**Supplementary Information**

**Spatial reactant distribution in CO\textsubscript{2} electrolysis: Balancing CO\textsubscript{2} utilization and Faradaic Efficiency**

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**Experimental**

All experiments were performed in a 5 cm\textsuperscript{2} area membrane electrode assembly (Dioxide materials) having a serpentine flow channel on both the anode and cathode endplates. Sigracet 38 BC gas diffusion layers (GDL) of 6.25 cm\textsuperscript{2} area (2.5cm x 2.5cm) was used as the porous transport layer. Ag catalyst layer was deposited on top of microporous layer of GDL by direct current magnetron sputtering to obtain a thickness of 100 nm. Nickel foam (3 cm x 3 cm ) was used as the anode. Ag GDE and Ni foam were combined with an oversized 16 cm\textsuperscript{2} (4cm x 4cm) Sustainion anion exchange membrane (X37-50 Grade RT) to assemble the MEA (Fig. S2). An exchange MEA configuration using 1M KOH as the anolyte and humidified CO\textsubscript{2} as reactant at the cathode were fed into the reactor.

![Flow diagram](image)

**Fig. S1:** Flow diagram of the experimental setup used for CO\textsubscript{2} electroreduction in an exchange MEA.
CO₂ was humidified by bubbling dry CO₂ into a water bath at room temperature and the relative humidity was measured using a humidity sensor. The MEA was prepared by physical compression of the electrodes and endplates using a torque wrench which were tightened to 4 Nm. This value was chosen to enhance the contact between the GDE and membrane while simultaneously ensuring that no physical damage occurred to the carbon GDE.

A series of constant current electrolysis experiments with different reactant flow rates were performed and the gaseous products from the cell were analysed using an online gas chromatography connected to the outlet of the cell equipped with two thermal conductivity detectors and a flame ionization detector. All experiments were performed for 1 hour at a current density of 200 mA/cm². Aliquots were collected every 5 min during the reaction resulting in a total of 12 injections in 1 hour. The concentration of gaseous products (CO and H₂) were obtained from GC and the average of 12 injections was used to calculate their faradaic efficiencies. The anolyte samples were collected after each experiments to quantify liquid products produced using HPLC measurements (Agilent Technologies). Over long enough operating periods salt formation will occur in the GDL and in the CO₂ gas channel, impacting CO₂ transport and reaction selectivity. Within the designated operating current density and testing time of 1 hr however, we did not observe any notable changes in selectivity although some salt precipitation was observed.

Fig. S2: (a) Schematic of the membrane electrode assembly configuration used in the experiments. (b) Serpentine flow channel with alternating turns at the endplate and (c) Dioxide materials cathode endplate with Ag GDE used in the study.
The flow rate at the outlet of the reactor was measured using a mass flow meter (Bronkhorst) in order to estimate the faradaic efficiency of products accurately. A LABVIEW program was built and connected to the mass flow meter for continuous monitoring of the outlet flow rate. The experimental setup and the entire system design used is shown in Fig. S1. The outlet flow rate of the gas mixture (CO+H₂ + residual CO₂) from the reactor was measured \( \dot{V}_{\text{outlet}} \) using the mass flow meter and the mole fractions of CO \( (x_{\text{CO}}) \) and H₂ \( (x_{\text{H₂}}) \) were estimated from the GC injections. All the calculated values are reported in Table S2.

**Faradaic efficiency calculation**

To estimate the Faradaic efficiency of gaseous products, the mole fractions of CO and H₂ were estimated from GC injections. The volume fraction of gas products from GC is equal to the mole fraction for ideal gases. The mole fraction of water vapour exiting the reactor was measured using a humidity sensor and found to be 78\% \( (x_{\text{H₂O}} = 0.023) \). Since the sum of mole fractions is equal to 1, the mole fraction of CO₂ exiting was calculated as,

\[
x_{\text{CO₂, out}} = 1 - (x_{\text{CO}} + x_{\text{H₂O}} + x_{\text{H₂}})
\]  
(S1)

After calculating the mole fractions of all gaseous products, the volumetric flow rate at the outlet of the reactor measured with the MFM and used to calculate the moles of each product.

\[
n_{\text{CO}} = \frac{\dot{V}_{\text{outlet}} \times x_{\text{CO}}}{RT}
\]  
(S2)

\[
n_{\text{H₂}} = \frac{\dot{V}_{\text{outlet}} \times x_{\text{H₂}}}{RT}
\]  
(S3)

\[
FE_{\text{CO}} = \frac{n_{\text{CO}} \times n_e \times F}{I} \times 100 \%
\]  
(S4)

Here: \( n_{\text{CO}} \) – moles/s of CO produced, \( n_e \) - number of electrons involved in CO₂RR (2 for CO), \( F \) - 96485 C/mol and \( I \) - applied current (in Amperes).

**Sample calculation of FE of gas products**

For an inlet flow rate of 50 sccm, the measured outlet flow rate was 39.08 ml/min which is a mixture of CO, H₂, H₂O (g) and residual CO₂. Since the mass flow meter was calibrated for CO₂, a correction factor based on the gas conversion factors for each of the gases was used to correct the outlet flow rate. The gas conversion factor for the gas mixture outlet is given by,

\[
\frac{1}{C_{\text{mix}}} = \frac{V_1}{C_1} + \frac{V_2}{C_2} + \frac{V_3}{C_3} + \frac{V_4}{C_4}
\]  
(S5)
Here $C_{\text{mix}}$ is gas conversion factor for outlet gas mixture, $V_i$ is the volume fraction of gas ‘i’ in the outlet of reactor measured from GC and $C_i$ is gas conversion factor for gas ‘i’.

### Table S1: Gas conversion factors and volume fraction of gases measured from GC.

| Species | Volume fraction ($V_i$) | Gas conversion factor |
|---------|-------------------------|-----------------------|
| CO      | 0.153                   | $C1 = 1$              |
| $H_2$   | 0.0067                  | $C2 = 1.01$           |
| $H_2O$  | 0.023                   | $C3 = 0.74$           |
| CO$_2$  | 1-(0.153+0.0067+0.023) = 0.817 | $C4 = 0.79$ |

\[
\frac{1}{C_{\text{mix}}} = \frac{0.153}{1} + \frac{0.0067}{1.01} + \frac{0.023}{0.79} + \frac{0.817}{0.74}
\]

\[
\Rightarrow C_{\text{mix}} = 0.773
\]

\[
\dot{V}_{\text{outlet}} = \frac{39.08}{0.74} \times C_{\text{mix}} = 40.84 \text{ ml/min}
\]

\[
FE_{CO} = \frac{2 \times 96485 \text{ Cmol}^{-1} \left( \frac{0.153 \times \frac{40.82}{60} \times 10^{-6} \text{ m}^3 \text{s}^{-1}}{8.314 \text{ J/mol} \times 273K} \right) \times 101325 \text{ Pa}}{1.25 A} \times 100 = 71.7 \%
\]

\[
FE_{H2} = \frac{2 \times 96485 \text{ Cmol}^{-1} \left( \frac{0.007 \times \frac{40.82}{60} \times 10^{-6} \text{ m}^3 \text{s}^{-1}}{8.314 \text{ J/mol} \times 273K} \right) \times 101325 \text{ Pa}}{1.25 A} \times 100 = 3.15 \%
\]

### Carbon balance on the cathode side

The following equations were then used to calculate the CO$_2$ consumption with OH$^-$ ions and make a carbon balance on the cathode side.

\[
\dot{V}_{\text{CO}_2 \rightarrow CO} = x_{CO} \times \dot{V}_{\text{outlet}} \quad (S6)
\]

\[
\dot{V}_{H2} = x_{H2} \times \dot{V}_{\text{outlet}} \quad (S7)
\]

\[
\dot{V}_{\text{residual CO}_2} = \dot{V}_{\text{outlet}} - (\dot{V}_{\text{CO}_2 \rightarrow CO} + \dot{V}_{H2}) \quad (S8)
\]
\[
\dot{V}_{CO_2 \to HCOO^-} = ((1 - x_{CO} - x_{H_2}) \times \frac{j \times A}{n \times F} \text{ mol s}^{-1} \times 22.4 \text{ L mol}^{-1} \times 60 \text{ s} \times 1000 \text{ ) ml/min} 
\]

(S9)

\[
\dot{V}_{OH^-} = \dot{V}_{\text{inlet}} - (\dot{V}_{\text{residual CO}_2} + \dot{V}_{CO_2 to CO} + \dot{V}_{CO_2 to HCOO^-}) 
\]

(S10)

\[
CO_2 \text{ utilization} = \left( \frac{\dot{V}_{CO_2 to CO} + \dot{V}_{CO_2 to HCOO^-}}{\dot{V}_{\text{inlet}}} \right) \times 100\% 
\]

(S11)

\[
\dot{j}_{\text{loss}} = \frac{n \times \dot{V}_{CO_2 to OH^-} \times F}{A} 
\]

(S12)

Table S2 shows the carbon balance performed on the cathode side from which the fraction of CO\(_2\) reacting with OH\(^-\) ions was calculated. Here, measuring the flowrate of gas products at the outlet of the reactor is an important factor in the estimation of FE of gas products and CO\(_2\) losses.

We observed that the sum of FE of CO and H\(_2\) did not add up to 100% which is possibly due to the formation of some liquid products. To determine this, we collected the anolyte (1M KOH) samples post electrolysis and conducted high performance liquid chromatography (HPLC) analysis. Formate (HCOO\(^-\)) was the only product detected showing that formate ions produced at the cathode migrate to the anolyte through the AEM. The sum of FE of CO, H\(_2\) and formate reached 96-97.5% for most of the studied inlet flow rates and we suspect that the remaining formate ions possibly oxidized to CO\(_2\) at the anode as reported previously. After this confirmation, we calculated the FE of formate produced as 100- (FE\(_{CO}\)+FE\(_{H2}\)) in order to make a carbon balance at the cathode side with the assumption that no non-faradaic reactions take place. The amount of CO\(_2\) lost to OH\(^-\) ions was then calculated for all the studied inlet flow rates.
Table S2: CO\textsubscript{2} losses, utilization rate and modified inlet flow rates and \(j_{\text{loss}}\) used in the model at an applied current density of 200 mA/cm\textsuperscript{2}.

| Inlet flow rate (sccm) | \(\dot{V}_{\text{CO}_2 \text{ to CO}}\) (ml/min) | \(\dot{V}_{\text{CO}_2 \text{ to } HO\text{CO}}\) (ml/min) | \(\dot{V}_{\text{residual }\text{CO}_2}\) (ml/min) | \(\dot{V}_{\text{OH}^-}\) (ml/min) | CO\textsubscript{2} utilization (%) | Case B- Modified inlet flow rate for the model (ml/min) | Case C- \(j_{\text{loss}}\) due to CO\textsubscript{2} lost to OH\textsuperscript{-} ions (mA/cm\textsuperscript{2}) |
|------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|----------------------------------------------------------|------------------------------------------|
| 10                     | 3.13                                     | 1.95                                     | 0.69                                     | 4.41                                     | 50.8                                     | 5.59                                                     | 106.4                                     |
| 12.5                   | 3.72                                     | 2.55                                     | 0.81                                     | 5.55                                     | 50.1                                     | 6.95                                                     | 127.5                                     |
| 15                     | 4.15                                     | 3.29                                     | 1.67                                     | 6.19                                     | 49.6                                     | 8.81                                                     | 142.2                                     |
| 17.5                   | 4.41                                     | 3.63                                     | 2.58                                     | 6.78                                     | 45.9                                     | 10.72                                                    | 155.7                                     |
| 20                     | 5.49                                     | 2.65                                     | 4.83                                     | 7.35                                     | 40.7                                     | 12.65                                                    | 168.9                                     |
| 25                     | 5.65                                     | 2.2                                      | 10.61                                    | 7.41                                     | 31.4                                     | 17.59                                                    | 170.3                                     |
| 30                     | 5.93                                     | 2.14                                     | 14.40                                    | 8.01                                     | 26.9                                     | 21.99                                                    | 184                                       |
| 40                     | 6.17                                     | 2.02                                     | 23.80                                    | 8.78                                     | 20.5                                     | 31.22                                                    | 201.7                                     |
| 50                     | 6.18                                     | 2.24                                     | 33.25                                    | 9.31                                     | 16.8                                     | 40.69                                                    | 214.1                                     |

(\(\dot{V}_{\text{CO}_2 \text{ to CO}}\) : consumed CO\textsubscript{2} flow rate which is electrochemically converted to gas product (CO); \(\dot{V}_{\text{residual }\text{CO}_2}\) : unreacted CO\textsubscript{2} flowrate in the gas outlet; \(\dot{V}_{\text{OH}^-}\) : consumed CO\textsubscript{2} flowrate via the reaction with OH\textsuperscript{-}.)
Modified current density used in the model

![Graph showing modified current density vs. inlet flow rate of CO2](image)

**Fig S3.** Modified current density used in the model after taking into account of the fraction of CO2 lost to hydroxide ions from carbon balance.

Outlet flow rate and Faradaic efficiency measurement during electrolysis

(a) Measured outlet flowrate during electrolysis at 200 mA/cm² for an inlet flow rate of 50 sccm. The dip in the peaks occurring every 5 min are due to the periodic GC injections. (b) Faradaic efficiency of CO and H₂ measured from the GC injections.

![Graph showing outlet flow rate and Faradaic efficiency](image)
Flow rate of humidified CO$_2$

The flowrate of humidified CO$_2$ entering the reactor varies slightly for each CO$_2$ flow rate. So we measured the flowrate of humidified CO$_2$ to make the carbon balance accurately, specifically in the determination of the amount of CO$_2$ reacting with OH$^-$ ions since it depends on the inlet flowrate as shown in equation S10.

**Table S3:** Flowrate of humidified CO$_2$ used in the experiments

| Inlet flowrate of CO$_2$ (sccm) measured from MFC | Inlet flowrate of humidified CO$_2$ (sccm) |
|-------------------------------------------------|------------------------------------------|
| 10                                              | 10.1                                     |
| 12.5                                            | 12.6                                     |
| 15                                              | 15.1                                     |
| 17.5                                            | 17.6                                     |
| 20                                              | 20.2                                     |
| 25                                              | 25.3                                     |
| 30                                              | 30.5                                     |
| 40                                              | 40.8                                     |
| 50                                              | 51.0                                     |

Humidity measurements

![Graph](image.png)

**Fig. S5.** Relative humidity measured at the exit of the reactor during electrolysis at 200 mA/cm$^2$ for an inlet flow rate of 50 sccm.
The relative humidity (R.H) at the outlet of the reactor was measured during electrolysis and it remained constant throughout 1 hour electrolysis. It did not vary significantly for different inlet flow rates. The measured R.H for an inlet flow rate of 50 sccm of CO$_2$ is shown in Fig S5. As shown here, R.H at outlet was 78% corresponding to a mole fraction of 0.023 for H$_2$O which was used in FE calculation.

**Table S4: Liquid products analysis using HPLC**

| Inlet flow rate (sccm) | HCOO$^-$ detected from HPLC (in ppm) | FE of HCOO$^-$ (%) | Predicted FE of HCOO$^-$ (100-FE$_{CO}$-FE$_{H2}$ %) | Missing FE (%) |
|------------------------|--------------------------------------|-------------------|-------------------------------------------------|---------------|
| 10                     | 2228.05                              | 21.23             | 25.16                                           | 3.92          |
| 12.5                   | 2953.5                               | 28.14             | 31.94                                           | 3.79          |
| 15                     | 2546.5                               | 24.28             | 33.41                                           | 9.13          |
| 17.5                   | 2372.9                               | 22.61             | 32.2                                            | 9.59          |
| 20                     | 2955.1                               | 28.16             | 30.54                                           | 2.38          |
| 25                     | 2681.1                               | 25.54             | 29.66                                           | 4.11          |
| 30                     | 2164.9                               | 20.63             | 22.98                                           | 2.34          |
| 40                     | 1976.1                               | 18.83             | 22.71                                           | 3.87          |
| 50                     | 1582.1                               | 15.07             | 24.6                                            | 9.73          |

**Faradaic efficiency of Formate from HPLC**

Sample calculation: The formate ions present in the anolyte were detected from HPLC measurements and the faradaic efficiency was calculated using the following equation. Here a sample calculation using 40 sccm as inlet flow rate is shown.

$$[\text{HCOO}^-] \text{ detected} = 1976.1 \text{ ppm} = 1.976 \text{ gL}^{-1}$$

*Molecular weight of HCOO$^-$ = 45 g mol$^{-1}$

*Volume of anolyte used = 0.1 L

*Moles of HCOO$^-$ = $\frac{1.976 \text{ gL}^{-1}}{45 \text{ g mol}^{-1}} \times 0.1 \text{ L} = 4.39 \times 10^{-3} \text{ moles}$

$$FE_{\text{HCOO}^-} = \frac{\text{Moles of HCOO}^- \times n^e \times F}{I \times t} \times 100\% = \frac{4.39 \times 10^{-3} \times 2 \times 96485}{1.25 A \times 3600 \text{ s}} = 18.83\%$$

*Sum of FE of products = $FE_{CO} + FE_{HCOO}^- + FE_{H2} = (71.5 + 18.83 + 5.7)\% = 96.03\%$
Model description

A 3D geometry of the cathode compartment (5cm² area) comprising of the serpentine flow channel with a series of alternating 180° turns and 12 ribs with same length (2.25 cm), width (1 mm) and depth (1 mm) was modeled in COMSOL Multiphysics. A carbon GDL of dimensions (2.5 cm x 2.5 cm x 0.325 cm) was placed in contact with the flow channel (Fig.10 (b)). The numerical simulations were performed using a MUMPS general solver with a relative tolerance of 0.001 to calculate the CO₂ concentration gradient in the gas channels and catalyst surface. For Case A and Case B, a current density of 200 mA/cm² was applied at the catalyst surface. For Case C, the modified current density for each of the inlet flow rate was used to estimate the concentration gradient.

Electrochemical reduction of CO₂ to CO was modelled and the competing hydrogen evolution reaction was not taken into account. The electrochemical reduction reaction occurring at the cathode is a 2 e⁻ reduction reaction:

\[
\text{CO}_2 \text{ RR : } \text{CO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{CO} + 2\text{OH}^- \tag{3.1}
\]

All parameters used in the model were taken from the experimental setup. The following assumptions were made in the model:

i) The system operates at steady-state conditions
ii) Carbon GDL is assumed to be isotropic with constant porosity and permeability since the in-plane diffusion is higher than the through plane diffusion
iii) Both diffusion and convection from the channel to the catalyst surface are taken into account
iv) A uniform current distribution is assumed on the catalyst surface
v) Isothermal at 298 K with no thermal diffusion gradients
Brinkmann equation and mixture diffusion model

The fluid flow in the serpentine channels was modelled using the Brinkmann equations which is a modified form of the Navier stokes equation for porous media flows. A no-slip boundary condition was imposed on the channel walls. A slip condition was used at the channel-GDL interface since the normal component of velocity is zero at this interface. Single phase compressible flow was assumed. An inlet boundary condition was given by a normal inflow velocity defined by the flowrate ($\dot{V}_{in}$) over inlet cross sectional area of the channel (Dirichlet boundary condition). $\dot{V}_{in}$ varied from 10 to 50 sccm which was used in the experiments. A zero pressure boundary condition was imposed at the outlet (Neumann boundary condition) with the suppression of backflow.

The Brinkman equation solves for the velocity and pressure distribution in the GDL. It was coupled with the mixture diffusion model taking into account of the diffusion and convection through the GDL. All parameters used in the model can be found in Table S5. For the meshing, a free tetrahedral mesh with a fine mesh size was used for the channels and a swept mesh was used for the GDL (98023 domain elements, 24196 domain elements and 2894 edge elements) resulting in a run time for 45 minutes for every simulation. The velocity and pressure field in the gas channels were solved using:

$$ \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \left[ -p \mathbf{I} + \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \right] + \mathbf{F} \quad (S13) $$

$$ \nabla \cdot (\rho \mathbf{u}) = 0 \quad (S14) $$

In the GDL, the velocity and pressure was calculated using:

$$ \frac{1}{\varepsilon_p} \rho (\mathbf{u} \cdot \nabla) \mathbf{u} \frac{1}{\varepsilon_p} = \nabla \cdot \left[ -p \mathbf{I} + \frac{1}{\varepsilon_p} \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu \frac{1}{\varepsilon_p} (\nabla \cdot \mathbf{u}) \mathbf{I} \right] - \left( \mu \kappa^{-1} + \frac{Q_m}{\varepsilon_p^2} \right) \mathbf{u} + \mathbf{F} \quad (S15) $$

$$ \nabla \cdot (\rho \mathbf{u}) = Q_m \quad (S16) $$

In these equations,

$\rho$ is the density of the fluid, $\mu$ is the dynamic viscosity of the fluid, $p$ is the pressure, $\mathbf{u}$ is the velocity, $\mathbf{F}$ is the force term, $\kappa$ is the permeability of the GDE, $\varepsilon_p$ is the porosity of the GDE and $Q_m$ is the mass source.

Mixture diffusion model

To solve for the species transport in the system, a mixture diffusion model was used. Relative humidity in the inlet stream was ignored since the humidity measured experimentally at the inlet remained constant at 75%. So, we accounted for only 2 species which are CO$_2$ and CO. The molar flux of the species were calculated using the following equations:

$$ \nabla \cdot j_i + \rho (\mathbf{u} \cdot \nabla) \omega_i = R_i \quad (S17) $$
\[ N_j = j_i + \rho u \omega_i \]  
(S18)

\[ j_i = -(\rho D_{im}^m \nabla \omega_i + \rho \omega_i D_{im}^m \frac{\nabla M_n}{M_n}) \]  
(S19)

\[ R_i = \frac{v_{j_i}}{nF} \]  
(S20)

Here:

\( N \) is the total flux vector of species \( i \), \( R_i \) is the reaction rate for species \( i \), \( u \) is the fluid velocity, \( j_i \) is the relative mass flux due to molecular diffusion of species \( i \), \( \omega_i \) is the mass fraction of species \( i \), \( v \) is the volumetric current density, \( F \)- Faraday’s constant. Here, equation S18, represents the convection-diffusion equation with the first term representing diffusion and second term representing convection the magnitude of which depends on the inlet velocity ‘\( u \)’.

**Mesh independence study**

A mesh independence study was performed to ensure that the right mesh size was chosen. An element size of 0.5 mm was chosen for the free tetrahedral mesh that generated a total of 98023 domain elements. Fig. S7 shows the mesh independence study performed to estimate the average \( CO_2 \) concentration at the catalyst surface for an inlet flowrate of 50 sccm and 200 mA/cm\(^2\).

![Fig. S7. A mesh independence study performed with different mesh element sizes at an inlet flowrate of 50 sccm and a current density of 200 mA/cm\(^2\). The average \( CO_2 \) concentration at the catalyst surface was calculated and did not vary within the shown number of domain elements.](image-url)
Simulation results

The simulation results of CO$_2$ concentration in the gas channels and at the catalyst surface are shown in Fig.S8 for an inlet flow rate of 10 sccm. Here the CO$_2$ losses to OH$^-$ ions are ignored (Case A).

**Fig. S8.** CO$_2$ concentration at the catalyst surface for an inlet flow rate of 10 sccm and current density of 200 mA/cm$^2$ without accounting for the fraction of CO$_2$ reacting with hydroxide ions.
**CO$_2$ concentration at different inlet flow rates**

![Figure S9](image)

**Fig. S9.** CO$_2$ concentration at the cathode for different inlet flow rates using a modified current density approach (Case C). Here, the CO$_2$ losses to OH$^-$ occurring homogenously throughout the catalyst surface are considered.

![Figure S10](image)

**Fig. S10.** The average CO$_2$ concentration at catalyst surface for each of the inlet flow rate studied calculated from the model (Case C).
Cumulative distribution plots of CO$_2$ concentration at the catalyst surface

**Fig. S11:** Cumulative distribution plots of CO$_2$ concentration at the catalyst surface for various inlet flow rates using a modified current density approach (Case C).
Catalyst area having \([\text{CO}_2]= 0\) at different inlet flowrates

**Fig. S12:** Percentage of catalyst surface area having \([\text{CO}_2]= 0\) for various inlet flowrates using a modified current density approach (Case C).

**Other Figures and Tables**

**Fig. S13.** (a) Variation of cell voltage with time during \(\text{CO}_2\) electrolysis for various inlet \(\text{CO}_2\) flow rates. (b) Cell voltage for various inlet \(\text{CO}_2\) flowrates at a current density of 200 mA/cm².
Material characterization

Fig. S14. SEM images of Ag catalysts coated on microporous layers of Sigracet 38 BC gas diffusion layers.

Fig. S15: XRD pattern of Ag GDE before and after CO₂ electrolysis showing the presence of Ag (111) facet. Potassium bicarbonate salt peaks are visible due to salt precipitation at the cathode.
**Fig. S16:** XPS analysis of Ag catalysts coated on microporous layers of Sigracet 38 BC gas diffusion layers.

**Fig. S17:** Components used in the MEA setup. 1: Nuts and bolts, 2: Ni porous medium, 3: GDE with Ag sputtered catalyst layer, 4: Titanium anode endplate, 5: Silicone gasket for anode, 6: PTFE gasket for cathode, 7: Stainless steel cathode endplate.
Table S5: Parameters used in the 3D mass transport and fluid flow model

| Parameter                              | Symbol | Value      | Units     | Reference |
|----------------------------------------|--------|------------|-----------|-----------|
| Temperature                            | T      | 298        | K         | This work |
| Reference pressure                     | P      | 1          | atm       | This work |
| Diffusivity of CO into CO₂             | D_{CO₂CO} | 1.52 × 10^{-5} | m²s⁻¹   | [1]       |
| Porosity of GDE                         | eps_gdl| 0.8        | –         | [2]       |
| Permeability of GDE                    | kappa_gdl | 7 × 10^{-12} | m²       | [2]       |
| Inlet flowrate                          | Q_{sccm}| 10-50      | sccm      | This work |
| Applied current density                | i_{loc} | -2000      | Am⁻²      | This work |

Table S6: Electrochemical and homogenous reactions occurring at the cathode of the electrolyzer.

| Reaction                           | Equation                               | (S)   |
|------------------------------------|----------------------------------------|-------|
| CO₂RR to CO                         | CO₂ + H₂O + 2e⁻ → CO + 2OH⁻             | (S12) |
| HER                                | 2H₂O + 2e⁻ → H₂ + 2OH⁻                  | (S13) |
| CO₂RR to HCOO⁻                     | CO₂ + H₂O + 2e⁻ → HCOO⁻ + 2OH⁻          | (S14) |
| HCO₃⁻ formation                    | CO₂ + OH⁻ ↔ HCO₃⁻                       | (S15) |
| CO₃²⁻ formation                    | HCO₃⁻ + OH⁻ ↔ CO₃²⁻                     | (S16) |

References

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