

Supplementary Information for

Energy conversion efficiency comparison of different aqueous and semi-aqueous  
CO<sub>2</sub> electroreduction systems

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**Table S1.** Standard chemical potentials of chemicals appearing in CO<sub>2</sub>-reduction reactions (taken from Pourbaix diagrams).<sup>S1,S2</sup>

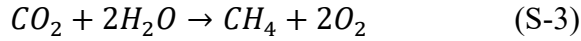
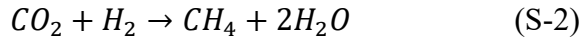
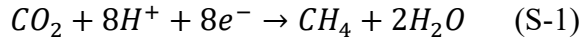
Chemicals	Standard chemical potential ( $\mu^{\circ}$ ) [kJ/mol]
CH <sub>4</sub>	-50.8
CO <sub>2</sub>	-394.4
H <sub>2</sub> O	-237.2
H <sub>2</sub>	0
H <sup>+</sup>	0
O <sub>2</sub>	0
CO	-137.3
C <sub>2</sub> H <sub>4</sub>	-198.5
HCOOH	-356.1
CH <sub>3</sub> OH	-166.3
C <sub>2</sub> H <sub>5</sub> OH	-174.8

(S1) M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*; National Association of Corrosion Engineers: Texas, 1974.

(S2) P. Atkins and J. de Paula, *Elements of Physical Chemistry*; 6th ed.; Oxford University Press: Oxford, 2013.

### ***Detail of the assumption of employing the H<sub>2</sub>O oxidation reaction as a reference***

The theoretical potential of CH<sub>4</sub>-generation reaction is derived in the cases of following three reactions (S-1), (S-2), and (S-3).



For Eq. (S-1), based on Table 1 and Eq. (2),  $\Delta G^o = -130,667.6$  [J/mol] is derived. Substituting the obtained  $\Delta G^o$ ,  $n = 8$ , and  $F = 96,485$  [C/mol] into Eq. (1) gives  $E^o = 0.169$  [V].

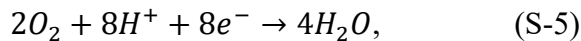
For Eq. (S-2), considering it the sum of the two reactions of Eq. (S-1) and the following equation:



$\Delta G^o = -130,667.6$  [J/mol] is derived. Therefore,  $E^o = 0.169$  [V] is obtained using Eq. (1).

In other words, the standard electrode potential of the targeted half-reaction (Eq. (1)) can be obtained by employing  $2H^+ + 2e^- \rightarrow H_2$  with  $\Delta G^o = 0$  as the counter-electrode reaction. However, when the energy conversion efficiency of Eq. (S-1) is calculated as a reference of H<sub>2</sub> oxidation, the calculation is incorrect because  $\varepsilon_{ec} < 0$  is often obtained due to  $V_0 < 0$ .

For Eq. (S-3), considering it the sum of the two reactions of Eq. (S-1) and the following equation:



$\Delta G^o = -817,189.2$  [J/mol] is obtained. Substituting the obtained  $\Delta G^o$ ,  $n = 8$ , and  $F = 96,485$  [C/mol] into Eq. (1) gives  $E^o = 1.059$  [V]. In this case, O<sub>2</sub> reduction reaction (reverse reaction of H<sub>2</sub>O oxidation;  $E^o = 1.228$  [V]) is the standard, resulting in obtaining the theoretical potential of Eq. (1) of  $E^o = 1.228 - 1.059 = 0.169$  [V]. Therefore, it is possible to calculate and compare the energy conversion efficiency of half-cell CO<sub>2</sub> reductions in the aqueous and semi-aqueous systems by employing H<sub>2</sub>O oxidation reaction without overvoltage ( $\eta_A = 0$ ) as a reference.

**Table S2.** Energy conversion efficiencies for the production of **(a)** CO, **(b)** HCOOH, **(c)** C<sub>2</sub>H<sub>4</sub>, and **(d)** CH<sub>4</sub> under each CO<sub>2</sub> reduction condition. Data are taken from Table 2. Note that  $T$ ,  $E_{\text{red}}$ ,  $i$ ,  $\eta_C$ ,  $\varepsilon_F$ , and  $\varepsilon_{\text{ec}}$  represent the temperature, electrode potential at which CO<sub>2</sub> reduction occurs, current density, cathodic overpotential, faradaic efficiency, and energy conversion efficiency, respectively. The full name of RHE is reversible hydrogen electrode.

**(a) CO production**

No	Electrocatalyst	Electrolyte	Product	$T / \text{K}$	pH	$E_{\text{red}}$	$i / \text{mA cm}^{-2}$	$\eta_C / \text{V}$	$\varepsilon_F / \%$	$\varepsilon_{\text{ec}} / \%$	Ref.
3	ZnO sheet	0.1 M KHCO <sub>3</sub>	CO	298	6.8	-1.399 V vs. SHE	11.5	1.29	85	43.2	(15)
4	Cornstarch-N-Ni	0.5 M KHCO <sub>3</sub>	CO	298	7.2	-0.8 V vs. RHE	11.6	0.694	92	60.5	(16)
9	Pt/C	Nafion	CO <sub>ads</sub>	313	-0.4	0.175 V vs. SHE	3.7	-0.281	75	95.0	(20)
11	FeN <sub>4</sub> /C	0.1 M KHCO <sub>3</sub>	CO	298	6.7	-0.6 V vs. RHE	13	0.494	93	67.9	(21)
13	Cu-Ni hollow fibre	0.1 M KHCO <sub>3</sub>	CO	293	6.7	-1.3 V vs. RHE	13.6	1.19	77.5	40.9	(23)
15	Bi single atoms	0.1 M NaHCO <sub>3</sub>	CO	298	6.7	-0.5 V vs. RHE	4	0.394	97	74.9	(25)
17	Zn/Ag foams	0.1 M KHCO <sub>3</sub>	CO	298	6.7	-1.24 V vs. RHE	9.5	1.13	73.3	39.6	(26)
24	Au	0.2 M KHCO <sub>3</sub>	CO	298	6.8	-0.39 V vs. RHE	0.017	0.284	30	24.7	(30)
25	Co-N <sub>5</sub>	0.2 M NaHCO <sub>3</sub>	CO	298	6.9	-0.73 V vs. RHE	4.5	0.624	99	67.4	(31)
29	Ag nanoplate	0.1 M KHCO <sub>3</sub>	CO	298	6.7	-0.85 V vs. RHE	1.25	0.744	96.8	62.1	(35)
30	Ni-N <sub>4</sub> -C	0.5 M KHCO <sub>3</sub>	CO	298	7.3	-0.81 V vs. RHE	28.6	0.704	99	64.8	(36)
31	Au nanoparticle	0.5 M KHCO <sub>3</sub>	CO	298	7.3	-0.47 V vs. RHE	8	0.364	80	62.9	(37)
32	Li-Zn	0.1 M KHCO <sub>3</sub>	CO	298	6.7	-1.17 V vs. RHE	30	1.06	80	44.5	(38)
34	SnO <sub>2</sub> porous nanowires	0.1 M KHCO <sub>3</sub>	CO	298	6.7	-0.8 V vs. RHE	6.0	0.694	11	7.24	(39)
35	Zn	0.5 M KCl	CO	298	4.0	-1.1 V vs. RHE	4.3	0.994	95	54.4	(40)
44	Ag/C	0.5 M KHCO <sub>3</sub>	CO	298	7.3	-1.00 V vs. RHE	125 mA mg <sup>-1</sup>	0.894	85.9	51.4	(48)
45	Au	0.5 M KHCO <sub>3</sub>	CO	298	7.2	-0.35 V vs. RHE	15	0.244	95	80.3	(49)
46	Oxide-derived-Cu	0.1 M KHCO <sub>3</sub>	CO	298	6.7	-0.6 V vs. RHE	4.5	0.494	90	65.7	(50)
49	Cu-Sn alloy	0.1 M KHCO <sub>3</sub>	CO	298	6.8	-0.6 V vs. RHE	1	0.494	90	65.7	(52)
51	Sn	0.1 M KHCO <sub>3</sub>	CO	298	6.7	-1.36 V vs. RHE	17.1	1.25	11.8	6.08	(53)
57	Ag	0.5 M KHCO <sub>3</sub>	CO	298	7.2	-0.75 V vs. RHE	10	0.644	79.2	53.4	(58)
54	Cu	0.1 M KHCO <sub>3</sub>	CO	298	6.8	-0.847 V vs. RHE	1	0.741	6.12	4.65	(63)
69	Cu nanoparticles	0.1 M KHCO <sub>3</sub>	CO	298	6.7	-1.1 V vs. RHE	23	0.994	5	2.87	(65)
71	Cu-In alloy	0.1 M KHCO <sub>3</sub>	CO	298	6.7	-0.60 V vs. RHE	0.6	0.494	85	62.0	(66)
72	Au nanoparticles	0.5 M KHCO <sub>3</sub>	CO	298	7.3	-0.67 V vs. RHE	5 A g <sup>-1</sup>	0.564	90	63.3	(67)
73	Au	0.5 M NaHCO <sub>3</sub>	CO	298	7.2	-0.35 V vs. RHE	4	0.244	96	81.2	(68)

75	ZnO	0.1 M KHCO <sub>3</sub>	CO	298	6.7	-1.45 V vs. RHE	7.0	1.34	80	39.9	(70)
82	Cu	0.1 M KHCO <sub>3</sub>	CO	298	6.7	-1.44 V vs. RHE	5.0	1.33	1.3	0.650	(72)
84	Au					-1.14 V vs. RHE	5.0	1.03	87.1	49.1	
86	Ag					-1.37 V vs. RHE	5.0	1.26	81.5	41.8	
88	Zn					-1.54 V vs. RHE	5.0	1.43	79.4	38.3	
91	Pd					-1.20 V vs. RHE	5.0	1.09	28.3	15.5	
93	Ga					-1.24 V vs. RHE	5.0	1.13	23.2	12.5	
96	In					-1.55 V vs. RHE	5.0	1.44	2.1	1.01	
98	Sn					-1.48 V vs. RHE	5.0	1.37	7.1	3.50	
101	Cd					-1.63 V vs. RHE	5.0	1.52	13.9	6.49	

### (b) HCOOH production

No	Electrocatalyst	Electrolyte	Product	T / K	pH	$E_{red}$	$i / \text{mA cm}^{-2}$	$\eta_c / \text{V}$	$\epsilon_F / \%$	$\epsilon_{cc} / \%$	Ref.
2	CuS nanosheet	0.5 M KHCO <sub>3</sub>	HCOO <sup>-</sup>	298	7.2	-0.7 V vs. RHE	50	0.501	70.2	52.0	(14)
19	Zn/Ag foams	0.1 M KHCO <sub>3</sub>	HCOO <sup>-</sup>	298	6.7	-1.24 V vs. RHE	0.3	1.10	2.1	1.16	(26)
20	Zr-organic frameworks	0.5 M KHCO <sub>3</sub>	HCOOH	298	7.3	-1.89 V vs. RHE	20	1.75	4.2	1.84	(27)
26	Pt-Ru black	Nafion	HCOOH	343	-0.4	0.053 V vs. SHE	30	-0.252	4.5×10 <sup>-4</sup>	5.5×10 <sup>-4</sup>	(32)
33	SnO <sub>2</sub> porous nanowires	0.1 M KHCO <sub>3</sub>	HCOOH	298	6.7	-0.8 V vs. RHE	6.0	0.601	80	56.3	(39)
36	SnO <sub>2</sub>	0.5 M NaHCO <sub>3</sub>	HCOOH	298	7.2	-0.975 V vs. SHE	50	0.776	87	56.4	(41)
37	Ag-Sn core-shell nanostructure	0.5 M NaHCO <sub>3</sub>	HCOOH	298	7.2	-0.8 V vs. RHE	16	0.601	80	56.3	(42)
43	Ultrathin Co <sub>3</sub> O <sub>4</sub> Layers	0.1 M KHCO <sub>3</sub>	HCOOH	298	6.7	-0.88 V vs. SHE	0.68	0.681	60	40.6	(47)
47	Oxide-derived-Cu	0.1 M KHCO <sub>3</sub>	HCOOH	298	6.7	-0.6 V vs. RHE	0.3	0.401	5	3.90	(50)
50	Sn	0.1 M KHCO <sub>3</sub>	HCOO <sup>-</sup>	298	6.7	-1.36 V vs. RHE	17.1	1.16	71.6	39.5	(53)
58	Pd-Pt-C	0.1 M KH <sub>2</sub> PO <sub>4</sub> /0.1 M K <sub>2</sub> HPO <sub>4</sub>	HCOOH	298	6.7	-0.4 V vs. RHE	5	0.201	91.8	80.5	(59)
61	Pd/C	0.5 M NaHCO <sub>3</sub>	HCOO <sup>-</sup>	298	7.2	-0.35 V vs. RHE	3.45	0.151	88	79.6	(61)
65	Cu	0.1 M KHCO <sub>3</sub>	HCOOH	298	6.8	-0.847 V vs. RHE	1	0.648	12.14	10.2	(63)
66	SnO <sub>2</sub>	0.1 M NaHCO <sub>3</sub>	HCOOH	298	6.7	-1.8 V vs. SHE	9.5	1.60	93	43.8	(64)
70	Cu nanoparticles	0.1 M KHCO <sub>3</sub>	HCOOH	298	6.7	-1.1 V vs. RHE	23	0.901	5	3.06	(65)
74	SnO <sub>x</sub> /Sn	0.1 M KHCO <sub>3</sub>	HCOO <sup>-</sup>	298	6.7	-1.36 V vs. RHE	17.1	1.16	71.6	39.5	(69)
83	Cu	0.1 M KHCO <sub>3</sub>	HCOO <sup>-</sup>	298	6.7	-1.44 V vs. RHE	5.0	1.24	9.4	5.03	(72)
85	Au		HCOO <sup>-</sup>			-1.14 V vs. RHE	5.0	0.94	0.7	0.422	
87	Ag		HCOO <sup>-</sup>			-1.37 V vs. RHE	5.0	1.17	0.8	0.439	
89	Zn		HCOO <sup>-</sup>			-1.54 V vs. RHE	5.0	1.34	6.1	3.14	

92	Pd		HCOO <sup>-</sup>			-1.20 V vs. RHE	5.0	1.00	2.8	1.65	
94	Pb		HCOO <sup>-</sup>			-1.63 V vs. RHE	5.0	1.43	97.4	48.6	
95	Hg		HCOO <sup>-</sup>			-1.51 V vs. RHE	0.5	1.31	99.5	51.9	
97	In		HCOO <sup>-</sup>			-1.55 V vs. RHE	5.0	1.35	94.9	48.7	
99	Sn		HCOO <sup>-</sup>			-1.48 V vs. RHE	5.0	1.28	88.4	46.6	
102	Cd		HCOO <sup>-</sup>			-1.63 V vs. RHE	5.0	1.43	78.4	39.1	
103	Tl		HCOO <sup>-</sup>			-1.60 V vs. RHE	5.0	1.40	95.1	48.0	
105	Ni		HCOO <sup>-</sup>			-1.48 V vs. RHE	5.0	1.28	1.4	0.738	

### (c) C<sub>2</sub>H<sub>4</sub> production

No	Electrocatalyst	Electrolyte	Product	T / K	pH	E <sub>red</sub>	i / mA cm <sup>-2</sup>	η <sub>C</sub> / V	ε <sub>F</sub> / %	ε <sub>ec</sub> / %	Ref.
5	CuO	0.1 M KHCO <sub>3</sub>	C <sub>2</sub> H <sub>4</sub>	298	6.7	-1.1 V vs. RHE	3	1.18	26.8	13.2	(17)
6	Sn-doped CuO						6		48.5	23.9	
21	Cu oxides/ZnO	0.1 M KHCO <sub>3</sub>	C <sub>2</sub> H <sub>4</sub>	298	6.7	-2.3 V vs. RHE	7.5	2.77	91.1	29.8	(28)
27	Cu nanoparticles	Nafion	C <sub>2</sub> H <sub>4</sub>	298	7.3	-0.8 V vs. RHE	7.5	0.874	92.8	52.8	(33)
52	Cu nanocubes	0.1 M KHCO <sub>3</sub>	C <sub>2</sub> H <sub>4</sub>	298	6.7	-1.1 V vs. RHE	5.6	1.18	41	20.2	(54)
54	Pyridinic-N rich graphene/Cu	0.5 M KHCO <sub>3</sub>	C <sub>2</sub> H <sub>4</sub>	298	7.3	-0.90 V vs. RHE	7.7 A g <sup>-1</sup>	0.979	19	10.3	(56)
59	Cu <sub>2</sub> O	0.1 M KHCO <sub>3</sub>	C <sub>2</sub> H <sub>4</sub>	298	6.7	-0.99 V vs. RHE	30	1.07	39	20.2	(60)
68	Cu nanoparticles	0.1 M KHCO <sub>3</sub>	C <sub>2</sub> H <sub>4</sub>	298	6.7	-1.1 V vs. RHE	23	1.18	20	9.87	(65)
77	Cu	0.1 M KHCO <sub>3</sub>	C <sub>2</sub> H <sub>4</sub>	298	6.7	-1.36 V vs. RHE	2.5	1.44	21.7	9.63	(71)
80	Cu	0.1 M KHCO <sub>3</sub>	C <sub>2</sub> H <sub>4</sub>	298	6.7	-1.44 V vs. RHE	5.0	1.52	25.5	11.0	(72)

### (d) CH<sub>4</sub> production

No	Electrocatalyst	Electrolyte	Product	T / K	pH	E <sub>red</sub>	i / mA cm <sup>-2</sup>	η <sub>C</sub> / V	ε <sub>F</sub> / %	ε <sub>ec</sub> / %	Ref.
1	Pt black	Nafion	CH <sub>4</sub>	313	-0.4	0.155 V vs. SHE	0.0023	0.0141	23.2	22.9	(13)
7	Pt <sub>0.8</sub> Ru <sub>0.2</sub> /C	Nafion	CH <sub>4</sub>	313	-0.4	0.175 V vs. SHE	0.14	-0.0063	18.2	18.3	(18)
8	Pt/C	Nafion	CH <sub>4</sub>	313	-0.4	0.135 V vs. SHE	0.06	0.0337	12.3	11.9	(19)
10	Pt/C	Nafion	CH <sub>4</sub>	313	-0.4	0.075 V vs. SHE	11.8	0.0937	6.8	6.25	(20)
12	La <sub>2</sub> CuO <sub>4</sub>	1 M KOH	CH <sub>4</sub>	298	9.6	-1.4 V vs. RHE	117	1.57	56.3	22.7	(22)
14	Pt/C	Nafion	CH <sub>4</sub>	333	-0.4	0.134 V vs. SHE	18.2	0.0353	0.4	0.387	(24)
16	Zn/Ag foams	0.1 M KHCO <sub>3</sub>	CH <sub>4</sub>	298	6.7	-1.24 V vs. RHE	0.4	1.41	3.1	1.33	(26)
42	Cu nanoparticles	Nafion	CH <sub>4</sub>	298	7.3	-1.6 V vs. RHE	7.5	1.77	12.1	4.53	(46)
48	Mo <sub>2</sub> C	0.1 M KHCO <sub>3</sub>	CH <sub>4</sub>	298	6.7	-1.1 V vs. RHE	13.62	1.27	29	13.2	(51)
63	Cu	0.1 M KHCO <sub>3</sub>	CH <sub>4</sub>	298	6.8	-0.847 V vs. RHE	1	1.02	2.57	1.31	(63)

67	Cu nanoparticles	0.1 M KHCO <sub>3</sub>	CH <sub>4</sub>	298	6.7	-1.1 V vs. RHE	23	1.27	57	25.9	(65)
76	Cu	0.1 M KHCO <sub>3</sub>	CH <sub>4</sub>	298	6.7	-1.36 V vs. RHE	2.5	1.53	22.3	9.13	(71)
79	Cu	0.1 M KHCO <sub>3</sub>	CH <sub>4</sub>	298	6.7	-1.44 V vs. RHE	5.0	1.61	33.3	13.2	(72)
80	Pd					-1.20 V vs. RHE	5.0	1.37	2.9	1.26	
100	Cd					-1.63 V vs. RHE	5.0	1.80	1.3	0.482	
104	Ni					-1.48 V vs. RHE	5.0	1.65	1.8	0.704	