

Electronic Supplementary Information

Broad parameter range of selective methane production with bicarbonate solution in electrochemical
CO₂ reduction

Hiroshi Hashiba,^{*,1,2} Hiroki K. Sato,¹ Satoshi Yotsuhashi,¹ Katsushi Fujii,³ Masakazu Sugiyama⁴
and Yoshiaki Nakano^{2,4}

1. Advanced Research Division, Panasonic Corporation, Sôraku-gun, Kyoto 619-0237, Japan
2. Research Centre for Advanced Science and Technology, The University of Tokyo, Meguro-ku, Tokyo 153-8904, Japan
3. Institute of Environmental Science and Technology, The University of Kitakyushu, Kitakyushu, Fukuoka 808-0135, Japan
4. Department of Electrical Engineering and Information Systems, Graduate School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

*E-mail: hashiba.hiroshi@jp.panasonic.com

Experimental methods

Figure S1 (a) shows the combinatorial instrumentation, which was able to perform eight experimental trials in parallel while varying parameters such as stirring speed, reaction voltage (or current density), CO₂ pressure and temperature. Rectangular Cu plates (Nilaco, Japan, 99.99%) with an active surface area of 1 cm² were used as the cathode electrodes during CO₂ reduction, as shown in Fig. S1 (b). The cathode surfaces were chemically polished using a mixture of nitric and phosphoric acids (S-710, Sasaki Chemical, Japan). Platinum wire (BAS, Japan) was employed as the anode electrode and saturated Ag/AgCl (Corr instruments, US) was used as the reference electrode. Each cell was divided into cathode and anode compartments using Nafion 424 (Aldrich, US). The cathode and anode electrolytes were made by dissolving KCl (Wako, Japan, >99.9%) and KHCO₃ (Wako, Japan, >99.5%) salts in distilled water. The cathode electrolytes tested were 0.5 M KCl, 0.25 M KHCO₃ and 0.5 M KHCO₃ (pH values under CO₂-saturated conditions at ambient pressure were 3.8, 7.2 and 7.5, respectively). The anode electrolyte was either 3.0 M or 1.5 M KHCO₃ (Wako, Japan) depending on the reaction temperature. More details regarding the combinatorial system are available elsewhere.¹

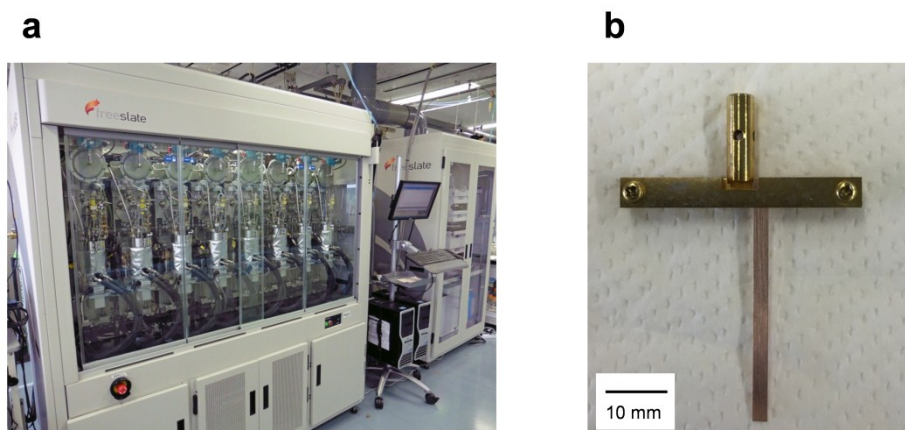


Figure S1 Photographs of (a) the combinatorial screening system and (b) the cathode electrode.

Prior to an experiment, each reactor was first bubbled with Ar and then with CO₂, each for 60 min and at a flow rate of 125 sccm. The reactors were sealed after being pressurised with CO₂ to the desired experimental value. Electrochemical measurements were performed to ascertain the current density while also controlling the stirring speed inside the reactor. Galvanostatic measurements with BT2000 (Arbin, TX, USA) multi-channel potentiostats were performed up to 100 C, with a different current density employed in each reactor to ascertain the current density dependence of the product distribution for each experiment. Unless otherwise noted, the temperature inside the reactor was 25 °C. Following the galvanostatic measurements, gas samples from each reactor were sequentially transferred to a 7890A (Agilent, CA, USA) gas chromatograph (GC) to allow for quantitative analysis of the reaction products. A thermal conductivity detector was used for measurements of H₂ and a flame ionisation detector for CO, CH₄ and C₂H₄. Gas sampling was carried once per reactor. Liquid products were analysed with a Prominence (Shimadzu, Japan) high-performance liquid chromatograph (HPLC) to determine formate (HCOO⁻) levels, and with a GC-17A (Shimadzu, Japan) with a TurboMatrix40 (PerkinElmer, MA, USA) headspace (HS) system for the detection of aldehydes and alcohols. Faradaic efficiencies (FEs) were calculated by dividing the charge ascribed to each product by the total charge that was passed through the system.

Graphs of experimental data

The variation in FE with current density for H₂ and CH₄ in all experiments is shown in Figs. S2(a–c). Figures S3(a–c) present the results for minor products, such as CO, C₂H₄, HCOO[−], and alcohols and aldehydes (specific products are denoted in Table S1), which are collectively labelled as “Others” in Fig. S2.

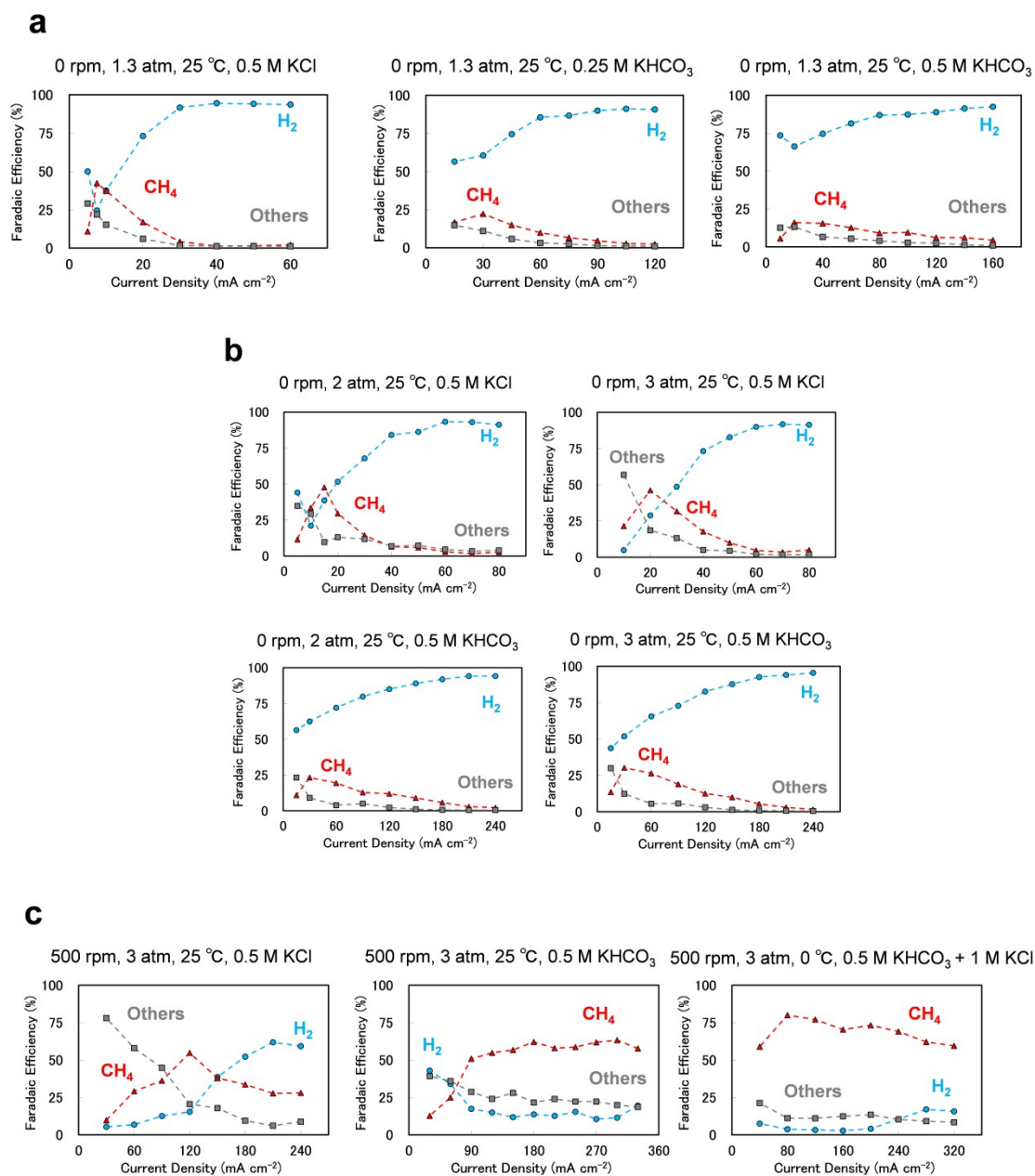


Figure S2. Variation in Faradaic efficiency with current density for H₂ (light blue circles), CH₄ (red triangles) and other products of the CO₂ reduction reaction (gray squares) for all experiments. (a) Electrolyte dependence at 0 rpm, 1.3 atm, 25 °C, (b) Pressure dependence at 0 rpm, 25 °C in 0.5 M KCl (upper row) and 0.5 M KHCO₃ (lower row), (c) Electrolyte and temperature dependence at 500 rpm and 3 atm

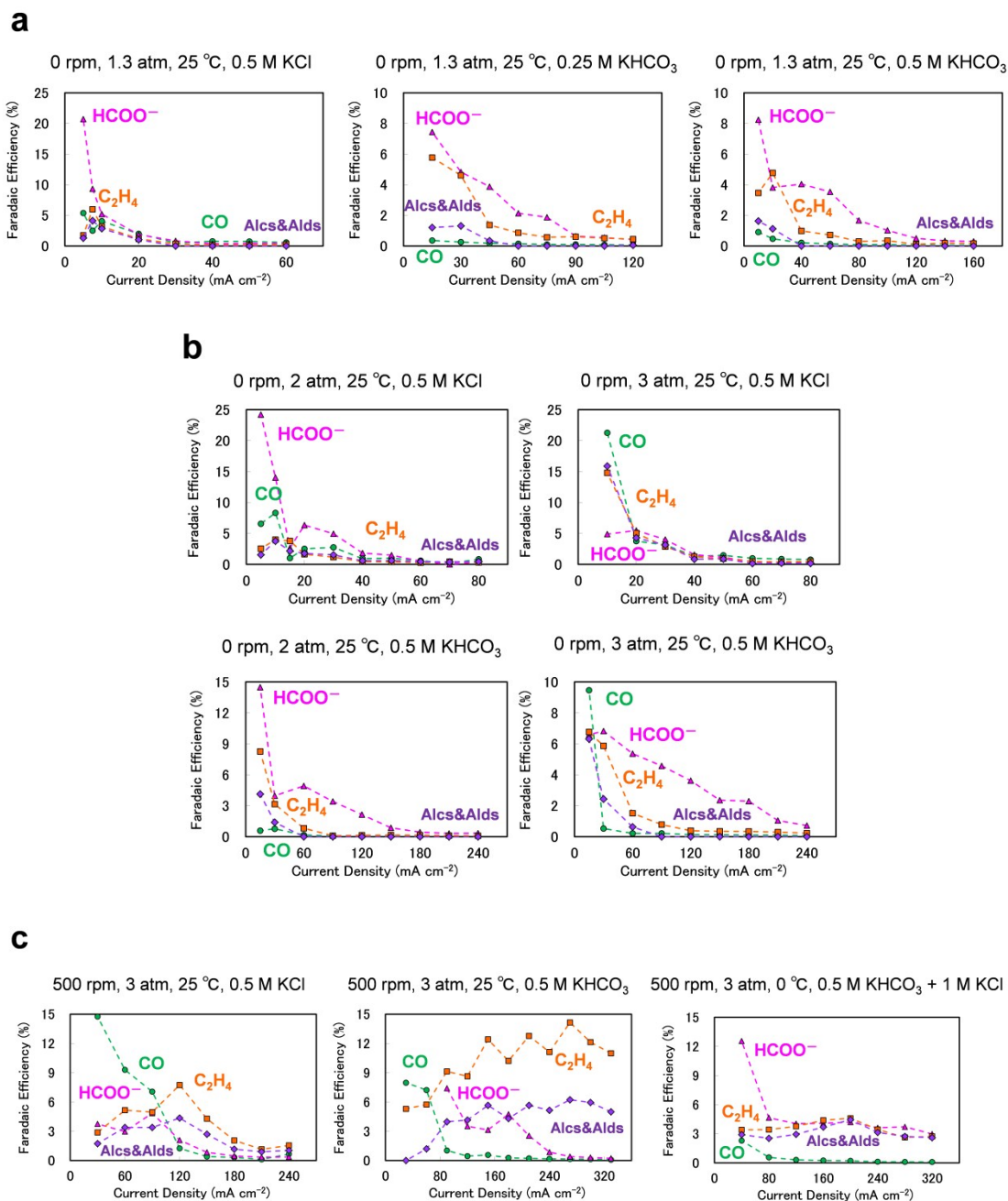


Figure S3. Variation in Faradaic efficiency with current density for CO (green circles), C₂H₄ (orange squares), HCOO⁻ (pink triangles) and alcohols & aldehydes (purple diamonds) for all experiments. (a) Electrolyte dependence at 0 rpm, 1.3 atm, 25 °C, (b) Pressure dependence at 0 rpm, 25 °C in 0.5 M KCl (upper row) and 0.5 M KHCO₃ (lower row), (c) Electrolyte and temperature dependence at 500 rpm and 3 atm.

Summary of experimental data

Table S1 summarises the experimental conditions, current densities and FEs for each reaction product for each experimental trial. Here, CD represents current density, and MeCHO, PrCHO and EtOH represent acetaldehyde, propionaldehyde and ethanol, respectively. E represents an average potential applied to the cathode during the electrolysis without iR compensation. The typical value of iR resistance in this system was approximately 3~5 ohm at 25 °C in 0.5 M KCl, 7~9 ohm at 25 °C in 0.25 M KHCO₃, 4~5 ohm at 25 °C in 0.5 M KHCO₃, 8~10 ohm at 0 °C in 0.5 M KHCO₃ and 3~4 ohm at 0 °C in 0.5 M KHCO₃ + 1 M KCl, which were measured with ALS-760C (BAS, Japan) potentiostat. The term “Others” indicates the sum total of the methanol, allyl alcohol and n-propanol produced by the reaction. Note that, in addition to the products shown below, trace amounts of ethane were also observed.

Table S1. Experimental conditions, current densities and Faradaic efficiencies for each of the products for all experiments.

Experimental conditions: 0.5 M KCl, 1.3 atm, 0 rpm, 25 °C

E (V vs. Ag/AgCl)	CD (mA cm ⁻²)	Faradaic Efficiency (%)								
		H ₂	CH ₄	CO	C ₂ H ₄	HCOO ⁻	MeCHO	PrCHO	EtOH	Others
-2.08	60	93.6	2.2	0.6	0.3	0.4	0.0	0.0	0.0	0.0
-1.99	50	94.1	1.5	0.7	0.2	0.4	0.0	0.0	0.0	0.0
-1.89	40	94.5	1.3	0.8	0.2	0.4	0.0	0.0	0.0	0.0
-1.92	30	91.6	4.2	0.5	0.3	0.8	0.0	0.0	0.0	0.0
-1.94	20	73.1	17.0	2.0	1.2	1.9	0.4	0.0	0.6	0.0
-1.87	10	37.6	37.4	4.1	3.2	5.2	0.9	0.1	1.8	0.0
-1.81	7.5	24.5	42.4	2.5	6.0	9.3	0.2	0.3	1.7	1.8
-1.75	5	50.0	10.9	5.4	1.7	20.7	0.4	0.2	0.6	0.0

Experimental conditions: 0.25 M KHCO₃, 1.3 atm, 0 rpm, 25 °C

E (V vs. Ag/AgCl)	CD (mA cm ⁻²)	Faradaic Efficiency (%)								
		H ₂	CH ₄	CO	C ₂ H ₄	HCOO ⁻	MeCHO	PrCHO	EtOH	Others
-3.13	120	90.7	2.3	0.1	0.4	0.4	0.1	0.0	0.0	0.0
-2.95	105	91.1	2.7	0.1	0.5	0.5	0.0	0.0	0.0	0.0
-2.75	90	89.9	4.7	0.1	0.6	0.6	0.0	0.0	0.0	0.0
-2.53	75	86.7	6.6	0.1	0.6	1.9	0.0	0.0	0.0	0.0
-2.43	60	85.5	9.9	0.1	0.9	2.1	0.0	0.0	0.0	0.0
-2.20	45	74.5	15.0	0.2	1.4	3.9	0.1	0.0	0.3	0.0
-1.98	30	60.5	22.2	0.3	4.6	4.8	0.1	0.1	1.1	0.0
-1.78	15	56.5	16.7	0.4	5.8	7.4	0.2	0.2	0.9	0.0

Experimental conditions: 0.5 M KHCO₃, 1.3 atm, 0 rpm, 25 °C

E (V vs. Ag/AgCl)	CD (mA cm ⁻²)	Faradaic Efficiency (%)								
		H ₂	CH ₄	CO	C ₂ H ₄	HCOO ⁻	MeCHO	PrCHO	EtOH	Others
-2.75	160	92.4	4.4	0.0	0.2	0.7	0.0	0.0	0.0	0.0
-2.64	140	91.3	6.0	0.1	0.2	1.0	0.0	0.0	0.0	0.0
-2.44	120	88.8	6.1	0.1	0.1	2.3	0.0	0.0	0.0	0.0
-2.33	100	87.3	9.5	0.1	0.3	2.4	0.0	0.0	0.0	0.0
-2.16	80	86.9	9.0	0.1	0.3	3.6	0.0	0.0	0.0	0.0
-1.99	60	81.4	12.7	0.1	0.7	4.6	0.0	0.0	0.0	0.0
-1.86	40	74.6	15.5	0.2	1.0	5.4	0.0	0.0	0.0	0.0
-1.69	20	66.2	16.0	0.5	4.8	6.8	0.1	0.0	1.0	0.0
-1.62	10	73.5	5.5	0.9	3.5	6.6	0.1	0.1	1.4	0.0

Experimental conditions: 0.5 M KCl, 2 atm, 0 rpm, 25 °C

E (V vs. Ag/AgCl)	CD (mA cm ⁻²)	Faradaic Efficiency (%)								
		H ₂	CH ₄	CO	C ₂ H ₄	HCOO ⁻	MeCHO	PrCHO	EtOH	Others
-2.22	80	91.2	2.7	0.8	0.3	0.4	0.8	0.0	1.6	0.0
-2.16	70	93.0	1.6	0.2	0.5	0.0	0.8	0.0	1.9	0.0
-2.10	60	93.3	2.9	0.6	0.3	0.5	1.0	0.0	2.2	0.0
-2.04	50	86.2	5.8	1.0	0.4	1.5	1.4	0.1	3.0	0.0
-2.03	40	84.2	6.5	0.9	0.5	1.8	1.3	0.1	2.3	0.0
-1.99	30	67.8	14.3	2.8	1.2	4.9	1.0	0.2	1.8	0.0
-1.96	20	51.6	29.5	2.5	1.6	6.3	0.9	0.2	1.5	0.0
-1.88	15	38.6	47.7	1.0	3.8	2.7	0.4	0.0	1.7	0.0
-1.85	10	21.1	33.5	8.3	4.0	14.0	1.4	0.3	1.3	0.0
-1.74	5	44.1	11.5	6.6	2.5	24.2	0.5	0.3	0.8	0.0

Experimental conditions: 0.5 M KCl, 3 atm, 0 rpm, 25 °C

E (V vs. Ag/AgCl)	CD (mA cm ⁻²)	Faradaic Efficiency (%)								
		H ₂	CH ₄	CO	C ₂ H ₄	HCOO ⁻	MeCHO	PrCHO	EtOH	Others
-2.23	80	91.3	5.0	0.8	0.5	0.4	0.2	0.0	0.0	0.0
-2.21	70	91.7	3.5	0.9	0.4	0.4	0.1	0.1	0.0	0.0
-2.17	60	89.9	4.7	1.0	0.5	0.4	0.2	0.0	0.0	0.0
-2.11	50	82.7	9.9	1.5	0.9	1.1	0.3	0.0	0.6	0.0
-2.05	40	73.1	17.7	1.3	1.2	1.6	0.3	0.1	0.5	0.0
-2.01	30	48.6	31.7	3.1	2.9	4.0	0.7	0.1	2.4	0.0
-1.93	20	28.8	46.2	3.8	5.0	5.5	1.1	0.1	3.1	0.0
-1.78	10	4.8	21.5	21.3	14.8	4.9	4.2	0.6	8.9	2.1

Experimental conditions: 0.5 M KHCO₃, 2 atm, 0 rpm, 25 °C

E (V vs. Ag/AgCl)	CD (mA cm ⁻²)	Faradaic Efficiency (%)								
		H ₂	CH ₄	CO	C ₂ H ₄	HCOO ⁻	MeCHO	PrCHO	EtOH	Others
-3.24	240	94.2	2.2	0.0	0.1	0.4	0.0	0.0	0.0	0.0
-3.10	210	94.2	2.9	0.0	0.1	0.3	0.0	0.0	0.0	0.0
-2.89	180	91.9	5.7	0.0	0.1	0.5	0.0	0.0	0.0	0.0
-2.70	150	89.0	8.9	0.1	0.2	0.8	0.0	0.0	0.0	0.0
-2.48	120	85.1	11.9	0.1	0.1	2.1	0.0	0.0	0.0	0.0
-2.24	90	79.8	12.8	0.1	0.1	4.9	0.0	0.0	0.0	0.0
-2.02	60	72.1	19.4	0.2	0.8	3.0	0.0	0.0	0.0	0.0
-1.81	30	62.4	23.2	0.8	3.2	3.8	0.3	0.2	0.9	0.0
-1.66	15	56.4	10.9	0.6	8.3	10.2	0.2	0.3	1.7	1.8

Experimental conditions: 0.5 M KHCO₃, 3 atm, 0 rpm, 25 °C

E (V vs. Ag/AgCl)	CD (mA cm ⁻²)	Faradaic Efficiency (%)								
		H ₂	CH ₄	CO	C ₂ H ₄	HCOO ⁻	MeCHO	PrCHO	EtOH	Others
-3.29	240	95.5	1.6	0.1	0.2	0.2	0.0	0.0	0.0	0.0
-3.08	210	94.1	3.0	0.1	0.3	0.3	0.0	0.0	0.0	0.0
-2.85	180	92.6	5.4	0.1	0.3	0.4	0.0	0.0	0.0	0.0
-2.67	150	87.7	9.9	0.1	0.3	0.9	0.0	0.0	0.0	0.0
-2.67	120	82.6	12.6	0.1	0.4	2.5	0.0	0.0	0.0	0.0
-2.25	90	72.9	18.9	0.2	0.8	4.7	0.0	0.0	0.0	0.0
-2.01	60	65.6	26.4	0.2	1.5	3.1	0.2	0.0	0.5	0.0
-1.78	30	51.9	30.3	0.5	5.9	3.5	0.4	0.2	1.9	0.0

Experimental conditions: 0.5 M KCl, 3 atm, 500 rpm, 25 °C

E (V vs. Ag/AgCl)	CD (mA cm ⁻²)	Faradaic Efficiency (%)								
		H ₂	CH ₄	CO	C ₂ H ₄	HCOO ⁻	MeCHO	PrCHO	EtOH	Others
-3.00	240	59.3	28.1	0.7	1.5	5.5	0.3	0.1	0.6	0.0
-2.90	210	61.9	27.8	0.1	1.2	3.9	0.3	0.0	0.6	0.0
-2.69	180	52.3	33.7	0.3	2.1	5.9	0.4	0.1	0.7	0.0
-2.59	150	38.7	37.9	0.4	4.3	10.4	1.0	0.1	1.6	0.0
-2.41	120	15.4	54.8	1.2	7.7	7.3	1.6	0.1	2.6	0.0
-2.28	90	12.6	36.2	7.1	5.0	29.3	1.3	0.3	1.8	0.0
-2.42	60	6.8	29.2	9.3	5.2	40.1	1.5	0.3	1.6	0.0
-1.92	30	5.4	9.8	14.8	2.9	58.7	1.0	0.1	0.7	0.0

Experimental conditions: 0.5 M KHCO₃, 3 atm, 500 rpm, 25 °C

E (V vs. Ag/AgCl)	CD (mA cm ⁻²)	Faradaic Efficiency (%)								
		H ₂	CH ₄	CO	C ₂ H ₄	HCOO ⁻	MeCHO	PrCHO	EtOH	Others
-3.66	330	19.5	57.7	0.1	11.0	2.6	1.2	0.3	3.5	0.0
-3.45	300	11.5	63.3	0.1	12.1	1.7	1.5	0.4	4.1	0.0
-3.25	270	10.5	61.8	0.2	14.1	1.7	1.6	0.4	4.2	0.0
-3.12	240	15.4	58.7	0.2	11.1	5.8	1.3	0.4	3.5	0.0
-2.87	210	12.7	58.0	0.2	12.8	5.3	1.5	0.5	3.7	0.0
-2.72	180	13.7	62.1	0.3	10.2	6.8	1.2	0.5	2.7	0.0
-2.55	150	11.8	56.7	0.6	12.4	9.4	1.6	0.8	3.2	0.0
-2.37	120	14.9	54.8	0.5	8.6	10.8	1.1	0.6	2.0	0.5
-2.15	90	17.4	50.8	1.0	9.1	14.6	1.2	0.8	2.0	0.0
-2.00	60	34.0	25.0	7.2	5.7	21.8	0.1	0.1	0.9	0.0
-1.77	30	42.9	12.7	8.0	5.3	26.0	0.0	0.0	0.0	0.0

Experimental conditions: 0.5 M KHCO₃, 3 atm, 500 rpm, 0 °C

E (V vs. Ag/AgCl)	CD (mA cm ⁻²)	Faradaic Efficiency (%)								
		H ₂	CH ₄	CO	C ₂ H ₄	HCOO ⁻	MeCHO	PrCHO	EtOH	Others
-3.41	160	4.6	66.6	0.1	7.5	1.8	1.7	0.3	2.6	0.0
-3.33	140	9.4	64.1	0.1	6.2	2.8	1.3	0.3	2.4	0.0
-2.99	120	4.9	71.7	0.1	6.9	2.4	1.5	0.3	2.2	0.0
-2.81	100	4.2	73.4	0.2	6.4	3.2	1.4	0.4	2.0	0.0
-2.58	80	6.4	76.6	0.2	5.7	5.0	0.9	0.4	1.5	0.0
-2.33	60	7.7	73.7	0.2	4.2	6.7	0.8	0.3	1.2	0.0
-2.10	40	8.0	72.3	0.5	4.0	8.6	0.7	0.5	1.1	0.0
-1.83	20	21.8	44.2	1.9	2.7	22.2	0.5	0.4	0.8	0.0

Experimental conditions: 0.5 M KHCO₃ + 1 M KCl, 3 atm, 500 rpm, 0 °C

E (V vs. Ag/AgCl)	CD (mA cm ⁻²)	Faradaic Efficiency (%)								
		H ₂	CH ₄	CO	C ₂ H ₄	HCOO ⁻	MeCHO	PrCHO	EtOH	Others
-2.86	320	15.7	59.5	0.1	2.7	3.0	0.8	0.0	1.7	0.0
-2.85	280	17.1	62.1	0.1	2.6	3.7	0.8	0.0	1.9	0.0
-2.60	240	10.5	69.1	0.1	3.4	3.6	1.0	0.0	2.2	0.0
-2.49	200	4.0	73.3	0.2	4.6	4.2	1.4	0.1	3.0	0.0
-2.32	160	2.8	70.4	0.3	4.4	4.1	1.3	0.1	2.3	0.0
-2.14	120	3.3	77.1	0.3	3.8	4.0	1.0	0.2	1.8	0.0
-2.02	80	3.8	80.0	0.6	3.4	4.6	0.9	0.2	1.5	0.0
-1.83	40	7.5	58.9	2.3	3.4	12.6	1.4	0.3	1.3	0.0

Reproducibility of the experimental results

Figure S4 shows the FEs of the reaction products for five separate experiments taken from different reactors that were all operating under the same experimental conditions (stirring speed: 500 rpm, CO₂ pressure: 3 atm and temperature: 25 °C at 240 mA cm⁻²). The measurement time was 417 s and 100 C of charge had been passed in all experiments. No major variation of product distribution was observed.

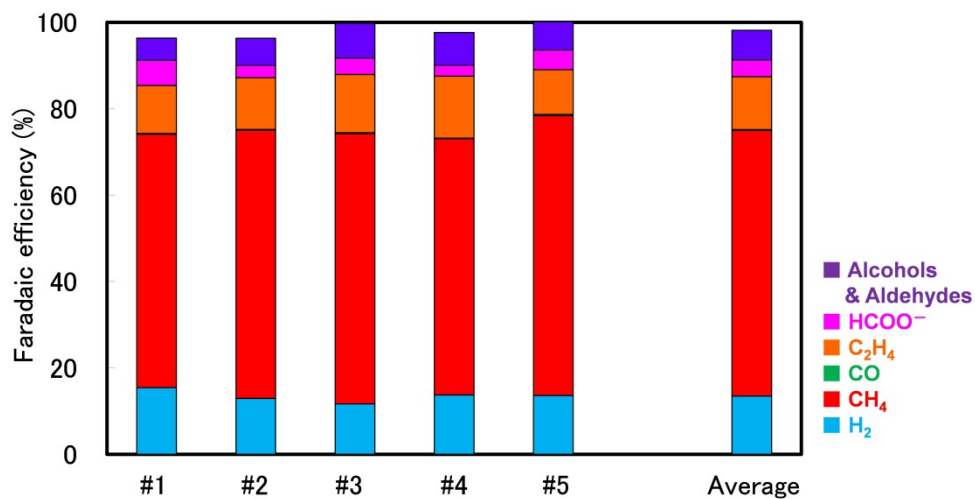


Figure S4. Individual and averaged product selectivity for five parallel experiments for measurements carried out at 240 mA cm⁻², 500 rpm, 3 atm and 25 °C.

Variation in product potential and selectivity with time

The time dependence of FE values for the reaction products is shown in Fig. S5(a). Measurements were performed under 500 rpm, 3 atm, 25 °C and 240 mA cm^{-2} in 0.5 M KHCO_3 for reaction times of 417, 834, 1668 and 2502 s (corresponding to 100, 200, 400 and 600 C, respectively). Here, we confirmed the increase of H_2 FE and the decrease of C_2H_4 FE with increasing reaction time. Although it appeared to decrease slightly initially, the magnitude relative to changes in other FE values was very small and we consider that the results suggest the FE of CH_4 was relatively constant over time. The potential vs. time profile is shown in Figure S5 (b). The potential is stable at around -3.1V vs. Ag/AgCl within the measured time region. Note that this potential is included IR losses.

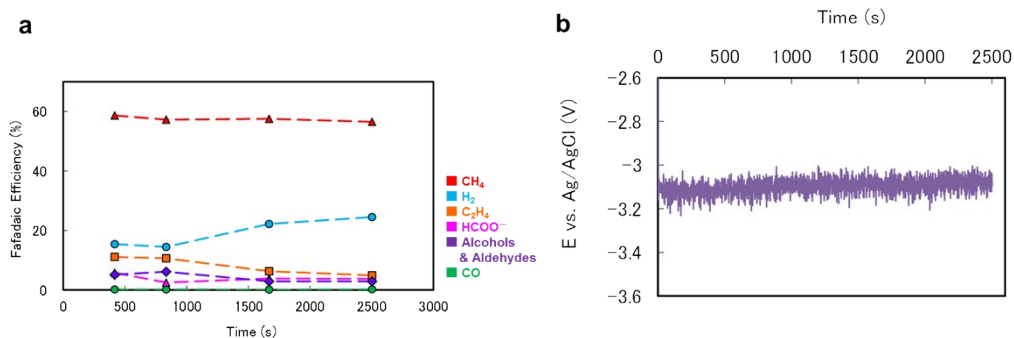


Figure S5. (a) Reaction time dependence of FEs of the reaction products at 240 mA cm^{-2} , 500 rpm, 3 atm and 25 °C. (b) Potential profile of the measurement of 2502 s.

Effects of adding KCl to KHCO_3 solutions

The effects of adding KCl to the KHCO_3 electrolyte were assessed by comparing the CH_4 FE values obtained using either 0.5 M KHCO_3 or 0.5 M KHCO_3 + 1 M KCl solutions. These experiments were performed at 3 atm, 500 rpm and 0 °C. As can be seen from Fig. S6, the plots of CH_4 FE against current density had very similar shapes regardless of the presence of KCl in the electrolyte.

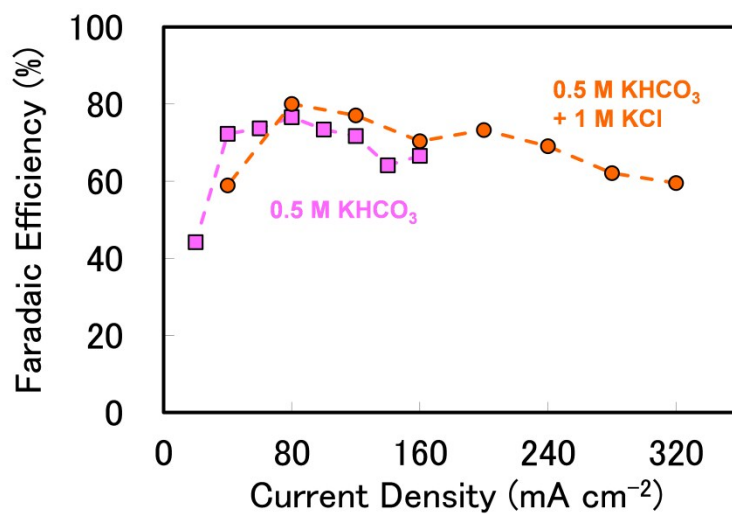


Figure S6. CH_4 Faradaic efficiencies as functions of current density in different electrolytes at 3 atm, 500 rpm and 0 °C. Green triangles: 0.5 M KHCO_3 and orange circles: 0.5 M KHCO_3 + 1 M KCl.

Effects of CO₂ pressure and stirring speed on product selectivity

Figure S7 presents the effects of CO₂ pressure and stirring speed on the FEs for H₂ (light blue circles), CH₄ (red triangles) and other CO₂-related products (gray squares) in 0.5 M KHCO₃ solution. The minimum H₂ FE significantly decreased, from 66.2% to 10.5%, with increasing pressurisation and stirring (on changing conditions from 1.3 atm and 0 rpm to 3 atm and 500 rpm).

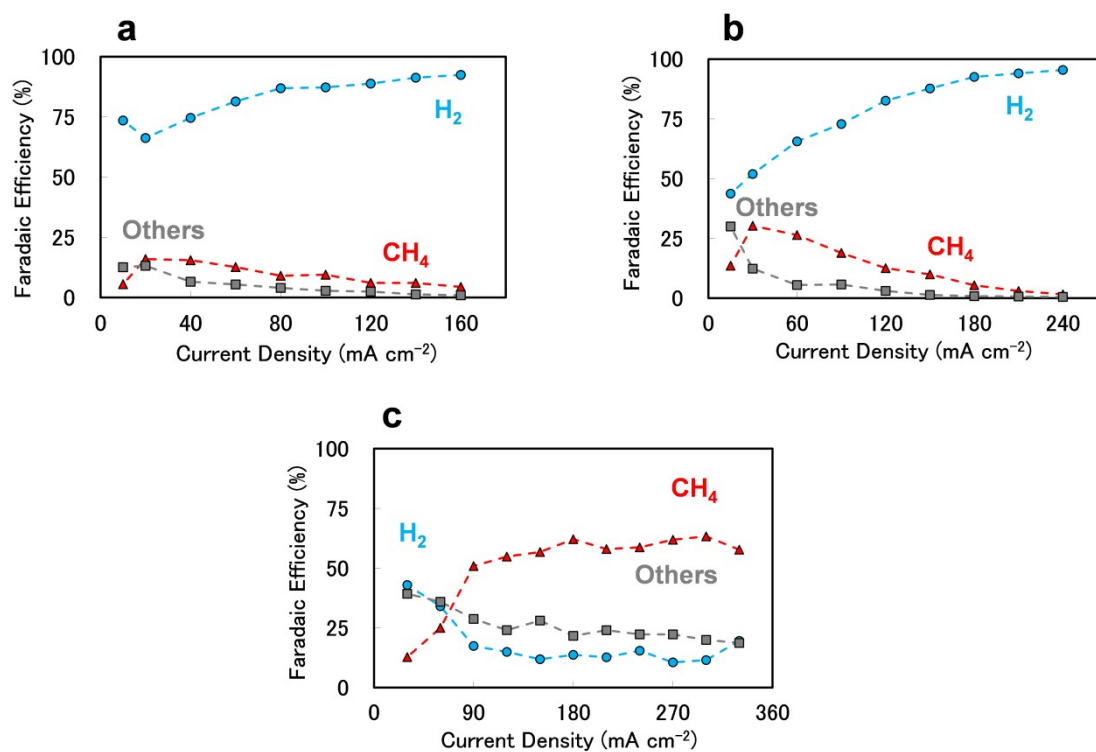


Figure S7. Faradaic efficiencies as functions of current density in 0.5 M KHCO₃ at 25 °C and (a) 1.3 atm and 0 rpm, (b) 3 atm and 0 rpm and (c) 3 atm and 500 rpm.

Figure S8 presents the effects of CO₂ pressure and stirring speed on the FEs for H₂ (light blue circles), CH₄ (red triangles) and other CO₂-related products (gray squares) in 0.5 M KCl solution. Unlike with 0.5 M KHCO₃, the minimum H₂ FE was below 25% regardless of the experimental conditions when KCl was used.

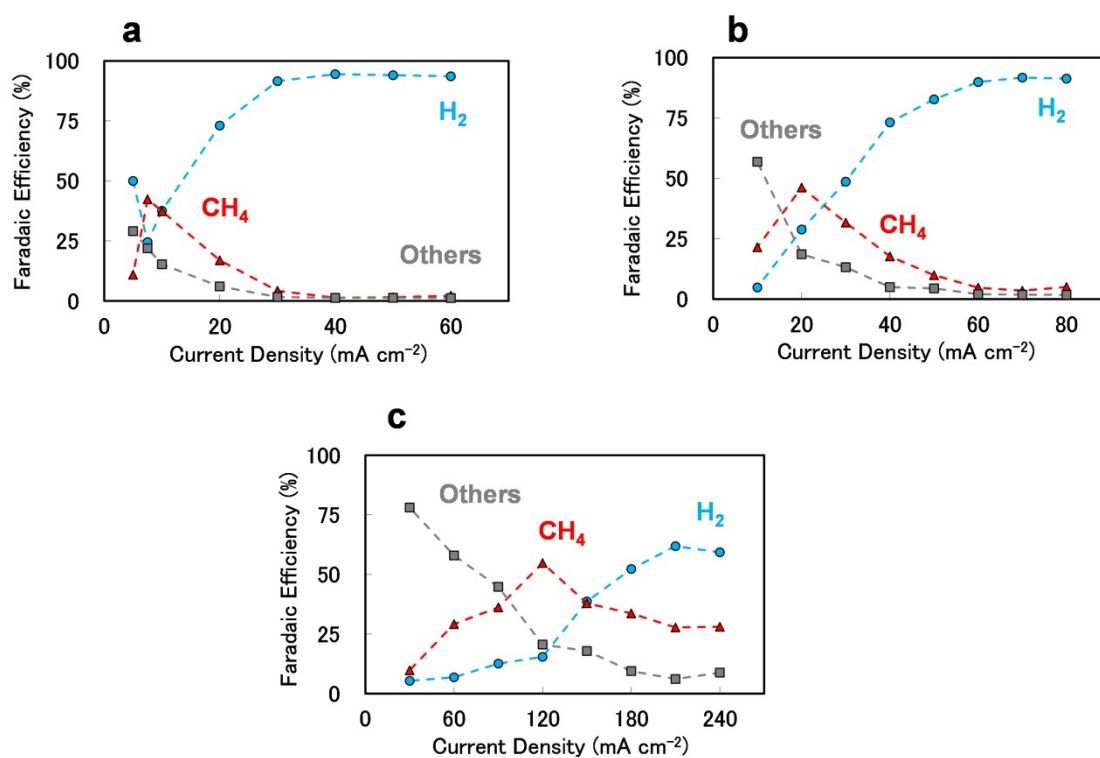


Figure S8. Faradaic efficiencies as functions of current density in 0.5 M KCl at 25 °C and (a) 1.3 atm and 0 rpm, (b) 3 atm and 0 rpm and (c) 3 atm and 500 rpm.

Limiting current densities for all experimental conditions in this study

Table S2 summarises the effect of parameters on limiting current density (LCD) for CO₂ reduction (which is also partly shown in Fig. 5 in the main report). We note that in several experiments (denoted with *), LCD could not be obtained because of experimental limitations. In those cases, we instead report the maximum observed value.

Table S2. LCDs for CO₂ reduction for all experimental conditions. Data are summarised by parameter (electrolyte, pressure, stirring and temperature).

Stirring: 0 rpm, Pressure: 1.3 atm and Temperature: 25 °C

Electrolyte	0.5 M KCl	0.25M KHCO ₃	0.5 M KHCO ₃
LCD (mA cm ⁻²)	5.3	10.0	12.3

Stirring: 0 rpm and Temperature: 25 °C in 0.5 M KCl

Pressure (atm)	1.3	2	3
LCD (mA cm ⁻²)	5.3	8.6	13.5

Stirring: 0 rpm and Temperature: 25 °C in 0.5 M KHCO₃

Pressure (atm)	1.3	2	3
LCD (mA cm ⁻²)	12.3	17.1	22.2

Pressure: 3 atm and Temperature: 25 °C in 0.5 M KCl

Stirring rate (rpm)	0	500
LCD (mA cm ⁻²)	13.5	90.4

Pressure: 3 atm and Temperature: 25 °C in 0.5 M KHCO₃

Stirring rate (rpm)	0	500*
LCD (mA cm ⁻²)	22.2	252

Stirring: 500 rpm and Pressure: 3 atm in 0.5 M KHCO₃

Temperature (°C)	0*	25*
LCD (mA cm ⁻²)	217	252

Comparison between experimental and theoretical LCDs

The LCDs shown in Table S2 were then compared with theoretical values given by Singh et al., as summarised in Table S3.² The electrolyte pH was obtained under ambient pressure. CO₂ concentration was calculated using a method defined in the literature.³ As noted in the main manuscript, we can clearly see from both experimental and theoretical results that LCD is dependent on the electrolyte's pH.

To carry out a quantitative comparison, we assumed a boundary layer thickness using the value we calculated previously using a semi-infinite diffusion model.¹ For the same boundary layer thickness, the CO₂-concentration-normalised LCD (at 33 mM) in this study is about four times larger than that in the simulation. We assume that the difference between these values derives from the differences in the main product: The simulation assumes production of CO is dominant (requiring 2 electrons per CO₂ molecule), while in our study the main product was CH₄ (requiring 8 electrons per molecule of CO₂). This means that the current would need to be approximately four times larger to consume the same amount of CO₂ in the experimental case. Thus, we conclude that our results show good agreement with those generated in the simulation by Singh et al.

Table S3. Comparison of experimentally and theoretically (Ref. 2) derived LCD values for CO₂ reduction

	LCD (mA cm ⁻²)	Electrolyte pH ^a (1 atm)	CO ₂ concentration (mM)	Normalized LCD at 33 mM (mA cm ⁻²)	Boundary layer thickness (μm)	Notes
Singh et al.	~ 7.5	3.8	33	~7.5	100	Ref. 2
Singh et al.	~ 17	7.5	33	~17	100	Ref. 2
0.5 M KCl	90.4	3.8	94 (Ref. 3)	31.8	~100 (Ref. 1)	This work (500 rpm, 3 atm, 25 °C)
0.5 M KHCO ₃ *	252	7.5	109 (Ref.3)	76.3	~100 (Ref. 1)	This work (500 rpm, 3 atm, 25 °C)

Surface morphology and orientation for Cu electrode in this study

To investigate the morphology of the electrode in this study, we performed Scanning Electron Microscopy (SEM) and Electron BackScattering Pattern (EBSP) analysis for the chemically-polished Cu electrode, as shown in Fig. S9. Although the surface appears relatively smooth when viewed at the micrometre-scale, we confirmed surface roughness of the order of several tens of nanometres (Figs. S9(a,b)). Figure S9(c) shows the EBSP pattern of the electrode, where the polycrystalline pattern is confirmed. The surface orientation that is favourable for CH₄ production (shown in Fig. S9(d) as red circles⁴) appeared to be dominant (estimated to be over 70% of the total area by Adobe Photoshop Elements 13), suggesting that this may assist selective CH₄ production.

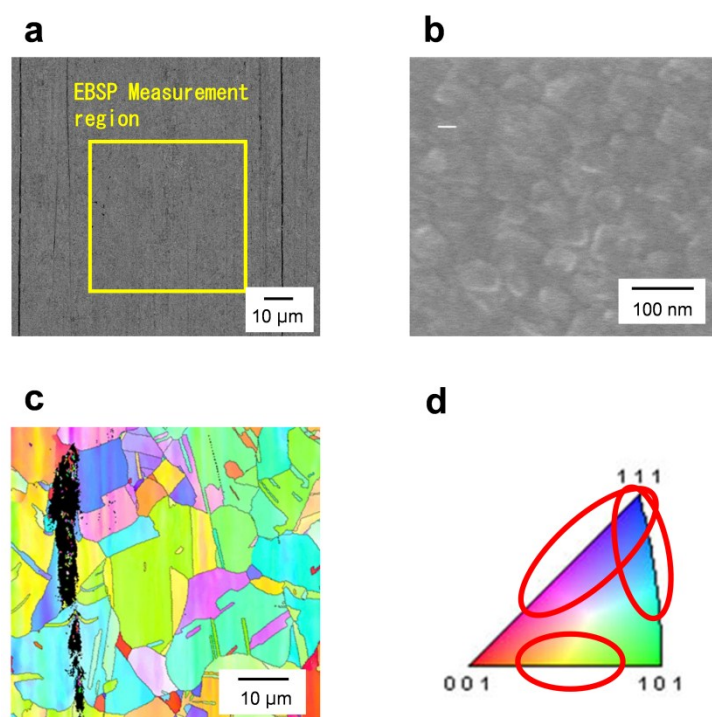


Figure S9. (a,b) SEM images of the surface of chemically-polished Cu electrode. (c) EBSP analysis of the Cu electrode. (d) Colour indication of the surface direction. The red ellipses represent the surface directions that favour CH₄ production according to Ref. 4.

References

1. H. Hashiba, S. Yotsuhashi, M. Deguchi and Y. Yamada, *ACS Comb. Sci.*, 2016, **18**, 203-208.
2. M. R. Singh, E. L. Clark and A. T. Bell, *Phys. Chem. Chem. Phys.*, 2015, **17**, 18924-18936.
3. H. Zhong, K. Fujii, Y. Nakano and F. Jin, *J. Phys. Chem. C*, 2015, **119**, 55-61.
4. Y. Hori, I. Takahashi, O. Koga and N. Hoshi, *J. Mol. Catal. A: Chem.*, 2003, **199**, 39-47.