Supplementary Information for

Energy conversion efficiency comparison of different aqueous and semi-aqueous CO_2 electroreduction systems

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Table S1. Standard chemical potentials of chemicals appearing in CO_2-reduction reactions (taken from Pourbaix diagrams).[S1,S2]

Chemicals	Standard chemical potential (μ^o) [kJ/mol]
CH_4	-50.8
CO_2	-394.4
H_2O	-237.2
H_2	0
H^+	0
O_2	0
CO	-137.3
C_2H_4	-198.5
HCOOH	-356.1
CH_3OH	-166.3
C_2H_5OH	-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_2O oxidation reaction as a reference

The theoretical potential of CH_4-generation reaction is derived in the cases of following three reactions (S-1), (S-2), and (S-3).

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad \text{(S-1)}$$

$$CO_2 + H_2 \rightarrow CH_4 + 2H_2O \quad \text{(S-2)}$$

$$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2 \quad \text{(S-3)}$$

For Eq. (S-1), based on Table 1 and Eq. (2), $\Delta G^o = -130{,}667.6$ [J/mol] is derived. Substituting the obtained ΔG^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:

$$8H^+ + 8e^- \rightarrow 4H_2, \quad \text{(S-4)}$$

$\Delta G^o = -130{,}667.6$ [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_2 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:

$$2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O, \quad \text{(S-5)}$$

$\Delta G^o = -817{,}189.2$ [J/mol] is obtained. Substituting the obtained ΔG^o, $n = 8$, and $F = 96{,}485$ $[C/mol]$ into Eq. (1) gives $E^o = 1.059$ [V]. In this case, O_2 reduction reaction (reverse reaction of H_2O 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_2 reductions in the aqueous and semi-aqueous systems by employing H_2O oxidation reaction without overvoltage (η_A= 0) as a reference.

Table S2. Energy conversion efficiencies for the production of **(a)** CO, **(b)** HCOOH, **(c)** C_2H_4, and **(d)** CH_4 under each CO_2 reduction condition. Data are taken from Table 2. Note that T, E_{red}, i, η_C, ε_F, and ε_{ec} represent the temperature, electrode potential at which CO_2 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 / K	pH	E_{red}	i / mA cm^{-2}	η_C / V	ε_F / %	ε_{ec} / %	Ref.
3	ZnO sheet	0.1 M $KHCO_3$	CO	298	6.8	-1.399 V vs. SHE	11.5	1.29	85	43.2	(15)
4	Cornstarch-N-Ni	0.5 M $KHCO_3$	CO	298	7.2	-0.8 V vs. RHE	11.6	0.694	92	60.5	(16)
9	Pt/C	Nafion	CO_{ads}	313	-0.4	0.175 V vs. SHE	3.7	-0.281	75	95.0	(20)
11	FeN_4/C	0.1 M $KHCO_3$	CO	298	6.7	-0.6 V vs. RHE	13	0.494	93	67.9	(21)
13	Cu-Ni hollow fibre	0.1 M $KHCO_3$	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 $NaHCO_3$	CO	298	6.7	-0.5 V vs. RHE	4	0.394	97	74.9	(25)
17	Zn/Ag foams	0.1 M $KHCO_3$	CO	298	6.7	-1.24 V vs. RHE	9.5	1.13	73.3	39.6	(26)
24	Au	0.2 M $KHCO_3$	CO	298	6.8	-0.39 V vs. RHE	0.017	0.284	30	24.7	(30)
25	Co-N_5	0.2 M $NaHCO_3$	CO	298	6.9	-0.73 V vs. RHE	4.5	0.624	99	67.4	(31)
29	Ag nanoplate	0.1 M $KHCO_3$	CO	298	6.7	-0.85 V vs. RHE	1.25	0.744	96.8	62.1	(35)
30	Ni-N_4-C	0.5 M $KHCO_3$	CO	298	7.3	-0.81 V vs. RHE	28.6	0.704	99	64.8	(36)
31	Au nanoparticle	0.5 M $KHCO_3$	CO	298	7.3	-0.47 V vs. RHE	8	0.364	80	62.9	(37)
32	Li-Zn	0.1 M $KHCO_3$	CO	298	6.7	-1.17 V vs. RHE	30	1.06	80	44.5	(38)
34	SnO_2 porous nanowires	0.1 M $KHCO_3$	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 $KHCO_3$	CO	298	7.3	-1.00 V vs. RHE	125 mA mg^{-1}	0.894	85.9	51.4	(48)
45	Au	0.5 M $KHCO_3$	CO	298	7.2	-0.35 V vs. RHE	15	0.244	95	80.3	(49)
46	Oxide-derived-Cu	0.1 M $KHCO_3$	CO	298	6.7	-0.6 V vs. RHE	4.5	0.494	90	65.7	(50)
49	Cu–Sn alloy	0.1 M $KHCO_3$	CO	298	6.8	−0.6 V vs. RHE	1	0.494	90	65.7	(52)
51	Sn	0.1 M $KHCO_3$	CO	298	6.7	-1.36 V vs. RHE	17.1	1.25	11.8	6.08	(53)
57	Ag	0.5 M $KHCO_3$	CO	298	7.2	-0.75 V vs. RHE	10	0.644	79.2	53.4	(58)
54	Cu	0.1 M $KHCO_3$	CO	298	6.8	-0.847 V vs. RHE	1	0.741	6.12	4.65	(63)
69	Cu nanoparticles	0.1 M $KHCO_3$	CO	298	6.7	-1.1 V vs. RHE	23	0.994	5	2.87	(65)
71	Cu–In alloy	0.1 M $KHCO_3$	CO	298	6.7	-0.60 V vs. RHE	0.6	0.494	85	62.0	(66)
72	Au nanoparticles	0.5 M $KHCO_3$	CO	298	7.3	-0.67 V vs. RHE	5 A g^{-1}	0.564	90	63.3	(67)
73	Au	0.5 M $NaHCO_3$	CO	298	7.2	-0.35 V vs. RHE	4	0.244	96	81.2	(68)

75	ZnO	0.1 M $KHCO_3$	CO	298	6.7	-1.45 V vs. RHE	7.0	1.34	80	39.9	(70)
82	Cu					-1.44 V vs. RHE	5.0	1.33	1.3	0.650	
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	0.1 M $KHCO_3$	CO	298	6.7	-1.20 V vs. RHE	5.0	1.09	28.3	15.5	(72)
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 / mA cm^{-2}	η_C / V	ε_F / %	ε_{ec} / %	Ref.
2	CuS nanosheet	0.5 M $KHCO_3$	$HCOO^-$	298	7.2	-0.7 V vs. RHE	50	0.501	70.2	52.0	(14)
19	Zn/Ag foams	0.1 M $KHCO_3$	$HCOO^-$	298	6.7	-1.24 V vs. RHE	0.3	1.10	2.1	1.16	(26)
20	Zr-organic frameworks	0.5 M $KHCO_3$	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^{-4}	5.5×10^{-4}	(32)
33	SnO_2 porous nanowires	0.1 M $KHCO_3$	HCOOH	298	6.7	-0.8 V vs. RHE	6.0	0.601	80	56.3	(39)
36	SnO_2	0.5 M $NaHCO_3$	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 $NaHCO_3$	HCOOH	298	7.2	-0.8 V vs. RHE	16	0.601	80	56.3	(42)
43	Ultrathin Co_3O_4 Layers	0.1 M $KHCO_3$	HCOOH	298	6.7	-0.88 V vs. SHE	0.68	0.681	60	40.6	(47)
47	Oxide-derived-Cu	0.1 M $KHCO_3$	HCOOH	298	6.7	-0.6 V vs. RHE	0.3	0.401	5	3.90	(50)
50	Sn	0.1 M $KHCO_3$	$HCOO^-$	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_2PO_4/0.1 M K_2HPO_4	HCOOH	298	6.7	-0.4 V vs. RHE	5	0.201	91.8	80.5	(59)
61	Pd/C	0.5 M $NaHCO_3$	$HCOO^-$	298	7.2	-0.35 V vs. RHE	3.45	0.151	88	79.6	(61)
65	Cu	0.1 M $KHCO_3$	HCOOH	298	6.8	-0.847 V vs. RHE	1	0.648	12.14	10.2	(63)
66	SnO_2	0.1 M $NaHCO_3$	HCOOH	298	6.7	-1.8 V vs. SHE	9.5	1.60	93	43.8	(64)
70	Cu nanoparticles	0.1 M $KHCO_3$	HCOOH	298	6.7	-1.1 V vs. RHE	23	0.901	5	3.06	(65)
74	SnO_x/Sn	0.1 M $KHCO_3$	$HCOO^-$	298	6.7	-1.36 V vs. RHE	17.1	1.16	71.6	39.5	(69)
83	Cu		$HCOO^-$			-1.44 V vs. RHE	5.0	1.24	9.4	5.03	
85	Au	0.1 M $KHCO_3$	$HCOO^-$	298	6.7	-1.14 V vs. RHE	5.0	0.94	0.7	0.422	(72)
87	Ag		$HCOO^-$			-1.37 V vs. RHE	5.0	1.17	0.8	0.439	
89	Zn		$HCOO^-$			-1.54 V vs. RHE	5.0	1.34	6.1	3.14	

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

(c) C_2H_4 production

No	Electrocatalyst	Electrolyte	Product	T / K	pH	E_{red}	i / mA cm^{-2}	η_C / V	ε_F / %	ε_{ec} / %	Ref.
5	CuO	0.1 M $KHCO_3$	C_2H_4	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 $KHCO_3$	C_2H_4	298	6.7	-2.3 V vs. RHE	7.5	2.77	91.1	29.8	(28)
27	Cu nanopartcles	Nafion	C_2H_4	298	7.3	-0.8 V vs. RHE	7.5	0.874	92.8	52.8	(33)
52	Cu nanocubes	0.1 M $KHCO_3$	C_2H_4	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 $KHCO_3$	C_2H_4	298	7.3	-0.90 V vs. RHE	7.7 A g^{-1}	0.979	19	10.3	(56)
59	Cu_2O	0.1 M $KHCO_3$	C_2H_4	298	6.7	-0.99 V vs. RHE	30	1.07	39	20.2	(60)
68	Cu nanoparticles	0.1 M $KHCO_3$	C_2H_4	298	6.7	-1.1 V vs. RHE	23	1.18	20	9.87	(65)
77	Cu	0.1 M $KHCO_3$	C_2H_4	298	6.7	-1.36 V vs. RHE	2.5	1.44	21.7	9.63	(71)
80	Cu	0.1 M $KHCO_3$	C_2H_4	298	6.7	-1.44 V vs. RHE	5.0	1.52	25.5	11.0	(72)

(d) CH_4 production

No	Electrocatalyst	Electrolyte	Product	T / K	pH	E_{red}	i / mA cm^{-2}	η_C / V	ε_F / %	ε_{ec} / %	Ref.
1	Pt black	Nafion	CH_4	313	-0.4	0.155 V vs. SHE	0.0023	0.0141	23.2	22.9	(13)
7	$Pt_{0.8}Ru_{0.2}/C$	Nafion	CH_4	313	-0.4	0.175 V vs. SHE	0.14	-0.0063	18.2	18.3	(18)
8	Pt/C	Nafion	CH_4	313	-0.4	0.135 V vs. SHE	0.06	0.0337	12.3	11.9	(19)
10	Pt/C	Nafion	CH_4	313	-0.4	0.075 V vs. SHE	11.8	0.0937	6.8	6.25	(20)
12	La_2CuO_4	1 M KOH	CH_4	298	9.6	-1.4 V vs. RHE	117	1.57	56.3	22.7	(22)
14	Pt/C	Nafion	CH_4	333	-0.4	0.134 V vs. SHE	18.2	0.0353	0.4	0.387	(24)
16	Zn/Ag foams	0.1 M $KHCO_3$	CH_4	298	6.7	-1.24 V vs. RHE	0.4	1.41	3.1	1.33	(26)
42	Cu nanopartcles	Nafion	CH_4	298	7.3	-1.6 V vs. RHE	7.5	1.77	12.1	4.53	(46)
48	Mo_2C	0.1 M $KHCO_3$	CH_4	298	6.7	-1.1 V vs. RHE	13.62	1.27	29	13.2	(51)
63	Cu	0.1 M $KHCO_3$	CH_4	298	6.8	-0.847 V vs. RHE	1	1.02	2.57	1.31	(63)

67	Cu nanoparticles	0.1 M $KHCO_3$	CH_4	298	6.7	-1.1 V vs. RHE	23	1.27	57	25.9	(65)
76	Cu	0.1 M $KHCO_3$	CH_4	298	6.7	-1.36 V vs. RHE	2.5	1.53	22.3	9.13	(71)
79	Cu	0.1 M $KHCO_3$	CH_4	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	