Supplementary Information

Selective electrochemical reduction of CO$_2$ to formic acid in gas phase reactor with by-product recirculation

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List of symbols and abbreviations

A	geometric surface area [cm²]
C_x	concentration of compound x in gas phase [mol/cm³]
CO_2RR	carbon dioxide reduction reaction
E_0	Nernstian standard half-cell reduction potential [V]
F	Faraday constant (96 485 C/mol)
HER	hydrogen evolution reaction
j_x	partial current density of compound x [mA/cm²]
j_0	exchange current density [mA/cm²]
j_{total}	total current density $(\sum j_x)$
L	membrane thickness [cm]
n	number of electrons transferred in the half-reaction
P_x	partial vapor pressure of compound x in gas phase
Q	reaction coefficient of the partial pressures of the involved species
R	universal gas constant (8.314 J/mol.K)
RH	relative humidity
RHE	reversible hydrogen electrode
R_x	production rate of compound x [mol/cm².s]
t	residence time in reactor [s]
T	temperature
V	gas volume in cathode compartment of reactor [cm³]
V_0	Nernstian half-cell reduction potential [V]
x_i	molar fraction of compound i in the liquid phase
Y_x	yield of product x per unit volume [mol/cm³]
σ	membrane conductivity [S/cm]
α_c	charge transfer coefficient

η   overpotential [V]

I.   Model description

The simulation of the looping system was performed using Excel. The governing parameters were: flow rate, reactor pressure, pressure release valve setpoint, electrode surface area, reactor cell temperature, reduction potential and condenser temperature. In the following, the equations and model assumptions will be discussed that were used to calculate the gas composition at points A-D of the looped system (Fig. S 1). Based on the changing partial pressures in the gaseous inflow of the electrochemical reactor cell, the current-voltage (IV) curves were continuously recalculated to determine the faradaic efficiency based on the partial current densities. For clarity, some constants for the conversion of units were left out of the equations.
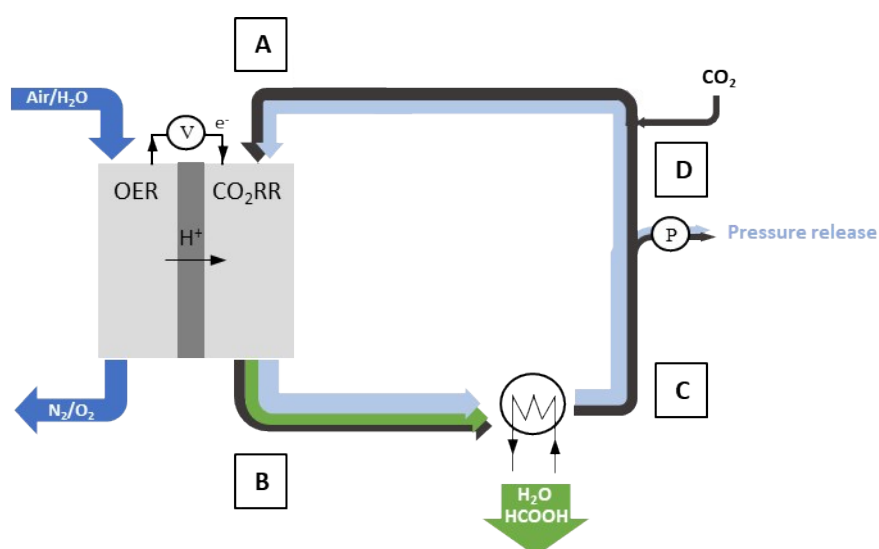

Fig. S 1. Gas phase electrochemical CO_2 reduction reactor with recirculation of by-products, maximizing formic acid production. The effect of recirculation on the reaction selectivity was simulated by calculating the changing partial pressures of the gases along the process steps (A - D).

A → B

The amount of H_2 and formic acid in the gas stream at the outlet of the electrochemical reactor are determined by the product yield. For H_2, and likewise for formic acid, this is calculated as follows :

$$C_{H2,B} = C_{H2,A} + Y_{H2}$$

$$Y_{H2} = \frac{R_{H2} * A * t}{V}$$

$$R = \frac{j_{H2}}{n * F}$$

With j_{H2} calculated numerically from IV-curves, that were simulated through following equations : [1]

$$V = V_0 + \eta_{Ohm} + \eta_{Act} + \eta_{Conc}$$

$$V_0 = E_0 - \frac{R * T_{reactor}}{n * F} * \ln Q$$

$$\eta_{Ohm} = \frac{j_{total} * L}{\sigma}$$

$$\eta_{Act} = \frac{RT}{nF\alpha_c} \ln \left(1 + \frac{j_{H2}}{j_{0,c}}\right)$$

$$\eta_{Conc} = a \, e^{bj_{H2}}$$

Herein, a [V] and b [m²/A] are phenomenological coefficients. The parameters were not reported for this dataset. Therefore, the parameters α, j_0, a and b were fitted to the experimental data and do not represent measured values for this reactor setup. If a parameter value was available in literature from a similar system, the literature reference is given in Table S 1. For the parameters for which no adequate literature value could be found, a tolerance interval is given, describing the range wherein the parameter could be varied in a realistic way.

Table S 1. Exchange current densities, charge transfer coefficients and phenomenological coefficients (a,b) used to fit the simulated IV-curves with the experimental data from Park *et al.*[2]

	CO$_2$RR to formate	Ref. / tolerance interval for parameter fitting	HER	Ref. / tolerance interval for parameter fitting
α_c	0.12	0.11 [3]	0.11	0.15 [4]
$j_{0,c}$ [mA/cm²]	(-) 0.410	0.41 [3]	(-) 0.003	0.003 ; calculated using j_0 = $C_m n_i k_i F$ with $k_{i,\,HER,Sn}$ = 1.39*10^{-9} mol/cm².s, from [5]
a [V]	0.040	0.001-0.100 [6]	0.085	0.001-0.100 [6]
b [cm²/mA]	0.035	0.001-0.100 [6]	0.015	0.001-0.100 [6]

For the calculation of η_{Ohm}, properties of a Nafion 117 membrane are assumed, with a membrane thickness of 0.0183 cm and a conductivity of 0.078 S/cm.[7]

A sensitivity analysis can be found in SI II, where the model parameters were varied.

When the amount of formic acid exceeds the maximum vapor pressure, not all formic acid that was produced can be carried out of the reactor cell due to saturation of the gaseous flow. Then, condensation occurs. The amount of condensed formic acid is determined by the liquid-vapor equilibrium at the reactor temperature.

$$C_{HCOOH,B} = C_{HCOOH,A} + Y_{HCOOH} - HCOOH_{liq}$$

Here, the Antoine equation was used, for which the constants can be found in Table S 2. If the formic acid concentration did not exceed its maximal concentration, this condensation term was set to 0.

$$HCOOH_{liq} = C_{HCOOH,A} + Y_{HCOOH} - C_{HCOOH,max}$$

$$\log P_x^0 = A - \frac{B}{T + C}$$

$$C_{HCOOH,max} = \frac{P_{HCOOH}^0[Pa]}{R * T_{reactor}}$$

Assuming that formic acid is the only C-containing compound that was formed :

$$C_{CO2,B} = C_{CO2,A} - Y_{HCOOH}$$

It was assumed that the gas coming out of the reactor has a RH of 50% due to the presence of a water-containing membrane. The accuracy of this assumption is dependent on several parameters, such as the type of membrane, the flow rate and the reactor dimensions. Due to the limited data on water evaporation from membranes during electrochemical operation, an accurate value is rather complex to determine. The assumption of a RH of 50% is expected to more accurately describe the situation in which a proton exchange membrane (PEM) is used than an anion exchange membrane (AEM), as with a PEM, the cathode side of the membrane is kept water loaded due to electro-osmotic drag. For an AEM, water is transported in the opposite direction, leading to a more dried out membrane and therefore presumably lower humidities of the gaseous reactor outflow.

$$C_{H2O,B} = \frac{P_{H2O}^0[Pa] * 0.5}{R * T_{reactor}}$$

Table S 2. Antoine constants used to calculate the vapor pressures of formic acid and water

	H$_2$O (T in °C ; P in mmHg)	HCOOH (T in °C, P in bar)
A	8.07	4.48
B	1730.63	1551.38
C	233.43	245.71

B → C

It is assumed that the permanent gases are not removed from the gas stream by the condenser, therefore:

$$C_{CO2,C} = C_{CO2,B}$$

$$C_{H2,C} = C_{H2,B}$$

Water and formic acid vapor are liquified inside the condenser if their concentration in the gas phase exceeds the maximal vapor pressure at the temperature of the condenser. The maximal vapor pressure is determined assuming that within the condenser, the gas is in equilibrium with the produced formic acid-water condensate, which is variable over time.

Hereby, Raoult's Law of ideal mixtures is followed:

$$P_i = x_i * P_i^0$$

The gas leaving the condenser carries the amount of water and formic acid according to their vapor pressure at the condenser temperature:

$$C_{i,C} = \frac{x_i * P_i^0 [Pa]}{R * T_{condenser}}$$

Thus, the amount of water and formic acid that is recovered inside the condenser is determined as follows:

$$condenser\ yield_i = C_{i,B} - C_{i,C}$$

As formic acid in water is, in practice, not an ideal mixture, this assumption will lead to a discrepancy. Formic acid forms an azeotrope in water, with the azeotropic composition also strongly depending on the temperature.[8] Due to limited availability of data, this effect was not taken into account. Based on the Antoine parameters for pure solutions, formic acid is calculated to be more volatile than water. However, for dilute formic acid-water mixtures, formic acid is slightly less volatile than water. Therefore, a slight error is made in positive direction: more formic acid will stay in the condensate than is obtained through the model, leading to a more concentrated product than what is now discussed.

C → D

In between point C and D in the recirculation system, there is an adjustable valve. A valve setting (P_D) at a lower pressure than the system pressure at point C is chosen in order be able to supply sufficient CO_2 reagent for the reaction to proceed efficiently, and tune the steady-state gas composition to the desired value.

The valve is simulated through following equation:

$$C_{i,D} = C_{i,C} * \frac{P_D}{P_C}$$

It is assumed that the gas is well-mixed and all gas- and vapor components are removed through the valve according to their relative abundance in the gas mixture at point C.

D → A

The gas composition values at point D are continuously re-inputted into the equations of the reactor cell to simulate the looping of the gas flows.

As CO_2 is supplied as a make-up gas, the CO_2 concentration going back into the reactor is determined through following equation :

$$C_{CO2,A'} = C_{CO2,D} + \frac{(P_A - P_D)}{R * T}$$

Additional model assumptions

As this model is used as a proof of concept and is therefore rather simplified, the following assumptions are made :

Firstly, it is assumed that the catalyst is stable over the course of the operation. This means that the faradaic efficiencies and current density do not shift due to inherent changes to the catalyst. Secondly, it is assumed that the recirculated gas phase products do not cause poisoning or other detrimental effects on the Sn catalyst. The local pH where the cathodic reaction occurs is assumed to be constant, with a proton activity of 1. Pressure increase is assumed to not results in an increase of the activity coefficient of the gases, for which an activity coefficient of 1 is assumed.[9] It is also assumed that the anode reaction (water

oxidation) does not work as a rate-limiting factor. Finally, it is assumed that there is no leaching of formic acid through the membrane to the anode side.

Furthermore, it was assumed that 99% of the gas is recycled and it is supplemented with 1% pure CO_2. For most calculations, the cell potential was chosen to be 2.3 V. For calculations at 0.2 MPa, The flowrate was set to 200 ml/min, with a reactor residence time of 1 second. The geometric electrode surface area was assumed to be 9 cm². Finally, the reactor and condenser temperature were assumed to be 70°C and 0°C respectively. The reactor temperature was chosen in accordance to the system discussed by Park *et al.*[2]

II.   Sensitivity analysis

The model parameters are highly dependent on the reaction conditions and catalyst choice. To analyse how universally this concept can be applied, it was assessed how heavily a change in these parameters affects the outcome. The output variable was chosen to be the percentage gain in faradaic efficiency towards formate after 5000 recycles as opposed to the faradaic efficiency in pure CO_2.

The cell potential (2.3 V), pressure (0.2 MPa), recycled fraction (99%) and flow rate (200 ml/min) were maintained constant. Therefore, the gas mixture composition after 5000 recycles varied for the varying parameter values. Linear trendlines were drawn through the simulated datapoints for a clear view of the trends.

Coefficients a and b

Coefficient a affects the slope of the linear region of the IV-curve. The larger a, the more linearly the current density increases with the applied voltage as opposed to exponentially when a is small. Coefficient b mostly affects the slope of the curve in the mass-transport limited region. The larger b, the smaller the limiting current density, representing a more mass-transport limited system.[10]

Fig. S 2 shows that if the HER has a strong exponential dependency on the potential (a(HER) small) or is less transport limited (b(HER) small), a larger gain in selectivity towards CO_2 reduction can be obtained after 5000 recycles under the given conditions. In these cases, H_2 accumulates quickly in the gas mixture and a potential shift of the HER curve as a result of the

increased hydrogen pressure causes a large difference in the HER partial current density. The gain in faradaic efficiency is less dependent on the curve shape of the CO_2RR.
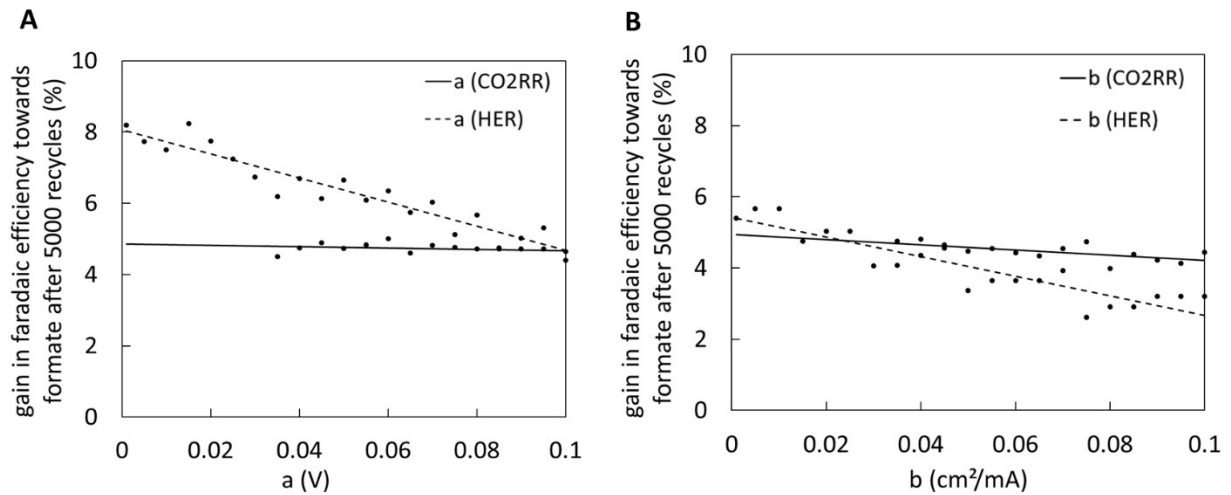

Fig. S 2. Simulated selectivity gain (%) after 5000 recycles in the recirculated reactor system for varying values of the phenomenological coefficients a and b.

Exchange current density ($j_{0,x}$)

Fig. S 3 shows the dependency of the selectivity gain on the exchange current density for both reactions. The most pronounced effect is that if hydrogen production is more kinetically favorable ($j_{0,HER}$ bigger), a larger gain in selectivity towards formate production can be achieved by recirculation (Fig. S 3B).
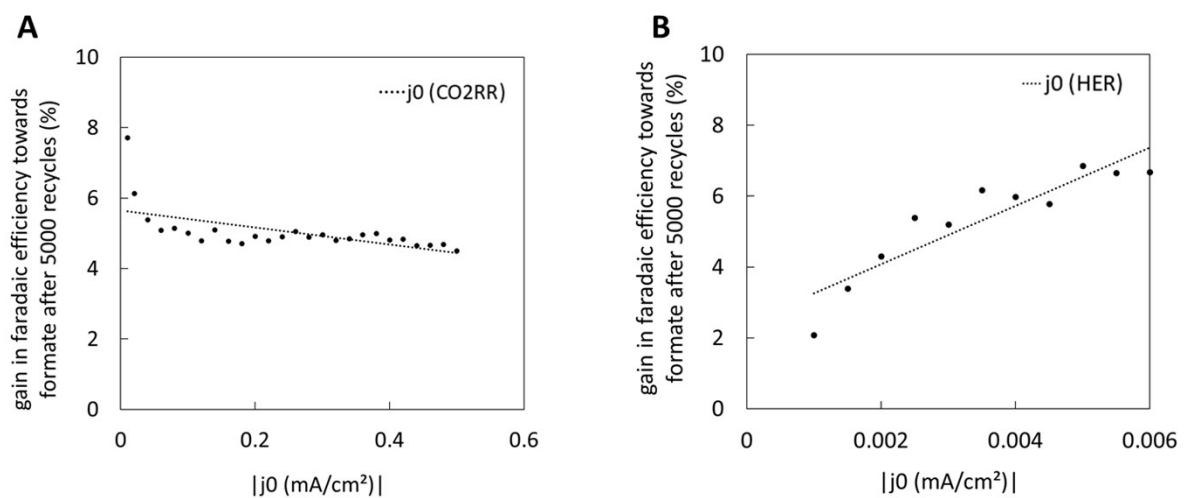
III.   Experimental Section

Reactor cell setup

A platinum on carbon cloth gas diffusion electrode (FuelCellStore, 0.5 mg/cm²) of 4 cm² was used as the anode electrocatalyst. Nafion ionomer (5 wt% in ethanol) was dropcasted onto the anode to ensure good contact with the proton exchange membrane (Nafion 117). The Nafion membrane was prepared by boiling it in a 5%-solution of H_2O_2, a 1M H_2SO_4 solution and milli-Q water for one, two and three hours at 120°C respectively. 100 ml of a 1M solution of KOH was recirculated through the anode compartment at a rate of 9 ml/min using a peristaltic pump. The cathode electrocatalyst also had a geometric surface area of 4 cm² was prepared by dipcoating carbon paper (QuinTech TP-060, untreated) into an ink with an intermediate drying step. The ink consisted of tin nanopowder (< 150 nm, Sigma Aldrich) and Nafion ionomer (5 wt% in ethanol) in a 3/1 Sn/ionomer weight ratio, dispersed in ethanol. Dipcoating led to a deposited mass of 1.13 mg (Sn + ionomer)/cm²$_{geom}$. Teflon gaskets were used in between anode and cathode.
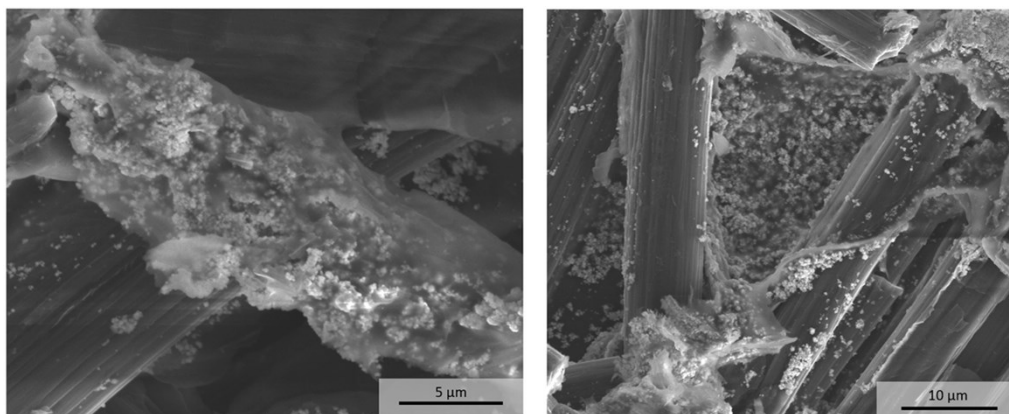

Fig. S 4. Scanning Electron Microscopy images of the cathode, consisting of tin nanopowder and Nafion ionomer deposited on a carbon paper support.

At the cathode, gaseous CO_2 and H_2 were mixed in varying concentrations using mass flow controllers (Gefran), with a constant total volumetric flow. The gas was humidified by going through a bubble humidifier at room temperature.

Electrochemical reaction

The electrochemical reactor operated at room temperature and was connected to a potentiostat (Ametek VersaSTAT 3) with VersaStudio software. Electrochemical characterization techniques were used including cyclic voltammetry at a scan rate of 10 mV/s, chronoamperometry at an applied cell potential of 2.6 V and Potentiostatic Electrochemical Impedance Spectroscopy. The cell potential on the x-axis of Fig. 7 was calculated as follows :

V (IR Corrected) = V (Applied) – j_{total} [A] * R [Ohm]

Product analysis

For hydrogen gas quantification, the gases were brought from the reactor to a gas chromatograph (Interscience CompactGC 4.0) through a line heater at 60°C. The chromatograph was equipped with a precolumn (Rt-QBond), molecular sieve column (Rt-Molsieve 5A) and thermal conductivity detector for analysis of permanent gases using argon carrier gas. For these measurements, the total flow was set at 10 ml/min, containing about 0.057 mg H_2O/cm².min. The volumetric concentrations of H_2 were determined from a linear calibration fitted over a range of 3 to 80 vol% H_2. The faradaic efficiency towards H_2 was calculated as follows :

$$FE\left(H_2\right), \% = \frac{P * \dfrac{\left(\dfrac{ml\, H_2}{s}\right)_{with\, reaction} - \left(\dfrac{ml\, H_2}{s}\right)_{without\, reaction}}{RT} * 10^{-6} * 2 * F}{j_{total}} * 100$$

For formate quantification, the cathodic outlet was connected to a base trap filled with 10 ml of a 0.5M $KHCO_3$ solution (pH ~ 7.3) to ensure complete dissociation of the product. The base trap was kept at a constant temperature of 10°C. The concentration of formate was determined through sampling from the base trap and analysis by ion chromatography (Metrohm, Metrosep A Supp 4 anion separation column). To aid evacuation of the aerosol from the reactor cell, a total flow of 150 ml/min was used, resulting in a water vapor content

of approximately 0.860 mg H_2O/cm^2.min. The faradaic efficiency towards formate (at moment t) was calculated as follows :

$$FE\left(HCOO^-\right), \% = \frac{mol\ HCOO^-_t * 2 * F}{charge\ passed_t\ [C]} * 100$$

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