# **Supporting Information For:**

## Bipotentiostatic Tandem Electrocatalysis of the CO<sub>2</sub> Reduction Reaction Yielding C<sub>2+</sub> Fuels

Joo Yeon Kim, Yeonsu Kim, C. Hyun Ryu, and Hyun S. Ahn\*

Contribution from: Department of Chemistry, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul, 03722 Republic of Korea

Email: ahnhs@yonsei.ac.kr

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## **Experimental**

**General.** All solutions were prepared using type I ultrapure water (Youngin Ins. Aquapuri 5: 18.2 M $\Omega$ ·cm, 3 ppb total oxidizable carbon). Potassium bicarbonate (KHCO<sub>3</sub>,  $\geq$  99.7%), Lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>,  $\geq$  99.0%), Cesium bicarbonate (CsHCO<sub>3</sub>  $\geq$  99.9%), Potassium hydroxide (KOH  $\geq$  99.99%) and ethylenediaminetetraacetic acid dipotassium salt (K<sub>2</sub>EDTA·2H<sub>2</sub>O, dihydrate  $\geq$  98%) were purchased from Sigma-Aldrich and used as received. Silver foil ( $\geq$  99.99%), Platinum foil ( $\geq$  99.9%), and Copper mesh ( $\geq$ 99.95%) were purchased from Goodfellow. A glassy carbon plate was obtained from Dasom RMS.

**Cu electrode.** Cu mesh was cut into a square shape  $(1.5 \times 2 \text{ cm}^2)$ , and the central opening was generated mirroring the WE1 dimensions. The mesh electrode was washed with acidic piranha solution (mixed solution of H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> as 7:3) and 2 M nitric acid before use.

Ag electrode. Ag foil was mechanically polished with 0.3  $\mu$ m de-agglomerated alumina powder and then cleaned thoroughly with 2 M nitric acid and deionized water.

Electrochemical measurement. All electrochemical measurements were conducted using Zive potentiostat (Zive MP2C, WonATech Co., Seoul, Korea). The Cu and Ag working electrodes were controlled independently by the grouped reference and counter electrodes. The volume of the cubic reactor where the tandem reaction occurs was 8-9 mL, and the storage volume contained 95 mL of the electrolyte solution (total volume of the storage compartment was 125 mL). The gaseous and liquid product was extracted from the head-space of the storage. Unless otherwise stated, 0.05M KHCO<sub>3</sub> was used as the electrolyte solution, and 34 µM EDTA was added to suppress Ag electrode fouling from Cu dissolution. Before running gas-tight CO2RR and CORR experiments, CO2 (99.999%, Shinyoung Gas Co., Seoul, Korea) and CO (99.9%, Shinyoung Gas Co., Seoul, Korea) gases were purged into the electrolyte solution for 60 minutes. In the CO<sub>2</sub> electroreduction experiments with online-GC product detection, the flow rate of the CO<sub>2</sub> was fixed at 50 (cc  $\cdot$  min<sup>-1</sup>). For the CO<sub>2</sub> electroreduction, Ag/AgCl (+0.196 V vs. RHE) filled with 1 M KCl and graphite rod was used as reference electrode and counter electrode, respectively. The potential applied on the Cu electrode was from -0.3 to -0.8 V(vs. RHE), which was insufficient to reduce  $CO_2$  to  $C_{2+}$  by itself. The applied potential on the Ag electrode was from -0.9 to -1.3 V (vs. RHE) to produce CO at sufficiently high Faradaic yields. CO<sub>2</sub> reduction reaction (CO2RR) in the gas-tight cell was carried out for 1-2 hours, and CO2RR at the GC-online cell was carried out for up to 4-5 hours. The applied potential value was corrected to reversible hydrogen electrode (RHE) values as shown in the following equation.

E (vs. RHE) = E (vs. Ag/AgCl) + 0.196 V + 0.059 × pH

### Product Analysis for Bipotentiostatic Tandem CO2RR

**Flow Reactor.** The electrochemical cell was custom designed (WizMac Co., Seoul, Korea) for delicate control of the distance between Cu-Ag electrodes. Poly(methyl methacrylate) (PMMA) was used as the base material, allowing the transparent window to monitor CO2RR. A reference electrode was positioned in the center of the reactor to minimize possible potential gradient. The proton exchange membrane (DuPont<sup>TM</sup> NR-212) used for cell separation (between the anode and the cathode compartments) was washed with 3% H<sub>2</sub>O<sub>2</sub> and then activated in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The membrane and anode reactor were positioned to face the cathode reactor as in a conventional stack cell.<sup>S1</sup> Both cathode and anode were supplied with the storage solution at constant flow by a diaphragm pump (KNF).



**Figure S1.** (a) Experimental configuration of the online-GC Product quantification of bipotentiostatic tandem electrocatalysis. Close-up images of the (b) WE1 Ag foil, (c) WE2 Cu mesh and (d) the electrode alignment. Before assembling the reactor stacks, we controlled the distance between the Cu and Ag based on Vernier Calipers measurements. To monitor any change in the Cu-Ag distance in the middle of the catalytic reaction, we customize the reactor with a transparent PMMA material. The distance between the electrodes in Figure(d) was 2 mm.

**Gaseous Product Quantification.** Gaseous products were collected from the head-space of the storage solution. For a gas-tight CO2RR experiment, gas quantification was performed manually on a gas chromatograph Agilent 7890B (Agilent). For a GC-online CO2RR experiment, the gaseous products were quantified by direct injection into the GC once every 30 minutes. In the online measurements, a dry ice trap was used to eliminate moisture from entering the gas sampling line. A thermal conductivity detector (TCD; equipped with Carboxen 1000 12 ft (Supelco)) was implemented for the detection and quantification of H<sub>2</sub>, CO, and CO<sub>2</sub>, and a flame ionization detector (FID; equipped with Rt-U-Bond 30 m (Restek)) was implemented for the detection of hydrocarbons  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_8$ . Helium (99.999%) was adopted as the carrier gas for an improved S/N ratio. Faradaic efficiencies of produced ethylene were calculated as follows:



**Figure S2.** Calibration curves for the quantification of (a) hydrogen, (b) carbon monoxide, (c) methane, and (d) ethylene.

For  $x_0$  ppm of ethylene, areas of standard gases were plotted versus mole of the known concentration (ppm).

$$n_{C_{2}H_{4}}(mol) = \frac{1 (atm) \times x_{0} \times V_{0}(L)}{0.082057 (L \cdot atm \cdot mol^{-1} \cdot K^{-1}) \cdot 298.15 (K)}$$

 $(V_0 = Volume \ of \ gas \ chromatography \ sample \ loop)$ 

(1.0 ml (FID),0.25 ml (TCD))

By replacing y values with the area measured from the sample mix gas, we obtained the concentration in the injected volume. Considering the head volume of the reactor cell, we can extrapolate the total amount of ethylene produced from the reaction.

$$N_{C_{2}H_{4}} = n_{C_{2}H_{4}}(mol) \times 96485 (C \cdot mol^{-1}) \times 12e^{-1}$$
$$FE = \frac{N_{C_{2}H_{4}}}{N_{total}} \times 100\%$$

 $(n_{C_2H_4} = Mole of ethylene filled in gas chromatography sample loop)$  $(N_{C_2H_4} = Mole of ethylene filled in reactor head space)$ 

Considering the  $CO_2$  purge flow rate and the volume ratio of ethylene in head space, we can calculate the Faradaic efficiency of ethylene in GC-online mode as follows:

$$i_{C_2H_4} = \frac{V_{C_2H_4} \times flow \ rate \ (mL \cdot min^{-1}) \times 96485 \ (C \cdot mol^{-1}) \times 12e^{-1}}{0.082057 \ (L \cdot atm \cdot mol^{-1} \cdot K^{-1}) \cdot 298.15(K)}$$

 $i_{total} = i_{Cu} (mA) + i_{Ag} (mA)$ 

$$FE = \frac{i_{C_2H_4} (mA)}{i_{total} (mA)} \times 100\%$$

 $V_{C_2H_4} = C_2H_4$  volume of gas chromatography sample loop) Flow rate =  $CO_2$  purging rate into storage solution, in the research we fixed it to 50 (mLmin<sup>-1</sup>)



**Figure S3.** Typical gas chromatogram of various products and their respective detection by (a) FID and (b) TCD.



**Figure S4.** Typical GC spectrum for the liquid product (1-PrOH) detection after a CO2RR electrolysis run. Gray-color and red-color spectrums represent the sample before exposure to CO2RR and after CO2RR. Green-color spectrum represents the standard solution of concentrated 1-PrOH. Sharp peaks displayed at a wide range of retention times were instrumental noise always accompanied when a liquid sample was injected.

**Liquid Product Quantification.** Liquid products were analyzed using nuclear magnetic resonance (NMR) AVANCE II 400 (Bruker Biospin). 600  $\mu$ l of the reaction mixture was transferred to an NMR tube after a CO<sub>2</sub> electroreduction experiment. Then, 100  $\mu$ l of the internal standard solution was injected into the NMR tube, and <sup>1</sup>H NMR spectrum was measured with a 400 MHz NMR spectrometer. In a GC-online CO2RR experiment, the liquid products were collected at 1 mL volume every 30 minutes for quantification. In a molar concentration calculation of the liquid product, the total volume over time was the result of subtracting the previous sampling volume extracted.

**Preparation of the Internal Standard Solution.** 122.5 mg of 1,3,5-benzenetricarboxylicacid (BTC) was dissolved in 15 ml of 1 M NaOH solution. Then, it was neutralized with 0.5 M HCl and diluted to 50 ml by the addition of H<sub>2</sub>O. 52.5 mg of 3-(Trimethylsilyl)propionic-2,2,3,3-d<sub>4</sub> acid sodium salt (TSP) was dissolved in 7 ml of D<sub>2</sub>O, and 1 ml of BTC solution was transferred to the solution. The mixture was diluted to 10 ml with H<sub>2</sub>O.<sup>S2</sup>



**Figure S5.** Typical NMR spectrum of the sample after a CO2RR electrolysis run. The spectrum was integrated for the quantification of liquid products.

### **COMSOL Multiphysics Simulation Details.**

This work uses laminar flow and transport of diluted species modules to simulate mass transport of the CO intermediate in Cu-Ag tandem operating conditions. We applied a CO<sub>2</sub>-bicarbonate-carbonate buffer system using the equilibrium equation following the approach of Gattrell and co-workers.<sup>S3-5</sup> Kinetic and transport parameters are listed in Table S1.



Figure S6. Cu-Ag tandem reactor model in COMSOL-based modeling and simulation.

$$CO_{2(aq)} + OH^{-} \leftrightarrow HCO_{3}^{-}$$

$$HCO_{3}^{-} + OH^{-} \leftrightarrow CO_{3}^{2-} + H_{2}O$$
(1)
(2)

<b>Table S1.</b> Kinetic and transport parameters for the simulatio	)n.
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Parameter	Value or Unit	Explanation
K1	4.42573*10	The equilibrium constant for
		reaction (1)
K2	$4.65*10^3$	The equilibrium constant for
		reaction (2)
D_CO	$2.05*10^{-9} [m^2/s]$	Diffusion coefficient of CO
D_CO2	$1.92*10^{-9} [m^2/s]$	Diffusion coefficient of CO <sub>2</sub>
D_HCO3	9.23*10 <sup>-9</sup> [m <sup>2</sup> /s]	Diffusion coefficient of HCO <sub>3</sub> -
D_CO3	$1.19*10^{-9} [m^2/s]$	Diffusion coefficient of CO <sub>3</sub> <sup>2-</sup>
D_OH	5.27*10 <sup>-9</sup> [m <sup>2</sup> /s]	Diffusion coefficient of OH-

Laminar Flow and Transport of Diluted Species. Figure S6 shows the three-dimensional geometric description of the Cu-Ag tandem operating cell, and the following parameters are listed in Table S2. For simulating the concentration and flux of CO, boundary conditions were the constant current density conversion of  $CO_2$  to CO at the Ag electrode and quantitative consumption of the arriving CO species at the Cu electrode. The fluid was saturated with  $CO_2$  at 33 mM concentration and flushed into the cubic reactor at a 100 cc/min rate.

Parameter	Value or Unit	Explanation
Width	10.4 [mm]	Cell width
Depth	25 [mm]	Cell depth
Height	25 [mm]	Cell height
Radius	1.5 [mm]	The radius of the inlet and outlet hole
Cu_Width	0.25 [mm]	Cu electrode width
Cu_Depth	2 [cm]	Cu electrode depth
Cu_Height	1.5 [cm]	Cu electrode height
Ag_Width	0.25 [mm]	Ag electrode width
Ag_Depth	1.5 [cm]	Ag electrode depth
Ag_Height	1 [cm]	Ag electrode height
Distance	2 [mm]	Distance between Cu and Ag electrode
Cu_x_axis_coordinate	5 [mm]	Cu electrode wall
Ag_ x_axis_coordinate	5 [mm]	Ag electrode wall
SCCM	100 [ml/min]	Flux velocity
Ag_Current	4.15 [mA]	Ag electrode current
Ag_Area	$1.5 [\mathrm{cm}^2]$	Ag electrode area
Re_Height	13 [mm]	Reference electrode height
Re_Radius	3 [mm]	Reference electrode radius
CO2_conc	33.4 [mM]	CO <sub>2</sub> concentration
OH_conc	10 <sup>7.2</sup> [M]	OH <sup>-</sup> concentration
pН	6.8	Electrolyte pH

Table S2. Geometry and operating parameters for the simulation.



Figure S7. The Faradaic efficiency distributions of (a) Ag and (b) Cu independent CO2RR.



(c) Faradaic efficiencies of Cu-Ag tandem CO2RR at varying Cu-Ag distances.



**Figure S9.** (a) COMSOL-derived local CO concentrations plot and (b) CO gradient at varying the opening area of Cu WE2. (c) Average current density, (d) Faradaic efficiency of CO and  $C_2$ , and (e) total product distribution at varying Cu-Ag distances. Products depicted as  $C_2$  include  $C_2H_4$ , EtOH, Acetate, and Acetaldehyde.



**Figure S10.** Various types of Cu substrates were applied in the Cu-Ag tandem CO<sub>2</sub> electrolysis. The red arrow represents the width of the woven mesh. The wire diameters of woven meshes were 0.230 mm, 0.140 mm, and 0.115 mm, respectively in (a-c). SEM images of (a) 310  $\mu$ m, (b) 190  $\mu$ m, and (c) 150  $\mu$ m wire Cu mesh, described as Cu Mesh I, II, and III in (d-f). (d) Average current density, (e) Faradaic efficiency of CO and C<sub>2</sub>, and (f) total product distribution in Cu-Ag tandem CO<sub>2</sub> electrolysis applied with the Cu meshes (a-c) and typical Cu foil. Products depicted as C<sub>2</sub> include C<sub>2</sub>H<sub>4</sub>, EtOH, Acetate, and Acetaldehyde.

## **Double Layer Capacitances Evaluation of Cu Substrates**

**ECSA Measurement.** The electrochemically active surface area (ECSA) of each catalyst was calculated by double-layer capacitance measurements by plotting each non-Faradaic current as a function of scan rates. The potential ranges for the measurements were set where only non-Faradaic charging current occurs. After obtaining the double layer capacitances of each electro from non-Faradaic charging experiments, the obtained numeric values can be converted to roughness factors ( $R_f$ ; a measure of surface roughness, a flat metallic surface has a  $R_f$  of 1, see **Table S3**) by dividing the double layer capacitance of a sample by that of an atomically flat surface (see equation below).

 $C_{dl} = \frac{d_i}{d_V d_V}$   $(C_{dl} = Double \ layer \ of \ capacitance \ )$ 

Roughness factor calculation for catalyst electrode samples

 $=\frac{Average \ Capacitance \ of \ the \ Metallic \ Surface \ (\mu C \cdot cm^{-2})}{Capacitance \ of \ Electropolished \ Copper \ (29\mu C \cdot cm^{-2})}$ 

Table S3. Double layer capacitances of Cu substrates candidates and resultant roughness factor.

Cu Substrate Type	Double Layer Capacitance of the Metal Surface (µFcm <sup>-2)</sup>	Roughness Factor		
Cu Mesh I	104	3.6		
Cu Mesh II	54	1.86		
Cu Mesh III	93	3.2		
Cu Foil	29	1.00		



**Figure S11.** Total product distribution of Cu-Ag tandem electrocatalysis at varying flow rates. A  $0.1 \text{ M KHCO}_3$  solution was used as the electrolyte and other experimental parameters (applied potential and electrode configurations) were the same as optimized above.



**Figure S12.** Results from electrochemical CO reduction on an independently operated Cu electrode are displayed. The total product distribution at (a) Potassium-containing electrolytes (1 M and 0.1 M KOH + 34  $\mu$ M K<sub>2</sub>EDTA·2H<sub>2</sub>O) and (b) Cesium-containing electrolytes (0.05 M CsHCO<sub>3</sub>+ 34  $\mu$ M K<sub>2</sub>EDTA·2H<sub>2</sub>O). The pulsed potential programs shown in (b) are identical to those applied at Cu in Cu-Ag tandem electrocatalysis. Due to the alkalinity in CORR experiments, Hg/HgO (0.110 V vs. RHE) was used as a reference electrode instead, and applied potential was corrected to those vs. RHE for reporting in the above figures.



**Figure S13.** (a) Average current density, (b) total Faradaic efficiencies, and (c)  $CH_4$  current density of Cu-M tandem CO2RR (M: Platinum and Glassy carbon). The applied potential on Platinum (Pt), and Glassy carbon (GC) was (-0.8 V, -1.1 V, and -1.3 V vs. RHE). Except for the metal type, other experimental parameters are the same as optimized above.



**Figure S14.** (a) Average current density, (b) Faradaic efficiency of  $CH_4$  and  $C_2$ , and (c) total product distribution in Cu-Ag tandem electrocatalysis at a varying CO volume ratio mixed into  $CO_2$ . Products depicted as  $C_2$  include  $C_2H_4$ , EtOH, and Acetaldehyde.



**Figure S15.** The H<sub>2</sub> and CO current density in Ag of Cu-Ag tandem electrocatalysis at varying applied potential on Ag (-0.9 V  $\sim$  -1.3 V vs. RHE). We assumed the Faradaic efficiency of H<sub>2</sub> and CO at Ag in bipotentiostatic CO2RR is the same as in Ag independent operation.



**Figure S16.** (a) Schematic of Cu-Ag tandem electrocatalysis. (b) Experimental and (c) COMSOL-based CO molar flux. Details in the calculation are presented in S7-S8.



**Figure S17.** COMSOL-based CO concentration map at varying applied potentials on Ag ((a)  $-0.9 \text{ V} \sim (e) -1.3 \text{ V}$  vs. RHE). (f) A plot of the Cu (WE2) plane's maximum CO concentration as a function of applied potential at Ag (WE1).



Figure S18. Total product distribution of Cu-Ag tandem electrocatalysis at varying applied potentials on (a) Ag (-0.9 V  $\sim$  -1.3 V vs. RHE) and (b) Cu (-0.3 V  $\sim$  -0.8 V vs. RHE), respectively.

#### **CO** Conversion Efficiency Calculations.

**Gaseous Product Analysis.** In our potentiostatic system, CO produced from Ag is consumed as a reactant toward  $C_{2+}$  production at the copper electrode. Because CO2RR product distribution in such a system display all chemicals produced from Ag and Cu operation, additional indicator was necessary to assess how efficiently CO tandem reaction occurs. Based on prior research works<sup>S4,5</sup>, we suggest a CORR efficiency calculation as follows:

 $CORR \ efficiency(\%)$   $= \frac{i_{CO \ to \ C_{2+}} \ (mA)}{i_{CO_{2} \ to \ CO} \ (mA)}$   $= \frac{Charge \ consumed \ in \ CO_{2} \ to \ CO_{C_{2+}} \ (C)}{Charge_{Ag} \ (C)}$   $= \frac{[Molar \ CO \ consumed \ for \ C_{2+} \ production] \ (mol) \times 2e^{-} \times 96485 \ (C \cdot mol^{-1})}{Charge_{Ag} \ (C)}$ 

 $(CO_{C_{2+}} = Molar CO consumed for C_{2+} production)$ 

We subtracted a slight amount of ethylene (8.5%) produced in Cu independent operation from the C<sub>2+</sub> product distribution under tandem catalysis conditions (see also Table S5). When x(%)F.E. of C<sub>2</sub>H<sub>4</sub> is achieved in Cu-Ag, moles of CO consumed for the corresponding C<sub>2</sub>H<sub>4</sub> production is calculated as shown below. *C0 consumed for* C<sub>2</sub>H<sub>4</sub> *production (mol)* 

$$= 2 \times \left( \frac{\left[ (Charge_{Cu} + Charge_{Ag})(C) \times x \ (\%) \right]}{96485 \ (C \cdot mol^{-1}) \times 12 \ e^{-}} - \frac{(Charge_{Cu}(C) \times 8.5 \ (\%)}{96485 \ (C \cdot mol^{-1}) \times 12 \ e^{-}} \right) \right)$$

When x(%) F.E. of 1–PrOH (C<sub>3</sub>H<sub>7</sub>OH) is achieved in Cu-Ag, moles of CO consumed for the corresponding 1-PrOH production is calculated as shown below.

CO consumed for 1-PrOH production (mol)

$$= 3 \times \left( \frac{[(Charge_{Cu} + Charge_{Ag})(C) \times x (\%)]}{96485 (C \cdot mol^{-1}) \times 18 e^{-1}} \right)$$

Calibrated by such procedure, we can consider moles of  $C_{2+}$  chemicals produced as the product of (CO<sub>2</sub>-CO-C<sub>2+</sub>) cascade of reactions from Cu-Ag tandem electrocatalysis, and from the CO Faradaic current at WE1 and the series of calculations above, overall electrosynthetic CO utility (in percent) can be deduced.

## Experimental Calculation of CO Flux between Cu-Ag tandem electrodes.

For x(%) F.E. of C<sub>2</sub>H<sub>4</sub> produced at Cu-Ag, CO flux at Cu is calculated below.

$$CO \ flux \ at \ Cu \ (10^{-4} mol \cdot m^{-2} \cdot s^{-1}) = \frac{\{[(i_{Cu} + i_{Ag})(mA \cdot) \times x \ (\%) - [i_{Cu} \times F.E. \ for \ C_2H_4 \ in \ Cu \ sole \ operation]\} \times 2}{96485 \ (C \cdot mol^{-1}) \times 12e^{-}} \times \frac{1}{0.002 \ \times 0.015 \ (m^2)}$$

Based on y(%) F.E. of CO produced at Ag independent operation, CO flux at Ag can be calculated from the equation below.

 $CO \ flux \ at \ Ag \ (10^{-4} \cdot mol \cdot m^{-2} \cdot s^{-1})$  $= \frac{i_{Ag} \times y \ (\%) \times 2}{96485 \ (C \cdot mol^{-1}) \times 12e^{-}} \times \frac{1}{0.002 \times 0.015 \ (m^2)}$ 



**Figure S19.** Total product distribution of Cu-Ag tandem electrocatalysis at varying (a) Pulse time and (b) anodic potential, respectively.



**Figure S20.** (a) Average current density, (b) total product distribution, and (c) Faradaic efficiency of  $CH_4$  and  $C_2$  in Cu-Ag tandem electrocatalysis at varying KHCO<sub>3</sub> concentration. Products depicted as  $C_2$  include  $C_2H_4$  and EtOH.



**Figure S21.** (a) Average current density, (b) Faradaic efficiency of  $CH_4$  and  $C_{2+}$ , and (c) total product distribution in Cu-Ag tandem electrocatalysis at varying electrolytes cations. Products depicted as  $C_{2+}$  include  $C_2H_4$ , EtOH, Acetate, Acetaldehyde, and 1-PrOH.



**Figure S22.** The CO<sub>2</sub> electroreduction stability was monitored at the GC-online flow cell for 7200 s. (a) Average current density, (b) Faradaic efficiency of  $C_2$  ( $C_2H_4$ , EtOH, Acetaldehyde and Acetate), and (c) total product distribution of Cu-Ag tandem electrocatalysis over time. CO<sub>2</sub> was purged constantly at the reaction condition of displaying the best  $C_2$  Faradaic yields in the gas-tight reactor. The electrolyte consists of 0.05 M KHCO<sub>3</sub> and other experimental parameters (applied potential and electrode configurations) are the same as optimized above. See S2-S6 for experimental details of the GC-online measurement.



**Figure S23.** The CO<sub>2</sub> electroreduction stability was monitored at the GC-online flow cell for 9000 s. (a) Average current density, (b) Faradaic efficiency of  $C_2$  ( $C_2H_4$ , EtOH, Acetaldehyde and Acetate), and (c) total product distribution of Cu-Ag tandem electrocatalysis over time (-1.2 V at Ag -0.65 V/+0.45 V at Cu). The electrolyte consists of 0.05 M KHCO<sub>3</sub> and other experimental parameters (electrode configurations) are the same as optimized above.



**Figure S24.** The CO<sub>2</sub> electroreduction stability was monitored at the GC-online flow cell for 7200 s. (a) Average current density, (b) Faradaic efficiency of  $C_2$  ( $C_2H_4$ , EtOH, Acetaldehyde and Acetate), and (c) total product distribution of Cu-Ag tandem electrocatalysis over time (-1.3 V at Ag -0.65 V/+0.45 V at Cu). The electrolyte consists of 0.05 M KHCO<sub>3</sub> and other experimental parameters (electrode configurations) are the same as optimized above.



**Figure S25.** The CO<sub>2</sub> electroreduction stability was monitored at the GC-online flow cell for 14400 s. (a) Average current density, (b) Faradaic efficiency of  $C_{2+}$  ( $C_2H_4$ , EtOH, Acetaldehyde, Acetate, and 1-PrOH), and (c) total product distribution of Cu-Ag tandem electrocatalysis over time (-1.1 V at Ag and -0.65 V/+0.45 V at Cu vs. RHE). The electrolyte consists of 0.05 M CsHCO<sub>3</sub> + 34  $\mu$ M K<sub>2</sub>EDTA·2H<sub>2</sub>O, and other experimental parameters are the same as optimized above.

## Cyclic Voltammogram (CV) for the Quantification of Dissolved Cu Species

**Peak Analysis.** CV study was performed to adjust additive concentration so that fouling of the Ag electrode by dissolved Cu may be prevented. When applying a pulsed potential of -0.65 V/+0.45 V and a constant potential of -1.3 V on the Cu and GC electrodes for an hour, some of the dissolved Cu species were electrodeposited on GC. An oxidation peak on the first scan corresponds to a stripping of the deposited Cu on GC during the reaction. To prevent the Ag electrode from similar fouling, we added Ethylenediaminetetraacetic Acid (EDTA) complex, which chelates the dissolved Cu species. The amount of dissolved Cu ion was calculated as follows:



**Figure S26.** (a) Schematic of Cu-GC tandem electrocatalysis. (b) CV of GC electrode after CO2RR.

Stripping peak area

= Cu stripping peak area per unit area( $\mu$ C · cm<sup>2</sup>) × GC substrate area (cm<sup>2</sup>)

 $9.1 (\mu C \cdot cm^2) \times 1.5 (cm^2) = 13.7 (\mu C)$ 

Mol of dissolved Cu ion

 $=\frac{Cu \ stripping \ peak \ area \ (\mu C)}{96485 \ (C \cdot mol^{-1}) \times 2e^{-}} = 71 \ (pmol)$ 

EDTA mole in electrolyte

= EDTA concentration( $\mu$ M) × Electrolyte (mL) = 34( $\mu$ M) × 94 (mL) = 3.2 ( $\mu$ mol)

Mole of Cu ion dissolved during CO<sub>2</sub>RR / EDTA in electrolyte

 $=\frac{71\times10^{-12}(mol)}{3.2\times10^{-6}(mol)}\times100~(\%)=0.0022~(\%)$ 

Considering the amount of dissolved Cu ion, relatively low concentration  $(34 \,\mu\text{M})$  of the EDTA additive was sufficient to keep our Cu-Ag tandem electrocatalysis for up to 4 hours without significant Ag electrode fouling.

## **Turnover Frequency (TOF) of the C-C Bond Formation Reaction on a Surface Copper Atom at WE2**

The TOF in our research represents the number of  $C_2$  molecules produced per second at a single copper atom<sup>S13</sup>. Amounts of  $C_2$  molecules produced at the Cu-Ag tandem electrocatalysis were used for calculation after subtracting the  $C_2$  molecules produced in the Cu -only operation.



**Figure S27.** Schematic representation of TOF in Cu-Ag tandem electrocatalysis. Representatively,  $C_2H_4$  was displayed as a product of CO reduction.

 $C_2$  molecules production rate at a single Cu atom site (s<sup>-1</sup>)

 $= \frac{(n_{C_2H_4} + n_{Acetaldehyde} + n_{Acetate} + n_{EtOH})(mol) \times N_A}{Reaction time (s) \times Number of Cu atoms in ECSA}$  $= \frac{(i_{C_2H_4} + i_{Acetaldehyde} + i_{Acetate} + i_{EtOH})(mA) \times N_A}{Number of Cu atoms in ECSA}$  $(N_A = 6.02 \times 10^{23})$ 

The number of Cu atoms in ECSA is calculated below (see also Table S3):

Number of Cu atoms in ECSA

 $= \left(\frac{\text{Double layer capacitance of the Cu mesh } (\mu F \cdot cm^{-2})}{\text{Double layer capacitance of the Cu foil } (\mu F \cdot cm^{-2})}\right) \times \frac{\text{Geometric surface area } (cm^2)}{\text{Surface area of Cu single atom } (cm^2)}$  $= \left(\frac{54 \ (\mu F \cdot cm^{-2})}{29 \ (\mu F \cdot cm^{-2})}\right) \times \frac{3 \ (cm^2)}{4\pi r_{Cu}^2 \ (cm^2)}$  $= 2.7 \times 10^{15} \\ (r_{Cu} = 128 \ pm)$ 

**Table S4.** C-C bond formation TOF per single Cu atom in Cu-Ag tandem electrocatalysis.



**Figure S28.** Schematic representation and product distribution at varying Cu-Ag alignment in tandem CO<sub>2</sub> catalysis.

	H <sub>2</sub>	со	CH <sub>4</sub>	нсоон	C <sub>2</sub> H <sub>4</sub>	СН <sub>3</sub> СНО	Acetate	EtOH	1-PrOH	Total
Ag	3.0	99								102
Cu	61	15.3	10.5	8.9	8.5					104
CullAg	15.8	9.6	8.0	5.4	35	4.2	2.5	19.1	6.5	106

Table S5. The total Faradaic efficiency of Ag, Cu, and Cu-Ag tandem CO2RR.

Table

**S6.** 

	Cu Current Density (mAcm <sup>-2</sup> )	Ag Current Density (mAcm <sup>-2</sup> )
Ag		5.3
Cu	1.09	
CullAg	6.6	4.2

Average current Density of Ag, Cu, and Cu-Ag tandem CO2RR.

Table S7. The Faradaic efficiency of CO and  $C_{2^+}$  at tandem catalysis and benchmarks.

	CO Faradaic Efficiency (%)	C <sub>2+</sub> Faradaic Efficiency (%)
Ag	99	
Cu	15.3	8.5
CullAg	16.0	67.3

Potential V vs. RHE	H <sub>2</sub>	со	CH₄	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
-0.9	21	67								88
-1.0	5.0	73		12.0						90
-1.1	3.0	99								102

-1.2	24	59	6.6			90
-1.3	10.0	69	11.0			90

**Table S8.** The total Faradaic efficiency of Ag CO2RR at varying applied potential (-0.9V  $\sim$  - 1.3V).

Potential V vs. RHE	H <sub>2</sub>	со	CH <sub>4</sub>	нсоон	$C_2H_4$	СН₃СНО	Acetate	EtOH	1-PrOH	Total
-0.65	62	25		10.7						98
-0.65 (pulse)	61	15.3	10.6	9.0	8.5					104
-0.9	55	3.4	1.20	32	0.96					92
-1.0	39	6.8	5.5	27	6.7					85
-1.1	29	7.6	12.8	34	10.3			10.0		104

Table S9. The total Faradaic efficiency of Cu CO2RR at varying applied potential (-0.65V  $\sim$  -

1.1V).

mm	H <sub>2</sub>	со	CH <sub>4</sub>	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
4	40	42	13.8	2.4	11.0					109
3	24	24	18.4	3.3	22	2.7	4.3	11.4		110
2	13.5	7.4	30		22			37		110
1	24	17.5	20		21	5.3		12.3		100

Table S10. The total Faradaic efficiency of tandem CO2RR at varying Cu-Ag distances.

Table local	S11. CO			COMSOL-Derived Concentrations.
		Distance between Cu II Ag (mm)	Maximum CO Concentration (mM)	
		1.0	2.0	-
		1.5	0.87	-
		2.0	0.64	-
		2.5	0.28	-
		3.0	0.163	-
		3.5	0.170	-
		4.0	0.129	-
		4.5	0.22	-
		5.0	0.24	-

mm	Cu Current Density (mAcm <sup>-2</sup> )	Ag Current Density (mAcm <sup>-2</sup> )
4	5.0	5.5
3	5.5	3.5
2	7.3	3.8
1	4.9	2.5

Average current density of Cu-Ag tandem CO2RR at varying Cu-Ag distances.

## Table S13. CO and $C_2$ Faradaic efficiency of Cu-Ag tandem CO2RR at varying Cu-Ag

mm	CO Faradaic Efficiency (%)	C <sub>2</sub> Faradaic Efficiency (%)
4	11.0	42
3	41	24
2	59	9.0
1	39	17.5

distances.

Hole Size of Cu (cm <sup>2</sup> )	H <sub>2</sub>	со	CH4	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
0	21	37	25	4.0	14.8			9.4		111
0.95	28	26	11.0	7.6	15.0	6.2		24		118
1.2	22	15.0	17.0	2.8	25		1.98	28		112
1.5	13.5	7.4	30		22			37		110

Table S14. The total Faradaic efficiency of tandem CO2RR at varying areas of the central

opening of Cu WE2.

Table S15. Average current density of Cu-Ag tandem CO2RR at varying areas of the central

Hole Size of Cu (cm²)	Cu Current Density (mAcm <sup>-2</sup> )	Ag Current Density (mAcm <sup>-2</sup> )
0	3.4	5.1
0.95	3.1	2.3
1.2	4.8	3.4
1.5	7.3	3.8

opening of Cu WE2.

**Table S16.** CO and C<sub>2</sub> Faradaic efficiency of Cu-Ag tandem CO2RR at varying areas of the central

Hole Size of Cu (cm²)	CO Faradaic Efficiency (%)	C <sub>2</sub> Faradaic Efficiency (%)
0	38	24
0.95	26	45
1.2	14.7	55
1.5	7.4	59

opening of Cu WE2.

Cu Substrate Type	H <sub>2</sub>	со	CH₄	нсоон	C <sub>2</sub> H <sub>4</sub>	CH <sub>3</sub> CH O	Acetate	EtOH	1-PrOH	Total
Cu Mesh I	15.3	37	4.1	3.8	18.1	3.6		21		103
Cu Mesh II	13.5	7.4	30		22		37			110
Cu Mesh III	14.0	23	8.4	8.2	23	2.7	1.70	14.9		96
Cu Foil	25	26	23	5.9	16.0		3.0	11.8		111

Table S17. The total Faradaic efficiency of tandem CO2RR at varying areas of the central

opening of Cu WE2.

**Table S18.** Average current density of Cu-Ag tandem CO2RR at varying areas of the central

Cu Substrate Type	Cu Current Density (mAcm <sup>-2</sup> )	Ag Current Density (mAcm <sup>-2</sup> )
Cu Mesh I	5.0	4.7
Cu Mesh II	7.3	3.8
Cu Mesh III	2.9	4.2
Cu Foil	4.9	3.9

opening of Cu WE2.

Cu Substrate Type	CO Faradaic Efficiency (%)	C <sub>2+</sub> Faradaic Efficiency (%)
Cu Mesh I	37	43
Cu Mesh II	7.4	59
Cu Mesh III	23	42
Cu Foil	26	31

**Table S19.** CO and C<sub>2</sub> Faradaic efficiency of Cu-Ag tandem CO2RR at varying areas of the central

opening of Cu WE2.

Flow Rate	H <sub>2</sub>	со	CH4	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
10	33	12.3	42	4.5	10.5			7.6		110
50	32	8.9	30	1.96	21			12.6		106
70	31	10.6	25	2.6	24			11.8		105
100	18	9.8	36		21			24		109
160	36	10.1	23	3.7	9.9		3.0	6.0		92

Table S20. The total Faradaic efficiency of Cu-Ag tandem CO2RR at varying flow rate.

Table S21. The CORR total product distribution at Potassium-containing electrolytes (1 M and

Electrolyte Potential (V vs. RHE)	H <sub>2</sub>	CO	CH4	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
1 M KOH -0.6	88				16.1					104
0.1 M KOH -0.7	62				27			10		99

 $0.1 \text{ M KOH} + 34 \mu \text{M K}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ ).

Table S22. The CORR total product distribution at Cesium-containing electrolytes (0.05 M

Potential (V vs. RHE)	H <sub>2</sub>	CO	CH4	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
-0.6	94									94
-0.85	85		2.0		1.96					89
-0.65 pulse	81		4.2		14.7					100
-0.85 pulse	103				9.4					112

 $CsHCO_3 + 34 \mu M K_2EDTA \cdot 2H_2O$ ).

Cu∥M (M: Pt, GC)	H <sub>2</sub>	со	CH4	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
Cu	61	15.3	10.5	8.9	8.5					104
Cu∥Pt	61	8.1	9.3	12.8	10.5					102
Cu∥GC	73	8.7	12.5		4.0					98
Cu∥GC	52	6.2	22	5.0	6.2					91

**Table S23.** The total Faradaic efficiencies of Cu-M tandem CO2RR (M: Platinum and Glassy carbon).

 Table S24. Average current density of Cu-M tandem CO2RR (M: Platinum and Glassy carbon).

	Cu Current Density (mAcm <sup>-2</sup> )	M Current Density (mAcm <sup>-2</sup> ) (M: Pt, GC)
Cu	1.09	
Cu∥Pt	1.20	1.03
CullGC	0.99	2.9
CullGC	1.63	5.8

Table S25. CH<sub>4</sub> current density of Cu-M tandem CO2RR (M: Platinum and Glassy carbon).

	CH <sub>4</sub> Current Density (mAcm <sup>-2</sup> )
Cu	0.115
Cu    Pt	0.21
CullGC	0.48
CullGC	1.66

CO (%)	H <sub>2</sub>	со	CH <sub>4</sub>	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
0	13.5		30		22			37		110
10	17.2		28	4.1	18.6	5.8		15.8		90
25	12.4		30	4.5	17.1	2.9		16.5		83
50	13.7		27	3.8	14.2	7.3		16.5		82
75	50		34		5.4	3.8				93

**Table S26.** The total Faradaic efficiencies of Cu-Ag tandem CO2RR at varying CO volume ratio mixed into CO<sub>2</sub>.

**Table S27.** Average current density of Cu-Ag tandem CO2RR at varying CO volume ratio mixed into  $CO_2$ .

CO (%)	Cu Current Density (mAcm <sup>-2</sup> )	Ag Current Density (mAcm <sup>-2</sup> )
0	7.3	3.8
10	4.3	3.0
25	3.8	3.2
50	4.0	3.9
75	4.1	3.1

**Table S28.** The  $CH_4$  and  $C_2$  Faradaic efficiencies of Cu-Ag tandem CO2RR at varying CO volume ratio mixed into  $CO_2$ .

CO (%)	CH₄ Faradaic Efficiency (%)	C <sub>2</sub> Faradaic Efficiency (%)
0	30	59
10	28	40
25	30	36
50	27	37
75	34	9.2

Ag (V vs. RHE)	H <sub>2</sub>	со	CH4	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
-0.9	43	10.2	12.2	6.9	15.3			6.2		94
-1.0	16.5	15.6	24	2.7	22	9.8		16.4		107
-1.1	13.5	7.4	30		22			37		110
-1.2	12.9	24.8	19.8	5.6	16.7	5.4	3.1	13.0		101
-1.3	5.8	18.94	33	4.0	25	3.0	1.24	9.3		100

Table S29. The total Faradaic efficiency of Cu-Ag tandem CO2RR at varying applied

potentials on Ag.

Table

and CC

 $\textbf{S30.}\,\mathrm{H}_2$ 

CO	Ag (V vs. RHE)	H <sub>2</sub> Current densities (mAcm <sup>-2</sup> )	CO Current densities (mAcm <sup>-2</sup> )					
	-0.9	0.33	1.09					
	-1	0.110	1.60					
	-1.1	0.116	3.8					
	-1.2	1.47	3.6					
	-1.3	0.89	6.1					

average current density in Ag of Cu-Ag tandem electrocatalysis at varying applied potentials on Ag.

**Table S31.** Average current density of Cu-Ag tandem CO2RR at varying applied potentials on Ag.

Ag (V vs. RHE)	Cu Current Density (mAcm <sup>-2</sup> )	Ag Current Density (mAcm <sup>-2</sup> )
-0.9	2.7	1.67
-1.0	4.1	2.2
-1.1	7.3	3.8
-1.2	6.7	6.1
-1.3	8.0	8.9

Ag (V vs. RHE)	Ag CO flux (10 <sup>-4</sup> molm <sup>-2</sup> s <sup>-1</sup> )	Cu CO flux (10 <sup>-4</sup> molm <sup>-2</sup> s <sup>-1</sup> )
-0.9	2.9	0.92
-1	4.1	3.9
-1.1	9.9	8.3
-1.2	9.3	5.9
-1.3	15.8	7.4

 Table S32. CO flux in Ag of Cu-Ag tandem electrocatalysis at varying applied potentials on

 Ag.

**Table S33.** CO and  $C_2$  Faradaic efficiencies of Cu-Ag tandem CO2RR at varying applied potentials on Ag.

Ag (V vs. RHE)	CO Faradaic Efficiency (%)	C <sub>2</sub> Faradaic Efficiency (%)
-0.9	10.2	20
-1.0	21	47
-1.1	9.0	59
-1.2	25	27
-1.3	18.9	18.7

Table S	534.	The	total	Faradaic	efficiency	of	Cu-Ag	tandem	CO2RR	at	varying	app	liec	l
							<u> </u>							

Cu (V vs. RHE)	H <sub>2</sub>	со	CH4	нсоон	$C_2H_4$	СН₃СНО	Acetate	EtOH	1-PrOH	Total
-0.3	20	42	14.0	20	14.3					110
-0.4	23	24	25	10	19.2			15.7		117
-0.5	20	23	23	6.4	21					93
-0.6	18.3	11.5	27	4.0	24	4.3		16.7		106
-0.65	13.5	7.4	30		22			37		110
-0.8	34	13.3	29	4.9	10.0	1.67		12.9		106

potentials on Cu.

Cu V(vs. RHE)	Cu Current Density (mAcm <sup>-2</sup> )	Ag Current Density (mAcm <sup>-2</sup> )
-0.3	1.90	3.0
-0.4	6.0	4.4
-0.5	5.8	3.0
-0.6	5.9	4.5
-0.65	7.3	3.8
-0.8	6.7	3.8

**Table S35.** Average current density of Cu-Ag tandem CO2RR at varying applied potentials on Cu.

Table S36. CO and C2 Faradaic efficiencies of Cu-Ag tandem CO2RR at varying applied

Cu V(vs. RHE)	CO Faradaic Efficiency (%)	C <sub>2</sub> Faradaic Efficiency (%)
-0.3	42	14.3
-0.4	25	35
-0.5	23	38
-0.6	11.5	45
-0.65	7.4	59
-0.8	13.3	25

potentials on Cu.

Step Time (s)	H <sub>2</sub>	со	CH4	нсоон	$C_2H_4$	СН <sub>3</sub> СНО	Acetate	EtOH	1-PrOH	Total
0.15	18.4	15.5	31	3.2	23			20		111
0.25	14.9	14.9	29	3.5	28	3.5		20		114

0.35	13.5	7.4	30		22		37	110
0.50	15.2	15.1	22	7.0	23		31	113
1.00	14.3	27	22	7.4	19.2		15.4	105
i-t	39	12.9	20	7.0	11.8		11.8	102

 Table S37. The total Faradaic efficiency of Cu-Ag tandem CO2RR at varying pulse time applied on Cu.

Anodic Potential (V vs. RHE)	H <sub>2</sub>	со	CH4	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
0.55	10.2	11.8	39	4.0	31			11.0		107
0.45	13.5	7.4	30		22			37		110
0.35	17.6	20	30	6.7	13.4	4.3	1.49	13.7		107

Table S38. The total Faradaic efficiency of Cu-Ag tandem CO2RR at varying anodic potential

applied on Cu.

Table S39. The total Faradaic efficiency of Cu-Ag tandem CO2RR at varying KHCO3

Con. (M)	H <sub>2</sub>	СО	CH4	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
0.05	13.5	7.4	30		22			37		110
0.1	18.0	9.8	36		21			24		109
0.2	27	9.1	41	4.6	6.6			15.0		103

concentration.

Cation	H <sub>2</sub>	со	CH4	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
Li <sup>+</sup>	62	2.9	29		0.80					95
<b>K</b> <sup>+</sup>	13.5	7.4	30		22			37		110
$Cs^+$	15.6	9.6	8.0	5.4	35	4.2	2.5	19.1	6.5	106

Table S40. The total Faradaic efficiency of Cu-Ag tandem CO2RR with various cations.

Table S41. Average current density of Cu-Ag tandem CO2RR with various cations.

Cation	Cu Current Density (mAcm <sup>-2</sup> )	Ag Current Density (mAcm <sup>-2</sup> )
Li <sup>+</sup>	7.4	5.3
$K^+$	7.3	3.8
$Cs^+$	6.6	4.2

Table				S42.
CH <sub>4</sub>	Cation	CH <sub>4</sub> Faradaic Efficiency (%)	C <sub>2</sub> Faradaic Efficiency (%)	$-$ and $C_2$
	Li+	29	0.77	_
	K+	30	59	_
	Cs <sup>+</sup>	8.0	67.3	

Faradaic efficiencies of Cu-Ag tandem CO2RR with various cations.

Ta	ble	<b>S43.</b> T	he total	prod	luct	distri	butio	n of Cu-Ag	tandem e	lectrocat	alys	is over tir	ne. (-	-1.1 V
at	Ag	-0.65	V/+0.4	5 V	at	Cu).	The	electrolyte	consists	of 0.05	М	KHCO <sub>3</sub>	and	other

Time (s)	H <sub>2</sub>	со	CH4	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
1800	12.0	11.5	22	3.8	28			12.0		89
3600	15.0	9.8	23	2.6	36	3.8	1.30	11.0		102
5400	11.4	6.0	19.7	4.0	36		0.86	11.8		90
7200	8.6	10.9	17.1	4.3	34		1.70	16.0		93

experimental parameters (electrode configurations) are the same as optimized above.

Table

S44.

Time (s)	Cu Current Density (mAcm <sup>-2</sup> )	Ag Current Density (mAcm <sup>-2</sup> )
1800	7.0	3.7
3600	6.9	4.0
5400	6.9	4.4
7200	6.9	4.6

Average current density of Cu-Ag tandem CO2RR over time.

	Faradaic	tondone	
Time (s)	C <sub>2</sub> Faradaic Efficiency (%)	over time.	tandem
1800	40		
3600	52		
5400	49		
7200	52		
	Time (s)         1800         3600         5400         7200	Time (s)         C2 Faradaic Efficiency (%)           1800         40           3600         52           5400         49           7200         52	Time (s)         C2 Faradaic Efficiency (%)         Faradaic Ag over time.           1800         40           3600         52           5400         49           7200         52

Time (s)	н	00	СН	нсоон	С.Н.	СНСНО	Acatata	EtOH	1 PrOH	Total
	112			neoon	C2114	Chigeno	Actiate	Eton	1-11011	10141
1800	11.1	16.3	32	6.5	23	5.4	1.44	13.4		99
3600	19.3	12.8	34	4.0	26	1.72		10.8		109
5400	16.9	8.5	41	5.1	28	1.5	1.30	10.3		113
7200	18.6	8.5	40	6.0	28	1.42	1.14	8.7		112
9000	17.6	7.5	37	8.4	24	1.34	1.43	8.9		106

**Table S46.** The total product distribution of Cu-Ag tandem electrocatalysis over time. (-1.2 V at Ag -0.65 V/+0.45 V at Cu). The electrolyte consists of 0.05 M KHCO<sub>3</sub> and other

experimental parameters (electrode configurations) are the same as optimized above.

Table S47. Average current density of Cu-Ag tandem CO2RR over time.

Time (s)	Cu Current Density (mAcm <sup>-2</sup> )	Ag Current Density (mAcm <sup>-2</sup> )
1800	6.6	4.9
3600	6.8	5.2
5400	7.0	5.5
7200	6.9	5.2
9000	6.8	6.7

		Faradaic	
Time (s)	C2 Faradaic Efficiency (%)	<ul> <li>Ag over time.</li> </ul>	tandem
1800	43		
3600	38		
5400	41		
7200	39		
9000	36		
	Time (s)         1800         3600         5400         7200         9000	Time (s)         C2 Faradaic Efficiency (%)           1800         43           3600         38           5400         41           7200         39           9000         36	Time (s)       C2 Faradaic Efficiency (%)       Faradaic Ag over time.         1800       43         3600       38         5400       41         7200       39         9000       36

Ta	able	<b>S49.</b> 1	The total	proc	luct	distri	butio	n of Cu-Ag	tandem e	elect	rocata	lysi	is over ti	me. (•	-1.3 V
at	Ag	-0.65	V/+0.4	5 V	at	Cu).	The	electrolyte	consists	of	0.05	М	KHCO <sub>3</sub>	and	other

Time (s)	H <sub>2</sub>	со	CH4	нсоон	C <sub>2</sub> H <sub>4</sub>	СН₃СНО	Acetate	EtOH	1-PrOH	Total
1800	5.6	25	28	4.4	22			10.2		95
3600	5.8	25	33	4.0	25	3.0	1.24	9.3		106
5400	5.3	20	34	4.3	27	3.4	2.1	8.7		105
7200	11.6	15.1	40	3.8	28	1.58	1.96	10.6		113

experimental parameters (electrode configurations) are the same as optimized above.

 Table S50. Average current density of Cu-Ag tandem CO2RR over time.

Time (s)	Cu Current Density (mAcm <sup>-2</sup> )	Ag Current Density (mAcm <sup>-2</sup> )
1800	6.8	7.0
3600	7.0	7.8
5400	7.1	8.1
7200	7.2	8.7

Table S51. C<sub>2</sub> Faradaic efficiencies of Cu-Ag tandem electrocatalysis over time.

Time (s)	C <sub>2</sub> Faradaic Efficiency (%)
1800	32
3600	38
5400	41
7200	42

Time (s)	$H_2$	со	CH4	нсоон	$C_2H_4$	СН₃СНО	Acetate	EtOH	1-PrOH	Total
1800	18.8	23	5.8	8.6	15.9	3.5	2.3	18.5		96
3600	23	11.0	9.4	5.5	32	9.2	3.0	14.6		108
7200	15.8	9.6	8.0	5.4	35	4.2	2.5	19.1	6.5	106
10800	18.5	11.4	6.2	7.2	37	2.7	1.20	14.0	5.8	104

**Table S52.** The total product distribution of Cu-Ag tandem electrocatalysis over time (-1.1 V at Ag and -0.65 V/+0.45 V at Cu vs. RHE). The electrolyte consists of 0.05 M CsHCO<sub>3</sub> + 34

 $\mu$ M K<sub>2</sub>EDTA·2H<sub>2</sub>O, and other experimental parameters are the same as optimized above.

 Table S53. Average current density of Cu-Ag tandem CO2RR over time.

Time (s)	Cu Current Density (mAcm <sup>-2</sup> )	Ag Current Density (mAcm <sup>-2</sup> )		
1800	6.4	3.8		
3600	6.6	4.2		
7200	6.6	4.9		
10800	6.2	5.4		

<b>Table S54.</b> C <sub>2+</sub>	Faradaic	efficiencies	of Cu-Ag tand	lem electrocata	lysis over time
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C <sub>2+</sub> Faradaic Efficiency (%)				
59				
67.3				
60				
58				

Reference Number	Electrolyte	Potential (V)	H <sub>2</sub>	C <sub>2+</sub>	C <sub>3</sub>	Enhancement factor (CuAg/Cu)	Substrate
6	0.1M KHCO <sub>3</sub>	-1.2	18.0	46	4.0	2	Glassy carbon
7	0.1M KHCO <sub>3</sub>	-1.1	35	52		3	Glassy carbon
8	0.1M KHCO <sub>3</sub>	-1.2	23	41	2.5	3	Glassy carbon
9	0.1M KHCO <sub>3</sub>	-0.98	21	65	3.4	1.2	Carbon paper
10	0.1M CsHCO <sub>3</sub>	-1.0	27	64	6.0	1.4	Glassy carbon
11	0.1M CsHCO <sub>3</sub>	-1.05	17.0	60	10.0	1.1	Si wafer (100)
12	0.2M KCl	-1.2	38	44		1.6	Gas diffusion layer
13	0.1M KHCO <sub>3</sub>	-1.05	25	76	5.6	1.4	Cu Film

Table S55. The records of  $C_{2+}$  selectivity enhanced at CuAg single channel catalyst usage.

Reference	Electrolyte	Potential (V)	H <sub>2</sub>	C <sub>2+</sub>	C <sub>3</sub>	Enhancement factor (CuAg/Cu)	Substrate
5	0.1M CsHCO <sub>3</sub>	-1.0	25	65	2.5	1.3	Au or Ag/Cu interdigitated device
14	0.1M KHCO <sub>3</sub>	-1.2	70	8		1.4	Glassy carbon
15	1M KHCO <sub>3</sub>	-0.8	17.5	62	7.5	2.0	Gas diffusion layer
This work	0.05M CsHCO <sub>3</sub>	-0.65V/+0.45V	15.8	67.3	6.5	6.4	Cu Mesh

**Table S56.** The records of  $C_{2+}$  selectivity enhanced at Cu-Ag bipotentiostatic system.

### C<sub>2</sub> partial current analysis on Cu Ag tandem CO2RR

The product distribution and current densities of CO2RR in Cu and Cu  $\parallel$  Ag were from CO<sub>2</sub> purged 0.05 M KHCO<sub>3</sub> of gas-tight reactor (see also Table S17). Applied potential on Cu for both were -0.65 V/+0.45 V 350 ms pulse. Applied potential of Ag was -1.1 V.



Figure S29. Schematic representations for  $CO_2$ -CO- $C_2H_4$  serial reaction based on (a) CO2RR and (b) CORR at Cu.

Condition	Cu Current (mA)	Ag Current (mA)
Cu	3.3	
CullAg	22	5.7
[Cu∥Ag]-[Cu]	18.7	

Average current density of Cu and Cu-Ag tandem CO2RR.

Condition	H <sub>2</sub>	со	CH4	нсоон	C <sub>2</sub> H <sub>4</sub>	СН3СНО	Acetate	EtOH	1-PrOH	Total (mA)
Cu	1.99	0.50	0.34	0.29	0.28	0.00	0.00	0.00	0.00	3.40
C <sub>2</sub> from CO2RR			7.94		5.79			10.21		23.94
C <sub>2</sub> from CORR			7.94		3.86			6.81		18.61

Table S58. Partial current density of product in Cu and Cu-Ag tandem CO2RR.

The C<sub>2</sub>-product currents increased at Cu in CuAg operation, and the 8-electron reduction (reduction of Ag produced CO) model fits well with the data. If Cu-derived CO participated in the C<sub>2</sub> production at significant portions, 12-electron reduction model should be more appropriate (CO2RR at copper yielding CO and then subsequent reduction to ethylene and ethanol), which is clearly not the case. Accordingly, we ascertain that CO produced at Cu exhibited minimal interferences with the C<sub>2+</sub> producing reaction in the tandem mode via electrochemically produced CO from Ag WE1.



**Figure S30.** COMSOL-based pH maps at varying flow rates. When the surface reaction current on Ag is off (a). When the flow rate is set at (b) 0 sccm, (c) 10 sccm, (d) 50 sccm, (e) 100 sccm, and (f) 160 sccm. Ag reaction rate applied in the simulation corresponds to that listed in Table S57.



**Figure S31.** COMSOL-based CO and pH maps at Cu opening size of (a)  $0.00 \text{ cm}^2$ , (b)  $0.95 \text{ cm}^2$ , (c)  $1.20 \text{ cm}^2$ , and (d)  $1.50 \text{ cm}^2$ . The surface reaction current on Cu was set as same as listed in Table S15.

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