%) = \frac{n_{c \ in \ products} + n_{c \ in \ CO_3^2} + n_{c \ in \ residual \ CO_2}}{n_{c \ in \ CO_2 \ input}} \times 100\%$$
(S24)

Consequently, the fraction of carbon element in each part and carbon balance on Cu GDE under each current density can be estimated in **Table S8**. The results show a carbon balance very close to 100%, demonstrating the effectiveness of our proposed flow-cell measurement system.

						Elec	trochemical reductio	n of CO2 to C	0				
Reactor	Catholyte	Catalyst	IEM	j _{total} (mA cm ⁻²)	GDE area (cm²)	CO2 inlet flowrate (mL min ⁻¹)	FE calculation method	Main products FE (%)	CO2 outlet flowrate (ml min ⁻¹)	Gas bubbles accumulation	Products in anolyte	Products in exhaust	Reference
Flow cell	1 M KOH	Ag NP	No	300	1	7	Based on GC and CO_2 flowrate	95% CO	Unspecified	Unspecified	_	_	J. Power Sources, 2016, 312, 192-198
Flow cell	3 М КОН	Ag NP	No	430	1	17	Based on GC and CO ₂ flowrate	~100% CO	Unspecified	Unspecified	_	_	Phys.Chem.Chem. Phys., 2016, 18, 7075
Flow cell	1 М КОН	Ag NP	No	340	1	7	Based on GC and CO ₂ flowrate	~100% CO	Unspecified	Unspecified	_	-	J. Mater. Chem. A , 2016, 8573-8578
Flow cell	1 M NaHCO ₃	Ag NP	BPM	200	4	100	Based on GC and CO ₂ flowrate	50% CO	Unspecified	Unspecified	_	_	ACS Energy Lett., 2018, 3, 149–154
Flow cell	1 М КОН	Ag NP	AEM	170	1	50	Based on GC and CO_2 flowrate	>92% CO	Unspecified	Unspecified	_	_	ACS Energy Lett., 2018, 3, 2835–2840
Flow cell	1 М КОН	Ag NP	AEM	300	1	50	Based on GC and CO ₂ flowrate	84% CO	Unspecified	Unspecified	_	_	Energy Environ. Sci., 2018,11, 2531-2539
Flow cell	1 М КОН	CoPc-CN	AEM	146	0.1	20	Based on GC and CO_2 flowrate	56% CO	Unspecified	Yes	_	_	ACS Energy Lett., 2018, 3, 2527–2532
Flow cell	2 М КОН	Au/MW CNT	AEM	180	1	17	Based on GC and CO ₂ flowrate	85% CO	Unspecified	Yes	_	_	ACS Energy Lett., 2018, 3, 193–198
Flow cell	2 М КОН	Ag NP	AEM	106	1	17	Based on GC and CO ₂ flowrate	93% CO	Unspecified	No	_	_	Nat. Energy, 2019, 4, 466–474

 Table S1 Experimental details of the flow cell setup and measurements procedures from previous publications.

Flow cell	1 M KHCO ₃	Ag-NOLI	AEM	400	0.3	40	Based on GC and CO ₂ flowrate	>95% CO	Unspecified	Unspecified	-	-	Nat. Energy, 2020, 5, 1032-1042
Flow cell	5 М КОН	CdS needle	AEM	222	Unspecified	60	Based on GC and CO ₂ flowrate	96% CO	Unspecified	Unspecified	_	_	Angew. Chem. Int. Ed., 2020, 59, 8706-8712
Flow cell	5 М КОН	Au cluster	AEM	540	2	20	Based on GC and CO ₂ flowrate	~100% CO	Unspecified	Unspecified	_	_	ACS Energy Lett., 2020, 5, 749–757
Flow cell	1 M KHCO ₃	Ag NP	AEM	100	1	19.2	Based on GC and CO ₂ flowrate	80% CO	Unspecified	Unspecified	_	_	Nat. Commun., 2020, 11, 5856
Flow cell	1 М КОН	Pd/C- PDDA	AEM	300	1	Unspecified	Based on GC and CO ₂ flowrate	~100% CO	Unspecified	Unspecified	_	_	J. Mater. Chem. A, 2020, 8, 15884- 15890
Flow cell	0.5 M KHCO3	NiSA/PC FM	CEM	330	4	20	Based on GC and CO ₂ flowrate	~90% CO	Unspecified	Unspecified	_	_	Nat. Commun., 2020, 11, 593
Flow cell	1 M KHCO ₃	NiPc-OMe MDE	AEM	400	0.5	20	Based on GC and CO ₂ flowrate	~99% CO	Unspecified	Unspecified	_	_	Nat. Energy, 2020, 5, 684-692
Flow cell	0.5 M KOH	CoPc/Fe- N-C	AEM	296	Unspecified	50	Based on GC and CO ₂ flowrate	93% CO	Unspecified	Unspecified	_	_	Adv. Mater., 2019, 31, 1903470
Flow cell	1 М КОН	CoPc/XC -72R	AEM	225	Unspecified	30	Based on GC and CO ₂ flowrate	90% CO	Unspecified	Unspecified	_	_	Angew. Chem. Int. Ed., 2020, 59, 22408-22413
Flow cell	1 М КОН	ZnCu	BPM	150	1	75	Based on GC and CO ₂ flowrate	80% CO	Unspecified	Unspecified	_	_	Chem Catal., 2021. DOI:10.1016/j.checat.2 021.05.006
						Electro	ochemical reduction	of CO2to form	nate				
Reactor	Catholyte	Catalyst	IEM	j _{total} (mA cm ⁻²)	GDE area (cm²)	CO2 inlet flowrate (mL min ⁻¹)	FE calculation method	Main products (%)	CO2 outlet flowrate (ml min ⁻¹)	Gas bubbles accumulation	Products in anolyte	Products in exhaust	Reference
Flow cell	1 M KOH	SnO ₂ /CN T	AEM	236	0.1	20	Based on NMR	83% formate	Unspecified	_	Unspecified	-	ACS Energy Lett., 2018, 3, 2527–2532

Flow cell	1 М КОН	SnO ₂	AEM	67	1	Unspecified	Based on NMR	74% formate	Unspecified	_	Unspecified	_	J. Mater. Chem. A, 2018,6, 10313- 10319
Flow cell	1 M KHCO ₃	Bi NS	AEM	285	1	Unspecified	Based on NMR	95% formate	Unspecified	_	Unspecified	_	Adv. Funct. Mater., 2021, 31, 2006704.
Flow cell	1 М КОН	Bi NS	AEM	400	Unspecified	20	Based on NMR	90% formate	Unspecified	_	Unspecified	_	Adv. Energy Mater., 2020, 10, 2001709.
Flow cell	1 М КОН	Bi NTs	AEM	220	16	80	Based on NMR	98% formate	Unspecified	_	Unspecified	_	Nat. Commun., 2019, 10, 2807.
Flow cell	1 М КОН	SnO ₂ /Cu O	Unspec ified	300	6	15	Based on NMR	85% formate	Unspecified	_	Unspecified	_	ChemSusChem, 2021, 14, 2112- 2125.
Flow cell	1 M KOH	SnO ₂	AEM	300	0.5	Unspecified	Based on NMR	70.8% formate	Unspecified	_	18.7% formate	_	J. Catal., 2020, 385, 140-145.
Flow cell	1 М КОН	Sn _{2.7} Cu	AEM	400	2	30	Based on NMR	90% formate	Unspecified	_	Unspecified	_	Angew. Chem. Int. Ed., 2020, 59, 4814-4821.
Flow cell	1 М КНСО3	In-MOF	AEM	140	1	20	Based on NMR	90% formate	Unspecified	_	Unspecified	_	Angew. Chem. Int. Ed.,2021,DOI:10.10 02/anie.202107523
					Elec	ctrochemical	reduction of CO2 to h	ydrocarbons	and oxygenate	25			
Reactor	Catholyte	Catalyst	IEM	<i>j</i> total (mA cm ⁻²)	GDE area (cm²)	CO ₂ inlet flowrate (mL min ⁻¹)	FE calculation method	Main products (%)	CO2 outlet flowrate (ml min ⁻¹)	Gas bubbles accumulation	Products in anolyte	Products in exhaust	Reference
Flow cell	1 M KOH	Cu NP	AEM	200	1	7	Based on GC/NMR and CO ₂ flowrate	46% C ₂ H ₄ , 17% EtOH	Unspecified	Unspecified	Unspecified	Unspecified	J. of Power Sources, 2016, 301, 219-228
Flow cell	1 M KOH	CuDAT- wire	AEM	~200	1	Unspecified	Based on GC/NMR and CO ₂ flowrate	37% C ₂ H ₄ , 25% EtOH	Unspecified	Few or no	Unspecified	Unspecified	ACS Catal., 2017, 7, 3313–3321

Flow cell	1 M KOH	CuDAT-	AEM	~166	1	Unspecified	Based on GC/NMR	20% C ₂ H ₄ ,	Unspecified	Yes	Unspecified	Unspecified	ACS Catal., 2017,
		dot				_	and CO ₂ flowrate	12% EtOH	_				7, 3313–3321
Flow cell	10 M KOH	Cu NP	AEM	275	Unspecified	50	Based on GC/NMR	66% C2H4	Unspecified	Unspecified	Unspecified	Unspecified	Science, 2018, 360,
	10 M Roll	Curti	712.101	275	Chiptenneu	50	and CO ₂ flowrate	0070 02114	Chispeennea	onspectited	Chispeenieu	enspeemea	783-787
		CuAa					Deced on CC/NMD	550/ C H					J. Am. Chem. Soc.,
Flow cell	1 M KOH	CuAg-	AEM	311	1	7	and CO. flowrate	260/ E+OU	Unspecified	Unspecified	Unspecified	Unspecified	2018, 140,
		wire					and CO_2 howrate	2070 EIOH					5791-5797
	A. 1. WOW			100		50	Based on GC/NMR	60 % C ₂ H ₄ ,					Adv. Mater., 2018,
Flow cell	3 M KOH	Cu	AEM	400	1	50	and CO ₂ flowrate	20% EtOH	Unspecified	Unspecified	Unspecified	Unspecified	30, 1804867
		Cu/MWC						2004 G H					
Flow cell	1 M KOH	NT(0.6 mg	AEM	663	1	10	Based on GC/NMR	$39\% C_2H_4,$	Unspecified	No	Unspecified	Unspecified	Adv. Mater., 2018,
		cm ⁻²)					and CO_2 flowrate	17% EtOH					30, 1803111
		Cu/MWC						2004 G H					4.1. 14.4. 2010
Flow cell	1 M KOH	NT(1.0 mg	AEM	663	1	10	Based on GC/NMR	$39\% C_2H_4,$	Unspecified	Yes	Unspecified	Unspecified	Adv. Mater., 2018,
		cm ⁻²)					and CO ₂ flowrate	17% EtOH					30, 1803111
	11/19/100	Cu/		200		T 0	Based on GC/NMR	38% C ₂ H ₄ ,					Nat. Catal., 2020,
Flow cell	1M KHCO ₃	FeTPP	AEM	300	I	50	and CO ₂ flowrate	41% EtOH	Unspecified	Unspecified	Unspecified	Unspecified	3,75-82
		<u> </u>											J. Am. Chem. Soc.,
Flow cell	1 M KOH	CuAg	AEM	250	Unspecified	Unspecified	Based on GC/NMR	35% C ₂ H ₄ ,	Unspecified	Unspecified	Unspecified	Unspecified	2019, 141,
		alloy					and CO ₂ flowrate	41% EtOH					8584-8591
		Cu/Ce(O					Based on GC/NMR	28% C ₂ H ₄ ,					Nat. Commun.,
Flow cell	1 M KOH	H)x	AEM	300	1	50	and CO ₂ flowrate	43% EtOH	Unspecified	Unspecified	Unspecified	Unspecified	2019, 10, 5814
	1.1.1.1.0.11	Cu/Ag					Based on GC/NMR	5 00(G					Joule, 2020, 4,
Flow cell	1 М КОН	NP	AEM	320	Unspecified	25	and CO ₂ flowrate	50% C ₂₊	Unspecified	Unspecified	Unspecified	Unspecified	1688–1699
F1 11	1 M KOU	1.00.04		200		20	Based on GC/NMR	5(0/ CH	TT : C 1	TT : C 1		TT : C 1	ACS Catal., 2020,
Flow cell	1 М КОН	La2CuO4	AEM	200	Unspecified	20	and CO ₂ flowrate	56% CH4	Unspecified	Unspecified	Unspecified	Unspecified	10, 4640–4646
Elan 11	10 M 201	C /D 4		27	1	7	Based on GC/NMR	970/ 0 11	Linen (C. 1	I.I	Then 10 1	Then 10 1	Nat. Catal., 2021,
Flow cell	10 M KOH	Cu/PA	AEM	37	1	/	and CO ₂ flowrate	$8 / \% C_2 H_4$	Unspecified	Unspecified	Unspecified	Unspecified	4, 20–27
				~200			Based on GC/NMR	65-75%					Science, 2020, 661-
Flow cell	7 М КОН	Cu/CIBH	AEM	0	1	50	and CO ₂ flowrate	C_2H_4	Unspecified	Unspecified	Unspecified	Unspecified	666

Flow cell	1 M	Cu/	AEM	320	1	50	Based on GC/NMR	72% CaH	Unspecified	Unspecified	Unspecified	Unspecified	Nature, 2020, 577,
TIOW CCII	КНСОЗ	molecule	ALM	520	1	50	and CO ₂ flowrate	7270 02114	onspecified	onspectified	Onspectited	onspecifica	509–513
Flow cell	1 M	Cu NP	AFM	300	2	45	Based on GC/NMR	45% C ₂ H ₄ ,	Ves	NR	Ves	NR	Energy Environ.
TIOW CCII	KHCO3	Culvi	ALM	500	2	45	and CO ₂ flowrate	20% EtOH	103	N.K.	103	IV.IX.	Sci., 2020, 13, 977
Flow cell	1 M	Cu NP	AFM	200	2	45	Based on GC/NMR	42% C ₂ H ₄ ,	Ves	Unspecified	Ves	Ves	Chem. Sci., 2020,
TIOW CCII	KHCO ₃	Culvi	ALM	200	2	45	and CO ₂ flowrate	20% EtOH	103	onspectived	103	103	11,8854-8861
Flow cell	1 М КОН	Cu-F NP	AFM	1600	1	50	Based on GC/NMR	65% C ₂ H ₄ ,	Unspecified	Unspecified	Unspecified	Unspecified	Nat. Catal., 2020,
How cell	I WI KOII	Cu-P NI	ALM	1000	1	50	and CO ₂ flowrate	12% EtOH	Onspecified	Onspectified	Onspecified	Onspecified	3, 478–487
Flow coll		Cu ND	AEM	300	0.5	50	Based on GC/NMR	$45\% C_2 H_4,$	Unerpairfied	Uneposition	Vos	Vos	J. Catal., 2020,
Flow cell	I M KOH	CUINF	ALM	300	0.5	50	and CO ₂ flowrate	22% EtOH	Unspecified	Unspecified	105	105	385, 140–145
Flow coll	1 M	OD Cu	AEM	300	2	20	Based on GC/NMR	37% C ₂ H ₄ ,	Unerpairfied	Uneposition	Unerpairfied	Unspecified	Joule, 2020, 4, 1–
Flow cell	KHCO ₃	OD-Cu	ALM	300	2	20	and CO ₂ flowrate	12% EtOH	Unspecified	Unspecified	Unspecified	Olispecified	17
Flow coll	7 M KOH	Cu	AEM	580	1	50	Based on GC/NMR	70% C ₂ H ₄ ,	Unerpairfied	Uneposition	Unerpairfied	Unspecified	Nat. Catal., 2020,
Flow cell	/ WI KOII	Cu	ALM	580	1	50	and CO ₂ flowrate	10% EtOH	Unspecified	Unspecified	Unspecified	Olispecified	3, 98-106
							Based on GC/NMP	37% C-H					J. Am. Chem. Soc.
Flow cell	2 M KOH	OD-Cu	AEM	355	1	24	and CO. flowrate	26% EtOH	Unspecified	Unspecified	Unspecified	Unspecified	2020, 142, 6400 -
							and CO ₂ nowrate	2070 EtOIT					6408
		Cu					Based on GC/NMR	32% C-H					J. Am. Chem. Soc.,
Flow cell	1 M KOH	dendrites	AEM	300	1	24	and CO. flowrate	22% EtOH	Yes	Unspecified	Unspecified	Unspecified	2021, 143, 8011-
		dendrites						2270 EtOI1					8021
Flow cell	1 M	OD-Cu	AFM	700	Unspecified	50	Based on GC/NMR	33% C ₂ H ₄ ,	Unspecified	Unspecified	Unspecified	Unspecified	Nat. Commun.,
Flow cell	KHCO3	OD-Cu	ALM	700	onspecified	50	and CO ₂ flowrate	12% EtOH	Onspecified	Onspectified	Onspecified	Onspecified	2021, 12, 794
Flow coll		Cu ND	AEM	500	Unspecified	5	Based on GC/NMR	$30\% C_2 H_4,$	Unerpairfied	Unerposition	Unerpairfied	Unspecified	Nat. Commun.,
Flow cell	1 M KOH	Cultr	ALM	500	onspecified	5	and CO ₂ flowrate	15% EtOH	Unspecified	Unspecified	Unspecified	Olispecified	2021, 12, 136
Flow cell	1 М КОН	Cu/C NP	AEM	400	Unspecified	50	Based on GC/NMR	71% C ₂ H ₄ ,	Vos	Unspecified	Unspecified	Unspecified	Nat. Commun.,
Flow cell	I WI KOII	Cu/C NI	ALM	400	onspecified	50	and CO ₂ flowrate	18% CO	105	Onspectified	Onspectited	Onspecified	2021, 12, 3765
							Based on GC/NMP	34% CaH					Angew. Chem. Int.
Flow cell	1 M KOH	Cu/CuI	AEM	700	Unspecified	30	and CO ₂ flowrate	25% EtOH	Unspecified	Unspecified	Unspecified	Unspecified	Ed. 2021, 60,
							and CO ₂ nowrate	2370 EtOH					14329-14333.

Current density	CO ₂ inlet flowrate	CO ₂ outlet flowrate		FE without CO ₂ consu	considering mption (%)			FE con CO ₂ consu	sidering mption (%)			Overestimat	tion ratio (%)	
(mA cm ²)	(ml min ⁻¹)	(ml min ⁻¹)	H ₂	СО	CH ₄	C_2H_4	H ₂	СО	CH ₄	C_2H_4	H ₂	СО	CH_4	C_2H_4
100.00	30.00	29.59	18.18	24.62	5.92	21.31	18.44	24.96	6.01	21.02	1.39	1.39	1.39	1.39
200.00	30.00	28.65	10.00	20.55	3.94	39.31	10.47	21.52	4.12	37.54	4.71	4.71	4.71	4.71
300.00	30.00	27.77	7.21	19.34	3.19	45.80	7.79	20.89	3.45	42.39	8.03	8.03	8.03	8.03
400.00	30.00	26.94	7.67	15.28	1.38	50.51	8.54	17.02	1.54	45.36	11.36	11.36	11.36	11.36
500.00	30.00	26.09	10.62	12.41	3.43	49.03	12.21	14.27	3.95	42.64	14.99	14.99	14.99	14.99
300.00	10.00	7.53	8.84	15.87	1.96	41.37	11.74	21.08	2.60	54.94	32.80	32.80	32.80	32.80
300.00	20.00	17.75	7.96	18.44	1.63	42.74	8.97	20.78	1.84	48.15	12.68	12.68	12.68	12.68
300.00	30.00	27.77	7.21	19.34	3.19	42.39	7.79	20.89	3.45	45.80	8.03	8.03	8.03	8.03
300.00	40.00	37.68	7.31	18.68	1.96	42.40	7.76	19.83	2.08	45.01	6.16	6.16	6.16	6.16
300.00	50.00	47.95	6.68	18.77	2.80	43.08	6.96	19.58	2.92	44.92	4.28	4.28	4.28	4.28

Table S2 Faradaic efficiency for gas products on magnetron-sputtered Cu GDE in 1 M KHCO₃ (corresponding to Fig. 2 in Main text).

Current density	CO ₂ inlet	CO ₂ outlet		FE without CO ₂ consur	considering			FE con	nsidering)		Overestimat	ion ratio (%)	
(mA cm ⁻²)	flowrate (ml min ⁻¹)	flowrate (ml min ⁻¹)	H ₂	СО	CH ₄	C ₂ H ₄	H ₂	СО	CH ₄	C ₂ H ₄	H ₂	СО	CH4	C ₂ H ₄
100.00	30.00	27.23	8.26	17.06	2.33	51.19	9.07	18.74	2.56	56.23	9.85	9.85	9.85	9.85
200.00	30.00	26.48	6.65	10.84	2.76	53.92	7.51	12.25	3.12	60.93	12.99	12.99	12.99	12.99
300.00	30.00	25.69	8.53	5.08	6.45	53.52	9.94	5.93	7.52	62.38	16.55	16.55	16.55	16.55
400.00	30.00	24.99	12.84	7.70	8.49	44.93	15.35	9.21	10.15	53.73	19.57	19.57	19.57	19.57
500.00	30.00	24.36	15.30	8.26	9.56	39.12	18.82	10.16	11.76	48.12	23.00	23.00	23.00	23.00
300.00	10.00	4.80	21.57	1.02	2.75	49.82	44.94	2.12	5.72	108.49	108.49	108.49	108.49	108.49
300.00	20.00	15.76	7.82	6.88	5.46	52.81	9.93	8.73	6.92	26.90	26.90	26.90	26.90	26.90
300.00	30.00	25.74	8.53	5.08	6.45	53.52	9.94	5.93	7.52	16.55	16.55	16.55	16.55	16.55
300.00	40.00	36.28	7.85	6.57	5.59	51.62	8.65	7.24	6.16	10.26	10.26	10.26	10.26	10.26
300.00	50.00	46.22	7.82	9.30	3.89	49.92	8.46	10.06	4.21	8.17	8.17	8.17	8.17	8.17

Table S3 Faradaic efficiency for gas products on magnetron-sputtered Cu GDE in 1 M KOH (corresponding to Fig. S11 in SI).

Current density	Catalyst loading		FE for g	as products			FE for gas pr	roducts in gas	; 6)	Overestimated FE for	Overestimation ratio for
$(mA cm^{-2})$	(mg cm ⁻²)	H ₂	CO	CH ₄	C ₂ H ₄	H ₂	СО	CH ₄	C ₂ H ₄	all gas products (%)	all gas products (%)
100.00		20.92	34.02	3.00	20.78	21.01	36.01	3.62	21.17	3.08	3.77
200.00		21.95	8.72	3.03	23.82	30.99	11.47	7.66	26.93	19.53	25.34
300.00	1.00	24.25	6.08	1.35	19.48	30.81	7.57	5.34	31.18	23.73	31.68
400.00	1.00	23.26	5.33	1.57	14.98	33.85	6.10	7.75	25.72	28.29	38.53
500.00		27.30	2.46	3.66	12.84	41.02	3.37	11.46	21.94	31.54	40.55
100.00		26.11	33.57	3.90	15.24	27.44	32.90	2.98	16.04	_	_
200.00		14.91	18.31	4.04	35.28	14.05	17.26	3.81	33.26	-	-
300.00	0.50	16.11	8.22	4.15	34.23	17.32	7.38	5.28	35.42	-	-
400.00		18.39	13.70	7.98	35.88	20.64	13.26	5.32	34.91	_	_
500.00		26.33	9.30	4.37	34.82	27.15	7.29	6.13	34.49	_	_

Table S4 Faradaic efficiency for gas products on airbrushed Cu GDE (corresponding to Fig. 3 in Main text and Fig. S19 in SI).

Current		Catholyte	F	E for products	in catholyte (%)		FE for produc	ts in anolyte (%)		Crossover	ratio (%)	
density	IEM	volume	formate	acetate	FtOH	n-PrOH	formate	acetate	EtOH	n-PrOH	formate	acetate	FtOH	n-PrOH
(mA cm-2)		(mi)	Tormate	accute	Lion	ii mon	Tormate	accuate	LIOII		Iormate	accuate	Lion	in mon
100.00			10.00	0.68	7.48	3.86	1.12	0.16	0.29	0.00	10.03	18.52	3.73	0.00
200.00			3.24	1.41	16.91	5.11	0.98	0.87	0.91	0.12	23.22	38.18	5.13	2.21
300.00		10.00	2.12	1.63	17.65	4.51	0.96	1.84	1.51	0.31	31.26	53.06	7.90	6.40
400.00			1.59	2.02	19.47	3.84	1.03	3.65	2.40	0.56	39.31	64.35	10.97	12.79
500.00	AEM		1.11	2.82	18.55	2.82	0.76	6.46	2.72	0.40	40.75	69.64	12.79	12.39
100.00	AEM		18.08	1.08	5.73	2.71	1.46	0.18	0.00	0.00	7.28	12.76	0.00	0.00
200.00			5.72	2.00	14.82	4.35	0.76	0.37	0.07	0.00	11.57	15.41	2.71	0.00
300.00		20.00	3.18	2.19	17.81	3.81	0.71	0.86	0.26	0.00	18.31	28.14	5.23	0.00
400.00			2.35	3.41	19.42	2.98	0.75	1.84	0.43	0.00	23.95	34.65	7.84	0.00
500.00			1.70	4.64	18.54	2.20	0.73	3.89	0.72	0.00	28.57	44.58	9.37	0.00
100.00			13.87	1.22	6.79	4.66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
200.00			5.42	3.02	17.43	4.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
300.00	CEM	20.00	3.49	5.07	22.00	3.19	0.00	0.01	0.03	0.00	0.00	0.14	0.15	0.00
400.00			3.41	5.75	23.29	2.02	0.00	0.00	0.01	0.00	0.00	0.07	0.06	0.00
500.00			2.85	5.90	21.15	1.39	0.00	0.01	0.03	0.00	0.00	0.10	0.13	0.00
100.00			10.88	1.02	8.15	3.81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
200.00]		3.16	2.65	17.29	4.27	0.00	0.05	0.00	0.00	0.00	1.79	0.00	0.00
300.00	BPM	20.00	2.44	3.98	23.25	2.82	0.02	0.10	0.00	0.00	0.98	2.46	0.00	0.00
400.00	1		1.78	7.03	22.24	1.20	0.05	0.23	0.14	0.00	2.71	3.23	0.65	0.00
500.00	1		1.34	5.53	22.08	1.57	0.06	0.31	0.14	0.00	4.01	5.32	0.63	0.00

 Table S5 Faradaic efficiency for main liquid products on magnetron-sputtered Cu GDE (corresponding to Fig. 4 in Main text and Figs. S26 and 28 in SI).

Current density	CO ₂ inlet flowrate	FE	for products i	n catholyte (%)	FE	for products in	n outlet gas (%)		Evaporation	n ratio (%)	
(mA cm ⁻²)	(ml min ⁻¹)	formate	Acetate	EtOH	n-PrOH	formate	Acetate	EtOH	n-PrOH	formate	Acetate	EtOH	n-PrOH
100.00		18.08	1.08	5.73	2.71	0.00	0.00	0.32	0.20	0.00	0.00	5.34	6.94
200.00		5.72	2.00	14.82	4.35	0.00	0.00	1.13	0.40	0.00	0.00	7.08	8.47
300.00	30.00	3.18	2.19	17.81	3.81	0.00	0.00	1.56	0.42	0.00	0.00	8.04	9.98
400.00		2.35	3.41	19.42	2.98	0.00	0.00	1.94	0.41	0.00	0.00	9.10	12.17
500.00		1.70	4.64	18.54	2.20	0.00	0.00	2.22	0.34	0.00	0.00	10.70	13.55
300.00	10.00	3.93	2.94	20.00	3.84	0.00	0.00	0.49	0.10	0.00	0.00	2.74	2.42
300.00	20.00	4.55	2.61	18.15	4.57	0.00	0.00	0.90	0.18	0.00	0.00	5.11	5.64
300.00	30.00	4.36	3.45	17.81	3.81	0.00	0.00	1.55	0.41	0.00	0.00	8.04	9.98
300.00	40.00	3.21	3.33	17.99	3.84	0.00	0.00	1.64	0.47	0.00	0.00	9.20	11.55
300.00	50.00	4.10	2.35	18.19	4.00	0.00	0.00	1.79	0.55	0.00	0.00	9.69	12.28

Table S6 Faradaic efficiency for main liquid products on magnetron-sputtered Cu GDE (corresponding to Fig. 5 in Main text).

Table S7 Faradaic efficiency for products on magnetron-sputtered Cu GDE tested in the modified measurement system (corresponding to Fig. S33 in SI).

Current							FE (%)					
density (mA cm-2)	Н2	СО	CH4	C2H4	formate	acetate	СНЗСНО	EtOH	Ethylene glycol	n-PrOH	Acetone	total
100.00	22.77	11.60	9.30	30.40	5.91	0.94	0.09	13.93	0.60	5.29	0.18	101.01
200.00	11.78	7.68	6.10	45.06	3.12	1.30	0.23	19.48	0.52	5.00	0.16	100.43
300.00	8.97	5.00	2.57	49.45	1.65	1.91	0.33	25.07	0.62	4.50	0.10	100.17
400.00	11.22	5.43	2.67	45.67	1.42	3.31	0.32	28.00	0.27	2.56	0.09	100.97
500.00	15.09	6.23	2.85	38.40	1.15	4.99	0.42	28.66	0.27	2.39	0.08	100.54

j (mA cm ⁻²)	Gas flowrate (ml min ⁻¹)			FE (%)												C in	Cin	Carbon
	Inlet	Outlet	H ₂	со	CH4	C ₂ H ₄	formate	acetate	СН₃СНО	EtOH	Ethylene glycol	n-PrOH	Acetone	(mmol)	CO ₂ (mmol)	(mmol)	e (mmol)	(%)
100	30.00	29.59	22.77	11.60	9.30	30.40	5.91	0.94	0.09	13.93	0.60	5.29	0.18	40.18	39.24	0.35	0.91	100.80
200	30.00	28.65	11.78	7.68	6.10	45.06	3.12	1.30	0.23	19.48	0.52	5.00	0.16	40.18	37.84	0.68	1.84	100.46
300	30.00	27.77	8.97	5.00	2.57	49.45	1.65	1.91	0.33	25.07	0.62	4.50	0.10	40.18	36.55	0.98	2.77	100.32
400	30.00	26.94	11.22	5.43	2.67	45.67	1.42	3.31	0.32	28.00	0.27	2.56	0.09	40.18	35.15	1.30	3.73	99.99
500	30.00	26.09	15.09	6.23	2.85	38.40	1.15	4.99	0.42	28.66	0.27	2.39	0.08	40.18	33.62	1.59	4.63	99.15

Table S8 Carbon balance analysis for CO₂RR on magnetron-sputtered Cu GDE tested by the modified measurement system.

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