

Supporting information

**Assessing the electrochemical CO<sub>2</sub> reduction reaction performance requires more than reporting coulombic efficiency**

*Paniz Izadi<sup>1</sup>, Jia Song<sup>2</sup>, Chandani Singh<sup>2</sup>, Deepak Pant<sup>2,3</sup> and Falk Harnisch<sup>1\*</sup>*

<sup>1</sup> Department of Microbial Biotechnology, Helmholtz-Centre for Environmental Research - UFZ, Leipzig, Germany

<sup>2</sup> Separation & Conversion Technology, Flemish Institute for Technological Research (VITO), Mol, Belgium

<sup>3</sup> Center for Advanced Process Technology for Urban Resource Recovery (CAPTURE), Frieda Saeysstraat 1, 9000 Ghent, Belgium

\* E-mail: falk.harnisch@ufz.de

## Experimental Methods

**Reactor and setup:** The flow cell gas diffusion electrode (GDE) reactor (electrode area 10 cm<sup>2</sup>) used in this study was purchased from ElectroCell® (Micro Flow Cell, Denmark). Tin (Sn) based GDE (Sn-GDE, 10 cm<sup>2</sup>) manufactured by VITO (VITO CORE®) and platinum sheet (Goodfellow, Huntingdon, UK, 10 cm<sup>2</sup>) were used as cathode and anode, respectively. Each anodic and cathodic compartment had a net volume of 10 mL that were separated by cation exchange membrane (CEM, fumasep FKS-PET-130, FUMATECH BWT GmbH, Bietigheim-Bissingen, Germany). The solution in each compartment was recirculated using a reservoir tank. The reservoir tank used for the catholyte was 0.5 L Duran bottle (DWK Life Sciences GmbH, Germany), designed and operated with 6 extra ports with the following applications: catholyte inlet and catholyte outlet for the recirculation using a peristaltic pump (Masterflex® Ismatec®, flow of 50 mL min<sup>-1</sup>), pH and conductivity probes for continuous measuring, a gas sampling port connected to a mass flow meter and a gas chromatography (GC) for the inline gas detection, and a liquid sampling port (Figure S1). The reservoir tank used for the anolyte was a 1.0 L Duran bottle (DWK Life Sciences GmbH, Germany) with 2 extra ports for the anolyte recirculation using a peristaltic pump (Masterflex® Ismatec®, flow of 50 mL min<sup>-1</sup>). The system was operated and kept gas tight, and the solutions were stirred using two magnet stirrers at 1000 rpm during the experiments to keep the solutions homogenous.

Gaseous CO<sub>2</sub> (Air Products GmbH, 99.5%, 1 bar) was fed to a CO<sub>2</sub> rotameter (VAF-Fluid-Technik GmbH) and then to the gas chamber of the reactor in the back side of the GDE, when the CO<sub>2</sub> flow rate was adjusted at 35 ± 1 or 16 ± 1 mL min<sup>-1</sup> throughout the experiment. During the GDE activation, CO<sub>2</sub> was provided using flow by mode that is by adjusting the back pressure of the GDE to 8 ± 1 mbar, controlled by manometer (RS PRO, RS-8890, Differential pressure gauge ± 0.3%, -2 psi → 2psi). During the electrochemical CO<sub>2</sub> reduction reaction (eCO<sub>2</sub>RR), flow through mode was applied by closing the gas outlet, to assure preserving all the CO<sub>2</sub> in the system, as required for creating carbon balance.

The current or the voltage between the cathode and anode was fixed using a DC power source (2230-30-1 triple Channel DC Power Supply, Keithley/Tektronix GmbH, Köln, Germany), and the respective cell voltage or current between the anode and cathode was monitored. The negative and positive current of the DC power supply was connected to the cathode and anode, respectively.

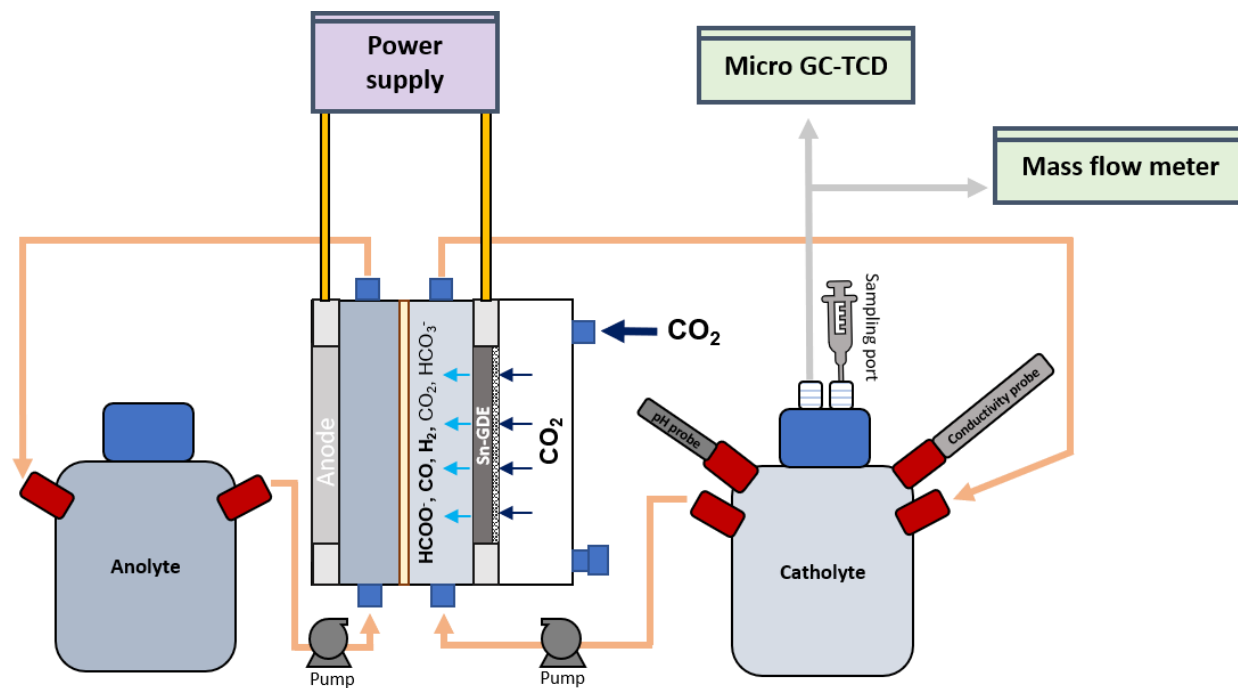


Figure S1. Schematic of the setup used in this study during electrochemical CO<sub>2</sub> reduction reaction (eCO<sub>2</sub>RR).

**GDE preparation:** Sn-GDE was prepared following the protocol mentioned in the patent application by VITO [1], using tin powder (99.8%, 325 mesh, Alfa Aesar), Polytetrafluoroethylene (PTFE) acquired from DuPont™ (PTFE- 669N X) and ammonium bicarbonate (ambic, NH<sub>4</sub>HCO<sub>3</sub> (98%, ACROS Organics)) and potassium bicarbonate (≥99.5%, VWR). A layer-by-layer approach was implemented to manufacture the GDE, which includes separately preparing the gas diffusion layer (GDL) and catalyst layer (CL). The GDL consists of primarily hydrophobic, porous layer of PTFE. The catalyst layer (CL) comprises Sn powder combined with PTFE as a binder. Both layers were mixed with ambic to introduce the porous structure in the GDE. Initially a cake of 10 × 10 cm<sup>2</sup> was prepared using a hydraulic press at 150 bar at 22 °C. These cakes were then cold rolled to form a separate sheet of GDL and CL, with a thickness of 0.40 - 0.45 mm each. The separate layer of CL and GDL were combined in the final stage to create a GDE 0.4 - 0.5 mm. The so prepared GDE is kept in an oven at 70 °C for 6 h, allowing the ambic to evaporate, forming a porous metal GDE.

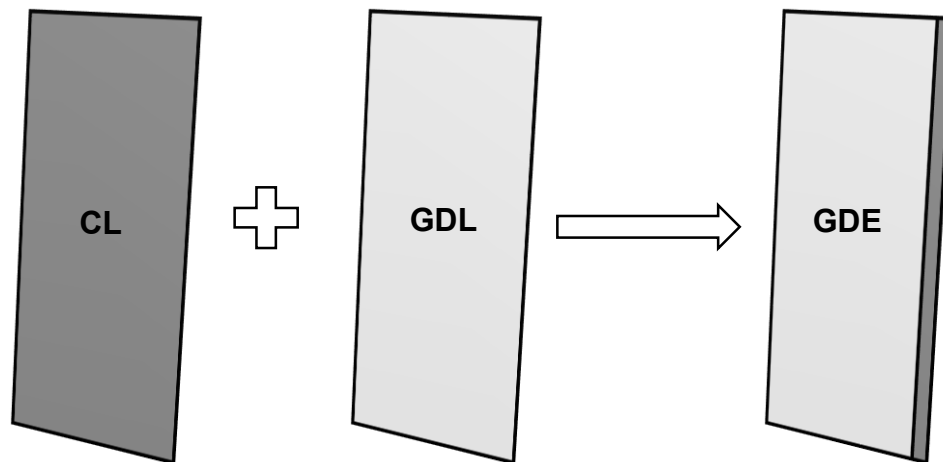


Figure S2. Schematic of gas diffusion electrode (GDE) preparation using catalyst layer (CL) and gas diffusion layer (GDL).

**GDE activation step:** The activation process was required after the electrode manufacturing and before the eCO<sub>2</sub>RR to make the pristine as prepared Sn-GDE conductive which is achieved by forming a thin Sn-film at the surface of the electrode. The process included increasing the cell potential gradually from 3 V up to 12 V between the anode and cathode using the DC power supply. (Therein the 10 cm<sup>2</sup> Sn-GDE served as a cathode, a 10 cm<sup>2</sup> platinum sheet as an anode, 0.5 M KHCO<sub>3</sub> as a catholyte, 5 M KOH as an anolyte and CEM was used to separate the anodic and cathodic compartments). The voltage was kept at 12 V and the current was monitored. GDE activation was achieved when the current reached the stable value of 600.0 ± 40.8 mA cm<sup>-2</sup>.

**eCO<sub>2</sub>RR step:** After GDE activation, the solutions were refreshed and the eCO<sub>2</sub>RR was carried out for 120 min at a room temperature ( $\varnothing = 24 \pm 1$  °C) under the fume hood, and a constant current density of 100 mA cm<sup>-2</sup>.

**Anolytes and catholytes:** During the GDE activation, anolyte and catholyte were 0.5 L of 5 M KOH and 0.3 L of 0.5 M KHCO<sub>3</sub>, respectively. During eCO<sub>2</sub>RR, 0.5 L KHCO<sub>3</sub> solution with different concentrations of 0.5, 0.05 and 0.005 M were used as catholyte, while anolyte was 1.0 L of 1.0 M KOH. Different concentrations of KHCO<sub>3</sub> (0.5, 0.05 and 0.005 M) were examined as the catholytes, since reaching the equilibrium of CO<sub>2</sub>/HCO<sub>3</sub><sup>-</sup> (and therefore catholyte pH) at each concentration was different. Therefore, CO<sub>2</sub> was purged in all the solutions before eCO<sub>2</sub>RR to achieve a stable pH value. Subsequently, after adjusting

the conductivity of 0.05 and 0.005 M KHCO<sub>3</sub> solutions using K<sub>2</sub>SO<sub>4</sub> (Table S1), 1 mL sample (being  $t_0$ ) was withdrawn and then eCO<sub>2</sub>RR was started.

Table S1. pH and conductivity of the catholytes after reaching the stable condition by purging CO<sub>2</sub> before electrochemical CO<sub>2</sub> reduction reaction (eCO<sub>2</sub>RR), conducted in triplicate (n=3).

Catholyte	pH	Conductivity (mS cm <sup>-1</sup> )
0.5 M KHCO <sub>3</sub>	7.45 ± 0.01	38.2 ± 0.2
0.05 M KHCO <sub>3</sub> (Conductivity adjusted by K <sub>2</sub> SO <sub>4</sub> )	6.56 ± 0.02	38.9 ± 0.1
0.005 M KHCO <sub>3</sub> (Conductivity adjusted by K <sub>2</sub> SO <sub>4</sub> )	5.73 ± 0.01	38.6 ± 0.3

**Liquid and gas analyses:** pH and conductivity (and temperature for quality control) were recorded using a SevenExcellence S470 (Mettler-Toledo, Greifensee, Switzerland) with an InLab Micro Pro pH probe and an InLab 710 conductivity probe (both Mettler-Toledo, Greifensee, Switzerland). Both probes were calibrated using commercial buffer solutions (Mettler-Toledo, Greifensee, Switzerland) before each experiment. The gas outlet port was connected to a N<sub>2</sub>-mass flow meter/controller (MFM; LOW- $\Delta$ P-FLOW F-101D, 60 mLn min<sup>-1</sup>, Bronkhorst High-Tech B.V., Ruurlo, Netherlands) controlled by a Flow-Bus (Bronkhorst High-Tech B.V., Ruurlo, Netherlands) with a micro GC (3000 Micro GC, INFICON, Cologne, Germany) in by-pass in order to determine the gas composition after calibrating the micro GC for O<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and CO detection, and their volume (details see below).

The collected liquid samples were analyzed by high-performance liquid chromatography (HPLC, Shimadzu Scientific Instruments, USA) and on total inorganic carbon (TIC) for detection of formate and dissolved CO<sub>2</sub>, respectively. HPLC was equipped with a refractive index detector (RID) (RID-20A, Shimadzu Scientific Instruments, Japan) Hi-Plex H column (300 mm × 7.7 mm ID, 8  $\mu$ m pore size, Agilent Technologies, Germany) with a pre-column (Carbo-H 4 mm × 3 mm ID, Security Guard, Phenomenex). Isocratic elution was performed with 0.005 M H<sub>2</sub>SO<sub>4</sub> at 0.5 mL min<sup>-1</sup> at 50 °C for 30 min<sup>-1</sup>. Since formate was the only product in the liquid phase, formate calibration (1.14 mM to 44.4 mM, five-point calibration with triplicate standards for each point, R<sup>2</sup>= 0.99) was carried out with external standards. TIC was measured by total carbon

analyzer (TOC-L, Shimadzu, Japan). The analysis for the TIC was performed after addition of diluted phosphoric acid at room temperature and measurement of the evolved CO<sub>2</sub> via non-dispersive infrared (NDIR) detector.

Sn in the catholyte was measured using a polarograph (797 VA Computrace, Metrohm, Switzerland) equipped with a platinum wire as a counter electrode and an Ag/AgCl saturated KCl as a reference electrode. Differential pulse (DP) mode with a hanging mercury drop electrode (HMDE) was used<sup>[2]</sup>. The external Sn<sup>2+</sup> standards were calibrated in the range of 1.08 μM to 1.08 mM (four-point calibration, R<sup>2</sup>= 0.99).

**Gas phase analysis:** During eCO<sub>2</sub>RR, gas composition was monitored as reported previously<sup>[3]</sup>, using a two channels of a four-channel micro GC equipped with a thermal conductivity detector (GC-TCD), which was calibrated before to analyze the experimental gas profile. The detailed information of the method used within micro GC-TCD is summarized in Table S2. Gas measurements were carried out at the beginning of the eCO<sub>2</sub>RR (*t*<sub>0</sub>) and every 30 min during the experiment.

From the mass flow meter, the volume  $v_{measured}^{norm}$  was recorded in mLn and the mole fraction  $y_i$  of each individual gas component  $i$  [%] was obtained from the micro GC-TCD measurement.

Table S2. The information of the method used for detection of gas composition using micro GC-TCD.

		Column	
Parameter	Unit	14 m Molsieve with 2 m Plot U pre-column, 1 μl backflush injector	8 m Plot Q, variable volume injector
Carrier gas		Argon	Helium
Sample inlet temperature	°C	100	100
Injector temperature	°C	100	100
Column temperature	°C	100	80

<b>Injection time</b>	ms	0	25
<b>Running time</b>	sec	420	420
<b>Column pressure</b>	psi	25	20
<b>Analyzed components</b>		O <sub>2</sub> , H <sub>2</sub> , N <sub>2</sub> , CO	CO <sub>2</sub>

**Calculation of  $i \times R$  drop:** the  $i \times R$  drop across the membrane is calculated based on Ohm's law.

Table S3 Thickness and swelling rate of the typical membranes used in eCO<sub>2</sub>RR system

Membrane	Thickness of the membrane (μm)	swelling rate
Nafion 117	183	20%
Fumasep FAA-3-50	50	2%

Table S4 Specific conductivity of the membranes soaked in the various solutions.

Nafion 117 [4]		Fumasep FAA-3-50	
Solution	Specific conductivity (S cm <sup>-1</sup> )	Solution	Specific conductivity (S cm <sup>-1</sup> )
1M HCl	0.074	1M KOH	0.009 [5]
1M NaCl	0.0135	1M HCl	0.005 [6]
1M KCl	0.0103	1M KHCO <sub>3</sub>	0.0014 [7]

**Calculation of production rate and efficiencies:** The rate of formate production ( $r_{HCOO^-}$ ) was calculated based on the amount of formate produced ( $n_{HCOO^-}$ ) between sampling points ( $dt$ ) using Eq. S1.

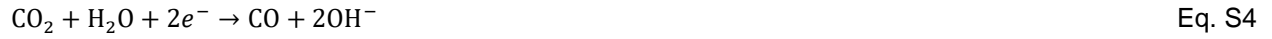
$$r_{HCOO^-} (mM h^{-1}) = \frac{n_{HCOO^-}}{dt} \quad \text{Eq. S1}$$

Coulombic efficiency ( $CE$ ) was calculated using Eq. S2, considering the theoretical charge required for production of each compound ( $Q_i$ ) and the experimentally supplied charge ( $Q_{total}$ ) by DC power supply:

$$CE_i = \frac{Q_i}{Q_{total}} \times 100\% = \frac{n_i \times z_i \times F}{\int i(t) dt} \times 100\% \quad \text{Eq. S2}$$

where  $n_i$  is the amount of each substance produced in mol,  $z_i$  is the number of transferred electrons per molecule and  $F = 96.485 \text{ C mol}^{-1}$  is the Faraday constant.  $n_i$  is the difference between the concentration of each product within sampling times, measured by micro GC-TCD or HPLC.  $z_i$  is 2 for all the products according to Eq. S3 – S8.

Under alkaline or neutral conditions:



Under acidic conditions:



Carbon conversion efficiency (*CCE*) of eCO<sub>2</sub>RR was calculated as a ratio of the molar amount of carbon that was found in all the products ( $\sum n_{C,products}$ ) detected by HPLC and micro GC-TCD, and the molar amount of carbon that was consumed as the substrate ( $n_{C,substrate}$ ), as depicted in Eq. S9.

$$CCE = \frac{\sum n_{C,products}}{\Delta n_{C,substrate}} \cdot 100\% \quad \text{Eq. S9}$$

$n_{C,substrate}$  was the carbon provided in form of bicarbonate in the catholyte measured by TIC, as well as the amount of carbon within the gaseous CO<sub>2</sub> fed during 120 min of experiment. The mol of CO<sub>2</sub> ( $n_{CO_2}$ ) was calculated using ideal gas law.

$$p \times V = n_{CO_2} \times R \times T \quad \text{Eq. S10}$$

where  $p$  is 1 bar as adjusted in the experiments,  $V$  is the volume of the gas depending on the adjusted flow rate during 120 min in L,  $R = 0.083144598 \text{ L bar mol}^{-1} \text{ K}^{-1}$  is a gas constant, and  $T$  is a temperature in K. The accuracy of the CO<sub>2</sub> calculation was also confirmed by measuring the CO<sub>2</sub> provided for 120 min using



the mass flow meter (MFM; LOW- $\Delta$ P-FLOW F-101D, 60 mLn min<sup>-1</sup>, Bronkhorst High-Tech B.V., Ruurlo, Netherlands).

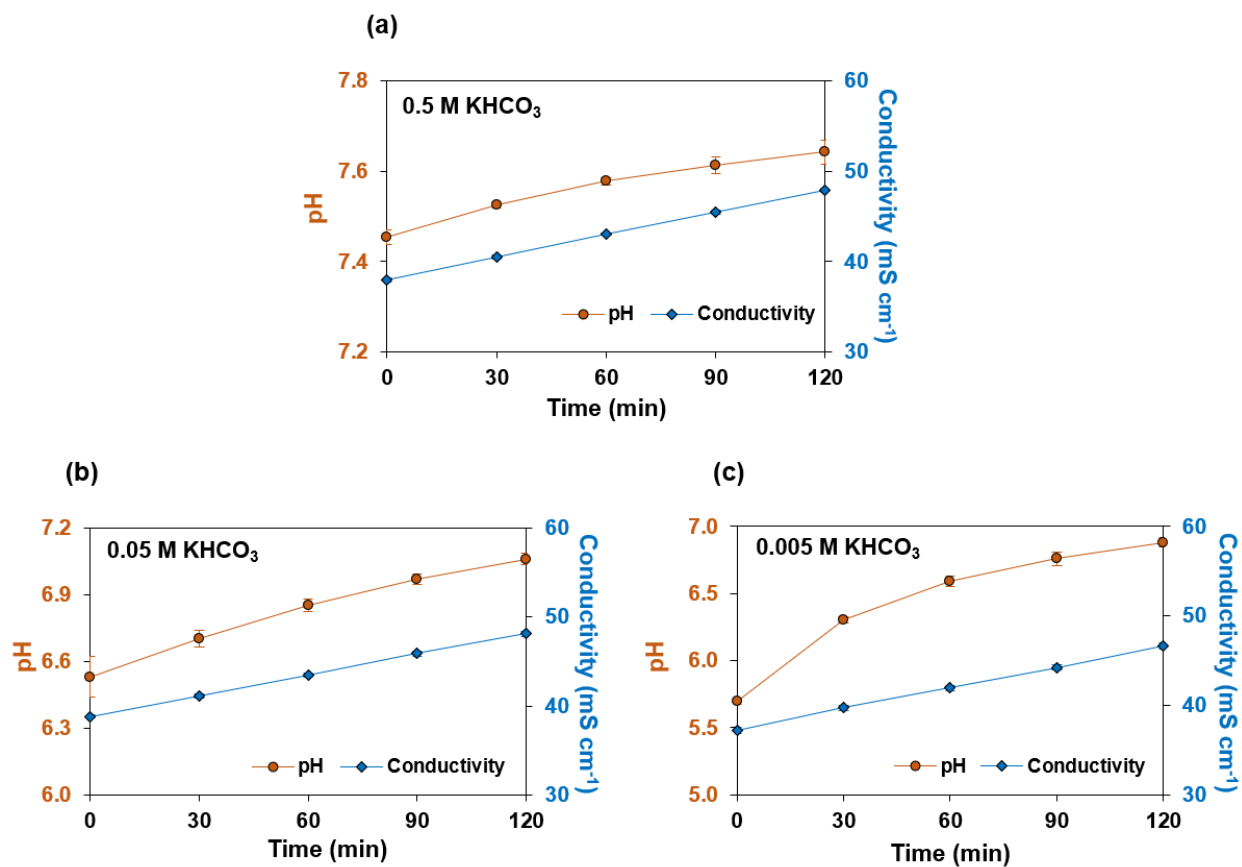


Figure. S3. pH and conductivity change over 120 min of eCO<sub>2</sub>RR in the catholytes of a) 0.5 M KHCO<sub>3</sub>, b) 0.05 M KHCO<sub>3</sub>, and c) 0.005 M KHCO<sub>3</sub> when inlet CO<sub>2</sub> flow rate was 35 ± 1 mL min<sup>-1</sup>. All experiments were conducted in triplicate (n=3).

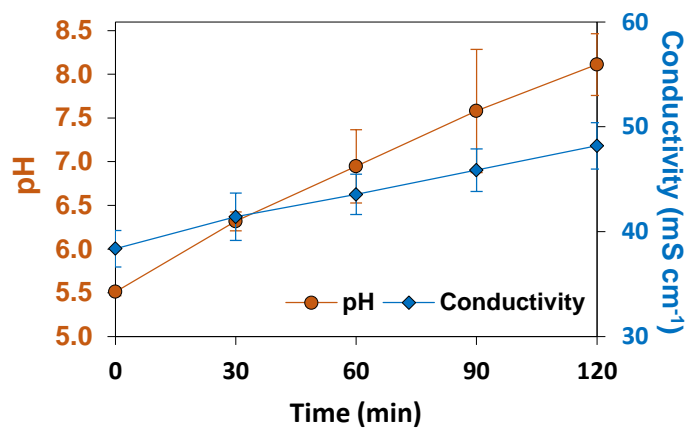


Figure S4. pH and conductivity change over 120 min of eCO<sub>2</sub>RR in the catholytes of 0.005 M KHCO<sub>3</sub> when inlet CO<sub>2</sub> flow rate was adjusted at 16 ± 1 mL min<sup>-1</sup>. All experiments were conducted in triplicate (n=3).

## References

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