Supplementary Information

Copper-Based Metal-Organic Frameworks for CO_2 Reduction: Selectivity Trends, Design Paradigms, and Perspectives

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Table S1: CO_2RR Faradaic Efficiencies for Cu MOF and Cu MOF Composites.

Ref	Cu MOF	Cluster or Node-based[1]	Secondary Building Unit	Cu Oxidation State	Electrolyte	Cell Type	FE CO_2RR[2]	Reported Potential (V)	Scale	Total Current Density (mA cm^{-2})[3]	Evidence of In Situ Transformation[4]
1	CuAdeAce	cluster	$Cu_2(ade)_2(ace)_2$	NR*	0.5 M $KHCO_3$	Flow	1.2	–1.75	Ag/AgCl	10	Yes
1	HKUST-1	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	15.9	–0.9	Ag/AgCl	10	Yes
2	CuBi9	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	55	–0.36	RHE	20	No
2	CuBi12	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	66.3	–0.21	RHE	20	Yes
2	CuBi84	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	61	–0.34	RHE	20	No
2	Cu100	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	40	–0.59	RHE	20	Yes
3	Cu-BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	70	–1.35	RHE	120	Yes
3	NH_2-Cu–BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	75	–0.85	RHE	60	Yes
3	OH-Cu-BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	66	–1.01	RHE	60	Yes
3	F-Cu-BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	81	–1.21	RHE	90	Yes
3	2F-Cu-BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	79	–1.45	RHE	150	Yes
4	NNU-50	cluster	Cu_6MePz	NR*	1 M KOH	Flow	87.49	–0.6	RHE	54	No
5	CR-MOF	node	CuN_2S_2	NR*	0.5 M $KHCO_3$	H	30	–1.6	SHE	20.95	No
6	$Cu_3(HHTP)_2$	node	CuO_4	NR*	0.1 M $KHCO_3$	H	1.9	–0.3	RHE	0.5	No
6	$Cu_3(HHTQ)_2$	node	CuO_4	+2	0.1 M $KHCO_3$	H	53.6	–0.4	RHE	0.5	No
7	HATNA-Cu-MOF	node	CuO_4	+1, +2	0.1 M $KHCO_3$	H	81	–1.5	RHE	10.5	No
8	Cu-DBC	node	CuO_5	+1, +2	0.1 M $KHCO_3$	H	68	–1.4	RHE	11.4	No
9	Cu-THQ	node	CuO_4	+1, +2	1 M choline chloride + 1 M KOH	H	91	–0.43	RHE	173	No
10	$Cu_3(HHTP)_2$	node	CuO_4	NR*	$KHCO_3$	H	4.3	–0.64	RHE	NR*	No
10	CoPc-Cu-O	node	CuO_4	+1, +2	$KHCO_3$	H	85	–0.74	RHE	17.1	No
10	CoPc-Cu-NH	node	CuN_4	+1, +2	$KHCO_3$	H	72	–0.74	RHE	11.6	No

10	NiPc-Cu-O	node	CuO_4	+1, +2	$KHCO_3$	H	56	–0.74	RHE	7.3	Yes
10	NiPc-Cu-NH	node	CuN_4	+1, +2	$KHCO_3$	H	43	–0.74	RHE	6.1	No
10	Pc-Cu-O	node	CuO_4	+1, +2	$KHCO_3$	H	5.6	–0.74	RHE	7.5	Yes
10	Pc-Cu-NH	node	CuN_4	+1, +2	$KHCO_3$	H	4.5	–0.74	RHE	8	No
10	$Cu_3(HITP)_2$	node	CuN_4	NR*	$KHCO_3$	H	3.3	–0.74	RHE	n/a	No
11	HKUST-1	cluster	$Cu_2(COO)_4$	+2	1 M KOH	Flow	57	–1.08	RHE	NR*	Yes
11	HKUST-1 (thermally treated)	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	70	–1.07	RHE	262	Yes
12	PcCu-Cu-O	node	CuO_4	+1, +2	0.1 M $KHCO_3$	H	68	–1.4	RHE	7.8	No
12	PcCo-Cu-O	node	CuO_4	NR*	0.1 M $KHCO_3$	H	60	–1	RHE	NR*	No
12	Cu-HHTP	node	CuO_4	NR*	0.1 M $KHCO_3$	H	50	–1.2	RHE	NR*	No
13	HKUST-1	cluster	$Cu_2(COO)_4$	0, +1, +2	0.01 M TBATFB/DMF	3EC^	51	–2.5	Ag/Ag^+	NR*	No
14	Cu_2O@Cu-MOF	cluster	$Cu_2(COO)_4$	0, +1, +2	0.1 M $KHCO_3$	H	89.1	–1.71	RHE	13.29	Yes
14	Cu-MOF	cluster	$Cu_2(COO)_4$	+1, +2	0.1 M $KHCO_3$	H	49.7	–1.71	RHE	n/a	Yes
15	PCZ-2	cluster	$Cu_2(COO)_4$	0, +1, +2	0.1 M $KHCO_3$	H	95	–0.75	RHE	2.6	No
16	Cu-MOF-74	cluster	Cu-O-C rod	+1, +2	0.1 M $KHCO_3$	H	87	–1.8	SCE	4	No
17	CuO/Cu-MOF	cluster	$Cu_2(COO)_4$	+2	0.1 M $KHCO_3$	H	65	–1.1	RHE	14	Yes
17	Cu-MOF	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	49	–1.1	RHE	12.7	No
17	2Cl-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	40	–1.1	RHE	10	No
17	2Br-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	44	–1.1	RHE	10	No
17	2OH-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	6	–1.1	RHE	NR*	No
17	$2NH_2$-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	9	–1.1	RHE	NR*	No
17	NH_2-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	8	–1.1	RHE	NR*	No
18	PA-Cu-DBC-1	node	CuO_5	+2	0.5 M $KHCO_3$	H	96.5	–1.1	RHE	47	No
18	PA-Cu-DBC-2	node	CuO_5	+2	0.5 M $KHCO_3$	H	71	–1.1	RHE	36	No
18	Cu-DBC	node	CuO_5	+2	0.5 M $KHCO_3$	H	54	-1	RHE	16	No

19	$Cu_2(CuTCPP)$	cluster	$Cu_2(COO)_4$	+1, +2	$CH_3CN/H_2O/EMIMBF_4$	H	97.2	–1.55	Ag/Ag^+	5.1	Yes
20	H-CuTCPP@$Cu(OH)_2$	cluster	$Cu_2(COO)_4$	0, +1, +2	$CH_3CN/H_2O/EMIMBF_4$	H	56	–1.7	Ag/Ag^+	10	Yes
20	nH-CuTCPP@$Cu(OH)_2$	cluster	$Cu_2(COO)_4$	0, +1, +2	$CH_3CN/H_2O/EMIMBF_4$	H	53	–1.7	Ag/Ag^+	8	Yes
21	Cu1	node	CuN_2	+1, +2	0.1 M $KHCO_3$	H	77.5	–0.89	RHE	4.5	Yes
21	Cu2	node	CuN_4	NR*	0.1 M $KHCO_3$	H	64.6	–0.96	RHE	4.5	No
21	Cu3	node	CuN_4	NR*	0.1 M $KHCO_3$	H	50.5	–0.99	RHE	4.4	No
22	Cu_2O@Cu-HHTP	node	CuO_4	+1, +2	0.1 M KCl + 0.1 M $KHCO_3$	H	80	–1.4	RHE	14.8	Yes
22	Cu-HHTP	node	CuO_4	+2	0.1 M KCl + 0.1 M $KHCO_3$	H	20	–1.4	RHE	9.5	Yes
23	Cu-DBC	node	CuO_5	+1, +2	1 M KOH	Flow	86.5	–0.9	RHE	203	No
23	Cu-HHTP	node	CuO_4	NR*	1 M KOH	Flow	88.5	–0.9	RHE	190	No
24	Cu(111)@Cu-THQ	node	CuO_4	0, +1, +2	0.1 M $KHCO_3$	H	78.2	–1.2	RHE	8.2	No
25	Cu-HITP	node	CuN_4	+2	0.1 M $KHCO_3$	H	82	–1.2	RHE	NR	No
25	Cu-HITP@PDA	node	CuN_4	+2	0.1 M $KHCO_3$	H	87.15	–1.2	RHE	4.76	No
25	Cu-HITP@PANI	node	CuN_4	+2	0.1 M $KHCO_3$	H	88.5	–1.2	RHE	NR	No
25	Cu-HITP@PPV	node	CuN_4	+2	0.1 M $KHCO_3$	H	71	–1.2	RHE	NR	No
26	PcCu-O_8-Cu	node	CuO_4	NR*	0.1 M $KHCO_3$	H	10	–1.1	RHE	16	No
26	PcZn-O_8-Cu	node	CuO_4	NR*	0.1 M $KHCO_3$	H	10	–1.1	RHE	10	No
27	CPF	cluster	$Cu_2(COO)_4$	+2	0.1 M $KHCO_3$	H	81.57	–1.4	RHE	10.1	Yes
28	CuBDC	cluster	$Cu_2(COO)_4$	+2	0.1 M KI	H	67	–1.1	RHE	NR*	No
28	Cu_2BDC	cluster	$Cu_2(OH)_2(COO)_4$	+1, +2	0.1 M KI	H	65	–1.3	RHE	NR*	No
29	Cu_4^{II}-MFU-4l	cluster	Cu_4Zn	+1, +2	0.5 M $NaHCO_3$	H	98	–1.2	RHE	10.65	No
30	MAF-2E	cluster	Cu_2N_4	+1	0.1 M $KHCO_3$	H	75.9	–1.3	RHE	10.9	No
30	MAF-2ME	cluster	Cu_2N_4	+1	0.1 M $KHCO_3$	H	68.6	–1.2	RHE	9	No
30	MAF-2P	cluster	Cu_2N_4	+1	0.1 M $KHCO_3$	H	81	–1.4	RHE	13	No

† name used in original publication. See Supplementary Data File for alternative names. * not reported. ^ three-electrode single compartment cell

Table S2: >2e⁻ Product Faradaic Efficiencies for Cu MOF and Cu MOF Composites.

Ref	Cu MOF	Cluster or Node-based[1]	Secondary Building Unit	Cu Oxidation State	Electrolyte	Cell Type	FE >2e^{-2}	Reported Potential (V)	Scale	Total Current Density (mA cm^{-2})[3]	Evidence of In Situ Transformation[4]
1	CuAdeAce	cluster	$Cu_2(ade)_2(ace)_2$	NR*	0.5 M $KHCO_3$	Flow	1.2	–1.75	Ag/AgCl	10	Yes
1	HKUST-1	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	15.9	–0.9	Ag/AgCl	10	Yes
2	CuBi9	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	31	–0.36	RHE	20	No
2	CuBi12	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	42.3	–0.21	RHE	20	Yes
2	CuBi84	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	9	–0.34	RHE	20	No
2	Cu100	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	20	–0.59	RHE	20	Yes
3	Cu-BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	50	–1.35	RHE	120	Yes
3	NH_2-Cu–BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	46	–1.62	RHE	180	Yes
3	OH-Cu-BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	44	–1.71	RHE	180	Yes
3	F-Cu-BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	54	–1.77	RHE	180	Yes
3	2F-Cu-BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	69	–1.45	RHE	150	Yes
4	NNU-50	cluster	Cu_6MePz	NR*	1 M KOH	Flow	81.5	–1	RHE	398.02	No
5	CR-MOF	node	CuN_2S_2	NR*	0.5 M $KHCO_3$	H	0	–1.6	SHE	20.95	No
6	$Cu_3(HHTP)_2$	node	CuO_4	NR*	0.1 M $KHCO_3$	H	1.9	–0.3	RHE	0.5	No
6	$Cu_3(HHTQ)_2$	node	CuO_4	+2	0.1 M $KHCO_3$	H	53.6	–0.4	RHE	0.5	No
7	HATNA-Cu-MOF	node	CuO_4	+1, +2	0.1 M $KHCO_3$	H	80	–1.5	RHE	10.5	No
8	Cu-DBC	node	CuO_5	+1, +2	0.1 M $KHCO_3$	H	67	–1.4	RHE	11.4	No
9	Cu-THQ	node	CuO_4	+1, +2	1 M choline chloride + 1 M KOH	H	0	–0.43	RHE	173	No
10	$Cu_3(HHTP)_2$	node	CuO_4	NR*	$KHCO_3$	H	0	–0.64	RHE	NR*	No
10	CoPc-Cu-O	node	CuO_4	+1, +2	$KHCO_3$	H	0	–0.74	RHE	17.1	No
10	CoPc-Cu-NH	node	CuN_4	+1, +2	$KHCO_3$	H	0	–0.74	RHE	11.6	No

10	NiPc-Cu-O	node	CuO_4	+1, +2	$KHCO_3$	H	0	–0.74	RHE	7.3	Yes
10	NiPc-Cu-NH	node	CuN_4	+1, +2	$KHCO_3$	H	0	–0.74	RHE	6.1	No
10	Pc-Cu-O	node	CuO_4	+1, +2	$KHCO_3$	H	0	–0.74	RHE	7.5	Yes
10	Pc-Cu-NH	node	CuN_4	+1, +2	$KHCO_3$	H	0	–0.74	RHE	8	No
10	$Cu_3(HITP)_2$	node	CuN_4	NR*	$KHCO_3$	H	0	–0.74	RHE	n/a	No
11	HKUST-1	cluster	$Cu_2(COO)_4$	+2	1 M KOH	Flow	30	–1.08	RHE	NR*	Yes
11	HKUST-1 (thermally treated)	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	45	–1.07	RHE	262	Yes
12	PcCu-Cu-O	node	CuO_4	+1, +2	0.1 M $KHCO_3$	H	68	–1.4	RHE	7.8	No
12	PcCo-Cu-O	node	CuO_4	NR*	0.1 M $KHCO_3$	H	12	–1.2	RHE	NR*	No
12	Cu-HHTP	node	CuO_4	NR*	0.1 M $KHCO_3$	H	0	–1.2	RHE	NR*	No
13	HKUST-1	cluster	$Cu_2(COO)_4$	0, +1, +2	0.01 M TBATFB/DMF	3EC^	51	–2.5	Ag/Ag^+	NR*	No
14	Cu_2O@Cu-MOF	cluster	$Cu_2(COO)_4$	0, +1, +2	0.1 M $KHCO_3$	H	83.5	–1.71	RHE	13.29	Yes
14	Cu-MOF	cluster	$Cu_2(COO)_4$	+1, +2	0.1 M $KHCO_3$	H	49.7	–1.71	RHE	n/a	Yes
15	PCZ-2	cluster	$Cu_2(COO)_4$	0, +1, +2	0.1 M $KHCO_3$	H	0	–0.75	RHE	2.6	No
16	Cu-MOF-74	cluster	Cu-O-C rod	+1, +2	0.1 M $KHCO_3$	H	0	–1.8	SCE	4	No
17	CuO/Cu-MOF	cluster	$Cu_2(COO)_4$	+2	0.1 M $KHCO_3$	H	57	–1.1	RHE	14	Yes
17	Cu-MOF	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	40	–1.1	RHE	12.7	No
17	2Cl-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	26	–1.1	RHE	10	No
17	2Br-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	30	–1.1	RHE	10	No
17	2OH-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	4	–1.1	RHE	NR*	No
17	$2NH_2$-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	6	–1.1	RHE	NR*	No
17	NH_2-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	5	–1.1	RHE	NR*	No
18	PA-Cu-DBC-1	node	CuO_5	+2	0.5 M $KHCO_3$	H	82.4	–1.1	RHE	47	No
18	PA-Cu-DBC-2	node	CuO_5	+2	0.5 M $KHCO_3$	H	42	–1.1	RHE	36	No
18	Cu-DBC	node	CuO_5	+2	0.5 M $KHCO_3$	H	12	–1	RHE	16	No

19	$Cu_2(CuTCPP)$	cluster	$Cu_2(COO)_4$	+1, +2	$CH_3CN/H_2O/EMIMBF_4$	H	16.8	–1.55	Ag/Ag^+	5.1	Yes
20	H-CuTCPP@$Cu(OH)_2$	cluster	$Cu_2(COO)_4$	0, +1, +2	$CH_3CN/H_2O/EMIMBF_4$	H	26.1	–1.6	Ag/Ag^+	8	Yes
20	nH-CuTCPP@$Cu(OH)_2$	cluster	$Cu_2(COO)_4$	0, +1, +2	$CH_3CN/H_2O/EMIMBF_4$	H	19.8	–1.6	Ag/Ag^+	7	Yes
21	Cu1	node	CuN_2	+1, +2	0.1 M $KHCO_3$	H	0	–0.89	RHE	4.5	Yes
21	Cu2	node	CuN_4	NR*	0.1 M $KHCO_3$	H	0	–0.96	RHE	4.5	No
21	Cu3	node	CuN_4	NR*	0.1 M $KHCO_3$	H	0	–0.99	RHE	4.4	No
22	Cu_2O@Cu-HHTP	node	CuO_4	+1, +2	0.1 M KCl + 0.1 M $KHCO_3$	H	76	–1.4	RHE	14.8	Yes
22	Cu-HHTP	node	CuO_4	+2	0.1 M KCl + 0.1 M $KHCO_3$	H	0	–1.4	RHE	9.5	Yes
23	Cu-DBC	node	CuO_5	+1, +2	1 M KOH	Flow	86	–0.9	RHE	203	No
23	Cu-HHTP	node	CuO_4	NR*	1 M KOH	Flow	83.5	–0.9	RHE	190	No
24	Cu(111)@Cu-THQ	node	CuO_4	0, +1, +2	0.1 M $KHCO_3$	H	76.4	–1.6	RHE	21	No
25	Cu-HITP	node	CuN_4	NR*	0.1 M $KHCO_3$	H	62	–1.2	RHE	NR*	No
25	Cu-HITP@PDA	node	CuN_4	+2	0.1 M $KHCO_3$	H	79.85	–1.2	RHE	4.76	No
25	Cu-HITP@PANI	node	CuN_4	NR*	0.1 M $KHCO_3$	H	73.5	–1.2	RHE	NR*	No
25	Cu-HITP@PPV	node	CuN_4	NR*	0.1 M $KHCO_3$	H	58	–1.2	RHE	NR*	No
26	PcCu-O_8-Cu	node	CuO_4	NR*	0.1 M $KHCO_3$	H	0	–1.1	RHE	16	No
26	PcZn-O_8-Cu	node	CuO_4	NR*	0.1 M $KHCO_3$	H	0	–1.1	RHE	10	No
27	CPF	cluster	$Cu_2(COO)_4$	+2	0.1 M $KHCO_3$	H	73.57	–1.4	RHE	10.1	Yes
28	CuBDC	cluster	$Cu_2(COO)_4$	+2	0.1 M KI	H	31	–1.4	RHE	NR*	No
28	Cu_2BDC	cluster	$Cu_2(OH)_2(COO)_4$	+1, +2	0.1 M KI	H	48	–1.3	RHE	NR*	No
29	Cu_4^{II}-MFU-4l	cluster	Cu_4Zn	+1, +2	0.5 M $NaHCO_3$	H	92	–1.2	RHE	10.65	No
30	MAF-2E	cluster	Cu_2N_4	+1	0.1 M $KHCO_3$	H	70.7	–1.4	RHE	16	No
30	MAF-2ME	cluster	Cu_2N_4	+1	0.1 M $KHCO_3$	H	57.9	–1.5	RHE	17.5	No
30	MAF-2P	cluster	Cu_2N_4	+1	0.1 M $KHCO_3$	H	77.1	–1.5	RHE	14	No

† name used in original publication. See Supplementary Data File for alternative names. * not reported. ^ three-electrode single compartment cell

Table S3: C_{2+} Product Faradaic Efficiencies for Cu MOF and Cu MOF Composites.

Ref	Cu MOF	Cluster or Node-based[1]	Secondary Building Unit	Cu Oxidation State	Electrolyte	Cell Type	FE C_{2+} [2]	Reported Potential (V)	Scale	Total Current Density ($mA\ cm^{-2}$)[3]	Evidence of In Situ Transformation[4]
1	CuAdeAce	cluster	$Cu_2(ade)_2(ace)_2$	NR*	0.5 M $KHCO_3$	Flow	0.5	–1.75	Ag/AgCl	10	Yes
1	HKUST-1	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	10.3	–0.9	Ag/AgCl	10	Yes
2	CuBi9	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	21	–0.36	RHE	20	No
2	CuBi12	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	33.3	–0.21	RHE	20	Yes
2	CuBi84	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	3	–0.34	RHE	20	No
2	Cu100	cluster	$Cu_2(COO)_4$	NR*	0.5 M $KHCO_3$	Flow	18	–0.59	RHE	20	Yes
3	Cu-BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	42	–1.35	RHE	120	Yes
3	NH_2-Cu–BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	24	–1.38	RHE	150	Yes
3	OH-Cu-BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	29	–1.71	RHE	180	Yes
3	F-Cu-BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	47	–1.21	RHE	90	Yes
3	2F-Cu-BDC	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	63	–1.45	RHE	150	Yes
4	NNU-50	cluster	Cu_6MePz	NR*	1 M KOH	Flow	29.12	–0.8	RHE	183	No
5	CR-MOF	node	CuN_2S_2	NR*	0.5 M $KHCO_3$	H	0	–1.6	SHE	20.95	No
6	$Cu_3(HHTP)_2$	node	CuO_4	NR*	0.1 M $KHCO_3$	H	1.9	–0.3	RHE	0.5	No
6	$Cu_3(HHTQ)_2$	node	CuO_4	+2	0.1 M $KHCO_3$	H	53.6	–0.4	RHE	0.5	No
7	HATNA-Cu-MOF	node	CuO_4	+1, +2	0.1 M $KHCO_3$	H	8	–1.2	RHE	4.2	No
8	Cu-DBC	node	CuO_5	+1, +2	0.1 M $KHCO_3$	H	16	–1.2	RHE	5	No
9	Cu-THQ	node	CuO_4	+1, +2	1 M choline chloride + 1 M KOH	H	0	–0.43	RHE	173	No
10	$Cu_3(HHTP)_2$	node	CuO_4	NR*	$KHCO_3$	H	0	–0.64	RHE	NR*	No
10	CoPc-Cu-O	node	CuO_4	+1, +2	$KHCO_3$	H	0	–0.74	RHE	17.1	No
10	CoPc-Cu-NH	node	CuN_4	+1, +2	$KHCO_3$	H	0	–0.74	RHE	11.6	No

10	NiPc-Cu-O	node	CuO_4	+1, +2	$KHCO_3$	H	0	–0.74	RHE	7.3	Yes
10	NiPc-Cu-NH	node	CuN_4	+1, +2	$KHCO_3$	H	0	–0.74	RHE	6.1	No
10	Pc-Cu-O	node	CuO_4	+1, +2	$KHCO_3$	H	0	–0.74	RHE	7.5	Yes
10	Pc-Cu-NH	node	CuN_4	+1, +2	$KHCO_3$	H	0	–0.74	RHE	8	No
10	$Cu_3(HITP)_2$	node	CuN_4	NR*	$KHCO_3$	H	0	–0.74	RHE	n/a	No
11	HKUST-1	cluster	$Cu_2(COO)_4$	+2	1 M KOH	Flow	13	–1.08	RHE	NR*	Yes
11	HKUST-1 (thermally treated)	cluster	$Cu_2(COO)_4$	+1, +2	1 M KOH	Flow	45	–1.07	RHE	262	Yes
12	PcCu-Cu-O	node	CuO_4	+1, +2	0.1 M $KHCO_3$	H	50	–1.2	RHE	7.3	No
12	PcCo-Cu-O	node	CuO_4	NR*	0.1 M $KHCO_3$	H	0	–1	RHE	NR*	No
12	Cu-HHTP	node	CuO_4	NR*	0.1 M $KHCO_3$	H	0	–1.2	RHE	NR*	No
13	HKUST-1	cluster	$Cu_2(COO)_4$	0, +1, +2	0.01 M TBATFB/DMF	3EC^	51	–2.5	Ag/Ag^+	NR*	No
14	Cu_2O@Cu-MOF	cluster	$Cu_2(COO)_4$	0, +1, +2	0.1 M $KHCO_3$	H	35.4	–1.31	RHE	7	Yes
14	Cu-MOF	cluster	$Cu_2(COO)_4$	+1, +2	0.1 M $KHCO_3$	H	12.9	–1.71	RHE	n/a	Yes
15	PCZ-2	cluster	$Cu_2(COO)_4$	0, +1, +2	0.1 M $KHCO_3$	H	0	–0.75	RHE	2.6	No
16	Cu-MOF-74	cluster	Cu-O-C rod	+1, +2	0.1 M $KHCO_3$	H	0	–1.8	SCE	4	No
17	CuO/Cu-MOF	cluster	$Cu_2(COO)_4$	+2	0.1 M $KHCO_3$	H	50	–1.1	RHE	14	Yes
17	Cu-MOF	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	40	–1.1	RHE	12.7	No
17	2Cl-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	20	–1.1	RHE	10	No
17	2Br-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	30	–1.1	RHE	10	No
17	2OH-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	0	–1.1	RHE	NR*	No
17	$2NH_2$-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	3	–1.1	RHE	NR*	No
17	NH_2-Cu-BDC	cluster	$Cu_2(COO)_4$	NR*	0.1 M $KHCO_3$	H	2	–1.1	RHE	NR*	No
18	PA-Cu-DBC-1	node	CuO_5	+2	0.5 M $KHCO_3$	H	8	–1	RHE	36	No
18	PA-Cu-DBC-2	node	CuO_5	+2	0.5 M $KHCO_3$	H	11	–1.1	RHE	36	No
18	Cu-DBC	node	CuO_5	+2	0.5 M $KHCO_3$	H	2	–1	RHE	16	No

19	Cu_2(CuTCPP)	cluster	$Cu_2(COO)_4$	+1, +2	$CH_3CN/H_2O/EMIMBF_4$	H	16.8	–1.55	Ag/Ag^+	5.1	Yes
20	H-CuTCPP@$Cu(OH)_2$	cluster	$Cu_2(COO)_4$	0, +1, +2	$CH_3CN/H_2O/EMIMBF_4$	H	26.1	–1.6	Ag/Ag^+	8	Yes
20	nH-CuTCPP@$Cu(OH)_2$	cluster	$Cu_2(COO)_4$	0, +1, +2	$CH_3CN/H_2O/EMIMBF_4$	H	19.8	–1.6	Ag/Ag^+	7	Yes
21	Cu1	node	CuN_2	+1, +2	0.1 M $KHCO_3$	H	0	–0.89	RHE	4.5	Yes
21	Cu2	node	CuN_4	NR*	0.1 M $KHCO_3$	H	0	–0.96	RHE	4.5	No
21	Cu3	node	CuN_4	NR*	0.1 M $KHCO_3$	H	0	–0.99	RHE	4.4	No
22	Cu_2O@Cu-HHTP	node	CuO_4	+1, +2	0.1 M KCl + 0.1 M $KHCO_3$	H	3	–1.4	RHE	14.8	Yes
22	Cu-HHTP	node	CuO_4	+2	0.1 M KCl + 0.1 M $KHCO_3$	H	0	–1.4	RHE	9.5	Yes
23	Cu-DBC	node	CuO_5	+1, +2	1 M KOH	Flow	19	–0.7	RHE	65	No
23	Cu-HHTP	node	CuO_4	NR*	1 M KOH	Flow	42	–0.8	RHE	105	No
24	Cu(111)@Cu-THQ	node	CuO_4	0, +1, +2	0.1 M $KHCO_3$	H	44.2	–1.2	RHE	8.2	No
25	Cu-HITP	node	CuN_4	NR*	0.1 M $KHCO_3$	H	43	–1.2	RHE	NR*	No
25	Cu-HITP@PDA	node	CuN_4	+2	0.1 M $KHCO_3$	H	75.21	–1.2	RHE	4.76	No
25	Cu-HITP@PANI	node	CuN_4	NR*	0.1 M $KHCO_3$	H	60.5	–1.2	RHE	NR*	No
25	Cu-HITP@PPV	node	CuN_4	NR*	0.1 M $KHCO_3$	H	24	–1.2	RHE	NR*	No
26	PcCu-O_8-Cu	node	CuO_4	NR*	0.1 M $KHCO_3$	H	0	–1.1	RHE	16	No
26	PcZn-O_8-Cu	node	CuO_4	NR*	0.1 M $KHCO_3$	H	0	–1.1	RHE	10	No
27	CPF	cluster	$Cu_2(COO)_4$	+2	0.1 M $KHCO_3$	H	32	–1.1	RHE	2	Yes
28	CuBDC	cluster	$Cu_2(COO)_4$	+2	0.1 M KI	H	29	–1.4	RHE	NR*	No
28	Cu_2BDC	cluster	$Cu_2(OH)_2(COO)_4$	+1, +2	0.1 M KI	H	47	–1.3	RHE	NR*	No
29	Cu_4^{II}-MFU-4l	cluster	Cu_4Zn	+1, +2	0.5 M $NaHCO_3$	H	0	–1.2	RHE	10.65	No
30	MAF-2E	cluster	Cu_2N_4	+1	0.1 M $KHCO_3$	H	51.2	–1.3	RHE	10.9	No
30	MAF-2ME	cluster	Cu_2N_4	+1	0.1 M $KHCO_3$	H	47.7	–1.3	RHE	10.2	No
30	MAF-2P	cluster	Cu_2N_4	+1	0.1 M $KHCO_3$	H	35.7	–1.2	RHE	7.5	No

† name used in original publication. See Supplementary Data File for alternative names. * not reported. ^ three-electrode single compartment cell

Tables S1 to S3 show the raw CO_2RR data used to generate Figures 14 and 17 in the main text. Note that to facilitate comparison, the tabulated potentials were converted from their reported values to the reversible hydrogen electrode using the following equations.

$$E_{RHE} = E_{Ag/AgCl} + 0.196\text{ V} + 0.0591\text{ V} \times \text{pH} \quad (1)$$

$$= E_{Ag/Ag^+} + 0.503\text{ V} + 0.0591\text{ V} \times \text{pH} \quad (2)$$

$$= E_{SHE} + 0.0591\text{ V} \times \text{pH} \quad (3)$$

$$= E_{SCE} + 0.241\text{ V} + 0.0591\text{ V} \times \text{pH} \quad (4)$$

Regarding (2), note that the Ag/Ag^+ couple refers to the reference electrode comprised of non-aqueous 10 mM $AgNO_3$ in acetonitrile. The value of 0.503 V is obtained from Coetzee and Campion.[31]

Finally, the numbered points below correspond to the superscripts in the tables.

1. If the secondary building unit features more than one metal atom, it is classified as cluster-based; otherwise, the secondary building unit is classified as node-based.
2. The listed faradaic efficiencies are based on values reported in the text or data tables of the original publication, where available; otherwise, the listed faradaic efficiencies are extracted from graphs.
3. Based on geometric area. The listed current densities are based on values reported in the text or data tables of the original publication, where available; otherwise, the listed current densities are extracted from graphs.
4. Evidence of an in situ transformation is classified as:
    - observed differences in Cu MOF properties between ex situ characterizations (e.g., XPS, XRD, SEM) before and after reaction
    - observed differences in Cu MOF properties between operando/in situ and ex situ characterizations (e.g., XPS, XRD, SEM)
    - periods of unstable CO_2RR performance (e.g., faradaic efficiency, current density, voltage) in chronoamperometric or galvanostatic measurements

Note that the purpose of this entry is to illustrate the dynamic nature of Cu MOF properties under CO_2RR conditions. That is, an entry of “Yes” or “No” is not intended to indicate the stability of a given Cu MOF. For example, an entry of “Yes” may be due to XPS measurements which indicate an increase in the Cu(I)/Cu(II) ratio; in general, this may or may not indicate the formation of a Cu_2O phase. Conversely, a study without post-reaction characterization or chronoamperometric measurements would receive an entry of “No” despite the unaddressed possibility of electrochemical reconstruction.

Data Aggregation Methodology

In tabulating the number of unique Cu MOFs with >$2e^-$ or C_{2+} product formation for Figures 14 and 17, we have excluded duplicate entries as follows. In the case of multiple reports of a Cu MOF with no explicit modifications to the Cu MOF itself, only one entry has been added to the total. Thus, the same Cu MOF under different reaction conditions was not considered as a unique instance of >$2e^-$ or C_{2+} product formation by that Cu MOF. Additionally, we have excluded reports of Cu MOF composite systems wherein the as-synthesized catalyst consists of a copper, copper oxide, or copper hydroxide phase or a non-copper-based MOF material (e.g., Bi-based MOF CAU-17 or PDA-functionalized Cu-HITP). In addition to all the data for Tables S1, S2, and S3, the Supplementary Data File contains the following details for each Cu MOF included in the study:

- alternative names used to refer to identical Cu MOFs
- the ligand constituting the Cu MOF
- the copper coordination geometry (excluding solvent molecules)
- the atoms directly bonded to copper ("Cu linking atoms")
- the presence of other transition metals in the Cu MOF catalyst ("Other TMs")
- the conductive additives used in preparing the electrode (e.g., carbon nanotubes)
- the method by which the Cu MOF is applied to the electrode (e.g., spray coating)
- faradaic efficiencies for all CO_2RR products observed under the conditions of highest CO_2RR, >$2e^-$, and C_{2+} product formation
- whether or not the reported potentials were iR corrected

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