Supporting Information

Accurate Assessment of Electrocatalytic Carbon Dioxide Reduction

Products at Industrial-Level Current Density

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Experimental section

Materials and chemicals: All the chemicals used for electrolytes, catalyst synthesis, and electrode preparation were purchased from Shanghai Aladdin Biochemical Technology Co., LTD. All those chemical reagents were used as received without any further purification. Nafion 117 membrane was purchased from Dupont. Deionized water (18.2 M Ω) was used in the experiments.

Revised formula derivation and verification: This experiment used the same type of thermal mass flowmeter (HORIBA S48-32/HMT) with different ranges. All mass flowmeters were calibrated using CO₂ at normal pressure and temperature (101325 Pa and 298 K). It uses the air flow through the capillary, changes the temperature distribution of the capillary, resulting in the upstream and downstream temperature difference method, and measures the gas mass flow. Another kind of flow meter that makes the upstream and downstream temperature constant by changing the heating temperature is shown in the Fig. S4. Its conversion coefficient is the same as the flowmeter used in the text.

Flow cell assembly: The flow cell setup was composed of three chambers: anolyte chamber, catholyte chamber, and gas chamber. The size of the exposed electrode was $0.5 \text{ cm} \times 2 \text{ cm}$. The cathode GDE was clamped between catholyte chamber and gas diffusion chamber, with the substrate side facing the gas chamber and catalyst side

facing the catholyte chamber. The IrO_2 -coating titanium sheet was employed as the counter electrode. The catholyte and anolyte chambers are separated by anion exchange membrane. The catholyte chamber contained an Ag/AgCl reference electrode (1 M KHCO₃).

Catholyte and anolyte were applied through separated silicone tubes that each connected to a peristaltic pump, offering a constant flow rate of approximately 30 mL min⁻¹. The electrolytes go through the pumps, and then enter each chamber from the bottom to the top, forming a close electrolyte cycle. For the gas supply, a digital mass flow controller was connected to gas cylinder to control the flow rate in gas flow chamber. The gas cylinders were purchased from Hunan Mander Gas Co. LTD.

Electrochemical measurement: All the electrochemical tests were carried out using an electrochemical workstation (DongHua Analytical, DH7002A). The CO₂RR performance was tested in a flow cell assembly under galvanostatic mode. 1 M potassium bicarbonate solution was used as cathode and anode electrolyte.

CO₂RR product analysis: The gas products were collected from the gas outlet channel of the flow cell, and were injected into a gas chromatograph. The gas chromatograph was equipped with a thermal conductivity detector (TCD) for detection of H_2 . And a flame ionization detector (FID) with a methanizer for the detection of CO and hydrocarbon species. For quantification, 1 mL of gas product was injected into the gas chromatograph, and the performance was evaluated as a function of current density,

gas flow rate and gas products fraction. Standard gases ranging from 10 ppm to 100,000 ppm were used to make standard curve.

During the evaluation of liquid products, the usual way is to sample a part of the electrolyte from the catholyte container. The concentration is analyzed by the hydrogen NMR (nuclear magnetic resonance) spectroscopy, and then the amount of product in the electrolyte and the FE are calculated. The calculation equation is (Detailed derivation of the process in Supporting Information Eqs. S14-S18).

As shown in Fig. S5a, the pipeline with a certain volume (V) is used to circulate the electrolyte in the flow cell. The dead volume effect of pipeline must be considered when calculating the FE. First, the product concentrations in the outlet pipe (red) of the cathode chamber, and in the catholyte bottle are compared (Fig. S5b) (detailed derivation of the process shown in Supporting Information Eqs. S19-25).

Obviously, the concentration of liquid products in the outlet section (red) of the cathode chamber is much higher than that in the inlet section (yellow). With the increase of reaction time, the product concentration in the catholyte bottle reaches equilibrium with the outlet pipe. When the reaction time is greater than 14 min, the influence of the concentration difference on the product concentration is less than 1%, and when the reaction time is greater than 27 min, the influence is less than 0.5%.

During continuous liquid product measurement of multiple reaction potentials, the electrolyte needs to be replaced. To prevent the catalyst from being destroyed, some electrolyte remains in the pipeline to protect the catalyst (Fig. S5a). We studied the errors caused by the volume of electrolyte in the pipeline and catholyte bottle (Fig. S5c)

(detailed derivation of the process shown in Supporting Information Eqs. S26-S27).

The smaller volume of pipeline and the larger the volume of electrolyte in catholyte bottle, the smaller error. To make the error less than 1%, it is necessary to control the electrolyte volume to more than 100 times the volume of pipeline. Though we can't guarantee a volume ratio of 100 between the outlet pipe of the cathode chamber and the electrolyte in the catholyte bottle, we can still correct the amounts of liquid products by continuously measuring the concentration in the electrolyte bottle and pipe volume.

In addition, we predicted the error due to electrolyte residue in various cases by Eq. S28. We found that this error can reach 30% (relative error) in some cases, and the effect on the total FE is generally in the range of 1% to 3% (Fig. S6). Therefore, when liquid products are in the majority, Eq. S28 should be considered for correction.

Derivation of Faradaic efficiency of gas products:

The original formula for the Faradaic efficiency of product i is

$$FE_i = \frac{Q_i}{Q_{total}} \#(S1)$$

Where Q_{tatal} is the total number of charges transferred in the reaction and Q_i is the number of charges transferred to form product i.

The total number of charges transferred can be obtained from the reaction current (I) and reaction time (t):

$$Q_{total} = It #(S2)$$

The number of charges transferred to form product i can be obtained from the amount of substance of product i (n_i), the number of electrons transferred to form a

single product $i(N_i)$, and the Faraday constant:

$$Q_i = n_i N_i F \# (S3)$$

The amount of product i is obtained from the outlet flow rate (ν), reaction time (t), and molar volume of the gas (V_n):

$$n_i = \frac{\nu t}{V_n} \#(S4)$$

The expression for the molar volume of gas is:

$$V_n = \frac{RT}{P} \#(S5)$$

Where R is the universal gas constant, T is the gas temperature, and P is the gas pressure.

By combining Eqs. S6-S10, the commonly used Faraday efficiency calculation formula is obtained:

$$FE_i = \frac{N_i P \nu C_i F}{IRT} \#(1)$$

Where, N_i is the number of transfer electrons of product i, P is the pressure of outlet gas product (pa), T is the temperature of outlet gas product (K), ν is the flow rate of gas at the outlet during reaction (sccm), C_i is the gas concentration of component i measured by gas chromatography (GC) (ppm), F is Faraday constant (96,485 C mol⁻¹). I is the average current during the measurement (A), and R is the universal gas constant (8.314).

When a CO₂-calibrated thermal mass flowmeter is used to measure substance i, the relationship between the indicated flow rate and the actual flow rate is:

$$\frac{v_{actual}}{B_i} = \frac{v_{indicated}}{B_{CO2}} \# (S6)$$

In the measurement of multi-component gas flow rate, each component gas is calculated separately:

$$\frac{c_i v_{actual}}{10^6 B_i} = \frac{v_{indicated,i}}{B_{CO2}} \# (S7)$$

Sum the left and right sides of the above formula separately:

$$\frac{\sum_{i} c_{i} v_{actual}}{10^{6} B_{i}} = \frac{\sum_{i} v_{indicated,i}}{B_{CO2}} \# (S8)$$

Simplify the formula and separate the component of CO₂:

$$v_{actual} = \frac{v_{indicated}}{\sum_{i} \frac{C_i B_{CO2}}{10^6 B_i} + \frac{10^6 - \sum_{i} C_i}{10^6} \#(S9)}$$

The error of the indicated flow rate can be obtained by bringing in different concentrations of each component by Eqs. S8 and S9:

$$error(\%) = \frac{\nu_{indicated} - \nu_{actual}}{\nu_{actual}} \times 100\% \# (S10)$$

These formulas are verified by the mixture of hydrogen and carbon dioxide at different ratios of flow rates. The accurate flow rate of hydrogen and carbon dioxide is obtained by the soap film flowmeter, and the flow rate is controlled by the mass flowmeter. Hydrogen is evenly mixed with carbon dioxide and then fed into a CO₂-calibrated thermal mass flowmeter. Read the indicated flow rate and measure the true flow rate using the soap film flowmeter (Fig. S2). The error value is calculated using the Eqs. S10.

Evaluation of gas products by internal standard: A propane standard gas $({}^{C}x_{0})$ with a fixed flow rate $({}^{V}x)$ is added to the product gas, mixed evenly and then passed into GC for measurement. After obtaining the diluted product concentration $({}^{C}i)$ and the

propane concentration (C_x), the flow rate ($^{\nu_{ture}}$) can be calculated using the Eq S3. After that, using Eq 1 to calculate the FE. In this experiment, the flow rate of carbon dioxide (99.99%) and propane standard gas (500 ppm) was 5 sccm.

If the pressure changes, the measurement of the concentration of all substances will change proportionally. If the pressure is α times the standard atmospheric pressure, then the measured concentration of all substances is α times the true value.

According to Eq. 1, the FE will be calculated as:

$$FE_i = \frac{N_i P \nu \alpha C_i F}{IRT} \#(S11)$$

When the internal standard method is used, the concentration of the internal standard increases and the calculated flow rate is calculated as:

$$v_{actual} = \frac{c_{x0}}{\alpha c_x} v_x \#(S12)$$

Combine Eqs. S16 and S17:

$$FE_{i} = \frac{N_{i}Pc_{x0}v_{x}\alpha C_{i}F}{\alpha c_{x}IRT} = \frac{N_{i}Pc_{x0}v_{x}C_{i}F}{c_{x}IRT} \#(S13)$$

The effect of pressure α is cancelled out, and the real FE is obtained.

Derivation of Faradaic efficiency of liquid products:

The original formula for the Faradaic efficiency of product i is

$$FE_i = \frac{Q_i}{Q_{tatal}} \#(S14)$$

Where Q_{tatal} is the total number of charges transferred in the reaction and Q_i is the number of charges transferred to form product i. The total number of charges transferred can be obtained from the reaction current (I) and reaction time (t):

$$Q_{tatal} = It #(S15)$$

The number of charges transferred to form product i can be obtained from the amount of substance of product i (n_i), the number of electrons transferred to form a single product i (N_i), and the Faraday constant:

$$Q_i = n_i N_i F \# (S16)$$

The amount of product i is obtained from the product concentration $(^{C_i})$, reaction time (t), and cathode electrolytic liquid volume (V):

$$n_i = C_i V \# (S17)$$

Where R is the universal gas constant, T is the gas temperature, and P is the gas pressure.

By combining Eqs. S16-S20, the commonly used Faraday efficiency calculation formula is obtained:

$$FE_i = \frac{N_i C_i VF}{It} \# (S18)$$

Where, N_i is the number of transferred electrons for one molecule generation, C_i is the product concentration of component $i \pmod{L^{-1}}$, V is the total volume of cathode electrolyte (L), F is the Faraday constant (96,485 C mol⁻¹), I is the average current (A) in the measurement process, and t is the time for the electrolyte to participate in the CO₂RR (s).

Derivation of liquid product distribution: It is assumed that catalyst has 20% Faradaic efficiency of ethanol at a current of 500 mA. Then the rate of ethanol

production ($v_n \mod s^{-1}$) is:

$$v_n = \frac{I(FE)_{ethanol}}{N_{ethanol}F} \#(S19)$$

Where *I* is current(A), $(FE)_{ethanol}$ is the Faradaic efficiency of ethanol, $N_{ethanol}$ is the number of electrons producing a single of molecular ethanol, F is the Faraday constant.

The growth rate of outlet pipeline product concentration (v_c mol L⁻¹s⁻¹) is:

$$v_c = \frac{v_n}{v_l} \#(S20)$$

Where v_l is the flow rate of electrolyte (L s⁻¹).

The product concentration in the electrolyte container (${}^{C_{c}}$ mol L⁻¹) is:

$$c_{c} = \frac{(t - \frac{V_{p}}{v_{l}})v_{n}}{V_{c} + 2V_{p}} \#(S21)$$

Where t is the duration of the reaction (s), V_p is the volume of outlet or inlet pipeline (L), V_c is the volume of electrolyte of container.

The product concentration in the pipeline (C_p mol L⁻¹) is:

$$c_p = c_c + v_c \#(S22)$$

The concentration difference of pipeline and container (blue) is:

$$difference_{bule}(\%) = \frac{c_p - c_c}{c_c} \times 100\% \#(S23)$$

The actual concentration after mixing (Cactual mol L⁻¹) is:

$$c_{actual} = \frac{v_n t}{V_c + 2V_p} \#(S24)$$

The concentration difference of measured value (red) and actual value is:

$$difference_{red}(\%) = \frac{c_{actual} - c_c}{c_{actual}} \times 100\% \# (S25)$$

Calculate the error caused by ignoring the pipe volume:

$$error(\%) = \frac{\frac{v_{n}t}{V_{c}} + \frac{v_{n}t}{V_{c} + 2V_{p}}}{\frac{v_{n}t}{V_{c} + 2V_{p}}} \times 100\%\#(S26)$$

And that simplifies it:

$$error(\%) = \frac{2V_p}{V_c} \times 100\% \#(S27)$$

$$n_{k+1} = c_{k+1} (V_{k+1} + V_{pipe}) - c_k V_{pipe} \# (S28)$$

Where k is the number of continuous measurements (k > 1), c_k is the concentration at the k th measurement (mol L⁻¹), V_k is the volume of the electrolyte replaced at the k th measurement (L), and V_{pipe} the volume of pipeline.



Fig S1. The change of pH value and outlet flow rate of the cathode solution after 30 min of carbon dioxide reduction under different current density in the cathode solution with different pH values.



Fig. S2. Experiment on error of different range flowmeters to low flow rate gas.



Fig. S3. Experimental diagram of mixing different kinds of gases to verify the flow correction formula.



Fig. S4. Another mass flow meter principle diagram, through different heating power to make the gas upstream and downstream temperature constant, in order to measure the gas flow rate. The arrows represent the direction of gas flow.



Fig. S5 (a) The error of flowmeter with different proportions of single gas product mixed with the CO_2 gas. (b) The error of flowmeter with the different CO_2 supply flow and different current in $FE_{CO}=95\%$, $FE_{H2}=5\%$ product mixture gases. (c) The error of flowmeter with the different CO_2 supply flow and different current in $FE_{C2H4}=60\%$, $FE_{CH4}=20\%$, $FE_{CO}=10\%$, $FE_{H2}=10\%$ product mixture gases. All the thermal mass flowmeters were calibrated with CO_2 gas. (d) The schematic diagram of the device for calculating outlet flow by internal (C_3H_8) standard method. (e) The FE calculated by the inlet flow rate (black) and outlet flow rate measured by the internal standard method (red).



Fig. S6. The relative and absolute errors of Faradaic efficiency of liquid product due to electrolyte residue varies with current density.