Supplementary Information (SI) for EES Catalysis.

Supporting information for 'Identification of catalyst optimization trends for electrocatalytic $CO_{(2)}$ reduction to ethylene'

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1. Dataset origins

The electrocatalysts described in this manuscript were obtained through various means over the course of ca. 2 years, including i) a very broad search term in SCOPUS, ii) going through various review articles regarding CO2RR electrocatalysts[1-83], iii) cross-referencing relevant publications for new citations and iv) catalyst summaries provided in the supporting information of numerous publications. For metallic copper and oxide-derived copper, we only included catalysts where the maximum C_2H_4 faradaic efficiency (FE) was ≥40%. For bi-elemental and multi-elemental catalysts, we decreased this selection criterium to catalysts making (approximately) ≥25% C_2H_4 to increase the likelihood of obtaining a statistically relevant quantity of sources on a per-element basis for those systems. Photocatalysts and pulse-operated catalysts were omitted from this work on account of us not having sufficient expertise in the field of photocatalysis, and pulsed operation representing dynamic catalyst conditions that cannot (in our opinion) be meaningfully compared to static (non-pulsed) operating conditions. However, we acknowledge that pulsing is a viable C_2H_4 improvement strategy[84-88] with various systems having been reported with high C_2H_4 selectivity[89-91], and refer the reader to reviews dedicated to this topic.[92] Throughout this SI, high performance will be used interchangeably with high selectivity. Finally, although we have opted to include alkaline CO_2 systems in our summary tables on account of their ubiquity in literature, we exclude these catalysts from our analysis whenever we feel the sample size is sufficient without these systems. We have opted for this approach because i) the pH effect[93] cannot realistically be deconvoluted from inherent catalytic activity and ii) the industrial irrelevance of such systems on account of the costs associated with maintaining a local alkaline pH in the presence of acidic CO_2.[94]

Faradaic efficiencies, current densities and voltages were preferentially extracted from tables provided in either the main manuscript or the supporting information, or alternatively from numbers provided in the text. If both are available, preference is given to tabulated values. If the sum of faradaic efficiencies in a table is significantly higher than 100%, the maximum C_2H_4 FE for a condition where the total FE is closer to 100% is reported instead. If no tabulated/written information was available, values were extracted through image analysis. If only a single electrolyte is stated, it is assumed that both anolyte and catholyte are of the same composition (if it concerns a cell configuration that has both anolyte and catholyte). If a range of current densities are given, the average is reported herein. Ambient conditions are taken to be standard temperature and pressure, which we report as 25 °C and 1 atm. If a cell is labeled as a 'flow cell', it is assumed that the electrolyte(s) is (are) actively circulated even if not specified in text. Nafion membranes are categorized as cation-exchange membranes (CEMs), even in such cases where the authors refer to it differently (e.g., anion-exchange membranes etc.). Footnotes have been added for those situations where we did not follow these rules or where we believe clarification to be necessary. For bi-elemental catalyst systems (excluding Cu/C systems) we tabulate a catalyst category, wherein we provide a description that we believe best suits the morphology of the catalyst. The following categories were identified over the course of this study: i) single atom-type, ii) alloyed/doped-type, iii) atomically-mixed/crystalline-type, iv) core/shell-type, v) mixed-phase/janus-type, vi) A-supports-B type and vii) overlayer-type systems.

Single atom-type catalysts have morphologies where one component is present in such a low quantity that no chemical bonds exist between two atoms of that component. Alloyed/doped-type catalysts have morphologies where one component can be considered to be dissolved into another component, but need not be homogeneously distributed throughout the system. Catalyst of the atomically-mixed/crystalline-type have morphologies where the catalyst forms a stable phase with a specific stoichiometry than can be observed via e.g., XRD. Core/shell-type catalysts consist of systems where a particle acts as a core and is fully surrounded by a second component. The surrounding layer is assumed to fully coat the surface of the core particle. Then we have the more generic mixed-phase/janus-type category which consists of catalysts where multiple phases are intermixed. If mixed phases exist, and one component is substantially larger than the other component and they are attached to one-another then we consider the catalyst to be of the A-supports-B type. Finally, if multiple catalyst layers with different components were sequentially deposited, we consider the catalyst system to be of the overlayer-type. Depending on the circumstances, a catalyst system can belong to multiple of these categories.

2. Dataset description

2.1. Metallic and oxide-derived Cu

2.1.1. Metallic copper

A summary of best-performing metallic copper catalysts is provided in Table S1. The metallic copper catalyst dataset is derived from 49 unique publications and comprises a total of 56 catalyst systems, with 15 using CO as a reactant and 15 having been identified as alkaline CO_2 systems. A total of 21 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55%, though 11 of those are reported under alkaline CO_2 reduction reaction (CO2RR) conditions. In our analysis, we will exclude such alkaline CO2RR systems, resulting in a final sample size of 41 catalysts. This number of catalysts is somewhat smaller than we would have initially expected, though it can be explained by realizing that we consider metallic copper to be different from oxide derived copper. As can be seen in Table S1, a maximum C_2H_4 FE of ca. 50%-60% can be reliably achieved on metallic copper catalysts using either CO_2 or CO as a reactant, with outliers yielding 77%[95] and (reportedly) 93%[96]. The fact that both CO and CO_2 reactants are present at the top-end of the spectrum serves to validate our decision to investigate both molecules as a potential feedstock from a catalyst perspective. Importantly, most of the high-performance catalysts have been shown to work under current densities >|-100| mA/cm^2, though this is not true for the two outliers. This observation is rather promising from an industrial perspective. However, we feel it is pertinent to point out that the metallic copper catalyst dataset is highly skewed, with a large proportion of metallic copper catalysts consisting of (arguably nearly identical) sputter-deposited Cu systems. As such, the number of unique catalysts is significantly smaller than the size of the table implies.

Table S1. Metallic Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	Commercial 70 nm Cu NPs with chitosan bio-based polymeric binder, on Toray TGP-H-60 GDL	Metallic Cu	Cu	Chitosan	(Gas-phase reactant, supplied from behind)	-	Sustainion X-37 50 grade	CO_2	-0.53 V vs. RHE	-10 mA/cm^2	94	[97]
2	Commercial Cu NPs (25 nm), on a GDL with custom MPL, hotpressed onto a Nafion membrane	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	-	Nafion 117	CO_2	-1.7 V vs. Ag/AgCl	-7.5 mA/cm^2	93	[96]
3	60 nm step site-rich Cu NPs blow-dried with Ar, on GDL	Metallic Cu	Cu	Sustainion XA-9	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAA-3-PK-75	CO_2	-0.58 V - iR vs. RHE	-710 mA/cm^2	80	[98]
4	CO_2RR pre-activated defective Cu NWs, on glassy carbon (tested in semi-pulsed electrolysis mode)	Metallic Cu	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion	CO_2	-1.01 V - iR vs. RHE	-22 mA/cm^2	77	[95]
5	Right bipyramidal (100)-rich Cu NPs with stacking faults, on GDL	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-75	CO_2	-0.63 V - iR vs. RHE	-325 mA/cm^2	67	[99]
6	Metallic Cu NPs mixed with PTFE, dropcast on GDL	Metallic Cu	Cu	Nafion, PTFE	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	Selemion DSVN	CO	-1.38 V - iR vs. RHE	-600 mA/cm^2	67	[100]
7	25 nm-thick Cu layer, evaporated on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	10 M KOH	Fumasep FAB-PK-130	CO_2	-0.54 V - iR vs. RHE	-275 mA/cm^2	66	[101]
8	25 nm-thick Cu layer, evaporated on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	5.5 M KOH + 4 M KI	Fumasep FAB-PK-130	CO_2	-0.62 V - iR vs. RHE	-500 mA/cm^2	65	[101]
9	Ultrasonically detached N2 atmosphere/high current density-electroplated Cu dendrites, on GDL	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	? (X37–50 Grade 60)	CO_2	-1.24 V vs. RHE	-37 mA/cm^2	60	[102]
10	(100)-rich Cu NCs, on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAB-PK-130	CO_2	-0.70 V - iR vs. RHE	-200 mA/cm^2	60	[103]
11	Cu NCs, on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	10.0 M KOH	Fumasep FAB-PK-130	CO_2	-0.47 V - iR vs. RHE	-75 mA/cm^2	60	[104]
12	Metallic Cu NPs, on GDL	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	NEOSEPTA, AHA	CO	-0.69 V - iR vs. RHE	?	60	[105]
13	Cu NPs, on GDL	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	2.5 M Kac (pH 8.6)	FAA-3-50	CO_2	-0.99 V - iR vs. RHE	-1250 mA/cm^2	59	[106]
14	Cu NWs after 15 h synthesis, on GDL	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-1.08 V vs. RHE	-123 mA/cm^2	59	[107]
15	Ultrasonically detached N2 atmosphere/high current density-electroplated Cu dendrites, on GDL	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	-	X37–50 Grade 60	CO_2	-1.0 V vs. RHE	-134 mA/cm^2	58	[102]
16	Cu nanorods (control sample), on GDL (poorly described synthesis, inaccurate reference)	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumapem FAA-3-PK-130	CO_2	-0.59 V - iR vs. RHE	?	57	[108]
17	Commercial Cu NPs, on GDL	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Sustainion, X37-50 Grade T	CO	?	-150 mA/cm^2	56	[109]
18	Commercial Cu NPs (100 nm), on GDL	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAA-PK-130	CO	-0.69 V - iR vs. RHE	-934 mA/cm^2	56	[110]
19	1000 nm-thick Cu layer, sputtered on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	"Fumasep"	CO_2	-4.23 V vs. Ag/AgCl	-250 mA/cm^2	56	[111]
20	Cu electrosputtered on electrospun PVDF-HFP-based GDL with 0.2 µm pore size	Metallic Cu	Cu	poly-(vinyliden-fluoride-co-hexafluorpropylene)	(Gas-phase reactant, supplied from behind)	1.0 M KCl	Nafion 117	CO_2	-1 V - iR vs. RHE	-200 mA/cm^2	55	[112]
21	25 nm-thick Cu layer, evaporated on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	5.38 M NaClO4	Nafion 117	CO_2	-0.88 V - iR vs. RHE	-106 mA/cm^2	55	[113]
22	In-house metallic Cu NPs, on mesoporous carbon/PTFE-modified carbon paper	Metallic Cu	Cu	Nafion	(Solution-phase reactant, supplied in front)	1.0 M KOH (pH 14)	?	CO	-0.70 V vs. RHE	-22 mA/cm^2	53	[114]
23	Cu layer sporting 50-80 nm Cu NPs, sputtered on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH + 0.2 M CsI	Fumasep FKS-50	CO_2	-0.63 V - iR vs. RHE	-247 mA/cm^2	53	[115]
24	Commercial Cu NPs (60-80 nm), on GDL	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0M KHCO3	Nafion 117	CO	?	-300 mA/cm^2	52	[116]
25	(100)-rich Cu NCs, on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	1.2 M KCl	Fumasep FAB-PK-130	CO_2	-0.80 V - iR vs. RHE	-200 mA/cm^2	52	[103]
26	Electropolished (i.e., defective) Cu(911) single crystal	Metallic Cu	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	-	CO_2	-1.36 V vs. RHE	-5 mA/cm^2	51	[117]
27	Star decahedron-shaped 30 nm Cu NPs, on glassy carbon RDE	Metallic Cu	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	?	CO_2	-0.98 V - iR vs. RHE	-17 mA/cm^2	51	[118]
28	275 nm-thick Cu layer, evaporated on e-PTFE GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	"Sustanion"	CO_2	-0.96 V - iR vs. RHE	-214 mA/cm^2	51	[119]
29	EDTA-assisted electrodeposited hollow porous copper microspheres, on carbon paper	Metallic Cu	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-0.82 V - iR vs. RHE	-8 mA/cm^2	50	[120]
30	60 nm step site-rich Cu NPs blow-dried with Ar, on GDL (6-cell stack)	Metallic Cu	Cu	Sustainion XA-9	(Gas-phase reactant, supplied from behind)	-	Home-made BPM	CO_2	-4.35 V vs. ANODE	-56 mA/cm^2	50	[98]
31	Mechanically polished and electropolished (i.e., defective) Cu(100) single crystal	Metallic Cu	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KI (pH 3.8)	Selemion CMV	CO_2	-1.18 V - iR vs. RHE	-7 mA/cm^2	49†–metallic,1	[121]
32	Electropolished Cu plate	Metallic Cu	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KClO4	"Selemion"	CO_2	-1.40 V - iR vs. NHE	-5 mA/cm^2	48	[122]
33	Electropolished Cu plate	Metallic Cu	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KCl	"Selemion"	CO_2	-1.44 V - iR vs. SHE	-5 mA/cm^2	48	[123]
34	Commercial metallic Cu NWs, on GDL	Metallic Cu	Cu	?	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO	-0.7 V vs. RHE	-92 mA/cm^2	48	[124]
35	Cu sputtered on PTFE GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	-	X37-50 Grade RT	CO	-2.2 V vs. ANODE	-25 mA/cm^2	48	[125]
36	Cu NPs (25 nm, Sigma Aldrich), on carbon paper GDL	Metallic Cu	Cu	LSC-D520 (Dupont, D-	(Gas-phase reactant,	-	Sustainion	CO_2	-3.69 V	-350	48	[126]

				520 = Nafion)	supplied from behind)		X37-50 Grade RT		vs. ANODE	mA/cm^2		
37	Commercial Cu NPs, on GDL	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FKB-PK-130	CO	-0.67 V - iR vs. RHE	-500 mA/cm^2	47	[127]
38	Commercial 50 nm Cu NPs, on GDL	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3 (CO atmosphere)	Nafion 117	CO	-1.04 V - iR vs. RHE	-300 mA/cm^2	46	[128]
39	Cu-sputtered on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-130	CO	-0.8 V vs. RHE	-93 mA/cm^2	46	[129]
40	Electropolished (i.e., defective) Cu(100) single crystal	Metallic Cu	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV	CO_2	-1.0 V vs. RHE	?	45	[86]
41	Cu overlayer sputtered on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	Fumasep FAA-3-PK-75	CO_2	-1.61 V - iR vs. SHE	-300 mA/cm^2	45	[130]
42	Magnetron sputtered Cu layer on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	0.5 M KOH	Fumasep FAA-3-PK-75	CO	-1.44 V - iR vs. SHE	-100 mA/cm^2	45	[131]
43	Cu electrosputtered on electrospun PVDF-HFP-based GDL with 0.2 µm pore size	Metallic Cu	Cu	poly-(vinyliden-fluoride-co-hexafluorpropylene)	(Gas-phase reactant, supplied from behind)	1.0 M KCl	Nafion 117	CO	?	-30 mA/cm^2	44	[112]
44	Commercial Cu NPs (25 nm) mixed with PTFE, on GDL	Metallic Cu	Cu	PTFE	(Gas-phase reactant, supplied from behind)	1.0 M KOH	"Sustanion"	CO	-0.60 V vs. RHE	-600 mA/cm^2	44	[132]
45	Metallic Cu layer, evaporated on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAA-PK-130)	CO	-0.64 V - iR vs. RHE	?	43	[133]
46	60 nm step site-rich Cu NPs blow-dried with Ar, on GDL	Metallic Cu	Cu	Sustainion XA-9	(Gas-phase reactant, supplied from behind)	-	Home-made BPM	CO_2	-4.3 V vs. ANODE	-300 mA/cm^2	43	[98]
47	In-house Cu NPs, on GDL	Metallic Cu	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-130,	CO	-0.88 V - iR vs. RHE	-818 mA/cm^2	43	[134]
48	Oleylamine-stabilized Cu-NWs on glassy carbon, cleaned (ligand removal) via photonic curing method	Metallic Cu	Cu	-	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.1 V - iR vs. RHE	-19 mA/cm^2	42	[135]
49	44 nm Cu NCs, on glassy carbon	Metallic Cu	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV	CO_2	-1.1 V vs. RHE	-3 mA/cm^2	41	[136]
50	Magnetron sputtered Cu layer (100 nm) on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	Nafion 212	CO_2	-3.4 V vs. RHE	-200 mA/cm^2	40	[137]
51	Cu(100) crystal prepared via PVD of Cu on Si(100) crystal	Metallic Cu	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Selemion AMV	CO_2	-0.97 V - iR vs. RHE	-4 mA/cm^2	39	[138]
52	Cu (400 nm) sputtered on a GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-50	CO_2	-0.69 V - iR vs. RHE	-200 mA/cm^2	38	[139]
53	Electrochemically polished Cu foil	Metallic Cu	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KOH	Selemion AMV	CO	-0.68 V vs. RHE	-1.4 mA/cm^2	38	[140]
54	Well-defined porous copper layer with controlled pore size (30 nm), depth (40 nm) and interspacing, on stainless steel	Metallic Cu	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV	CO_2	-1.7 V - iR vs. RHE	-15 mA/cm^2	37	[141]
55	Cu layer magnetron-sputtered on GDL	Metallic Cu	Cu	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-1.17 V vs. RHE	-222 mA/cm^2	37	[142]
56	60 nm step site-rich Cu NPs blow-dried with Ar, on GDL	Metallic Cu	Cu	Sustainion XA-9	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAA-3-PK-75	CO	-0.43 V - iR vs. RHE	-67 mA/cm^2	29	[98]
	[†_metallic,1]We report here the highest C2H4 value with a total FE close to 100% (being 49 % as opposed to 50 %)											

2.1.2. Oxide-derived copper

As a follow-up of metallic copper, we now address 'oxide-derived' copper systems. Herein, oxide-derived copper is liberally interpreted as including copper paired with any of the following elements: Li, Na, K, Rb, Cs, N, O, P, S, F, Cl, Br and/or I. We have decided on this grouping because all these catalysts share the same property, namely that one would expect these types of catalysts to reconstruct into (defective) metallic copper because of thermodynamic considerations, although this is not universally agreed upon by the community. Possibly more agreeable would be to state that these catalysts all share the property that they contain many undercoordinated, catalytically active sites such as e.g., kink sites, step sites, oxygen vacancies, defect sites etc.

Assuming herein that these oxide-derived copper systems typically reconstruct into defective metallic copper under CO2RR conditions, we consider it most logical to compare oxide-derived catalysts to metallic copper catalysts. A summary of best-performing oxide-derived catalysts for C_2H_4 production is given in Table S2. The oxide-derived copper catalyst dataset is derived from 134 unique publications and comprises a total of 157 catalyst systems, with 23 using CO as a reactant and 60 having been identified as alkaline CO_2 systems. A total of 83 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55%, though 37 of those were measured under alkaline CO2RR conditions. In our analysis, we will exclude such alkaline CO2RR systems, resulting in a total remaining sample size of 97 catalysts. Contrary to the size of the metallic Cu catalysts table, the quantity of oxide-derived catalysts matches better with expectations. Maximum C_2H_4 FEs for high performance oxide-derived catalysts are reliably observed in the 60%-70% range, with both CO and CO_2 reactants being well-represented. Outliers sporting maximum C_2H_4 FEs of 76%[143] and 78%[144], 83%[145] and 85%[146] are observed, with CO being used as a reactant for the catalysts yielding 76% and 78% C_2H_4. Regarding applied current densities, we find that most high-selectivity oxide-derived catalysts were measured at $<|-50|$ mA/cm^2. Thus, when we compare oxide-derived copper catalysts to metallic copper catalysts, we find that oxide-derived copper yields higher C_2H_4 FEs for top-performing systems (ca +10% in absolute terms), but at overall lower current densities. Both show a 'healthy' mix of CO and CO_2 being used as reactants (ca 1:1 ratio) for the high-performance segment, although we should clarify that this is only true because we specifically exclude alkaline CO2RR conditions in our analysis.

Having formed an informed opinion on what copper by itself is capable of, we now discuss catalyst systems where copper is paired with a second element; bi-elemental systems (Cu/M). We have opted to describe reported catalysts on a per-element basis, where we have grouped elements with similar behavior together. Importantly, as the sample sizes for the multi-elemental systems are too limited on a per-element basis for Cu/M systems we have opted to include alkaline CO2RR conditions in our analysis of these catalyst systems unless stated otherwise.

	Table S2. Oxide-derived Cu											
#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	Template-assisted electroplated nanoporous (20 nm pore diameter) CuOx overlayer on Cu foam	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	-	X37-50 Grade 60	CO_2	-3.0 V vs. ANODE	-368 mA/cm^2	86	147
2	Amorphous CuOx film evaporation-deposited on GDL	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	"Nafion"	CO_2	-1.3 V - iR vs. RHE	-32 mA/cm^2	85	146
3	KOH anodization-derived CuO nanoplate on Cu-sputtered GDL	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-50	CO_2	-0.81 V - iR vs. RHE	-100 mA/cm^2	84	148
4	Defective CuO-derived Cu nanosheets, on glassy carbon	Oxide-derived	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M K2SO4	Nafion 117	CO_2	-1.18 V - iR vs. RHE	-60 mA/cm^2	83	145
5	Pre-reduced, CuO-derived Cu quantum dots (5 nm), on a GDL	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-75	CO_2	-0.93 V -iR vs. RHE	-1100 mA/cm^2	82	149
6	Calcined (in Al foil!) electroplated Cu dendrites, on GDL	Oxide-derived	Cu, O, Al (?)	Nafion	(Gas-phase reactant, supplied from behind)	3.0 M KOH	Sustainion X37-50 Grade T	CO	?	-100 mA/cm^2	78	144
7	Amorphous CuOx film evaporation-deposited on GDL	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	-	FBAPK-13	CO_2	-1.75 V vs. ANODE	-113 mA/cm^2	78	146
8	Porous Cu2O microparticles, on PTFE-modified GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KCl + x M H2SO4 (pH 1.9)	Nafion 115	CO	?	-800 mA/cm^2	76	143
9	Defect-rich CuO NRs (800 nm) with HCOO- induced pores, on a GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	2.0 M KOH	Nafion 117	CO_2	-0.8 V -iR vs. RHE	-144 mA/cm^2	75	150
10	Star shaped (322)-rich Cu2O large NPs, on glassy carbon	Oxide-derived	Cu, O	Nafion D-521	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion	CO_2	-1.2 V vs. RHE	-11 mA/cm^2	74	151
11	N-doped CuOx NPs derived from calcination of Cu(OH)3NO3 precursor at 350 °C, on GDL	Oxide-derived	Cu, O, N	Nafion	(Gas-phase reactant, supplied from behind)	1 M KOH (pH 14)	Fumasep-FAA-3-PK-130	CO_2	-1.09 V - iR vs. RHE	-962$^{\dagger\_oxidic,2}$ mA/cm2	73	152
12	(220)-facet rich CuI nanodots (5.3 nm) prepared via in-situ reduction of (Cu(OH)2) NPs on carbon paper GDL in 0.1 M KHCO3 + 0.1 M KI	Oxide-derived	Cu, O, I	Nafion	(Gas-phase reactant, supplied from behind)	0.5 M KHCO3 + 0.5 M KI	FAA-3-PK -130	CO_2	-2.1 V vs. RHE	-800 mA/cm^2	72	153
13	Grainboundary-rich Cu2CO3(OH)2-derived Cu nanoribbons with Carbon NP midlayer and graphite toplayer, on PTFE GDL	Oxide-derived	Cu, O, C	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumapem FAA-3-PK-130	CO_2	-1.6 V vs. RHE	-700 mA/cm^2	71	154
14	Cu2O NCs on GDL, electrochemically pre-activated via in-situ reduction in the presence of CO_2	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Sustainion® X37-50 grade RT	CO_2	-0.6 V vs. RHE	-207 mA/cm^2	71	155
15	Defect-rich CuO NRs (800 nm) with HCOO- induced pores, on a GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	3.0 M KCl	Nafion 117	CO_2	-1.07 V -iR vs. RHE	-312 mA/cm^2	71	150
16	Sputtered Cu with Carbon NP midlayer and graphite toplayer, on PTFE GDL	Oxide-derived	Cu, C	-	(Gas-phase reactant, supplied from behind)	7.0 M KOH	Fumasep FAB-PK-130	CO_2	-0.57 V - iR vs. RHE	-100 mA/cm^2	70	156
17	Cu3(PO4)2 particles, on glassy carbon	Oxide-derived	Cu, O, P	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.45 V vs. RHE	-23 mA/cm^2	70	157
18	Iodine-doped copper oxychloride NPs, on glassy carbon	Oxide-derived	Cu, O, Cl, I	Nafion	(Solution-phase reactant, supplied in front)	0.05 M KHCO3	-	CO_2	-1.71 V vs. RHE	-29 mA/cm^2	70	158
19	Wet-chemical induced (NaOH / (NH4)2S2O8) high roughness nanoporous CuOx layer on Cu plate	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	1.0 M KOH	"Nafion"	CO	-0.8 V vs. RHE	-130 mA/cm^2	70	159
20	Template-assisted electroplated nanoporous (20 nm pore diameter) CuOx overlayer on Cu plate	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-0.99 V vs. RHE	-63 mA/cm^2	70	147
21	80-100 nm Cu2−xS NPs, on glassy carbon	Oxide-derived	Cu, S	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.2 V vs. RHE	-51 mA/cm^2	69	160
22	Cu nanoneedles electrodeposited on Cu-sputtered PTFE GDL	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	3.0 M KCl + x mM HCl (pH 1)	Nafion 117	CO_2	-2 V -iR vs. RHE	-1200 mA/cm^2	69	161
23	Branched/'spikey' CuO NPs derived from NH3-treated Cu2O NCs supported on Ketjen black, on on glassy carbon	Oxide-derived	Cu, O, C	Nafion (top-coat)	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.05 V -iR vs. RHE	-26 mA/cm^2	68	162
24	Calcined (in Al foil!) electroplated Cu dendrites, on GDL	Oxide-derived	Cu, O, Al (?)	Nafion	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-59 Grade 60	CO	-3.1 V vs. ANODE	-100 mA/cm^2	68	163
25	Electrochemical-assisted iodine-reconstructed Cu foil	Oxide-derived	Cu, O, I	-	(Solution-phase reactant, supplied in front)	1.0 M KOH (pH 14)	Nafion 117	CO	-0.56 V vs. RHE	-8 mA/cm^2	68	164
26	Cu3(PO4)2-derived Cu NPs on glassy carbon	Oxide-derived	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.48 V vs. RHE	-33 mA/cm^2	67	165
27	Grainboundary-rich Cu2CO3(OH)2-derived Cu nanoribbons, on carbon paper	Oxide-derived	Cu, O, C	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumapem FAA-3-PK-130	CO_2	-1.27 V vs. RHE	-700 mA/cm^2	67	154
28	(111)-facet rich octahedral Cu2O NPs supported on hydroxl-rich acetylene black carbon, on glassy carbon	Oxide-derived	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	?	CO_2	-1.1 V vs. RHE	-67 mA/cm^2	67	166
29	Electroplated (1 C/cm2) Cu2O from lactic-acid containing bath, on GDL	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	1 M KOH (pH 14)	-	CO_2	-0.8 V vs. RHE	-183 mA/cm^2	67	167
30	25 nm-thick Cu layer, evaporated on GDL	Oxide-derived	Cu	-	(Gas-phase reactant, supplied from behind)	10.0 M KOH	Fumasep FAB-PK-130	CO_2	-0.54 V - iR vs. RHE	-275 mA/cm^2	66	156
31	Cu3N-derived Cu NWs, on copper foam	Oxide-derived	Cu, N	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 115	CO_2	-1.0 V vs. RHE	-51 mA/cm^2	66	168
32	CuOx NPs electrodeposited in the presence of CTAB, on Cu plate	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.5 M KCl	Nafion 115	CO_2	-1.0 V vs. RHE	-18 mA/cm^2	66	169
33	In-situ reduced porous CuOx NPs derived from hydrothermal synthesis with tetrapropylammonium, on a GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	3.0 M KOH	FUMA-FAA-3-PK-130	CO_2	-1.25 V -iR vs. RHE	-536 mA/cm^2	66	170
34	Cu(OH)F-derived Cu/F, on GDL	Oxide-derived	Cu, O, F	-	(Gas-phase reactant, supplied from behind)	2.5 M KOH	NEOSEPTA	CO_2	-0.89 V - iR vs. RHE	-1600 mA/cm^2	65	171
35	Non-swelling anion exchange ionomer (AEI)-modified electroreduced CuO nanosheets, on GDL	Oxide-derived	Cu, O	AEI: Xenergy Pention D 18, PTFE	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAA PK 130	CO_2	-0.78 V - iR vs. RHE	-800 mA/cm^2	65	172
36	25 nm-thick Cu layer, evaporated on GDL	Oxide-derived	Cu	-	(Gas-phase reactant, supplied from behind)	5.5 M KOH + 4	Fumasep FAB-PK-130	CO_2	-0.62 V - iR vs. RHE	-500 mA/cm^2	65	156

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37	CuOx NP nanospheres, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAA-PK-130	CO	-0.72 V - iR vs. RHE	-1250 mA/cm^2	65	[173]
38	Anodization-dirived Cu2O NWs on Cu-sputtered FTO glass	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	-	CO_2	-0.8 V vs. RHE	-2 mA/cm^2	65	[174]
39	Electrochemical-assisted chlorine-reconstructed Cu NCs on hollow tubular novelty GDE	Oxide-derived	Cu, O, Cl	-	(Gas-phase reactant, forced through surface)	5.0 M KOH	Fumasep FAB-PK-130	CO	-0.8 V vs. RHE	-740 mA/cm^2	65	[175]
40	Cu2P2O7 particles, on glassy carbon	Oxide-derived	Cu, O, P	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.40 V vs. RHE	-18 mA/cm^2	64	[157]
41	Partially reduced, thermally annealed/oxidized electroplated Cu nanodendrites, on carbon paper	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 115	CO_2	-1.4 V (no iR) vs. RHE	-27 mA/cm^2	63	[176]
42	Ultrasonic-assisted defective CuO-derived Cu nanosheets, on GDL	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAA-3-PK-75	CO_2	-0.52 V - iR vs. RHE	-300 mA/cm^2	63	[177]
43	In-situ formed Cu NPs supported on CuO nanosheets, on hydrophobic carbon cloth	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	2.0 M KCl + 0.01 M HCl	"from Fumasep"	CO_2	-2.82 V vs. RHE	-700 mA/cm^2	63	[178]
44	In-situ reconstruction-driven (2D) defective CuO NWs, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAA-3-PK-75	CO_2	-0.56 V - iR vs. RHE	-324 mA/cm^2	62	[179]
45	In-situ reconstructed defective CuO NWs, on carbon paper	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-75	CO_2	-0.56 V - iR vs. RHE	-524 mA/cm^2	62	[179]
46	Chloride-derived CuOx NPs prepared via chemical oxidation (H2O2), on Cu-sputtered GDL	Oxide-derived	Cu, O, Cl	-	(Gas-phase reactant, supplied from behind)	3.0 M KOH	?	CO_2	-0.68 V -iR vs. RHE	-400 mA/cm^2	61	[180]
47	Metal–organic polyhedra-derived hollow CuOx NP based spheres	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-0.9 V - iR vs. RHE	-143 mA/cm^2	61	[181]
48	Cu3N NPs, on glassy carbon	Oxide-derived	Cu, N	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-0.8 V vs. RHE	-60 mA/cm^2	61	[182]
49	Polystyrene template-assisted interconnected mesoporous Cu2O NPs, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1 M KOH (pH 14)	Fumatech, FAA-3PK-130	CO_2	?	-1000 mA/cm^2	61	[183]
50	Hollow Cu2O NPs on GDL, electrochemically pre-activated via in-situ reduction in the presence of CO_2	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Sustainion® X37-50 grade RT	CO_2	-0.6 V vs. RHE	-200 mA/cm^2	61	[155]
51	O2 plasma-treated (2 min, 20 W) Cu plate	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion	CO_2	-0.9 V -iR vs. RHE	-10 mA/cm^2	60	[184]
52	Cu3N NCs_20nm supported on Ketjen Carbon, on carbon paper	Oxide-derived	Cu, N, C	Polyvinylidene fluoride (PVDF)	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 212	CO_2	-1.6 V vs. RHE	-30 mA/cm^2	60	[185]
53	Hybrid material composed of graphene oxide nanodots on CuO nanosheets, on GDL	Oxide-derived	Cu, O, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAA–PK–130)	CO_2	-0.82 V - iR vs. RHE	-500 mA/cm^2	60	[186]
54	Nitridized Cu NPs, on GDL	Oxide-derived	Cu, N	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Sustainion, X37-50 Grade T	CO	?	-100 mA/cm^2	60	[109]
55	Electrochemical-assisted iodine-reconstructed Cu foil	Oxide-derived	Cu, O, I	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.09 V vs. RHE	-26 mA/cm^2	60	[164]
56	Cu2(OH)2CO3 NPs, on glassy carbon	Oxide-derived	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	?	CO_2	-0.9 V vs. RHE	-50 mA/cm^2	60	[187]
57	Plasma-fluorinated Cu sputter-deposited on PTFE GDL	Oxide-derived	Cu, F	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	-0.57 V -iR vs. RHE	-250 mA/cm^2	60	[188]
58	Truncated octahedral Cu2O NPs having both (100) and (111) exposed facets supported on Carbon Black, on glassy carbon	Oxide-derived	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	?	CO_2	-1.1 V vs. RHE	-23 mA/cm^2	59	[189]
59	(100)-rich sputtered Cu in presence of gaseous O2, on GDL	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	2.0 M KOH	Fumatech FAA-3-PK-75	CO_2	-0.75 V vs. RHE	-122 mA/cm^2	59	[190]
60	Multi-shelled ("4.4") Cu2O spheres, on a GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1 M KOH (pH 14)	?	CO_2	-0.85 V - iR vs. RHE	-900 mA/cm^2	59	[191]
61	Cu-metal/CuOx co-catalyst NPs with intimate interfacial contact, on carbon paper	Oxide-derived	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.0 V vs. RHE	-15 mA/cm^2	59	[192]
62	Electroreduced KOH-derived Cu(OH)2 nanorods on Cu-sputtered carbon paper	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-0.54 V - iR vs. RHE	-250 mA/cm^2	58	[193]
63	Porous/partially hollow core/shell Cu2O microparticles, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	2.0 M KOH	Fumasep FAA-PK-130	CO_2	-1.1 V - iR vs. RHE	-260 mA/cm^2	58	[194]
64	O2-driven oxidized Cu NWs, on glassy carbon	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.03 V - iR vs. RHE	-34 mA/cm^2	58	[195]
65	(111)/(100) grain boundary-rich hexagonal-polyhedral Cu2O MPs (ca. 2 µm), on carbon paper	Oxide-derived	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.2 M KI	Nafion 117	CO_2	-1.3 V vs. RHE	-25 mA/cm^2	58	[196]
66	Crystalline CuO NPs embedded in amorphous CuO nanoflakes, on glassy carbon	Oxide-derived	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 115	CO_2	-1.08 V vs. RHE	-16 mA/cm^2	58	[197]
67	Cu2(OH)2CO3 MPs with amorphous layer induced by 15 min microwave treatment, on carbon paper	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	-2.0 V vs. RHE	-317 mA/cm^2	58	[198]
68	Water-optimized CO_2 feed reduction on Cu2O/Cu co-catalyst NPs derived from Cu2O/CuO precursor, on a GDL	Oxide-derived	Cu, O	Nafion, quaternary ammonia polysulphone (aQAPS-S14)	(Gas-phase reactant, supplied from behind)	-	QAPPT	CO_2	-3.8 V vs. RHE	-1000 mA/cm^2	58	[199]
69	Fragmented Cu2O NPs of originally 20 nm supported on carbon black, on glassy carbon	Oxide-derived	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV	CO_2	-1.1 V -iR vs. RHE	-18 mA/cm^2	57	[200]
70	Cu(OH)Cl-derived Cu/Cl, on GDL	Oxide-derived	Cu, O, Cl	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH + 0.5 M KF	NEOSEPTA	CO_2	-0.6 V - iR vs. RHE	-380 mA/cm^2	57	[171]
71	Grainboundary-rich defective Cu NCs derived from CO-assisted thermally reduced Cu2O NCs supported on carbon black (XC-72R), on GDL	Oxide-derived	Cu, O, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAB-PK-130	CO_2	-1 V - iR vs. RHE	-500 mA/cm^2	57	[201]
72	In-situ electroplated CuOx in Br-containing electrolyte, on GDL	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.1 M KBr + 0.01 M CuSO4 (pH 2.5)	Nafion 117	CO_2	-4.3 V vs. ANODE	-170 mA/cm^2	57†–oxidic, 5	[202]
73	Chloride-derived CuOx NPs prepared via chemical oxidation (H2O2), on Cu foil	Oxide-derived	Cu, O, Cl	-	(Solution-phase reactant, supplied in front)	0.05 M KHCO3	?	CO_2	-2.6 V -iR vs. Ag/AgCl	-16 mA/cm^2	56	[180]

74	Oxygen-assisted plasma induced N-doped CuO NPs supported on Ketjen Black, on glassy carbon	Oxide-derived	Cu, O, C, N	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMVN	CO_2	-1.1 V - iR vs. RHE	-25 mA/cm^2	56	[203]
75	Electrodeposited Cu(OH)x dendrites (-200 mA/cm^2 for 10 min from 0.05 M H2SO4/2.5 M KCl/7 mM CuSO4 bath with active CO_2 flow), on Cu-sputtered PTFE GDL	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	0.05 M H2SO4 + 2.5 M KCl	Nafion 117	CO_2	?	-200 mA/cm^2	56	[204]
76	Nitrogen vacancy-rich Cu3Nx NPs prepared via controlled lithiation/delithiation, on GDL	Oxide-derived	Cu, N, Li	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	X37-50 Grade T	CO_2	-1.15 V vs. RHE	-375 mA/cm^2	56	[205]
77	CuO NSs, on glassy carbon, pre-reduced in halide-containing electrolyte (0.1 M KHCO3 + 0.01 M KBr)	Oxide-derived	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 + 10 mM KBr$^{\dagger\_oxidic,3}$	Nafion 117	CO_2	-0.98 V - iR vs. RHE	-31 mA/cm^2	56	[206]
78	Pre-reduced CuO NSs ("CISC-24"), on a GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	3.0 M KOH	FAA-3-PK-130	CO_2	-0.55 V -iR vs. RHE	-753 mA/cm^2	56	[207]
79	Chloride-derived CuOx NPs prepared via chemical oxidation (H2O2), on Cu-sputtered GDL	Oxide-derived	Cu, O, Cl	-	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	?	CO_2	-1.8 V -iR vs. RHE	-450 mA/cm^2	55	[180]
80	Branched/'spikey' Cu NPs obtained from KOH addition to catalyst ink, on GDL	Oxide-derived	Cu, O	Nafion, KOH	(Gas-phase reactant, supplied from behind)	-	X37–50	CO_2	-3.25 V vs. ANODE	-281 mA/cm^2	55	[208]
81	Grainboundary-rich defective Cu NCs derived from CO-assisted thermally reduced Cu2O NCs supported on carbon black (XC-72R), on glassy carbon	Oxide-derived	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.0 V - iR vs. RHE	-3 mA/cm^2	55	[201]
82	Cu2O/Cu(OH)2 spherical and porous nanocages, on carbon paper	Oxide-derived	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.15 V vs. RHE	-31 mA/mg	55	[209]
83	Cu(OH)2-derived Cu NPs without additives (?), on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAB-PK-130	CO_2	-0.9 V -iR vs. RHE	-440 mA/cm^2	55	[210]
84	Electrodeposited Cu(100), on GDL	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-130	CO_2	-1.26 V vs. RHE	-200 mA/cm^2	54	[211]
85	Cu3(PO4)2 particles, on Cu-sputtered PTFE GDL	Oxide-derived	Cu, O, P	Nafion	(Gas-phase reactant, supplied from behind)	2.0 M KOH	?	CO_2	-2.4 V vs. RHE	-350 mA/cm^2	53	[157]
86	Commercial oxygen-passivated Cu NPs (<100 nm), on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3 (verify)	Nafion 117	CO	?	-300 mA/cm^2	53	[116]
87	Mixed valency CuOx/Cu NPs, on glassy carbon	Oxide-derived	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.3 V vs. RHE	-18 mA/cm^2	53	[212]
88	Cu(OH)F-derived Cu/F, on GDL	Oxide-derived	Cu, O, F	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	NEOSEPTA	CO	-0.6 V - iR vs. RHE	-440 mA/cm^2	52	[171]
89	Electrochemical-assisted chlorine-reconstructed Cu nanocrystals on a 920 nm-thick Cu layer, sputtered on GDL	Oxide-derived	Cu, O, Cl	-	(Gas-phase reactant, supplied from behind)	1 M KOH + 0.2 M CsI	Fumasep FKS-50	CO_2	-0.55 V - iR vs. RHE	-184 mA/cm^2	52	[115]
90	Lithiated CuOx MPs, on glassy carbon	Oxide-derived	Cu, O, Li	? polyvinylidene fluoride	(Solution-phase reactant, supplied in front)	0.1 M CsHCO3	Selemion AMV	CO_2	-0.9 V -iR vs. RHE	-13 mA/cm^2	52	[213]
91	Pre-reduced CuO NSs, on carbon paper	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.1 V vs. RHE	-12 mA/cm^2	52	[207]
92	Multi-shelled CuO microboxes, on carbon paper	Oxide-derived	Cu, O	Nafion D-521	(Solution-phase reactant, supplied in front)	0.1 M K2SO4 (pH 5.8)	Nafion 117	CO_2	-1.05 V vs. RHE	-28 mA/cm^2	51	[214]
93	Li-deficient Li2CuO2 microparticles	Oxide-derived	Cu, O, Li	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	X37-50 Grade T	CO_2	-0.85 V vs. RHE	-195 mA/cm^2	51	[215]
94	Octahedral 500 nm Cu2O particles, on glassy carbon	Oxide-derived	Cu, O	Nafion D-521	(Solution-phase reactant, supplied in front)	0.1 M CsHCO3	Nafion 117	CO_2	-1.2 V vs. RHE	-25 mA/cm^2	51	[216]
95	Partially thermally reduced electroplated Cu2Ox with NH4Cl-induced high step density, on plate	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-0.76 V - iR vs. RHE	-31 mA/cm^2	51	[217]
96	Electrochemical-assisted bromine-reconstructed Cu foil	Oxide-derived	Cu, O, Br	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.10 V - iR vs. RHE	-43 mA/cm^2	51	[218]
97	Vacancy-rich delithiated Li2-xCuO2 NPs, on GDL	Oxide-derived	Cu, Li, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	X37-50 Grade T	CO_2	-0.85 V vs. RHE	-200 mA/cm^2	51	[219]
98	Spherical Cu(OH)2 nanorod (250 nm individual diameters) aggregates, on GDL	Oxide-derived	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KCl	Nafion 115	CO_2	-1.08 V vs. RHE	-28 mA/cm^2	51	[220]
99	Commercial Cu NPs, on GDL with custom-tailored MPL	Oxide-derived	Cu	Nafion, Pention-D72 (Xergy)	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-50	CO_2	-1.44 V - iR vs. RHE	-1360 mA/cm^2	51	[221]
100	Electroplated CuOx catalyst forming highly porous structure during in-situ reduction, on glassy carbon	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	FAA-3-PK-75	CO_2	-0.8 V vs. RHE	-4 mA/cm^2	51	[222]
101	Cu(OH)Br-derived Cu/Br, on GDL	Oxide-derived	Cu, O, Br	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH + 0.5 M KF	NEOSEPTA	CO_2	-0.6 V - iR vs. RHE	-345 mA/cm^2	50	[171]
102	Spherical 20 nm CuO NPs with loading of 1.7 mg/cm2, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1 M KCl	Nafion 117	CO_2	-1.02 V vs. RHE	-1600 mA/cm^2	50	[223]
103	Electrochemical-assisted iodine-reconstructed Cu foil	Oxide-derived	Cu, O, I	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.09 V - iR vs. RHE	-40 mA/cm^2	50	[218]
104	Electrochemical-assisted chlorine-reconstructed Cu foil	Oxide-derived	Cu, O, Cl	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.11 V - iR vs. RHE	-40 mA/cm^2	50	[218]
105	O2 plasma (400 mTorr / 20 W / 2 min) treated Cu foil	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 + 0.3 M KCl	Nafion 211	CO_2	-1.04 V - iR vs. RHE	-53 mA/cm^2	50	[224]
106	Electrochemical-assisted chlorine-reconstructed Cu nanocrystals on a 920 nm-thick Cu layer, sputtered on GDL	Oxide-derived	Cu, O, Cl	-	(Gas-phase reactant, supplied from behind)	1 M KOH + 0.2 M CsI	Fumasep FKS-50	CO	-0.60 V - iR vs. RHE	-100 mA/cm^2	50	[115]
107	"Cu10Cs1" (wt%/at.% not reported) co-catalyst electroplated on carbon paper	Oxide-derived	Cu, Cs	-	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO_2	-1.4 V vs. RHE	-45 mA/cm^2	50	[225]
108	Porous iodine-doped (0.02 % I, ICP) CuO MPs, on carbon paper	Oxide-derived	Cu, O, I	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.2 V vs. RHE	-15 mA/cm^2	50	[226]
109	Electrochemical-assisted carbonate-reconstructed Cu foil	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV	CO_2	-0.96 V - iR vs. RHE	-3 mA/cm^2	49	[227]
110	O2 plasma (400 mTorr / 20 W) treated Cu foil	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.1 M CsHCO3	Selemion AMV	CO_2	-0.96 V - iR vs. RHE	-41 mA/cm^2	49	[228]
111	Cu2O/CuO NPs, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	?	CO_2	?	-400 mA/cm^2	49	[229]
112	N-doped Cu (Cu3N) NCs, on GDL	Oxide-derived	Cu, N,	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-130	CO_2	-1.13 V -iR vs. RHE	-1100 mA/cm^2	49	[230]

			O									
113	Porous CuO NSs (19.4 nm), on "PTFE GDL"	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	3.0 M KOH	FAB-PK-130	CO_2	-0.89 V -iR vs. RHE	-430 mA/cm^2	49	[231]
114	Cu2O NCs on GDL, electrochemically pre-activated via in-situ reduction in the presence of CO_2	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Sustainion® X37-50 grade RT	CO	-0.6 V vs. RHE	-184 mA/cm^2	48	[155]
115	Microwave-assisted additional Cu-induced activity enhanced CuO nanosheets, on glassy carbon	Oxide-derived	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.2 V - iR vs. RHE	-29 mA/cm^2	47	[232]
116	Defective CuO-derived Cu nanosheets, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	0.05M H2SO4 + 3 M KCl (pH 0.5)	Nafion 117	CO_2	-1.45 V - iR vs. RHE	-560 mA/cm^2	47	[233]
117	30 nm CuO NPs, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-50 grade T	CO	-2.44 V vs. ANODE	-1000 mA/cm^2	47	[234]
118	P-doped CuOx nm-sized spherical agglomerates, on GDL	Oxide-derived	Cu, O, P	Nafion	(Gas-phase reactant, supplied from behind)	1 M KOH (pH 14)	3PK-130	CO_2	-1.4 V vs. RHE	-350 mA/cm^2	47	[235]
119	CuBaCO3 NPs, on Cu-sputtered PTFE GDL	Oxide-derived	Cu, Ba, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-0.65 V vs. RHE	-400 mA/cm^2	47	[236]
120	F-doped CuO large NPs	Oxide-derived	Cu, O, F	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAA-3-PK-130	CO_2	-1.05 V - iR vs. RHE	-320 mA/cm^2	46	[237]
121	15 nm Cu2O NPs, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumatech	CO_2	-0.79 V - iR vs. RHE	-300 mA/cm^2	46	[238]
122	CuOx MPs electrodeposited on carbon paper	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-75	CO_2	-0.75 V - iR vs. RHE	-601 mA/cm^2	46	[239]
123	Ultrathin porous Cu foil chemically converted into Cu(OH)2 nanoneedles, reduced by H2 under slow temperature ramp. Hydrophobic, full-metal GDE	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	1.0 M KCl + 1.0 M HCl	Nafion 117	CO_2	-1.82 V vs. RHE	-600 mA/cm^2	46	[240]
124	P-doped pulse-electroplated Cu (Cu0.92P0.08) on carbon paper	Oxide-derived	Cu, P	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Nafion 115	CO_2	-0.72 V -iR vs. RHE	-210 mA/cm^2	46	[241]
125	Cu2O NPs , on GDL	Oxide-derived	Cu, O	Pention D18 (Xergy Co., Ltd.)	(Gas-phase reactant, supplied from behind)	-	In-house BPM with water splitting catalyst + perforated AEM	CO_2	-4.5 V vs. ANODE	-300 mA/cm^2	46	[242]
126	O2 plasma-treated (20 s, 20 W) chloride-derived CuOx NCs, on Cu plate	Oxide-derived	Cu, O, Cl	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 115	CO_2	-1.05 V -iR vs. RHE	-50 mA/cm^2	45	[243]
127	Electrochemically reduced CuO micropore nanowire-modified Cu foam; oxygen-bearing copper micropore NWs	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.0 V - iR vs. RHE	-100 mA/cm^2	45	[244]
128	Electrochemically restructured Cu by cycling in 0.1 M KHCO3 + 16 mM KCl as per [insert Robert Sloan ref], on Cu plate	Oxide-derived	Cu, O, Cl	-	(Solution-phase reactant, supplied in front)	0.1 M CsHCO3 (pH 6.8)	Selemion AMV	CO_2	-1 V - iR vs. RHE	-14 mA/cm^2	45	[245]
129	Pre-reduced (CO_2RR conditions) CuO NSs, on glassy carbon	Oxide-derived	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV	CO_2	-1.1 V - iR vs. RHE	-35 mA/cm^2	45	[246]
130	Porous Cu2O nanosphere superparticle, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	2.0 M KOH	Fumasep FAB-PK-130	CO_2	-0.75 V - iR vs. RHE	-700 mA/cm^2	45	[247]
131	(100)-rich Cu NPs derived from in-situ reduction of phosphate-doped copper oxychloride pre-cursor, on GDL	Oxide-derived	Cu, O, P, Cl	Nafion	(Gas-phase reactant, supplied from behind)	-	FAA-3-PK-130	CO	-2.23 V vs. ANODE	-700 mA/cm^2	45	[248]
132	Highly porous CuOx NWs derived from polymer templating strategy (poly(acrylonitrile-blockmethylmethacrylate)), on a GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH[†_oxidic,7]	Fumasep PK 130	CO_2	-0.98 V -iR vs. RHE	-238 mA/cm^2	45	[249]
133	CuO NRs, on a GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Selemion AMVN	CO	-3.2 V -iR vs. RHE	-900 mA/cm^2	45	[250]
134	Cu2(PO4)(OH) microrods, on GDL	Oxide-derived	Cu, O, P	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-1.38 V vs. RHE	-265 mA/cm^2	44	[251]
135	CuO nanoneedles, on Toray Carbon Paper (TGP-H-60)	Oxide-derived	Cu, O	Fluorinated ethylene propylene	(Gas-phase reactant, supplied from behind)	1 M KOH (pH 14)	?	CO_2	-0.76 V - iR vs. RHE	-975 mA/cm^2	44	[252]
136	CuOX NPs electrodeposited from 0.1 M CuCOOH + 0.1 M KHCO3 + sodium tartrate dibasic dihydrate under constant CO_2 bubbling, on GDL (?)	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	-	"Sustainion"	CO_2	-2.7 V vs. ANODE	-300 mA/cm^2	44	[253]
137	Mixed Cu-metal/Cu2O MPs with prism-shaped Cu2O shell, on glassy carbon	Oxide-derived	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	? 0.1 M KHCO3	Nafion 117	CO_2	-1.08 V vs. RHE	-15 mA/cm^2	44[†_oxidic,8]	[254]
138	Mixed CuOx MP catalyst containing Cu4O3 phase, on GDL	Oxide-derived	Cu, O	Sustainion XA-9	(Gas-phase reactant, supplied from behind)	Cs2SO4	Nafion 117	CO_2	-0.64 V vs. RHE	-300 mA/cm^2	43	[255]
139	(100)-rich Cu NPs derived from in-situ reduction of phosphate-doped copper oxychloride pre-cursor, on GDL	Oxide-derived	Cu, O, P, Cl	Nafion	(Gas-phase reactant, supplied from behind)	-	FAA-3-PK-130	CO_2	-3.26 V vs. ANODE	-400 mA/cm^2	43	[248]
140	Cu2O NPs , on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	0.9 M KHCO3 + 0.1 M KI	Nafion 115	CO_2	?	-300 mA/cm^2	43	[256]
141	In-situ reduced CuOx MPs under CO atmosphere, yielding small Cu NPs (ca. 3 nm) 'supported' on larger Cu MPs (ca. 300 nm) on a GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-PK-130	CO	-0.66 V -iR vs. RHE	-390 mA/cm^2	43	[257]
142	P-doped electroplated ("-0.5 V") Cu layer on carbon paper	Oxide-derived	Cu, O, P	-	(Solution-phase reactant, supplied in front)	0.1 M CsI	Nafion 117	CO_2	-1.2 V vs. RHE	-50 mA/cm^2	43	[258]
143	Water-quenced 500 C-warm CuO particles, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAB-PK-130	CO_2	-0.84 V - iR vs. RHE	-40 mA/cm^2	42[†_oxidic,1] (50)	[259]
144	CuO nanosheet-functionalized Cu GDL prepared via thermal evaporation	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Selemion AMVN	CO	-2.25 V - iR vs. NHE	-200 mA/cm^2	42[†_oxidic,4]	[260]
145	Partially oxidized Cu NPs, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	0.5 M KH2PO4 + 0.5 M K2HPO4 + 0.5 M KCl (pH 6.5)	Nafion 117	CO	?	-200 mA/cm^2	41	[261]
146	Pre-reduced (100)/(111)-interface rich CuOx NPs on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	?	CO_2	-1 V - iR vs. RHE	-300 mA/cm^2	41	[262]
147	Mixed valency CuOx/Cu aerogel, on carbon paper	Oxide-derived	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KCl	"Nafion"	CO_2	-1.1 V - iR vs. RHE	-79 mA/cm^2	40	[263]
148	Highly defective 150 nm Cu3N-derived CuOx NPs, on GDL	Oxide-derived	Cu,	Nafion	(Gas-phase reactant,	-	Sustainion	CO	-4.6 V	-500	40	[264]

			O, N		supplied from behind)		37-50		vs. ANODE	mA/cm²		
149	'Highly fragmented' CuO NPs, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1 M KOH (pH 14)	Fumasep FAA-PK-130)	CO	-0.66 V - iR vs. RHE	-175 mA/cm²	40	[133]
150	In-situ reduced, highly porous Cu2P2O7, on custom GDL	Oxide-derived	Cu, P, O	Nafion	(Gas-phase reactant, supplied from behind)	-	QAPPT	CO_2	-3.36 V vs. ANODE	-350 mA/cm²	40	[265]
151	Commercial um-sized CuCl reduced in-situ, on carbon paper	Oxide-derived	Cu, Cl	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV	CO_2	-1.06 V -iR vs. RHE	-39 mA/cm²	39	[266]
152	'Fragment' CuOx-derived Cu NPs, on GDL	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1 M KOH (pH 14)	Fumasep FAB-PK-130	CO	-0.76 V vs. RHE	-59 mA/cm²	38	[267]
153	CuOx NRs, on a "PTFE membrane"	Oxide-derived	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-130	CO	-0.7 V -iR vs. RHE	?	36	[268]
154	In-situ electroplated Cu NCs, prepared via oxidative/reductive cycling in Cl- containing solution, on carbon paper	Oxide-derived	Cu, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	"Selemion"	CO_2	-0.97 V - iR vs. RHE	-20 mA/cm²	35	[269]
155	Co-plated P-doped Cu NPs, on Cu substrate	Oxide-derived	Cu, O, P	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.15 V - iR vs. RHE	-16 mA/cm²	34	[270]
156	Electrodeposited Cu, on GDL	Oxide-derived	Cu, O	-	(Gas-phase reactant, supplied from behind)	-	FAA-3-50	CO	-0.98 V vs. RHE	-87 mA/cm²	33	[271]
157	P-doped Cu NPs (P/Cu of 0.075), on carbon paper	Oxide-derived	Cu, P	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 115	CO_2	-1.6 V vs. RHE	-58 mA/cm²	31	[272]
	[†_oxidic,1]Many of the total FE values in the publication were shown to be ca. 110 % - thus we report here the highest C2H4 value with a total FE close to 100% (being 42 % as opposed to 50 %)											
	[†_oxidic,2]Derived from FE(C2H4) and j(C2H4) as opposed to the reported LSV											
	[†_oxidic,3]SI table states 0.1 M KHCO3 without KBr, but text states with KBr											
	[†_oxidic,4]Disagreement between numbers in main text and SI, report here number provided in main text											
	[†_oxidic,5]Highly unstable signal due to continuous in-situ electrodeposition of Cu											
	[†_oxidic,7]Text denotes "CO_2-saturated 1.0 M KOH", but SI table says electrolyte is 1.0 M KOH											
	[†_oxidic,8]Reported total FE is unreasonably high: 106.6%											

2.2. Cu/M systems resembling oxide-derived copper: Al, B and Mg

2.2.1. Al/Cu

A summary of best-performing Cu/Al bi-elemental catalysts for C_2H_4 production is given in Table S3. The Cu/Al catalyst dataset is derived from 22 unique publications and comprises a total of 26 catalyst systems, with 1 using CO as a reactant and 17 having been identified as alkaline CO_2 systems. A total of 5 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55%, though 3 of those were measured under alkaline CO2RR conditions. The best catalyst yields 80% C_2H_4 and concerns an alkaline CO2RR system.[273] The highest non-alkaline catalyst system yields 79% C_2H_4 and uses CO_2 as the reactant.[274]

Cu/Al systems are mostly found in three forms; i) as alloys with relatively low Al content (alloyed/doped-type), ii) as a mix of different phases consisting of randomly distributed CuOx and AlOx particles (mixed-phase/janus-type), or iii) in the form of Cu NPs supported on Al_2O_3 or $AlCuO_4$ sheets (mixed-phase/janus-type and A-supports-B type). Low concentration Al-doped systems are common on account of the propensity of aluminum to selectively leach under alkaline conditions, allowing for the creation of highly porous materials with trace amounts of aluminum retained in the final product. Generally, we see that such alloyed systems yield C_2H_4 FEs between 30% and 55%, though a single outlier has reported such a system to make up to 80% C_2H_4.[273] Many of the mixed phase systems consist of CuOx NPs combined with (typically) amorphous AlOx particles. Such catalysts generally exhibit relatively poor C_2H_4 performance. The final category comprises Cu NPs supported on an AlOx phase and is an important category for Cu/Al catalysts, with the AlOx supporting phase typically consisting of Al-containing 2D nanosheets such as e.g., Al_2CuO_4 or Al_2O_3.[274-276] However, Cu can also be the 'support' such as is the case for this reference[276], wherein a thin layer of Al_2O_3 was selectively deposited on the Cu [111] sites. Importantly, there generally exists an intimate interface between the (oftentimes two-dimensional) Al-containing phase and the copper particles present in the system. This combination of properties results in systems that exhibit high C_2H_4 performance, with FEs ranging between 60%-80%. In general, an optimum in C_2H_4 is observed with respect to Al content[274,277-280] and disagreement exists regarding *in-situ* Al stability with some authors reporting that the Al dissolves[278,279] whilst other authors state that the catalyst is stable during operation.[273,275]

	Table S3. Al-based Cu											
#	**Electromaterial description**	**Catalyst type**	**Main elements**	**Polymeric / organic & inorganic additives**	**Reactant delivery mode**	**Catholyte**	**Membrane**	**Reactant**	**E**	**j**	**C_2H_4 FE**	**Reference**
1	CNP and graphite layer on top of chemically etched co-sputtered Cu/Al layer on PTFE GDL	Overlayer, Alloyed/Doped	Cu, Al, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	-1.67 V - iR vs. RHE	-400 mA/cm^2	80	[273]
2	CuO NPs supported on Al2CuO4 nanosheets, on glassy carbon	Mixed-phase/Janus, atomically mixed/crystalline, A-supports-B	Cu, Al, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Selemion AMV	CO_2	-0.99 V - iR vs. RHE	-2 mA/cm^2	79[†_Cu-Al,1]	[274]
3	CuOx nanocubes/rectangles supported on Al2O3 nanosheets having an Al2CuO2 interface layer, mixed with CNPs, on glassy carbon	Mixed-phase/Janus, atomically mixed/crystalline, A-supports-B	Cu, Al, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.2 V - iR vs. RHE	-60 mA/cm^2	71	[275]
4	CuO NPs supported on Al2CuO4 nanosheets, on GDL	Mixed-phase/Janus, atomically mixed/crystalline, A-supports-B	Cu, Al, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-130	CO_2	-2.03 V - iR vs. RHE	-600 mA/cm^2	70	[274]
5	Al2O3 partial overlayer (0.8 nm) specifically covering the (111) facets of Cu NPs (10 nm) supported on CNPs, on Ta-sputtered PTFE GDL	Core/shell, A-supports-B	Cu, Al, C, O, Ta	Nafion	(Gas-phase reactant, supplied from behind)	5.0 M KOH	FAB-PK-130	CO_2	-1.1 V - iR vs. RHE	-253 mA/cm^2	61	[276]
6	Al2O3 partial overlayer (0.8 nm) specifically covering the (111) facets of Cu NPs (10 nm) supported on CNPs, on GDL	Core/shell, A-supports-B	Cu, Al, C, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Selemion AMV	CO_2	-1.1 V - iR vs. RHE	-23 mA/cm^2	54	[276]
7	Al-doped (0.09 wt% > 0.27 at.%), agglomerated CuOx nanosheets, on carbon paper	Alloyed/Doped	Cu, Al, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 + 0.3 M KCl	Nafion 117	CO_2	-0.95 V - iR vs. RHE	-30 mA/cm^2	54	[279]
8	Al-doped CuOx NCs ("CuAl-II"), on Toray GDL	Alloyed/Doped	Cu, Al, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	?	-900 mA/cm^2	51	[277]
9	QAPEEK (anionic ionomer) layer on top of electrochemically leached (-150 mA in KOH) Cu/Al co-sputtered midlayer on PTFE GDL	Overlayer, Alloyed/Doped	Cu, Al	QAPEEK	(Gas-phase reactant, supplied from behind)	-	QAPPT	CO_2	-3.4 V vs. ANODE	-800 mA/cm^2	50	[281]
10	Electro-reduced KOH-treated Cu/Al LDHs, yielding AlOx decorated Cu NPs, supported on CNPs, on GDL (backside sealed with epoxy)	Mixed-phase/Janus, A-supports-B	Cu, Al, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	FAA-3-PK-130	CO_2	-1.06 V - iR vs. RHE	-48 mA/cm^2	50	[282]
11	Hollow Al-doped CuOx spheres obtained via pyrolisis of impregnated Cu-based MOF, on GDL	Alloyed/Doped	Cu, Al	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-1.377 V vs. RHE	-626 mA/cm^2	50	[283]
12	Al-doped (1.9 at%, ICP) CuOx nanoflakes derived from calcining Cu MOF, on a GDL	Alloyed/Doped	Cu, Al, O	Nafion	(Gas-phase reactant, supplied from behind)	0.5 M K2SO4 (pH 2)	Sustainion X37-50 Grade RT	CO_2	?	-700 mA/cm^2	49	[278]
13	CuO NPs supported on Al2CuO4 nanosheets, on GDL	Mixed-phase/Janus, atomically mixed/crystalline, A-supports-B	Cu, Al, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-130	CO	-0.56 V - iR vs. RHE	-500 mA/cm^2	48	[274]
14	Al-doped (0.09 wt% > 0.27 at.%), agglomerated CuOx nanosheets, on carbon paper	Alloyed/Doped	Cu, Al, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-130	CO_2	-0.88 V - iR vs. RHE	-700 mA/cm^2	46	[279]
15	Al-doped Cu2O microparticles, on carbon paper	Alloyed/Doped	Cu, Al, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.23 V vs. RHE	-12 mA/cm^2	45	[284]
16	Semi-porous Cu3Al-derived wires, on carbon paper - prepared by electrospinning metal salts with PVP, followed by calcination and alkaline Zn leaching step	Alloyed/Doped	Cu, Al	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-2.1 V vs. RHE	-600 mA/cm^2	44	[285]
17	Cu100Al7.88-OD nanosheets (number representing wt%), consisting of CuOx phases and amorphous Al2O3 phase mixed homogeneously, on GDL	Mixed-phase/Janus	Cu, Al, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FUMA-FAA-3-PK-130	CO_2	-1.68 V vs. RHE	-693 mA/cm^2	44	[280]
18	Al-doped Cu-based layered double hydroxide (LDH), on carbon paper	Alloyed/Doped	Cu, Al	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Nafion 115	CO_2	-1.4 V vs. RHE	-300 mA/cm^2	44	[286]
19	Al-doped ("5%") octahedral Cu2O NPs, on a GDL	Alloyed/doped	Cu, Al, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-1.1 V vs. RHE	-338 mA/cm^2	42	[287]
20	Al/Cu alloy layer (5% Al) (400 nm) sputtered on a GDL	Alloyed/Doped	Cu, Al	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-50	CO_2	-0.65 V - iR vs. RHE	-200 mA/cm^2	39	[139]
21	400 nm thick evaporated Cu/Al alloy (95:5), on GDL	Alloyed/Doped	Cu, Al	-	(Gas-phase reactant, supplied from behind)	-	AF1-HNN8-50-X	CO_2	?	-100 mA/cm^2	37	[288]
22	Electrochemically reduced nanosheet-like mixed metal Cu5Al1Ox, on GDL	Mixed-phase/Janus	Cu, Al, O	Nafion	(Gas-phase reactant, supplied from behind)	0.2 M KHCO3	-	CO_2	-1.2 V vs. RHE	-75 mA/cm^2	36	[289]
23	CNP and graphite toplayers, on CuO/CuAl2O4 catalyst prepared via co-precipitation and calcination (800 °C) midlayer , on Cu-sputtered PTFE GDL	Atomically mixed/Crystalline, A-supports-B	Cu, Al, O, C	Nafion	(Gas-phase reactant, supplied from behind)	2.0 M KOH	FAA-3-PK-130	CO_2	-1.1 V vs. RHE	-175 mA/cm^2	35	[290]
24	Porous Cu MPs prepared via dealloying Al2Cu pre-cursor, on GDL	Alloyed/Doped	Cu, Al	-	(Gas-phase reactant, supplied from behind)	-	AF1-HNN8⍰50-X	CO_2	-3.7 V vs. ANODE	-75 mA/cm^2	34	[291]
25	Calcined (800 °C) Cu/Al LDH pre-cursor, yielding CuAl2O4/CuO NPs, on GDL	Mixed-phase/Janus	Cu, Al, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	PK-3-K-130	CO_2	-0.92 V vs. RHE	-200 mA/cm^2	30	[292]
26	Thermally annealed Cu-Al LDH, on GDL	Alloyed/Doped	Cu, Al	Nafion	(Gas-phase reactant, supplied from behind)	? 1.0 M KOH	FAA-3-PK-130	CO_2	-0.9 V - iR vs. RHE	-951 mA/cm^2	28	[293]
	[†_Cu-Al,1] Main text states 79.4, SI states 82.4. Report here main text value											

2.2.2. B/Cu

A summary of best-performing Cu/B bi-elemental catalysts for C_2H_4 production is given in Table S4. The Cu/B catalyst dataset is derived from 17 unique publications and comprises a total of 20 catalyst systems, with 0 (none) using CO as a reactant and 9 having been identified as alkaline CO_2 systems. A total of 3 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55%, though 1 of those was measured under alkaline CO2RR conditions. The top-most catalyst yields 68% C_2H_4 and concerns an alkaline CO2RR system.[294] The highest non-alkaline system yields 59% C_2H_4 and uses CO_2 as the reactant.[295] The relatively large number of publications investigating the CO2RR performance of Cu/B systems can likely be (partially) attributed to an 'early' (in terms of new-era CO2RR research) publication by Yansong *et al.* (2018) who investigated the catalytic activity of porous dendritic Cu particles having a boron gradient, and found it to yield a maximum C_2H_4 FE of ca. 53%.[296] Virtually all Cu/B systems can be categorized as alloyed/doped-type systems, although the (bulk) boron contents are spread out between as little as 0.15 at.%[297] up to >12 at.%[298]. Furthermore, an uneven boron distribution is typically reported with boron having the propensity to be preferentially located at the surface. Some authors claim that B-doped Cu NPs will fragment upon application of reductive potentials[299], though this is not reported in other works. We find that the large heterogeneity of the overall Cu/B dataset makes generalization virtually impossible beyond stating that boron doping seems to have 'an effect'. Whether or not this effect is due to fragmentation (possibly) in concert with increased C_2H_4 performance for alkaline CO_2 reduction, or due to an increase in the number of oxygen vacancies, or due to boron gradients influencing the charge of the copper atoms at the interface is uncertain. Even purely morphological effects cannot be ruled out with the reported systems ranging from boron overlayers[270,288] to NPs with core/shell morphology[296,300] to doped 2D nanosheets[297] and nanowires[301,302] to ultra-small metallic copper nanoparticles derived the reductive fragmentation of B-doped CuOx.[299] Overall, the C_2H_4 activity of Cu/B catalyst systems is lackluster, ranging typically between 40%-50%, though outliers up to a maximum of 68% exist.[294]

Table S4. B-based Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	Thin quasi-graphitic carbon-shell functionalized, B-doped Cu NPs supported on carbon fibers, on GDL	Alloyed/Doped, Core/Shell	Cu, C, B	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Sustanion X37-50	CO_2	-0.55 V -iR vs. RHE	-300 mA/cm^2	68	294
2	Highly tensile strained Cu(100) NCs with boron nitride shell grown on top, mixed with CNPs and PTFE, on Cu-sputtered PTFE GDL	Core/shell	Cu, B, N	Nafion, PTFE	(Gas-phase reactant, supplied from behind)	3.0 M KCl ("pH = 1", according to paper)	Nafion 117	CO_2	-2.75 V vs. RHE	-1200 mA/cm^2	59	295
3	Oxygen-vacancy rich B-doped CuO ‘nanobundles’ (nanowires + nanosheets), on carbon paper	Alloyed/Doped	Cu, O, B	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.1 V vs. RHE	-20 mA/cm^2	58	302
4	Fragmented Cu NPs derived from B-doped (2.1 at. %) CuOx NPs (30 nm, with 2.7 nm B-enriched shell), on carbon paper	Alloyed/Doped (gradient)	Cu, O, B	Nafion	(Gas-phase reactant, supplied from behind)	7.0 M KOH	FAA-3-PK-130	CO_2	-0.69 V - iR vs. RHE	-300 mA/cm^2	53	299
5	Porous dendritic Cu with a boron gradient (higher surface B content), on glassy carbon	Alloyed/Doped (gradient)	Cu, B	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO_2	-1.1 V -iR vs. RHE	-55 mA/cm^2	52	296
6	B-doped CuO MPs consisting of aggregated NSs, on carbon paper	Alloyed/doped	Cu, O, B	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.2 V vs. RHE	-15 mA/cm^2	51	303
7	B-doped Cu (1.4 at. % B; NaBH4 as reductant and Boron source) NPs mixed with PTFE, on GDL	Alloyed/Doped	Cu, B	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-75	CO_2	-0.45 V -iR vs. RHE	-200 mA/cm^2	49	304
8	B-doped (“5 %” > 11.9 at. % from ICP) CuOx particles (B gradient at surface), on carbon paper	Alloyed/Doped (gradient)	Cu, O, B	Nafion	(Solution-phase reactant, supplied in front)	1.0 M KOH	Nafion 117 (?)	CO_2	-1.0 V vs. RHE	?	49	298
9	Calcined B-doped Cu(OH)2 nanorods yielding B-doped (8.2 at. %) CuOx NPs, on carbon paper	Alloyed/Doped	Cu, O, B	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	"Sustainion"	CO_2	-0.62 V vs. RHE	-167 mA/cm^2	48	305
10	Fragmented Cu NPs derived from B-doped (2.1 at. %) CuOx NPs (30 nm, with 2.7 nm B-enriched shell), on glassy carbon	Alloyed/Doped (gradient)	Cu, O, B	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-0.72 V - iR vs. RHE	?	46	299
11	Calcined B-doped Cu(OH)2 nanorods yielding B-doped (8.2 at. %) CuOx NPs, on carbon paper	Alloyed/Doped	Cu, O, B	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	Selemion AMV	CO_2	-1.01 V vs. RHE	-115 mA/cm^2	40	305
12	B/Cu alloy layer (5% B) (400 nm) sputtered on a GDL	Alloyed/doped	Cu, B	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-50	CO_2	-0.66 V - iR vs. RHE	-200 mA/cm^2	40	139
13	B-doped dendritic Cu (B gradient at surface) mixed with PTFE, on GDL	Alloyed/Doped (gradient)	Cu, O, B	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	-1.33 V vs. SHE	-200 mA/cm^2	39	300
14	B-doped (0.15 at. %) CuO NSs,on carbon paper	Alloyed/doped	Cu, O, B	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	?	CO_2	-1.2 V vs. RHE	-31 mA/cm^2	39	297
15	Cu-SAC (<1 wt%) on hetero-atom (B) doped C3N4 lamellae, on carbon paper	Single atom, Atomically mixed/Crystalline	Cu, C, N, B	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	"ion exchange membrane"	CO_2	-0.9 V vs. RHE	-14 mA/cm^2	34	306
16	Co-plated B-doped Cu NPs, on Cu substrate	Alloyed/Doped	Cu, O, B	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.08 V - iR vs. RHE	-10 mA/cm^2	32	270
17	B-doped CuOX NPs ("B0.02M"), on a GDL	Alloyed/Doped, Mixed-phase/Janus	Cu, B, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-0.97 V vs. RHE	-163 mA/cm^2	32	307
18	400 nm thick evaporated Cu/B alloy (95:5), on GDL	Alloyed/Doped	Cu, B	-	(Gas-phase reactant, supplied from behind)	-	AF1-HNN8-50-X	CO_2	?	-100 mA/cm^2	30	288
19	B-doped (“5 %” > 11.9 at. % from ICP) CuOx particles (B gradient at surface), on carbon paper	Alloyed/Doped (gradient)	Cu, O, B	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117 (?)	CO_2	-1.0 V vs. RHE	-35 mA/cm^2	30	298
20	B-doped Cu2O NWs, on Toray GDL	Alloyed/Doped	Cu, O, B	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.2 V vs. RHE	-32 mA/cm^2	26	301

2.2.3. Mg/Cu

A summary of best-performing Cu/Mg bi-elemental catalysts for C_2H_4 production is given in Table S5. The number of sources is small, comprising 6 unique publications describing 8 catalyst systems. However, considering one of the results looks incredibly promising we have opted for a brief individual discussion section. Specifically, Mingcan *et al.* report a maximum C_2H_4 FE of ca. 70% under alkaline CO2RR conditions for a *pseudo*-core/shell type of catalyst where a thin MgOx layer is deposited around Cu NPs.[105] Importantly, they also report on CO reduction and show similarly high catalytic activity – although optimum performance (CORR; 80% C_2H_4) was observed for partial pressures below 1 atm. Improved C_2H_4 performance for lower reactant partial pressures has been reported for other catalyst systems[173,308], though the reported maximum C_2H_4 FE for this Cu/Mg system is extraordinarily high even when accounting for modulated partial reactant pressure. However, this exceptional performance is not corroborated by the other sources. Ji *et al.* come closest, reporting a maximum C_2H_4 FE of ca. 59% under alkaline CO2RR conditions.[309] The other sources find significantly lower selectivities at <50%.[293,307,310,311] Although these selectivities are all well below what Mingcan *et al.* report, it is important to recognize that the reaction conditions (CORR at low partial pressure) are also significantly different. Hence, without a reproduction study, there is insufficient data available to draw any conclusions other than that Mg is a potentially interesting candidate.

	Table S5. Mg-based											
#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	Mg surface-doped CuOx NPs (Mg0.72Cu), on GDL	Alloyed/Doped	Cu, Mg, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	NEOSEPTA, AHA	CO	?	?	80	[105]
2	Mg surface-doped CuOx NPs (Mg0.72Cu), on GDL	Alloyed/Doped	Cu, Mg, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	NEOSEPTA, AHA	CO_2	-0.69 V - iR vs. RHE	-650 mA/cm^2	70	[105]
3	Mg surface-doped CuOx NPs (Mg0.72Cu), on GDL	Alloyed/Doped	Cu, Mg, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	NEOSEPTA, AHA	CO	?	?	61	[105]
4	Mg-doped CuOx NPs, on carbon paper	Alloyed/Doped	Cu, Mg, O	Nafion	(Solution-phase reactant, supplied in front)	1.0 M KOH	Nafion 117	CO_2	-1.07 V vs. RHE	-700 mA/cm^2	59	[309]
5	Mg-doped CuO NSs, on a GDL	Alloyed/Doped	Cu, Mg, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M CsI	?	CO_2	-1.3 V vs. RHE	-3 mA/cm^2	46	[310]
6	Mg-doped Cu(OH)2 NWs with a PTFE shell, on a GDL	Alloyed/Doped, Core/shell (in-)organic	Cu, Mg, O	PTFE	(Gas-phase reactant, supplied from behind)	-	X37-50 grade RT	CO_2	-3.72 V vs. ANODE	-400 mA/cm^2	39	[311]
7	Mg-doped CuOX NPs containing amorphous Mg(OH)2, on a GDL	Alloyed/Doped, Mixed-phase/Janus	Cu, Mg, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-1.37 V vs. RHE	-279 mA/cm^2	35	[307]
8	Thermally annealed Cu-Mg LDH, on GDL	Alloyed/Doped	Cu, Mg	Nafion	(Gas-phase reactant, supplied from behind)	? 1.0 M KOH	FAA-3-PK-130	CO_2	-1.0 V - iR vs. RHE	-505 mA/cm^2	28	[293]

2.3. Cu/M systems containing transition and post-transition metal co-elements: Zn, Sn, Pd, Pb, Ni, Co, Ga, Fe, Au, Ag

2.3.1. Zn/Cu

A summary of best-performing Cu/Zn bi-elemental catalysts for C_2H_4 production is given in Table S6. The Cu/Zn catalyst dataset is derived from 28 unique publications and comprises a total of 31 catalyst systems, with 3 using CO as a reactant and 14 having been identified as alkaline CO_2 systems. A total of 6 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55%, though 2 of those were measured under alkaline CO2RR conditions. The top-two catalysts yield 74%[312] and 91%[313] C_2H_4, both concerning non-alkaline systems. A wide range of Cu/Zn systems can be identified, starting with 'tandem-type' systems, where the Zn component is hypothesized to solely serve as a local CO forming agent. Such systems typically yield maximum C_2H_4 FEs in the 40%-50% range and yield little knowledge in the way of how to improve catalyst performance on account of the C_2H_4 forming component not being modified. Another commonly observed category of Cu/Zn catalysts are alloyed/doped-type systems, where Zn contents in the 5%-15% range generally yield optimal C_2H_4 activity. We find that C_2H_4 activities for this category vary widely, yielding anywhere between <30% all the way up to 73% C_2H_4.[314] A brass catalyst (containing 37% Zn) modified with a Nafion/PVDF coating is even reported to yield a maximum C_2H_4 FE of 74%[312], although this might be more-so related to the inorganic overlayer rather than the combination of Cu and Zn in the catalyst itself. Such inorganic overlayer effects are covered in more detail in section S2.8. Another category of Cu/Zn catalysts that is quite common are systems belonging to the mixed-phase/janus-type consisting of intermixed ZnOx and CuOx domains. The interfaces between the domains can be derived from simple mechanical mixing or generated via more intricate methods (e.g., Janus structures). Maximum C_2H_4 FEs for these systems typically range between 40%-50%, although an outlier reports (a rather high) C_2H_4 FE of 91%.[313] Finally, we are aware of two Cu/Zn sources wherein the active catalyst can be categorized as being of the a core/shell-type. However, the performance of these systems is poor, sporting a low maximum of 34% C_2H_4.[315]

Table S6. Zn-based Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	CuOx supported on ZnO , on carbon paper (TGP-H-60)	Mixed-phase/Janus, A-supports-B	Cu, Zn, O	Nafion	(Gas-phase reactant, supplied from behind)	-	Nafion 117	CO_2	-2.5 V vs. Ag/AgCl	-7.5 mA/cm^2	91	313
2	Brass foil (62% Cu, 37% Zn, trace amounts of Fe, Pb, Sn) with Nafion/PVDF (70:30 wt%) overlayer	Alloyed/Doped, Overlayer	Cu, Zn	Nafion, PVDF	(Solution-phase reactant, supplied in front)	0.1 M NaHCO3 (pH 6.8)	-	CO_2	-0.89 V vs. RHE	?	74	312
3	Highly porous Zn/Cu layer (10 at. % Zn) generated through partially leaching of co-sputtered Zn/Cu layer on PTFE substrate	Alloyed/Doped	Cu, Zn	-	(Gas-phase reactant, supplied from behind)	0.75 M KOH	Fumasep FAB-PK-130	CO_2	-1.1 V vs. RHE	-150 mA/cm^2	73	314
4	Highly porous Zn/Cu layer (10 at. % Zn) generated through partially leaching of co-sputtered Zn/Cu layer on PTFE substrate	Alloyed/Doped	Cu, Zn	-	(Gas-phase reactant, supplied from behind)	3.0 M KCl	Nafion 117	CO_2	-1.6 V vs. RHE	-300 mA/cm^2	64	314
5	Lattice-strained, Zn-doped CuO NPs, on carbon paper	Alloyed/Doped	Cu, Zn	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Nafion 117	CO_2	-0.95 V vs. RHE	-500 mA/cm^2	61	316
6	Nanosheet arrays containing homogeneously mixed Zn & Cu domains (Cu:Zn ratio of 24:76 via XPS), on Cu foam	Bi-phasic/Janus	Cu, Zn	-	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 211	CO_2	-1.14 V vs. RHE	-150 mA/cm^2	59	317
7	Zn-doped ("5%") octahedral Cu2O NPs, on a GDL	Alloyed/doped	Cu, Zn, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-1.1 V vs. RHE	-338 mA/cm^2	52	287
8	Phase-separated CuO and ZnO NPs (Cu:Zn ratio of 80:20) supported on Vulcan XC72, on GDL	Mixed-phase/Janus	Cu, Zn, O	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-75	CO_2	-0.75 V -iR vs. RHE	-367 mA/cm^2	51	318
9	Cu NP layer (1 mg/cm2) with ZnO overlayer (0.2 mg/cm2), on GDL	Overlayer, Tandem catalyst	Cu, Zn, O	Nafion	(Gas-phase reactant, supplied from behind)	1 M KOH	"Membrane"	CO_2	-0.73 V vs. RHE	-596 mA/cm^2	49	319
10	Zn/Cu alloy NRs (5 at.% Zn) prepared from oxide precursor, on a GDL	Alloyed/Doped	Cu, Zn, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Selemion AMVN	CO	?	-500 mA/cm^2	49	250
11	ZnO NPs supported on highly porous aggregrates of CuO NSs, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Zn, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	-	CO_2	-1.10 V vs. RHE	-21 mA/cm^2	46	320
12	Cu NP layer (0.4 mg/cm2) with ZnO overlayer (only present near CO_2 inlet, 5% of total area), on GDL	Overlayer, Tandem catalyst	Cu, Zn, O	Sustainion XA-9	(Gas-phase reactant, supplied from behind)	-	"Sustainion"	CO_2	-3.15 V vs. ANODE	-652 mA/cm^2	46	321
13	Chemically dezincified (through NaOH+(NH4)2S2O8 treatment) Zn-doped CuOx NWs, prepared from co-plated Zn/Cu alloy on carbon paper	Alloyed/Doped	Cu, Zn	-	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3 ("1.0 M KOH saturated with CO_2")	FAA-PK-130	CO_2	-0.8 V vs. RHE	-170 mA/cm^2	46	322
14	Zn-doped ("5%") CuOx NPs prepared via pyrolysis of Zn-impreganted Cu-based MOF (HKUST-1), on carbon paper	Alloyed/Doped	Cu, Zn	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	"anionic membrane"	CO_2	-1.0 V vs. RHE	-200 mA/cm^2	45	323
15	Zn/Cu alloy NRs (3 at.% Zn) prepared from oxide precursor, on a GDL	Alloyed/Doped	Cu, Zn, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Selemion AMVN	CO	-3.3 V -iR vs. RHE	-900 mA/cm^2	45	250
16	Cu90Zn10 alloy layer, on GDL - prepared via magnetron co-sputtering	Alloyed/Doped	Cu, Zn	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-1.27 V vs. RHE	-180 mA/cm^2	44	142
17	Cu2O NCs decorated with Zn ("4%"), on a GDL	Mixed-phase/Janus	Cu, Zn, O	-	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	Selemion AMV	CO_2	?	-500 mA/cm^2	43	324
18	Electrochemically cycled (e.g., oxide-derived) Cu75Zn25 alloy disk	Alloyed/Doped	Cu, Zn	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	AHO, AGC Inc.	CO_2	-1.10 V vs. RHE	?	41	325
19	Cu NPs (3 nm) supported on Zn-based MOF (zeolitic imidazolate framework-8), on GDL	Mixed-phase/Janus, A-supports-B	Cu, Zn	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-1.62 V vs. RHE	-400 mA/cm^2	41	326
20	Cu NWS decorated with a Zn-based MOF (ZIF-8), on carbon paper	Core/shell, mixed-phase/janus	Cu, Zn	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-0.7 V vs. RHE	-6 mA/cm^2	41	327
21	Cu/Zn mixed catalyst (Cu100Zn4.9), on carbon paper - prepared via co-plating	Mixed-phase/Janus	Cu, Zn	-	(Solution-phase reactant, supplied in front)	0.1 M CsI	Nafion 117	CO_2	-1.38 V vs. RHE	-40 mA/cm^2	40	328
22	Cu/Zn mixed catalyst co-electroplated from single plating bath, directly onto a GDL	Mixed-phase/Janus	Cu, Zn	-	(Solution-phase reactant, supplied in front)	2.0 M KCl + 0.01 M KHCO3	Nafion 117	CO_2	-1.36 V vs. RHE	-79 mA/cm^2	40	329
23	Zn-doped ("5%") CuOx NPs prepared via pyrolysis of Zn-impreganted Cu-based MOF (HKUST-1), mixed with carbon, on carbon paper	Alloyed/Doped, A-supports-B	Cu, Zn, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M K2SO4	"proton exchange membrane"	CO_2	-0.7 V vs. RHE	-7 mA/cm^2	40	323
24	Cu83Zn17 catalyst, on Au substrate - prepared via co-plating	Alloyed/Doped	Cu, Zn	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV	CO_2	-1.8 V vs. Ag/AgCl	?	35	330
25	Dual-single atom Cu/Zn (3:1 ratio) deposited on N-functionalized amorphous/graphitic carbon, on Toray carbon paper	Single atom	Cu, Zn, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.1 V vs. RHE	-22 mA/cm^2	35	331
26	Core/shell NPs with Cu2O shell (ca. 60 nm) and ZnO core (ca. 30 nm), on GDL	Core/shell	Cu, Zn, O	Nafion	(Solution-phase reactant, supplied in front)	1 M KHCO3 ("1 M KOH saturated with CO_2")	?	CO_2	-1.0 V vs. RHE	-33 mA/cm^2	34	315
27	Laser-prepared Cu/Zn alloy NPs (7-15 nm, 4:1 ratio), on glassy carbon	Alloyed/Doped	Cu, Zn	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	?	CO_2	-1.10 V vs. RHE	-6 mA/cm^2	33	332
28	Cu NWs decorated with Zn-TMC, on GDL	Core/shell, A-supports-B	Cu, Zn	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-1.0 V vs. RHE	?	30	333
29	Semi-porous Cu3Zn-derived NPs, on carbon paper - prepared by electrospinning metal salts with PVP, followed by calcination and alkaline Zn leaching step	Alloyed/Doped	Cu, Zn	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-2.15 V vs. RHE	-600 mA/cm^2	24	285
30	Thermodynamically unstable Cu9Zn1 NPs prepared via thermal shock, on carbon nanotubes	Alloyed/Doped, A-supports-B	Cu, Zn	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3	CO	-0.69 V -iR vs. RHE	-50 mA/cm^2	22	334
31	CNP and graphite layers on top of reduced CuZnO alloy catalyst prepared via co-precipitation and calcination (800 °C) midlayer, on Cu-sputtered PTFE GDL	Alloyed/Doped	Cu, Zn, C	Nafion	(Gas-phase reactant, supplied from behind)	2.0 M KOH	FAA-3-PK-130	CO_2	-1.15 V vs. RHE	-210 mA/cm^2	17	290

2.3.2. Sn/Cu

A summary of best-performing Cu/Sn bi-elemental catalysts for C_2H_4 production is given in Table S7. The Cu/Sn catalyst dataset is derived from 7 unique publications and comprises a total of 8 catalyst systems, with 2 using CO as a reactant and 3 having been identified as alkaline CO_2 systems. A total of 1 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55% (i.e., 57%[335]), being measured under alkaline CO2RR conditions. The majority of the Cu/Sn catalyst systems identified in this work are comprised of alloys (alloyed/doped-type) with low Sn content. Overall, the C_2H_4 performance of Cu/Sn based catalysts is poor, with relatively little information contained within the few sources available. The presence of vacancies and changes in oxophilicity are the dominant theories for any Sn-related changes in C_2H_4 performance. The heterogeneity of the dataset does not allow for additional insights at this stage, but the relatively low maximum C_2H_4 performance in concert with the low number of publications indicate that Sn is not an attractive research target for the electro formation of C_2H_4 in our opinion.

	Table S7. Sn-based Cu											
#	**Electromaterial description**	**Catalyst type**	**Main elements**	**Polymeric / organic & inorganic additives**	**Reactant delivery mode**	**Catholyte**	**Membrane**	**Reactant**	**E**	**j**	**C_2H_4 FE**	**Reference**
1	Co-plated Cu and Sn from a 1 mM 3,5-diamino-1,2,4-triazole containing plating bath, on a 10nm Cu-sputtered GDL	Alloyed/Doped	Cu, Sn	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	-	CO_2	-0.8 V vs. RHE	-226 mA/cm^2	57	[335]
2	Sn-doped CuO nanosheets (0.65%, 130 C), on carbon paper	Alloyed/Doped	Cu, Sn, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.1 V vs. RHE	-9 mA/cm^2	49	[336]
3	Sn-doped oxygen vacancy-rich CuO nanoribbons, on carbon paper	Alloyed/Doped	Cu, Sn, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	?	-6 mA/cm^2	40	[337]
4	SnO2-decorated (3 %) CuO nanosheets, on GDL	Mixed-phase/Janus, A-supports-B	Cu, Sn, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.0 V vs. RHE	-8 mA/cm^2	24	[338]
5	Cu/Sn alloy NPs (3 % Sn) mixed with Vulcan Carbon and polyvinylidene fluoride, on a GDL	Alloyed/Doped	Cu, Sn	Polyvinylidene fluoride	(Gas-phase reactant, supplied from behind)	-	X37–50 Grade RT	CO_2	-4.0 V vs. ANODE	?	24	[339]
6	Cu NPs in an ionic liquid polymer impregnated with SnCl2 (1 mol% vs. Cu), on GDL	Mixed-phase/Janus	Cu, Sn, O	Polymeric ionic liquid crosslinked with divinylbenzene	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO	?	-250 mA/cm^2	23	[340]
7	Thermodynamically unstable Cu9Sn1 NPs prepared via thermal shock, on carbon nanotubes	Alloyed/Doped, A-supports-B	Cu, Sn	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3	CO	-0.74 V -iR vs. RHE	-100 mA/cm^2	19	[334]
8	400 nm thick evaporated Cu/Sn alloy (95:5), on GDL	Alloyed/Doped	Cu, Sn	-	(Gas-phase reactant, supplied from behind)	-	AF1-HNN8-50-X	CO_2	?	-100 mA/cm^2	16	[288]

2.3.3. Pd/Cu

A summary of best-performing Cu/Pd bi-elemental catalysts for C_2H_4 production is given in Table S8. The Cu/Pd catalyst dataset is derived from 23 unique publications and comprises a total of 26 catalyst systems, with 5 using CO as a reactant and 8 having been identified as alkaline CO_2 systems. A total of 5 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55%, though 1 of those was measured under alkaline CO2RR conditions, The top two catalysts yield 64%[341] and 76%[222] C_2H_4, both concerning non-alkaline systems. High performance Cu/Pd-based C_2H_4 catalysts can be divided into three categories: alloyed/doped-type, core/shell-type and mixed-phase/janus-type systems. Alloyed/doped-type systems and mixed-phase/janus-type systems make up the top-segment of Cu/Pd systems in terms of C_2H_4 performance and can reliably yield 45%-55% C_2H_4. Oftentimes, such systems contain relatively low quantities of Pd (<1.4 at.%)[110,222,341-343], though mixed-phase/janus-type systems seem to be more forgiving in this aspect. An outlier does exist in the form of an alloyed/doped-type catalyst that yield a reasonably high maximum C_2H_4 FE of 45% at an elevated Pd concentration of ca. 13 at%.[344] Even though low Pd contents are generally best, lower isn't necessarily better considering that many of these systems exhibit volcano behavior in C_2H_4 performance w.r.t. Pd content.[345,346] As such, it is not unexpected that we then find that a CuN_3 pre-catalyst doped with ultralow amounts of Pd (ca. 0.002 at. %) yields a relatively low maximum C_2H_4 FE of ca. 25%.[347]

Core/shell-type catalyst systems make up the remainder of the identified Cu/Pd catalyst systems, but relatively poor maximum C_2H_4 activity (≤ 44%) is observed for such alloyed systems. In general, combining Pd and Cu to form a bi-elemental electrocatalyst is actually detrimental for C_2H_4 performance, with Cu/Pd systems generally i) enhancing EtOH performance[343,348,349], and ii) decreasing H_2 and CO FEs, whilst also typically resulting in iii) suppressed current densities. Interestingly, a relatively high number of Cu/Pd publications have managed to achieve industrially relevant current densities (≥|-200| mA/cm^2) with C_2H_4 FEs of ≥34%. In addition, the presence of Pd might have a stabilizing effect on catalyst morphology under CO2RR conditions[341], which would also be of considerable industrial importance.

Table S8. Pd-based Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	Dilute Cu/Pd alloy (1.4 at. % Pd) prepared via co-electrodeposition, on glassy carbon	Alloyed/Doped	Cu, Pd	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	FAA-3-PK-75	CO_2	-0.7 V vs. RHE	-3 mA/cm^2	76	222
2	Pd NP-decorated (50 nm) cubic Cu2O microparticles (1 µm) supported on carbon black, on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, Pd, C, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.1 V vs. RHE	-22 mA/cm^2	64	341
3	Ultralow (single atom, 0.36 wt%) surface Pd-doped Cu NCs, on a GDL	Alloyed/Doped, SAC	Cu, Pd	-	(Gas-phase reactant, supplied from behind)	0.5 M KHCO3	"Sustanion"	CO_2	-1.1 V vs. RHE	-184 mA/cm^2	61	350
4	Surface Pd-doped ("6.2%") Cu-sputtered PTFE GDL	Alloyed/Doped	Cu, Pd	-	(Gas-phase reactant, supplied from behind)	0.5 M K2SO4 + x M H2SO4 (pH 2)	Nafion 117	CO_2	?	-500 mA/cm^2	60	351
5	Ultrasmal PdOx NPs supported on Cu2O MPs, on a GDL	Mixed-phase/Janus, A-supports-B	Cu, Pd, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	-0.90 V - iR vs. RHE	-400 mA/cm^2	56	352
6	Pd doped Cu2O NCs (0.88 at. % Pd), on Toray YLS-30T GDL	Alloyed/Doped	Cu, Pd, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-130	CO_2	-0.87 V vs. RHE	-800 mA/cm^2	54	342
7	Cu2O microcubes (1 µm) decorated with small Pd NPs (20 nm), prepared via galvanic displacement, mixed with carbon black, on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, Pd, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.2 V vs. RHE	-29 mA/cm^2	53	353
8	Phase-separated Cu/Pd NPs (51.3:48.7 at. ratio), on GDL	Mixed-phase/Janus, A-supports-B	Cu, Pd	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	"Fumatech"	CO_2	-0.74 V - iR vs. RHE	-361 mA/cm^2	47	354
9	Co-electroplated Cu/Pd foam (6.83:1 at. ratio), on carbon paper	Alloyed/Doped	Cu, Pd	-	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO_2	-1.2 V vs. RHE	-17 mA/cm^2	45	344
10	Pd-doped Cu/Cu2O NPs (6 at. % Pd (?)), on a GDL	Alloyed/Doped	Cu, Pd, O	Nafion	(Gas-phase reactant, supplied from behind)	0.5 M K2SO4 + x M H2SO4 (pH 2)	Nafion 117	CO_2	-2.18 V vs. RHE	-615 mA/cm^2	45[†_Cu-Pd,1]	345
11	Cu1Pd0.004 NPs prepared via ultrasonic-assisted galvanic replacement of commercial Cu NPs (100 nm), on GDL	Core/shell	Cu, Pd	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-PK-130	CO	-0.65 V - iR vs. RHE	-581 mA/cm^2	44	110
12	CuOx NPs coated with an ultrathin Pd shell, on glassy carbon	Core/shell	Cu, Pd, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 115	CO_2	-1.05 V vs. RHE	-6 mA/cm^2	40	355
13	CuPd NPs (1:0.576 at. ratio) prepared via galvanic replacement of Cu NPs (100 nm), on SGL 29BC GDL	Core/shell	Cu, Pd	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO	?	-700 mA/cm^2	35	343
14	Pd surface doped (0.002 at. %) CuN3 NCs, on carbon paper	Alloyed/Doped	Cu, Pd, N	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	X37-50 grade 60	CO_2	-1.1 V vs. RHE	-88 mA/cm^2	35	347
15	Pd NCs (ca. 20 nm) with a 'thick' (15 nm) Cu shell,	Core/shell	Cu, Pd	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	-	CO_2	-1.0 V vs. RHE	-5 mA/cm^2	35	349
16	Ultrasmal PdOx NPs supported on Cu2O MPs, on a GDL	Mixed-phase/Janus, A-supports-B	Cu, Pd, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO	-0.77 V - iR vs. RHE	-44 mA/cm^2	35	352
17	CuPd NPs (1:0.576 at. ratio) prepared via galvanic replacement of Cu NPs (100 nm), on SGL 29BC GDL	Core/shell	Cu, Pd	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	Nafion 117	CO_2	?	-500 mA/cm^2	34	343
18	Janus catalyst composed of Cu decahedra NPs grown on Pd seed (46.2:1 at. ratio Cu/Pd), supported on Vulcan XC72, on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, Pd, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.0 V vs. RHE	-30 mA/cm^2	34	356
19	Phase-separated Cu/Pd NPs (98:2 wt. ratio) deposited via electroplating on GDL	Mixed-phase/Janus, A-supports-B	Cu, Pd	-	(Gas-phase reactant, supplied from behind)	1.0 M KCl	Nafion 117	CO_2	-1.15 V - iR vs. RHE	-200 mA/cm^2	34	346
20	CuPd NPs (1:0.383 at. ratio) prepared via galvanic replacement of Cu NPs (100 nm), on SGL 29BC GDL	Core/shell	Cu, Pd	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	-1.74 V vs. RHE	-500 mA/cm^2	31	343
21	Disordered Cu/Pd NPs (1.1:1 atomic ratio), on GDL	Alloyed/Doped	Cu, Pd	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-130,	CO	-0.54 V - iR vs. RHE	?	31	134
22	Pd/Cu alloy layer (5% Pd) (400 nm) sputtered on a GDL	Alloyed/doped	Cu, Pd	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-50	CO_2	-0.65 V - iR vs. RHE	-200 mA/cm^2	31	139
23	"CuPd(100) interface catalyst" prepared starting from Pd NPs, supported on Kochin black, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Pd, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	-	CO_2	-0.8 V vs. RHE	-14 mA/cm^2	29	357
24	Thermodynamically unstable Cu9Pd1 NPs prepared via thermal shock, on carbon nanotubes	Alloyed/Doped, A-supports-B	Cu, Pd	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3	CO	-0.66 V -iR vs. RHE	-25 mA/cm^2	27	334
25	Cu NPs mixed with (in-situ formed) PdO2 NPs 'dissolved'/dispersed in an IL polymer layer, on GDL	Mixed-phase/Janus	Cu, Pd, O	Polymeric ionic liquid crosslinked with divinylbenzene	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	-0.99 V - iR vs. RHE	-350 mA/cm^2	27	348
26	Pd-doped Cu prepared via co-sputtering on GDL (30 T)	Alloyed/Doped	Cu, Pd	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	?	-300 mA/cm^2	25	358
	[†_Cu-Pd,1] Report the value given in main text, as opposed to SI table (45 vs. 44%)											

2.3.4. Pb/Cu

A summary of best-performing Cu/Pb bi-elemental catalysts for C_2H_4 production is given in Table S9. The Cu/Pb catalyst dataset is derived from 4 unique publications and comprises a total of 4 catalyst systems, with 1 using CO as a reactant and 1 having been identified as an alkaline CO_2 system. A total of 1 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55% (i.e., 57%[359]), being measured under non-alkaline CO2RR conditions. Overall, we can say that only few Pb catalysts are reported to make appreciable amounts of C_2H_4, with very little overlap between these systems. Maximum C_2H_4 FEs range between 33% and 57%, and Pb doping is typically observed to improve CO formation at lower current densities in those cases where C_2H_4 formation still occurs. The best catalyst that contains Pb that we are aware of[359] is also the most difficult to interpret: a highly complex and heterogeneous catalytic surface composed of single atom Cu sites on top of polyaniline-modified carbon with PbOx NPs distributed across the surface. Although copper SACs typically exhibit poor C_2H_4 performance and favor instead CH_4, that the addition of an inorganic layer could serve to enhance C_2H_4 performance (as we have also hypothesized previously for a Cu/Zn system[312]). Hence, we believe that the presence of a polyaniline layer plays an important role in the high C_2H_4 activity for this specific Cu/Pb system.[359] This effect is described in more detail in section S2.8 during the discussion of inorganic overlayer-type catalyst systems.

Of potential interest are the results of an older publication, wherein improved performance for a Cu/Pb catalyst was observed under CORR conditions compared to alkaline CO2RR conditions.[360] Overall though, insufficient data exists to make reasonable inferences regarding Cu/Pb systems, though current-best performances can be considered poor.

Table S9. Pb-based Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	Phase-seggregated Cu/Pb bimetallic catalyst individually electroplated on polyaniline-modified carbon paper	Mixed-phase/Janus, Single atom	Cu, Pb, C	Polyaniline	(Solution-phase reactant, supplied in front)	0.1 M CsI	Nafion 117	CO_2	-1.2 V vs. RHE	-16 mA/cm^2	57	359
2	Cu NCs with 0.7 nm Pb shell, mixed with CNPs, on glassy carbon	Core/shell, A-supports-B	Cu, Pb, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.3 V vs. RHE	-18 mA/cm^2	40	361
3	Alloyed Pb/Cu NPs (Cu:Pb ratio of 0.2%, possibly phase-separated) mixed with CNPs, on GDL	Alloyed/Doped	Cu, Pb	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Nafion 117	CO	-2.4 V vs. SCE	-200 mA/cm^2	34	360
4	Pb-doped (3.4 wt%) Cu2O nanosheets, on GDL	Alloyed/Doped	Cu, Pb, O	Nafion	(Gas-phase reactant, supplied from behind)	3.0 M KOH	FAA-3-PK-130	CO_2	-1.1 V vs. RHE	-204 mA/cm^2	33	362

2.3.5. Ni/Cu

A summary of best-performing Cu/Ni bi-elemental catalysts for C_2H_4 production is given in Table S10. The Cu/Ni catalyst dataset is derived from 23 unique publications and comprises a total of 24 catalyst systems, with 1 using CO as a reactant and 13 having been identified as alkaline CO_2 systems. A total of 12 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55%, though 7 of those were measured under alkaline CO2RR conditions. The top-two catalysts yield 72%[363] and 81% C_2H_4[364], both being non-alkaline CO2RR systems. Cu/Ni catalysts are abundant and relatively straightforward, with a large proportion of Ni/Cu catalysts consisting of CuOx NPs mixed with a CO-forming Ni catalyst (tandem-type). Considering that these CO-forming Ni catalysts typically consist of single atom Ni sites on carbon, such tandem-type Cu/Ni catalysts bear striking resemblance to carbon-supported Cu catalysts (discussed in detail in the paragraph on Cu/C systems). Specifically in the case of Cu/Ni catalyst systems, tandem-type catalysts are observed to yield a broad range of C_2H_4 activities, being able to reach respectable maximum FEs of ca. 65%.[100,365,366] We are even aware of an outlier yielding an impressive 72% C_2H_4[363], although we hypothesize that mesoporosity/confinement effects are the driving force for the exceptional performance in that particular case. Overall, these Cu/Ni tandem-type systems seem to allow for relatively high C_2H_4 selectivities compared to other tandem-type systems, which seems to be related to the good match between the potential optimum for CO_2-to-CO conversion on the Ni-SAC sites and the CO-to-C_2H_4 conversion on copper sites.[100] In addition, most other CO-forming catalysts (e.g., Ag, Au or Zn based) would not require a carbon support to be present such as is the case for Ni SACs. Hence in the case of specifically Cu/Ni tandem-type catalysts, the CO-formation effect and catalyst-support effects are convoluted, possibly being responsible for the slightly improved performance of these Cu/Ni tandem-type systems.

The bulk of non-tandem type Cu/Ni catalysts comprise mixed-phase/janus-type and alloyed/doped-type systems. Out of these, the mixed-phase/janus-type catalysts yield overall higher C_2H_4 performance in the 50%-60% range[367-369] whilst alloyed/doped-type systems generally yield C_2H_4 FEs between 25%-40%.[334,370] Additionally, increasing the Ni content seems to be detrimental to C_2H_4 performance in general. However, a particular catalyst system is in direct opposition to this observation. Namely, 2D Cu/Ni alloy nanosheets with a 50 at.% Ni content, have been reported to yield maximum C_2H_4 FEs of 80.5%. We posit this deviation from the status quo for alloyed/doped-type systems is likely related to the 2D nanosheet morphology, an effect that we discuss in further detail in the main text. Overall, we observe that Ni is a very versatile co-element for modifying Cu-based catalysts yielding a large range of possible C_2H_4 activities, though current research lines focus mostly on its potential as a CO-forming additive.

Table S10. Ni-based Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	Ultrathin (ca. 4.8 nm) alloyed hexagonal CuNi nanosheets (ca. 1:1 atom ratio), on Ti mesh	Alloyed/Doped	Cu, Ni	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	?	CO_2	-1.5 V vs. RHE	-470 mA/cm^2	81	364
2	Cu NPs encapsulated in mesoporous Ni-SAC functionalized carbon, on GDL	Mixed-phase/Janus, A-supports-B	Cu, Ni, C, N	-	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	"Fuel Cell Store"	CO_2	-1.1 V -iR vs. RHE	-406 mA/cm^2	72	363
3	(100)-facet rich Cu NWs mixed with Ni-SAC and CNPs, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Ni, C, N	PVDF, NMP	(Gas-phase reactant, supplied from behind)	10 M KOH	-	CO_2	-0.5 V vs. RHE	-101 mA/cm^2	66	365
4	Ni-SAC layer on top of sputtered Cu layer, on GDL	Overlayer, Tandem catalyst	Cu, Ni, C, N	Nafion (?)	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-0.72 V -iR vs. RHE	-160 mA/cm^2	63	366
5	Ni-N/C layer on top of Cu NP layer, on a GDL	Overlayer, Tandem catalyst	Cu, Ni, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-75	CO_2	-0.70 V -iR vs. RHE	-593 mA/cm^2	62	371
6	Cu NPs supported on Ni-SAC mixed with PTFE, on GDL	Mixed-phase/Janus, A-supports-B	Cu, Ni, C, N	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	Selemion DSVN	CO_2	-1.33 V -iR vs. RHE	-600 mA/cm^2	62	100
7	Cu NPs mixed with Ni-SAC, on homemade GDL	Mixed-phase/Janus	Cu, Ni, C, N	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-130	CO_2	-0.58 V -iR vs. RHE	-308 mA/cm^2	61	372
8	Ni electroplated on Cu NW array-modified GDL	Mixed-phase/Janus, overlayer	Cu, Ni	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	3PK-130	CO_2	-1.1 V -iR vs. RHE	-432 mA/cm^2	59	373
9	Ni-doped (1.2 at.%) self-supporting Cu2O NWs arrays on Cu mesh substrate	Mixed-phase/Janus, A-supports-B	Cu, Ni, O	-	(Solution-phase reactant, supplied in front)	0.5 M KCl	Nafion 117	CO_2	-1.1 V -iR vs. RHE	-65 mA/cm^2	58	369
10	CU NPs supported on Ni-SAC layer, on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, Ni, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 + 0.1 M KCl	Nafion 117	CO_2	-1.1 V vs. RHE	-3 mA/cm^2	57[†–Cu-Ni,1]	374
11	CuOx NCs supported on Ni/C,N catalyst, on GDL	Mixed-phase/Janus, A-supports-B	Cu, Ni, C, N	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-50	CO_2	-0.60 V -iR vs. RHE	-127 mA/cm^2	55	375
12	Ni-doped Cu2(OH)3Cl pre-cursor reduced in-situ to form β nickel-oxide hydroxide (NiOOH)/Cu active phase, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Ni, C, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-130	CO_2	-1.25 V -iR vs. RHE	-400 mA/cm^2	55	368
13	CuO NPs supported on Ni-SAC, on GDL	Mixed-phase/Janus, A-supports-B	Cu, Ni, C, N	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Sustainion X37 50	CO_2	-0.89 V -iR vs. RHE	-1500 mA/cm^2	54	376
14	Cu-doped Ni MOF mixed with MWCNTs and PTFE, on GDL	Mixed-phase/Janus	Cu, Ni, C, O	PiperION-A5	(Gas-phase reactant, supplied from behind)	1.0 M KOH	PiperION-A40	CO_2	-1.3 V vs. RHE	-527 mA/cm^2	53	367
15	(100)-facet rich Cu NWs mixed with Ni-SAC and CNPs, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Ni, C, N	PVDF, NMP	(Gas-phase reactant, supplied from behind)	0.5 M KHCO3	Nafion 212	CO_2	-1.6 V vs. RHE	-78 mA/cm^2	51	365
16	Cu/Ni alloy NPs (7% Ni), co-sputtered on GDL	Alloyed/Doped	Cu, Ni	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Sustainion 37-50	CO_2	-0.9 V -iR vs. RHE	-200 mA/cm^2	41	370
17	Cu NWs decorated with Ni-TMC, on GDL	Core/shell, A-supports-B	Cu, Ni	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-1.0 V vs. RHE	?	37	333
18	Ni-based SAC mixed with Cu2O octahedra (ca. 200 nm), on a GDL	Mixed-phase/Janus, A-supports-B	Cu, Ni, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	"Selemion"	CO_2	-1.03 V -iR vs. RHE	-500 mA/cm^2	35	377
19	Coral-like catalyst obtained via thermal and electrochemical treatment of Ni-based metalloporphyrin intermixed in Cu-based MOF, on carbon paper	Mixed-phase/Janus	Cu, Ni, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 115	CO_2	-1.27 V vs. RHE	-49 mA/cm^2	32	378
20	Ni clusters deposited through galvanic displacement on CuS-derived roughened Cu foam	Mixed-phase/Janus	Cu, Ni	-	(Solution-phase reactant, supplied in front)	1.0 M KOH	Sustainion 37–50	CO_2	-0.88 V -iR vs. RHE	-268 mA/cm^2	32	379
21	Cu NPs supported on Ni-N/C , on glassy carbon	Tandem catalyst, A-supports-B	Cu, Ni, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.09 V -iR vs. RHE	-6 mA/cm^2	31	380
22	Thermodynamically unstable Cu9Ni1 NPs prepared via thermal shock, on carbon nanotubes	Alloyed/Doped, A-supports-B	Cu, Ni	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3	CO	-0.64 V -iR vs. RHE	-25 mA/cm^2	26	334
23	Air-oxidized Cu/Ni alloy NPs (19% Ni), on carbon paper	Alloyed/Doped	Cu, Ni	-	(Solution-phase reactant, supplied in front)	0.05 M KHCO3	-	CO_2	-1.2 V vs. RHE	-2 mA/cm^2	25	381
24	Ni-doped Cu(OH)2 NWs with a PTFE shell, on a GDL	Alloyed/Doped, Core/shell (in-)organic	Cu, Ni, O	PTFE	(Gas-phase reactant, supplied from behind)	-	X37-50 grade RT	CO_2	-3.4 V vs. ANODE	-200 mA/cm^2	10	311

[†–Cu-Ni,1] Main text states 57.3, SI states 57.8. Rounded down to 57

2.3.6. Co/Cu

A summary of best-performing Cu/Co bi-elemental catalysts for C_2H_4 production is given in Table S11. The Cu/Co catalyst dataset is derived from 16 unique publications and comprises a total of 19 catalyst systems, with 2 using CO as a reactant and 4 having been identified as alkaline CO_2 systems. A total of 7 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55%, though 3 of those were measured under alkaline CO2RR conditions. The top-two catalysts yield 76%[143] and 81% [382] C_2H_4, both being non-alkaline CO2RR systems. Cu/Co catalyst systems bear much resemblance to Cu/Ni systems, with a CO-forming Co-based MOF or TMC commonly being added to yield tandem-type catalyst systems.[143,383-386] These systems are observed to yield typical C_2H_4 FEs between 40%-50% , with a maximum of 54% reported by Ma *et al.*[386] for a catalyst system comprising a (CO-forming) Co MOF-based overlayer deposited onto Cu2O nanocubes. However, we consider such systems to be less interesting on account of intrinsic catalytic activity for making C_2H_4 not being strongly influenced besides (potentially) modulating the (local) CO pressure (P_{CO}) and CO surface coverage (θ_{CO}).

Rather, it is the non-tandem Cu/Co catalyst systems that have the potential for improving intrinsic catalytic activity and thus can provide clues on how to increase C_2H_4 performance. In this regard, we find that adding minor quantities of Co (between 0.2 at.%[387] – 1.5 at.%[388]) to alloyed/doped-type and mixed-phase/janus-type Cu/Co systems can improve catalyst performance w.r.t benchmark Cu catalysts, although adding too much Co worsens performance. Nonetheless, the overall performance of these types of systems tends to be relatively poor with maximum C_2H_4 FEs between 20%-45% C_2H_4.[333,387,388] Also, it is important to note that the number of alloyed/doped systems is limited at 3.

An outlier is observed in the form of a CoOx/CuOx mixed-phase/janus-type catalyst with a high Co content, having been prepared via co-reduction followed by post-treatment in cold H_2 plasma. XRD and EDS showed individual, but well mixed, CoOx and CuOx domains. This catalyst system has been reported to yield an impressive C_2H_4 FE of 70% when the Cu to Co ratio was 2:1 (i.e., 33. at. % Co).[389] However, it should be noted that the authors therein attributed this improved performance to spillover of CO from the Co (cobalt) sites to the Cu sites, which would make this system act as a tandem-type system. However, CoOx isn't known to be a good CO2-to-CO catalyst. As such, we do not categorize this catalyst as being of the tandem type herein. Another catalyst that looks to be an outlier is a system comprised of porous Cu_2O microparticles with a CO-forming Co-based TMC confined within its pores.[143] Normally this would fall under the tandem-type category as well, but selectivity was largely unchanged when CO instead of CO_2 was used as the reactant (making tandem-type catalysis impossible). As such, the cobalt component does not play a role here (but it was present and is thus listed in the table). Importantly, the excellent performance of this catalyst seems to be related to a nanoconfinement effect instead, which we have previously also hypothesized to be responsible for the exceptional performance of a similar Cu/Ni system which yielded 72% C_2H_4[363].

The best Cu/Co catalyst system identified in this study are 2D alloyed Co/Cu nanosheets (1:1 ratio, i.e., 50 at. % Co), yielding an impressive 81% FE for C_2H_4.[389] We would like to reiterate here the resemblance between Cu/Co and Cu/Ni systems, considering that a similar 2D alloyed Cu/Ni nanosheet catalyst with extraordinary CO_2-to-C2H_4 performance also exists.[364] However, we also must point out that both publications are by the same authors and their results have not been verified by an independent party, to the best of our knowledge. Overall, we observe that cobalt seems to be a very versatile co-element for Cu-based electrocatalyst allowing for enhanced C_2H_4 activity at both low and high Co contents, with alloyed/doped-type and mixed-phase/janus-type systems being most promising and allowing for exceptionally high faradaic efficiencies.

Table S11. Co-based Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	Ultrathin (ca. 46.3 nm) alloyed hexagonal CuCo nanosheets (ca. 1:1 atom ratio), on glassy carbon	Alloyed/Doped	Cu, Co	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.5 V vs. RHE	-400 mA/cm^2	81	[382]
2	Co-TMC (tetraphenylporphyrin) confined within the nanopores of porous Cu2O microparticles, on PTFE-modified GDL	A-supports-B, Mixed-phase/Janus	Cu, O, Co	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KCl + x M H2SO4 (pH 1.9)	Nafion 115	CO	?	-800 mA/cm^2	76	[143]
3	Cu2O NCs supported on cobalt phthalocyanine-modified-acetylene black, on GDL	A-supports-B, Mixed-phase/Janus	Cu, Co, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-20	CO_2	-0.76 V - iR vs. RHE	-317 mA/cm^2	71	[384]
4	Cold H2 plasma-treated porous mixed CoOx/CuOx, on glassy carbon	Mixed-phase/Janus	Cu, Co	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	?	CO_2	-1.0 V vs. RHE	-21 mA/cm^2	70	[389]
5	Vulcan XC-72 toplayer on Co-TMC midlayer, on Cu-sputtered PTFE GDL	Overlayer	Cu, Co, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Nafion 115	CO_2	-0.79 V - iR vs. RHE	-420 mA/cm^2	67	[383]
6	Cu2O NCs supported on cobalt phthalocyanine-modified-acetylene black, on glassy carbon	A-supports-B, Mixed-phase/Janus	Cu, Co, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.1 V - iR vs. RHE	-51 mA/cm^2	58	[384]
7	Cu NWs decorated with Co-TMC (phthalocyanine, mass ratio of 100:1 Cu/Co-TMC), on GDL	Core/shell, A-supports-B	Cu, Co	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-1.4 V vs. RHE	-350 mA/cm^2	58	[333]
8	Co-TMC shell around Cu2O NCs, on carbon paper	Core/shell	Cu, Co	-	(Gas-phase reactant, supplied from behind)	1.0 M KCl	Nafion 117	CO_2	-2.85 V vs. RHE	-500 mA/cm^2	54	[386]
9	Co-TMC (tetraphenylporphyrin) confined within the nanopores of porous Cu2O microparticles, on PTFE-modified GDL	A-supports-B, Mixed-phase/Janus	Cu, O, Co	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KCl + x M H2SO4 (pH 1.9)	Nafion 115	CO_2	-0.93 V - iR vs. RHE	-800 mA/cm^2	52	[143]
10	Co-TMC surface-modified Cu NCs supported on carbon black, on GDL substrate	Core/shell, A-supports-B	Cu, Co, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	FAB-PK-130	CO_2	?	-200 mA/cm^2	49	[385]
11	Co-containing (CO forming) TMC (porphyrin) coated on CuOx NW-modified Cu mesh substrate	Core/Shell, Mixed-phase/Janus	Cu, Co, O	-	(Solution-phase reactant, supplied in front)	0.5 M KCl (CO_2-saturated)	Nafion 117	CO_2	-0.8 V - iR vs. RHE	-22 mA/cm^2	48	[390]
12	Co (0.2 %)/CuO alloy NPs (ca. 16 nm) with single-atom Co prepared from Cu-MOF precursor, on carbon paper	Alloyed/Doped	Cu, Co	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	"Selemion"	CO_2	-1.01 V vs. RHE	-650 mA/cm^2	43	[387]
13	Co-doped (1.1 at.%) self-supporting Cu2O NWs arrays on Cu mesh substrate	Mixed-phase/Janus, A-supports-B	Cu, Co, O	-	(Solution-phase reactant, supplied in front)	0.5 M KCl	Nafion 117	CO_2	-1.1 V -iR vs. RHE	-58 mA/cm^2	42	[369]
14	Cu NWs decorated with Co-TMC (phthalocyanine, mass ratio of 100:1 Cu/Co-TMC), on GDL	Core/shell, A-supports-B	Cu, Co	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO	-1.2 V vs. RHE	?	38	[333]
15	Co TMC (porphyrin) coated on Cu-sputtered PTFE GDL	Overlayer	Cu, Co	-	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	FAA-3-PK-130	CO_2	?	?	37	[391]
16	Coral-like catalyst obtained via thermal and electrochemical treatment of Co-based metalloporphyrin intermixed in Cu-based MOF, on carbon paper	Mixed-phase/Janus	Cu, Co, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 115	CO_2	-1.17 V vs. RHE	-39 mA/cm^2	32	[378]
17	Co-doped ("0.4%") Cu NWs, grown on Cu foil	Mixed-phase/Janus, Core/Shell	Cu, Co, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	"Nafion"	CO_2	-1.0 V -iR vs. RHE	-22 mA/cm^2	27	[392]
18	Co-doped Cu(OH)2 NWs with a PTFE shell, on a GDL	Alloyed/Doped, Core/shell (in-)organic	Cu, Co, O	PTFE	(Gas-phase reactant, supplied from behind)	-	X37-50 grade RT	CO_2	-3.35 V vs. ANODE	-200 mA/cm^2	25	[311]
19	Cu/Co (4% Co) alloy NPs prepared via co-electroplating on Cu substrate	Alloyed/Doped	Cu, Co	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 212	CO_2	-1.19 V - iR vs. RHE	?	22	[388]

2.3.7. Ga/Cu

A summary of best-performing Cu/Ga bi-elemental catalysts for C_2H_4 production is given in Table S12. The Cu/Ga catalyst dataset is derived from 8 unique publications and comprises a total of 9 catalyst systems, with 1 using CO as a reactant and 6 having been identified as alkaline CO_2 systems. None of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55%. The top-most catalyst yields 45% C_2H_4 and concerns an alkaline CO2RR system. The highest non-alkaline system yields 43% C_2H_4 and uses CO as the reactant.[393]

Gallium-copper systems are typically reported in the form of alloys (alloyed/doped-type), with only a singular source reporting on an overlayer-type system (having low C_2H_4 activity). Ga contents vary considerably across sources (between 1.5 at.%[277] – 69 at.%[393] Ga), with maximum C_2H_4 FEs similarly varying considerably (between 20% – 45%). Although none of the sources exhibit particularly high C_2H_4 performance, one of the best catalyst systems (yielding 43% C_2H_4)[393] actually employed CO as a reactant rather than CO_2 – a measurement that is not often conducted, empirically. No consensus is reached between publications as to why activity is changed upon gallium addition. Explanations range from p-d orbital hybridization changing adsorption strength of key intermediates (CO_2, CO)[277] to suppression of copper oxidation by imparting electron density to Cu sites and gallium oxophilicity[293,394] to decreasing the C-C coupling barrier[288] to allowing for elevated CO coverage by reducing repulsion between *CO adsorbates[393]. Rather than enhancing C_2H_4 performance, it is commonly observed that EtOH formation is favored, whilst HER activity is suppressed.[277,293,395] The limited quantity of sources together with the significant heterogeneity of the Cu/Ga dataset makes meaningful discussion impossible in our opinion.

	Table S12. Ga-based Cu											
#	**Electromaterial description**	**Catalyst type**	**Main elements**	**Polymeric / organic & inorganic additives**	**Reactant delivery mode**	**Catholyte**	**Membrane**	**Reactant**	**E**	**j**	**C_2H_4 FE**	**Reference**
1	Ga-doped CuOx NCs (1.67 at.% Ga), on Toray GDL	Alloyed/Doped	Cu, Ga, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	-1.07 V - iR vs. RHE	-900 mA/cm^2	45	277
2	Cu4Ga9 intermetallic alloy NPs, on a GDL	Alloyed/Doped	Cu, Ga	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-130	CO	-1.15 V vs. RHE	?	43	393
3	400 nm thick evaporated Cu/Ga alloy (95:5), on GDL	Alloyed/Doped	Cu, Ga	-	(Gas-phase reactant, supplied from behind)	-	AF1-HNN8-50-X	CO_2	?	-100 mA/cm^2	37	288
4	Ga/Cu alloy layer (5% Ga) (400 nm) sputtered on a GDL	Alloyed/doped	Cu, Ga	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-50	CO_2	-0.65 V - iR vs. RHE	-200 mA/cm^2	34	139
5	Thermally annealed Cu-Ga LDH, on GDL	Alloyed/Doped	Cu, Ga	Nafion	(Gas-phase reactant, supplied from behind)	? 1.0 M KOH	FAA-3-PK-130	CO_2	-1.0 V - iR vs. RHE	-522 mA/cm^2	31	293
6	Cu4Ga9 intermetallic alloy NPs, on a GDL	Alloyed/Doped	Cu, Ga	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-130	CO_2	-1.49 V vs. RHE	-1800 mA/cm^2	31	393
7	Ga(OH)x overlayer on Cu-sputtered PTFE GDL	Overlayer, Mixed-phase/Janus	Cu, Ga, O	-	(Gas-phase reactant, supplied from behind)	1 M KOH	FAA-3-PK-130	CO_2	?	?	27	395
8	Cu/Ga alloy NPs (4 at. % Ga), on glassy carbon	Alloyed/Doped	Cu, Ga	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Selemion AMV	CO_2	-1.1 V - iR vs. RHE	-3 mA/cm^2	23	394
9	Alloy/mixed metal Ga/Cu (1:3 ratio) microparticles, on GDL - obtained via reduction of mixed nitrate salt with NaBH4 over 12h period	Alloyed/Doped	Cu, Ga	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	NEOSEPTA, AHA	CO_2	-0.6 V vs. RHE	-106 mA/cm^2	19	105

2.3.8. Fe/Cu

A summary of best-performing Cu/Fe bi-elemental catalysts for C_2H_4 production is given in Table S13. The Cu/Fe catalyst dataset is derived from 9 unique publications and comprises a total of 9 catalyst systems, with 0 (none) using CO as a reactant and 3 having been identified as alkaline CO_2 systems. A total of 1 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55% (specifically, 64%[321]), being measured under alkaline CO2RR conditions. The highest non-alkaline system yields 51% C_2H_4 and uses CO_2 as the reactant.[386] Cu/Fe catalyst systems predominantly take the form of tandem-type catalysts (with Fe-based component responsible for converting CO_2 to CO)[321,378,391,396], with only a single non-tandem publication reporting on a copper substrate containing single atom Fe sites being able to generate C_2H_4 at low overpotentials and low current densities (max C_2H_4 FE of ca. 30%).[397] However, the product spectrum quickly switches to CH_4 formation once the current is increased. Considering that tandem-type catalyst systems do not intrinsically change the catalytic activity of the C_2H_4-forming sites, existing literature regarding Cu/Fe systems does not allow for much insights in the way of how to improve C_2H_4 performance.

	Table S13. Fe-based Cu											
#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	Cu NP layer (0.8 mg/cm2) with Fe-N/C overlayer (only present near CO2 inlet, 5% of total area), on GDL	Overlayer, Tandem catalyst	Cu, Fe, C, N	Sustainion XA-9	(Gas-phase reactant, supplied from behind)	-	"Sustainion"	CO_2	-3.38 V vs. ANODE	-1200 mA/cm^2	64	321
2	Fe-TMC shell around Cu2O NCs, on carbon paper	Core/shell	Cu, Fe	-	(Gas-phase reactant, supplied from behind)	1.0 M KCl	Nafion 117	CO_2	-3.0 V vs. RHE	-500 mA/cm^2	51	386
3	Fe TMC (porphyrin) coated on Cu-sputtered PTFE GDL	Overlayer	Cu, Fe	-	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	FAA-3-PK-130	CO_2	?	?	41	391
4	Fe TMC (porphyrin) coated on Cu NCs, on glassy carbon	A-supports-B, Mixed-Phase/Janus	Cu, Fe	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	"Selemion"	CO_2	-1.05 V vs. RHE	-4 mA/cm^2	36	396
5	Coral-like catalyst obtained via thermal and electrochemical treatment of Fe-based metalloporphyrin intermixed in Cu-based MOF, on carbon paper	Mixed-phase/Janus	Cu, Fe, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 115	CO_2	-1.17 V vs. RHE	-38 mA/cm^2	33	378
6	Cu NWs decorated with Fe-TMC, on GDL	Core/shell, A-supports-B	Cu, Fe	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-1.0 V vs. RHE	?	31	333
7	Single atom Fe sites on a Cu-sputtered PTFE GDL	Single atom	Cu, Fe	-	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	?	CO_2	?	-100 mA/cm^2	31	397
8	Fe-doped (1.3 at.%) self-supporting Cu2O NWs arrays on Cu mesh substrate	Mixed-phase/Janus, A-supports-B	Cu, Fe, O	-	(Solution-phase reactant, supplied in front)	0.5 M KCl	Nafion 117	CO_2	-1.1 V -iR vs. RHE	-25 mA/cm^2	22	369
9	Fe-doped Cu(OH)2 NWs with a PTFE shell, on a GDL	Alloyed/Doped, Core/shell (in-)organic	Cu, Fe, O	PTFE	(Gas-phase reactant, supplied from behind)	-	X37-50 grade RT	CO_2	-3.9 V vs. ANODE	-300 mA/cm^2	17	311

2.3.9. Au/Cu

A summary of best-performing Cu/Au bi-elemental catalysts for C_2H_4 production is given in Table S14. The Cu/Au catalyst dataset is derived from 19 unique publications and comprises a total of 21 catalyst systems, with 2 using CO as a reactant and 7 having been identified as alkaline CO_2 systems. A total of 1 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55% (56%[371]), which was measured under alkaline CO2RR conditions. The highest non-alkaline system yields 45% C_2H_4 and uses CO_2 as the reactant.[398] By and large, reported Cu/Au systems fall into the category of tandem-type catalysts where the Au component serves to convert CO_2 into CO.[371,399-404] Thus, we are limited in how much we can learn from them with respect to improving C_2H_4 performance. However, a small number of publications report on catalyst systems that fall into other categories. To start, various works describe alloyed/doped-type catalyst systems. We find that such systems typically exhibit poorer C_2H_4 activity than pure copper systems, with the product spectrum shifted away from C_2H_4 to e.g., EtOH[405] or CH_4[124]. This is corroborated by Huang *et al.,* who show that Au/Cu nanoparticles with a pseudo-core/shell morphology (i.e., a Cu-rich shell with an Au-rich core) exhibit some activity for C_2H_4 formation at low overpotentials (ca. 20 %), but this activity is lost when looking at homogeneous Cu/Au alloy NPs.[406]

A second group of non-tandem type Cu/Au systems can be categorized as being of the mixed-phase/janus-type. It is shown that for Janus-type catalysts, the shape of the Au "seed" has an effect on the activity of the C_2H_4 performance[407] – which we interpret as Au playing a more active role than as solely serving as a CO donor (hence it not being designated as tandem-type herein). This is corroborated by physically mixing near-identical individual Au and Cu particles, which yielded worse C_2H_4 performance than the Au-derived Au/Cu Janus particles.[408] Other mixed-phase catalysts (e.g., Au NPs deposited/grown on Cu) are typically reported to function via a tandem mechanism though.[402,409] In general, we find that Cu/Au systems do not result in high C_2H_4 performance, and that the samples with the lowest Au contents typically perform best (albeit not necessarily better than the pure Cu benchmark).[124,408,410] Overall, we observe that Au does not seem to be a good candidate for improving C_2H_2 performance of Cu electrocatalysts.

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	Au NP layer on top of Cu NP layer, on a GDL	Tandem catalyst	Cu, Au	Nafion	(Gas-phase reactant, forced through surface)	1.0 M KOH	FAA-3-PK-75	CO_2	-0.70 V -iR vs. RHE	-596 mA/cm^2	56	[371]
2	Cu shell grown on top of Au nanoribbons with 4H phase supported on carbon black, on carbon paper	Core/Shell	Cu, Au, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.11 V -iR vs. RHE	-14 mA/cm^2	45	[398]
3	Au/Cu janus nanocrystals derived from penta-twinned Au nanobipyramids, on glassy carbon	Mixed-phase/Janus	Cu, Au	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-0.98 V -iR vs. RHE	-5 mA/cm^2	42	[407]
4	Au NPs ("large", order of a few nm) supported on Cu2O octahedra (ca. 200 nm) through galvanic displacement, on a GDL	Mixed-phase/Janus, A-supports-B	Cu, Au	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	"Selemion"	CO_2	-0.97 V -iR vs. RHE	-300 mA/cm^2	42	[377]
5	Au/Cu alloy hollow NWs (Cu:Au of 5:1) prepared via galvanic displacement, on GDL	Alloyed/Doped	Cu, Au	-	(Solution-phase reactant, supplied in front)	1.0 M KOH	?	CO	-0.6 V vs. RHE	-67 mA/cm^2	40	[124]
6	Au/Cu bimetallic (100)-facet rich penta-twinned nanorods (1 at. % Au, single atom sites), on carbon paper	Alloyed/Doped	Cu, Au	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	"Selemion"	CO_2	-0.62 V -iR vs. RHE	-200 mA/cm^2	40	[410]
7	Au NPs (0.7 at.%) supported on Cu NWs, on glassy carbon	A-supports-B	Cu, Au	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 + 0.1 M KCl	Nafion 117	CO_2	-1.4 V vs. RHE	-25 mA/cm^2	39	[411]
8	Au NPs supported on Cu2O NWs grown on Cu-sputtered, etched FTO substrate	A-supports-B	Cu, Au	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Fumasep FKS-50	CO_2	-1.05 V vs. RHE	-43 mA/cm^2	39	[400]
9	Air-annealed (400 °C/4h) Au/CuC2O4/C yielding nanoporous hollow Au/CuO–CuO tandem catalsyt, on carbon paper	Mixed-phase/Janus	Cu, Au, O	Nafion	?	1.0 M KOH	"Fumasep"	CO_2	-1.3 V vs. RHE	?	37	[402]
10	Air-annealed (400 °C/4h) Au/CuC2O4/C yielding nanoporous hollow Au/CuO–CuO tandem catalsyt, on carbon paper	Mixed-phase/Janus	Cu, Au, O	Nafion	?	1.0 M KOH	"Fumasep"	CO	-1.3 V vs. RHE	?	37	[402]
11	Au/Cu janus-type NPs consisting of concave Au NCs linked with hollow quasi-spherical Cu particles (ca. 118 nm) (Au:Cu ratio of 1:24), on a GDL	Mixed-phase/Janus	Cu, Au	Nafion	(Gas-phase reactant, supplied from behind)	3.0 M KOH	-	CO_2	-0.75 V -iR vs. RHE	-480 mA/cm^2	36	[408]
12	Au/Cu bimetallic (100)-facet rich nanocubes (2 at. % Au, single atom sites), on carbon paper	Alloyed/Doped	Cu, Au	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	"Selemion"	CO_2	?	-150 mA/cm^2	28	[410]
13	Au-doped Cu prepared via co-sputtering on GDL (30 T)	Alloyed/Doped	Cu, Au	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	?	-300 mA/cm^2	28	[358]
14	Au NPs supported on Cu2O NCs, on carbon paper	A-supports-B	Cu, Au	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	"Nafion"	CO_2	-1.3 V vs. RHE	-6 mA/cm^2	24	[401]
15	Au NPs (8 nm) linked via bipyridine to Cu NWs (50 nm) supported on CNPs, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Au, C	PVDF, NMP	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.5 V vs. RHE	?	23	[403]
16	Au/Cu alloy layer (5% Au) (400 nm) sputtered on a GDL	Alloyed/doped	Cu, Au	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-50	CO_2	-0.77 V - iR vs. RHE	-400 mA/cm^2	22	[139]
17	Galvanic displacement driven surface-Au doped Cu microcones on Cu foil	Core/shell	Cu, Au	-	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 115	CO_2	-1.1 V vs. RHE	-28 mA/cm^2	21	[405]
18	Hollow Cu NPs with Au NPs inside of them, on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, Au	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.05 V -iR vs. RHE	-28 mA/cm^2	21	[404]
19	Cu shell/Au core NPs (50 nm) with elemental gradient, on GDL	Core/shell (gradient)	Cu, Au	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-0.4 V vs. RHE	-0.1 mA/cm^2	20	[406]
20	Cu particles electroplated on 'wrinkled' Au substrate	Mixed-phase/Janus, A-supports-B	Cu, Au	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	?	CO_2	-1.05 V vs. RHE	-15 mA/cm^2	20	[412]
21	Au NPs (10 nm) on top of electropolished monocrystalline Cu substrate, restructuring in-situ to form core/shell structures	Core/shell	Cu, Au	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	FAA-3-PK130	CO_2	-1.03 V -iR vs. RHE	-10 mA/cm^2	8	[409]

2.3.10. Ag/Cu

A summary of best-performing Cu/Ag bi-elemental catalysts for C_2H_4 production is given in Table S15. The Cu/Ag catalyst dataset is derived from 71 unique publications and comprises a total of 77 catalyst systems, with 7 using CO as a reactant and 28 having been identified as alkaline CO_2 systems. A total of 12 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55%, though 8 of those were measured under alkaline CO2RR conditions. The top-two catalysts (consisting of non-alkaline CO2RR systems) both yield 78% C_2H_4, although originating from two publications by the same author.[413,414] The third-most selective catalyst yields 69% C_2H_4 and concerns an alkaline CO2RR system.[415] Cu/Ag catalyst systems are the most ubiquitous amongst the bi-elemental catalysts that make appreciable amounts of C_2H_4 (i.e., ≥25%). Although the dataset is diverse, we find that galvanic displacement of copper with silver is a popular method for creating Cu/Ag catalysts with various morphologies. The resulting systems consist of copper particles with a given morphology and size distribution being sparsely decorated with small Ag clusters, with the Ag sites presumed to be acting as the CO-formation sites and the morphology of the initial Cu particles mostly retained. These tandem-type catalyst systems generally result in rather ordinary C_2H_4 activity with maximum C_2H_4 FEs around 45%. Furthermore, when multiple concentrations of Ag are reported, the lowest Ag content typically yields the highest C_2H_4 selectivity – though this performance might well be lower than the (undoped) Cu NPs on their own. Rather than improving C_2H_4 performance, we observe that the presence of Ag promotes the formation of oxygenates such as e.g., EtOH and PrOH.[416]

A small number of publications exist that report C_2H_4 FEs between 45-55%, but these above-average (for Cu/Ag bi-elemental catalysts) performing systems exhibit high heterogeneity both in terms of catalyst characteristics and in terms of measurement methodology, making it impossible to pinpoint specific characteristics that make them better than others. Especially considering many of their characteristics are shared also with the poorer-performing systems. As such, we cautiously posit there must exist a delicate balance of several attributes for Cu/Ag systems to yield appreciable amounts of C_2H_4, with most catalyst systems ending up on the 'wrong' end of the balance.

Lastly, we have a look at the small number of Cu/Ag-based outliers, which sport C_2H_4 FEs of ≥60%. Specifically, 60%[417], 67%[418], 69%[415] and 76%[413,414] – although the lowest of these four corresponds to a publication wherein they report a doubling of the C_2H_4 FE (from 33% to 60%) after turning off the system overnight and starting it back up the following day. Considering they have provided no evidence regarding reproducing this behavior we consider this source unreliable and forego detailed discussion. The 3rd highest C_2H_4 FE (67%) was obtained on galvanically modified octahedral Cu NPs (mixed-phase/janus-type), tested in an H-cell environment.[418] From testing NPs with other morphologies, they found that the octahedral shape was paramount for increasing the catalytic performance, which they attributed to a high fraction of (111) facets. To continue, 69.2% C_2H_4 could be achieved on a porous alloyed Ag/Cu surface prepared via alternated magnetron sputtering of Cu and Ag targets on a GDL substrate (alloyed/doped-type).[415] The system was operated as an MEA-electrolyzer, with the C_2H_4 optimum observed at -450 mA/cm2 at a cell voltage of -3.8V. Although the combination of high C_2H_4 FE and high current density might give the impression of industrial relevance, the cell voltage is excessively high. In addition, the combination of CO_2 as a reactant with an anion exchange membrane (AEM) make this system an alkaline CO2RR configuration, further decreasing its industrial potential.

The maximum C_2H_4 FE of 76% (as far as we are aware) has been reported for a simple tandem-type catalyst where an optimized (commercial) Cu NP/Nafion layer was deposited on top of an Ag foil.[413,414] This effect is similar to another publication regarding a Cu/Zn catalyst modified with a Nafion/PVDF coating (yielding

74% C_2H_4)[312], and a publication concerning a Cu/Pb catalyst supported on a polyaniline-modified carbon substrate.[359] During our discussion of those systems, we already proposed that the enhancement in C_2H_4 might well be related to the presence of an inorganic layer rather than the fact that a bi-elemental catalyst is used. This effect is described in more detail in the main text. Overall, we conclude that Ag is not a very suitable candidate for improving the performance of Cu-based CO2RR catalysts for C_2H_4 formation.

	Table S15. Ag-based Cu											
#	**Electromaterial description**	**Catalyst type**	**Main elements**	**Polymeric / organic & inorganic additives**	**Reactant delivery mode**	**Catholyte**	**Membrane**	**Reactant**	**E**	**j**	**C_2H_4 FE**	**Reference**
1	Ag foil coated with Cu NP Nafion ink	Overlayer	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.1 M NaHCO3 (pH 6.8)	-	CO_2	-1.9 V vs. RHE	-21 mA/cm^2	76	413
2	Prepared by electrodepositing Cu on Ag surfaces	Overlayer	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.1 M NaHCO3 (pH 6.8)	-	CO_2	-1.9 V vs. RHE	-21 mA/cm^2	76	414
3	Cu/Ag obtained using magnetron sputtering, on a GDL	Mixed-phase/Janus	Cu, Ag, Al	Nafion	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-50 Grade 60	CO_2	-	-451 mA/cm^2	69	415
4	Ag flakes (10 mass% vs. Cu) supported on Cu2O NPs (12 nm), on a GDL (YLS-30 T)	Mixed-phase/Janus, A-supports-B	Cu, Ag, O	Nafion	(Gas-phase reactant, supplied from behind)	3.0 M KOH	Nafion 117	CO_2	?	-650 mA/cm^2	68	419
5	Cu NCs doped with AgNO3, on solid substrate	Cubes, Mixed-phase/Janus	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3 (pH 6.8)	Nafion 115	CO_2	-1.2 V vs. RHE	-27 mA/cm^2	67	418
6	Ag flakes (10 mass% vs. Cu) supported on Cu2O NPs (12 nm), on a GDL (YLS-30 T)	Mixed-phase/Janus, A-supports-B	Cu, Ag, O	Nafion	(Gas-phase reactant, supplied from behind)	3.0 M KCl	Nafion 117	CO_2	?	-650 mA/cm^2	66	419
7	Cu NWs from ACS Materials doped with AgNO3, on a GDL	Nanowire, Mixed-phase/Janus	Cu, Ag	-	(Gas-phase reactant, supplied from behind)	-	PiperIon 40 µm	CO_2	-3.2 V cell potential	-80 mA/cm^2	60	417
8	In-situ reduced Cu2CO3(OH)2/AgCl/C composite pre-catalyts (1.28 at.% Ag), on carbon paper	Mixed-phase/Janus	Cu, Ag, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	"Selemion"	CO_2	-0.85 V -iR vs. RHE	$-85^{\dagger\_\mathrm{Cu\text{-}Ag,1}}$ mA/cm^2	58	420
9	Ag-doped Cu MOF (Cu:Ag of 10:1) NPs, on carbon paper	Mixed-phase/Janus	Cu, Ag, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-1.3 V vs. RHE	-220 mA/cm^2	57	421
10	Homogenously dispersed Cu/Ag NPs in carbon matrix obtained via pyrolizing MOF-precursor, on GDL	Mixed-phase/Janus, A-supports-B	Cu, Ag, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-1.2 V vs. RHE	-200 mA/cm^2	56	422
11	CuAg by electrodeposited CuSO4 and Ag2SO4, on a GDL	Nanowire, Mixed-phase/Janus	Cu, Ag	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumatech	CO_2	-0.68 V vs. RHE	-313 mA/cm^2	55	423
12	Electroplating Ag with drop casted Cu, on a GDL	Mixed-phase/Janus	Cu, Ag	Thiadiazole (N2SN)	(Gas-phase reactant, supplied from behind)	-	Fumapem FAA-3-50	CO_2	-4.55 Vvs. ANODE	-320 mA/cm^2	55	424
13	Synthesis of Ag NCs doped with CuCl2, on glass carbon electrode	Mixed-phase/Janus, A-supports-B, cubes	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 212	CO_2	-1.2 V vs. RHE	-4 mA/cm^2	54	425
14	Ag-doped (4.3 at. % vs. Cu) CuO nanospheres consisting of aggregated platelets, on carbon paper	Mixed-phase/Janus	Cu, Ag, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 115	CO_2	-1.2 V vs. RHE	-25 mA/cm^2	51	426
15	Cu2O microcubes (1 µm) decorated with small Ag NPs (50 nm), prepared via galvanic displacement, mixed with carbon black, on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, Ag, C, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.2 V vs. RHE	-29 mA/cm^2	51	353
16	Synthesis of CuO NCs doped with AgCl2, on a GDL	Nanowire, Mixed-phase/Janus	Cu, Ag, O	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-0.6 V vs. RHE	-150 mA/cm^2	50	427
17	Cu needles with Ag NP, on a GDL	Janus, A-supports-B	Cu, Ag	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAS-50	CO_2	-0.93 V vs. RHE	-350 mA/cm^2	50	428
18	In-situ reduced Cu2CO3(OH)2/AgCl/C composite pre-catalyts (1.28 at.% Ag), on carbon paper	Mixed-phase/Janus	Cu, Ag, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KCl	Nafion 117	CO_2	-1.11 V -iR vs. RHE	-61 mA/cm^2	50	420
19	Synthesised CuO particles followed by AgNO3 doping, on a glassy carbon electrode	Mixed-phase/Janus	Cu, Ag, I, O	Nafion	(Solution-phase reactant, supplied in front)	0.25 M KHCO3	Nafion 117	CO_2	-1 V vs. RHE	-24 mA/cm^2	49	429
20	Homogenously dispersed Cu/Ag NPs in carbon matrix obtained via pyrolizing MOF-precursor, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Ag, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-0.7 V vs. RHE	-8 mA/cm^2	49	422
21	Ag NP layer on top of Cu NP layer, on a GDL	Overlayer, Tandem catalyst	Cu, Ag	Nafion	(Gas-phase reactant, forced through surface)	1.0 M KOH	FAA-3-PK-75	CO_2	-0.75 V -iR vs. RHE	-490 mA/cm^2	48	371
22	Galvanic replacement commercial Cu NPs and Ag+	Foam	Cu, Ag	Nafion	(Gas-phase reactant, forced through surface)	1.0 M KOH (pH 14)	Fumasep FAB-PK-130	CO_2	-0.65 V vs. RHE	-708 mA/cm^2	48	430
23	Defective Ag NPs obtained from in-situ reduction of AgIO3 NSs mixed with CuO NSs (Cu:Ag ratio of 6), deposited on a GDL	Mixed-phase/Janus, A-supports-B	Cu, Ag, O	Nafion	(Gas-phase reactant, supplied from behind)	0.5 M K2SO4 + x mM H2SO4 (pH 1.0)	-	CO_2	-2.0 V -iR vs. RHE	-1200 mA/cm^2	48	431
24	Cu NP layer (0.4 mg/cm2) with Ag overlayer (only present near CO_2 inlet, 5% of total area), on GDL	Overlayer, Tandem catalyst	Cu, Ag	Sustainion XA-9	(Gas-phase reactant, supplied from behind)	-	"Sustainion"	CO_2	-3.05 V vs. ANODE	-688 mA/cm^2	46	321
25	Cu NPs mixed with Ag NPs and PTFE, on GDL	Mixed-phase/Janus	Cu, Ag	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	Selemion DSVN	CO_2	-1.42 V -iR vs. RHE	-600 mA/cm^2	45	100
26	Ag NRs fully coated by Cu(NO3)2 solution	Core-shell, A-supports-B	Cu, Au	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.11 V vs. RHE	-100 mA/cm^2	45	398
27	Commercial Sigma-Aldrich Cu NP on GDL, immersed AgNO3 solution for various times.	Mixed-phase/Janus	Cu, Ag	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAB-PK-130	CO	-0.56 V vs. RHE	?	44	432
28	Core/shell NPs with Ag core and Cu shell, on a GDL	Core-shell, A-supports-B	Cu, Ag, C	Nafion	(Gas-phase reactant, supplied from behind)	1 M KHCO3 (pH 6.8)	Nafion 115	CO_2	-1.6 V vs. RHE	-299 mA/cm^2	44	433
29	Co-plated Cu and Ag from a 1 mM 3,5-diamino-1,2,4-triazole containing plating bath, on a 10nm Cu-sputtered GDL	Alloyed/Doped	Cu, Ag	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	-	CO_2	-0.8 V vs. RHE	-148 mA/cm^2	43	335

30	Core-shell NPs prepared by precipitation of Cu(OH)2 on Ag core, on a GDL	Core-shell, A-supports-B	Cu, Ag, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Not Found	CO_2	-0.64 V vs. RHE	-400 mA/cm^2	43	434
31	Ag-doped (2%) Cu2O NPs, on a GDL	Alloyed/Doped	Cu, Ag, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-0.74 V vs. RHE	-1350 mA/cm^2	43	435
32	The CuO supports prepared by precipitation method followed by Ag impregnation, On a GDL	Mixed-phase/Janus	Cu, Ag, O	Nafion 115	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.3 V vs. RHE	-10 mA/cm^2	42	436
33	Sythesyzed Cu nanocubes doped with AgNO3, On a GDL	Mixed-phase/Janus, A-supports-B, cubes	Cu O, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV, AGC Inc.	CO_2	-0.95 V vs. RHE	-10 mA/cm^2	42	437
34	CuO Nanowires modified with AgNO3	Mixed-phase/Janus, A-supports-B	Cu, Ag	-	(Solution-phase reactant, supplied in front)	0.2 M KHCO3 (pH 6.8)	-	CO_2	-1.05 V vs. RHE	-36 mA/cm^2	42	438
35	Ag-doped porous Cu NWs supported on CNPs (Ketjen 600C), on GDL	Mixed-phase/Janus, A-supports-B	Cu, Ag, C	Polyvinylidene difluoride	(Gas-phase reactant, supplied from behind)	0.1 M KHCO3 (pH 6.8)	Nafion 212	CO_2	-1.3 V vs. RHE	-33 mA/cm^2	42	439
36	Commercial Sigma-Aldrich Cu NP dispersed in methanol with Nafion deposited on GDL, immersed in aqueous AgNO3 solution for various times.	Core shell, Janus, A-supports-B, cubes	Cu, Ag	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAB-PK-130	CO_2	-1.31 V vs. RHE	?	41	432
37	The AgCu alloy catalyst was obtained via electroreduction, on a GDL	Alloyed/doped, Mixed-phase/Janus	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion	CO_2	-1.1 V vs. RHE	-6 mA/cm^2	41	440
38	Electroplated Cu NPs with Ag layer created by spincoating with AgNO3 solution, on a Cu foil	Mixed-phase/Janus, A-supports-B	Cu, Ag	-	(Gas-phase reactant, forced through surface)	0.5 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.2 V vs. RHE	-20 mA/cm^2	41	441
39	Ag NPs with a porous (40 nm thick) Cu2O shell, on glassy carbon	Core/shell	Cu, Ag, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.6 V vs. RHE	-21 mA/cm^2	41	442
40	AgNO3 doping of CuO particles	Mixed-phase/Janus, A-supports-B	Cu, Ag, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	?	-1200 mA/cm^2	40	443
41	Ag/Cu catalysts were deposited by cosputtering with Cu and Ag targets	Mixed-phase/Janus	Cu, Ag	-	(Gas-phase reactant, supplied from behind)	1 M KHCO3 (pH 6.8)	Fumasep FAA-3-PK-130	CO_2	?	-200 mA/cm^2	40	444
42	Ag surface-mofied CuO MPs, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3 (pH 6.8)	"Nafion"	CO_2	-1.1 V vs. RHE	-13 mA/cm^2	40	445
43	Ag-doped porous Cu NWs supported on CNPs (Ketjen 600C), on GDL	Mixed-phase/Janus, A-supports-B	Cu, Ag, C	Polyvinylidene difluoride	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	? Nafion 212	CO_2	-1.48 V vs. RHE	-500 mA/cm^2	40	439
44	Ag-doped porous Cu NWs supported on CNPs (Ketjen 600C), on GDL	Mixed-phase/Janus, A-supports-B	Cu, Ag, C	Polyvinylidene difluoride	(Gas-phase reactant, supplied from behind)	0.1 M KHCO3 (pH 6.8)	Nafion 212	CO	-1.2 V vs. RHE	?	40	439
45	Synthesis of Cu2O NCs doped by AgNO3, on a GDL	Core shell, Janus, A-supports-B, cubes	Cu, Ag, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAB–PK–130	CO_2	-2.1 V vs. RHE	800 mA/cm^2	39	446
46	Consecutive galvanic replacement-prepared Ag-doped (4 wt%, XPS) CuOx NPs, on Cu-sputtered PTFE GDL	Alloyed/Doped	Cu, Ag, O	Nafion	(Gas-phase reactant, supplied from behind)	-	"Sustainion"	CO	?	-600 mA/cm^2	37	447
47	Ag–Cu NDs were synthesized using a seed-mediated method, on a GDL	Mixed-phase/Janus	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion	CO_2	-1.1 V vs. RHE	-1 mA/cm^2	37	448
48	Cu NPs supported on Graphdiyne doped with Ag, on a GDL	Mixed-phase/Janus, A-supports-B	Cu, Ag, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion N-115	CO_2	-1.8 V vs. RHE	-50 mA/cm^2	36	449
49	Synthesised Ag NPs were doped with copper acetate and PVP, on a GDL	Core shell, Mixed-phase/Janus, A-supports-B	Cu, Ag	Nafion	(Gas-phase reactant, forced through surface)	3.0 M KOH	Nafion 115	CO_2	-1.1 V vs. RHE	-375 mA/cm^2	36	450
50	Cu-Ag bimetallic catalysts by simultaneous galvanic replacement, on a glass carbon electrode	Alloyed/doped, Mixed-phase/Janus	Cu, Ag, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.1 V vs. RHE	?	35	451
51	Mixed Ag/Cu-melamine complex, on carbon paper	Atomically mixed/Crystalline	Cu, Ag	Nafion, melamine	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-1.0 V vs. RHE	-50 mA/cm^2	35	452
52	Metal powder mixed and heated up to 2650 °C, on a GDL	Alloyed/doped	Cu, Ag, C	Teflon	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Nafion 117	CO	-2.3 V vs. SCE	-200 mA/cm^2	34	360
53	Synthesis of CuO NPs followed by addition of AgOCOCF3 making core shell, on a GDL	Core shell, Janus, A-supports-B, cubes	Cu, Ag, C, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumatech PK-75	CO_2	-0.75 V vs. RHE	-110 mA/cm^2	34	453
54	Exchange of Ag+ ions from Cu nanosheets, on a glass carbon electrode	Mixed-phase/Janus	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.05 M KHCO3	?	CO_2	-1.2 V vs. RHE	-10 mA/cm^2	34	454
55	Ag nanocrystals with copper overlayer, on a GDL	Core shell, Janus, A-supports-B,	Cu, Ag	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAB-PK-130	CO_2	-1.2 V vs. RHE	-102 mA/cm^2	33	455
56	Electrodeposited CuAgx on carbon support	Mixed-phae/Janus, A-supports-B, dendritic	Cu, Ag	?	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.23 V vs. RHE	-11 mA/cm^2	33	456
57	Synthesized Ag nanowires were mixed with Cu(OAc)2 generating Ag@CuOx-X	Core-shell, A-supports-B	Cu, Ag, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Fumasep FAA-3-PK-130	CO_2	-1.05 V vs. RHE	-16 mA/cm^2	32	457
58	Self prepared Cu np were doped with aqueous AgNO3 solution creating Ag shell	Core-shell, A-supports-B	Cu, Ag	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Nafion 115	CO_2	-1.1 V vs. RHE	-23 mA/cm^2	32	458
59	Ag NPs (25 wt%) anchored on Cu NWs with a 4, 4′-bipyridine linker, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.15 V -iR vs. RHE	?	32	459
60	Cu-BTC doped with aqueous AgNO3 solution, on a GDL	Mixed-phase/Janus, A-supports-B	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.2 V vs. RHE	-6 mA/cm^2	31	460
61	Ag2Cu2O3 synthesised from Cu(NO3)2 and AgNO3, on a GDL	Alloyed	Cu, Ag, O	Sustainion XA-9	(Gas-phase reactant, supplied from behind)	1 M CsHCO3	Fumasep FAB–PK–130	CO	?	-200 mA/cm^2	31	461
62	5 nm Ag layer sputter-deposited on Cu sputtered (100 nm) GDL	Overlayer	Cu, Ag	-	(Gas-phase reactant, supplied from behind)	-	?	CO_2	-2.82 V vs. ANODE	-200 mA/cm^2	31	462
63	Cu/Ag alloy NPs synthesized by polyol method, dropped on glassy carbon	Core shell, alloyed/doped	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.06 V vs. RHE	-2 mA/cm^2	30	463
64	Prepared by high-energy ball milling CuO particles with Ag powders, on a GDL	Mixed-phase/Janus	Cu, Ag, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Selemion AMVAGC Inc.	CO	-0.57 V vs. RHE	-133 mA/cm^2	30	464
65	Alloyed by melting and cryogrinding, on glassy carbon	Alloyed/doped	Cu,	Nafion	(Solution-phase reactant,	0.5 M	?	CO_2	-0.3 V vs.	-13	30	465

			Ag		supplied in front)	KHCO3 (pH 6.8)			RHE	mA/cm^2		
66	Cu cubes were synthesized and then doped with AgNO3 solution, on a GDL	Mixed-phase/Janus, A-supports-B	Cu, Ag	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	-	CO$_2$	-1.1 V vs. RHE	-233 mA/cm^2	30	[466]
67	Silicon wafers covered by Cu and Ag by reactive sputtering	Janus, two-phase	Cu, Ag, (Si)	?	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV	CO$_2$	-1.0 V vs. RHE	-10 mA/cm^2	30	[399]
68	AgNO3 doping of CuO NP	Mixed-phase/Janus, A-supports-B	Cu, Ag, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3 (pH 6.8)	Fumasep FAB–PK–130	CO$_2$	-0.99 V vs. RHE	-52 mA/cm^2	29	[467]
69	400 nm thick evaporated Cu/Ag alloy (95:5), on GDL	Alloyed/doped	Cu, Ag	-	(Gas-phase reactant, supplied from behind)	-	AF1-HNN8-50-X	CO$_2$	?	-100 mA/cm^2	28	[288]
70	Cu NCs with a non-equilibrium Cu/Ag alloy shell, on a GDL	Alloyed/Doped, core/shell	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	"Nafion"	CO$_2$	-1.1 V -iR vs. RHE	?	28	[468]
71	Ag-doped Cu prepared via co-sputtering on GDL (30 T)	Alloyed/Doped	Cu, Ag	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO$_2$	?	-300 mA/cm^2	28	[358]
72	Sytheses of NP with in AgNO3 and Cu(acac)2, on a GDL	Mixed-phase/Janus	Cu, Ag	Nafion	(Gas-phase reactant, supplied from behind)	2.0 M KOH	?	CO$_2$	-0.77 V vs. RHE	-6 mA/cm^2	27	[469]
73	Cu–Ag NCs synthesized by galvanic exchange of Cu(0) with Ag-trifluoroacetate (Ag-TFA), on a GDL	Mixed-phase/Janus	Cu, Ag, C	-	(Gas-phase reactant, supplied from behind)	1 M KHCO3 (pH 6.8)	Selemion DSVN	CO$_2$	-1.13 V vs. RHE	-288 mA/cm^2	26	[470]
74	Cu9Ag1 NPs prepared via thermal shock, on carbon nanotubes	Alloyed/Doped, A-supports-B	Cu, Ag	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3	CO	-0.65 V -iR vs. RHE	-25 mA/cm^2	25	[334]
75	Cu coated Ag core shell, on a GDL	Core-shell, A-supports-B	Cu, Ag	PTFE powder	(Gas-phase reactant, supplied from behind)	1 M KHCO3 (pH 6.8)	FAA-3-PK-75	CO$_2$	-0.8 V vs. RHE	-137 mA/cm^2	23	[471]
76	Galvanic replacement from Cu to Ag to achieve in situ formation of CuAg ensembles	Mixed-phase/Janus, A-supports-B	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	?	CO$_2$	-1.12 V vs. RHE	-2 mA/cm^2	22	[472]
77	Cu/Ag alloy NPs synthesized by polyol method, dropped on glassy carbon	Alloyed/Doped	Cu, Ag	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3 (pH 6.8)	Fumasep FAA-3-PK-130	CO$_2$	-1.1 V vs. RHE	-15 mA/cm^2	13	[473]
	[†_Cu-Ag,1] Used current density and FE described in text to calculate total current, as opposed to figure (ca. 85 mA/cm^2 vs. ca. 110 mA/cm^2)											

2.4. Elements forming non-reducible oxides: Zr, Hf, Ti, Si, and the lanthanide series

2.4.1. Zr & Hf/Cu (combined due to their chemical similarities)

A summary of best-performing Cu/Zr (Cu/Hf) bi-elemental catalysts for C_2H_4 production is given in Table S16 (S17). The Cu/Zr (Cu/Hf) catalyst dataset is derived from 10 (3) unique publications and comprises a total of 13 (5) catalyst systems, with 2 (1) using CO as a reactant and 6 (3) having been identified as alkaline CO_2 systems. A total of 3 (1) of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55 %, though 1 (1) of those was measured under alkaline CO2RR conditions. The top-most Cu/Zr catalyst yields 63% C_2H_4 and concerns a non-alkaline CO2RR system[474], with the top Cu/Hf catalyst (also) yielding 63% C_2H_4, but being an alkaline system instead.[475]

Cu/Zr catalyst systems are generally observed to form separate (phase-segregated) particles and are thus classified herein as being mixed-phase/janus-type catalysts, with the same being true for Cu/Hf systems. The degree of mixing is an important parameter, with well-mixed particles (such as achieved via co-precipitation methods) yielding better performance than e.g., mechanically mixed systems.[475] C_2H_4 FEs in the 50%-60% range are reliably observed when looking at the combination of the two catalyst systems. An important observation is that both Cu/Zr and Cu/Hf systems have been reported to also work for CO reduction (yielding maximum C_2H_4 FEs of 44%[476] and 51%[475], respectively). In addition, ZrOx domains and HfOx domains retain in their oxidized state *in-operando*, which some authors claim to be responsible for the observation that C_2H_4 activity goes through a maximum before decreasing with increasing oxide content, which they attribute to reduced conductivity.[476] The publications provide little insights as to why exactly C_2H_4 performance is improved upon ZrOx (HfOx) addition, though increased CO_2 (CO) adsorption capacity is commonly hypothesized as a potential contributor, besides the literature-pervasive "stabilization of Cuδ+" argument. Besides mixed-phase/janus-type systems, overlayer-type systems where a layer of component 'B' is deposited on top of layer 'A' are also reported specifically for Cu/Zr.[477,478] However, these systems exhibit lower C_2H_4 selectivity (ca. 45% C_2H_4), which might be correlated to a low quantity of intimate interfaces when considering that intricately mixed-particles exhibit superior performance in mixed-phase/janus-type systems.[475] (Supposed) alloyed/doped-type catalysts are also reported, but their activity is poor (≤15% C_2H_4).[105]

As a final consideration we would like to emphasize two publications with similar characteristics. To start, we highlight a publication regarding Cu-SAC sites dispersed within the nanopores of a Zr-based MOF which is found to be stable under operating conditions.[479] This system is reported to yield an impressive maximum C_2H_4 FE of 62% for the reduction of CO. Rather than being related to the presence of both Cu and Zr in the catalyst, it seems to be the confinement of CO within the pores that is responsible for the excellent performance. Secondly, we would like to highlight a publication by Li *et al.* regarding a mixed-phase/janus-type catalyst consisting of mixed ZrO_2 and CuO particles wherein they report on the importance of the presence of nanocavities for the enhancement of C_2H_4 performance.[476] Both these studies comprise a similar nanoconfinement effect as we have also previously hypothesized to exist for a particular Cu/Ni[363] and a Cu/Co[143] system, respectively.

Table S16. Zr-based Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	ZrO2 supported on Cu-Cu2O NPs prepared via co-precipitation, on carbon paper	Bi-phasic/Janus, A-supports-B	Cu, Zr, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO_2	-0.70 V vs. RHE	-24 mA/cm^2	63	[474]
2	Single atom Cu sites enclosed in a Zr-based MOF framework with rod-like morphology, on GDL	Single atom, Atomically mixed/Crystalline, MOF	Cu, Zr	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M phosphate buffer saline	Nafion 212	CO	?: -1.0 V vs. RHE	-125 mA/cm^2	62	[479]
3	NPs composed of a mix of ZrO2 and CuO, prepared via co-precipitation, on carbon paper	Bi-phasic/Janus	Cu, Zr, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Nafion 117	CO_2	?	-250 mA/cm^2	55	[476]
4	(SAA, ca. 2 at.%) Zr-doped Cu NPs mixed with CNPs, on a GDL	Mixed-phase/Janus	Cu, Zr	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-130	CO_2	-1.0 V vs. RHE	-730 mA/cm^2	50	[480]
5	NPs composed of a mix of ZrO2 and CuO, prepared via co-precipitation, on carbon paper	Bi-phasic/Janus	Cu, Zr, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.10 V vs. RHE	-11 mA/cm^2	48	[476]
6	NPs composed of a mix of ZrO2 and CuO, prepared via co-precipitation, on carbon paper	Bi-phasic/Janus	Cu, Zr, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KOH (pH 13)	Nafion 117	CO	-0.6 V vs. RHE	?	44	[476]
7	Porous ZrO2 layer on top of Cu plate - dropcast with Nafion binder, dried on hotplate at 110 C in air	Cu with overlayer	Cu, Zr, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	"Nafion"	CO_2	-1.05 V - iR vs. RHE	-24 mA/cm^2	44	[477]
8	Porous ZrO2 layer prepared via decomposition of UiO-66 (Zr-based MOF, 0.25 mg/cm2), on top of Cu plate - dropcast with Nafion binder, dried on hotplate at 110 C in air	Cu with overlayer	Cu, Zr, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	"Nafion"	CO_2	-1.05 V - iR vs. RHE	-26 mA/cm^2	43	[478]
9	CuO NPs mixed with amorphous ZrO2, on a GDL	Mixed-phase/Janus	Cu, Zr	Nafion	(Gas-phase reactant, supplied from behind)	-	X37-50 Grade RT	CO_2	-4.0 V vs. ANODE	-182 mA/cm^2	36	[481]
10	Cu impregnated into a Zr-based MOF (UiO-66), on carbon paper	Alloyed/Doped	Cu, Zr	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.0 V vs. RHE	-10 mA/cm^2	34	[482]
11	Zr(OH)x overlayer on Cu-sputtered PTFE GDL	Overlayer, Mixed-phase/Janus	Cu, Zr, O	-	(Gas-phase reactant, supplied from behind)	1 M KOH	FAA-3-PK-130	CO_2	?	?	17	[395]
12	Alloy/mixed metal Zr/Cu (1:1 ratio) microparticles, on GDL - obtained via reduction of mixed nitrate salt with NaBH4 over 12h period	Alloyed/Doped	Cu, Zr	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	NEOSEPTA, AHA	CO_2	-0.6 V vs. RHE	-102 mA/cm^2	15	[105]
13	Alloy/mixed metal Zr/Cu (1:1 ratio) microparticles, on GDL - obtained via reduction of mixed nitrate salt with NaBH4 over 12h period	Alloyed/Doped	Cu, Zr	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	NEOSEPTA, AHA	CO_2	-0.8 V vs. RHE	-170 mA/cm^2	15	[105]

Table S17. Hf-based Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	Co-precipitated HfOx and CuOx (2:3 ratio) mixed NPs, on carbon paper	Mixed-phase/Janus	Cu, Hf, O	Nafion	(Gas-phase reactant, supplied from behind)	0.1 M KOH	?	CO_2	?	-300 mA/cm^2	63	[475]
2	Co-precipitated HfOx and CuOx (2:3 ratio) mixed NPs, on glassy carbon (?)	Mixed-phase/Janus	Cu, Hf, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KOH	Nafion 117	CO	-0.4 V vs. RHE	?	51	[475]
3	Co-precipitated HfOx and CuOx (2:3 ratio) mixed NPs, on glassy carbon (?)	Mixed-phase/Janus	Cu, Hf, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.1 V vs. RHE	-1 mA/cm^2	49	[475]
4	Hf-doped Cu(OH)2 NWs with a PTFE shell, on a GDL	Alloyed/Doped, Core/shell (in-)organic	Cu, Hf, O	PTFE	(Gas-phase reactant, supplied from behind)	-	X37-50 grade RT	CO_2	-4.1 V vs. ANODE	-400 mA/cm^2	42	[311]
5	Alloy/mixed metal Hf/Cu (1:3 ratio) microparticles, on GDL - obtained via reduction of mixed nitrate salt with NaBH4 over 12h period	Alloyed/Doped	Cu, Hf	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	NEOSEPTA, AHA	CO_2	-0.8 V vs. RHE	-136 mA/cm^2	13	[105]

2.4.2. Ti/Cu

A summary of best-performing Cu/Ti bi-elemental catalysts for C_2H_4 production is given in Table S18. The Cu/Ti catalyst dataset is derived from 7 unique publications and comprises a total of 8 catalyst systems, with 3 using CO as a reactant and 3 having been identified as alkaline CO_2 systems. A total of 2 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55 %, both having been measured under non-alkaline CO2RR conditions. The top-most catalyst yields 71% C_2H_4 and concerns a CORR system.[483]

Although few Cu/Ti systems are reported to make C_2H_4 (typical C_2H_4 performance in the 45-55% range), a singular source reports on a highly active catalyst material. This material, comprising 2D Ti-based MXene nanosheets decorated with single atom copper sites (Cu-SAC/Ti3C2Tx; Tx=terminating group), could be considered as a multi-elemental catalyst on account of the presence of Cu, Ti, and C. However, considering we believe the activity mostly originates from the 2D structure (discussed in the main text) rather than the presence of additional elements we have opted to assign it to the Cu/Ti group. This particular catalyst exhibits exceptional performance, yielding 71% C_2H_4 during the reduction of CO.[483] This is noteworthy not only because of the high faradaic efficiency, but also because of i) the fact that CO is the reactant and ii) that the active sites consists of atomically dispersed copper. Especially the latter is interesting considering that SACs typically are not active for C-C coupling during CO(2) reduction.[484-486] Interestingly, copper NPs on top of the Ti-based MXene nanosheets were found to exhibit much poorer C_2H_4 activity, which we interpret as performance being strongly influenced by support-catalyst interactions. Importantly (in our opinion), the non-Cu doped Ti-based MXene support by itself is also active for C_2H_4 formation, albeit only a little. Such C_2H_4 activity of the Ti-based support is also identified in an unrelated publication, who find that the pristine (non-Cu) Ti nanotube-functionalized Ti foil substrate they use is itself active to a certain degree for forming C_2H_4.[487]

Such C_2H_4 activity of non-Cu containing catalysts is an anomaly in literature, observed only sporadically.[488] Possibly the fact that the support material itself is capable of making ethylene is what allows a Cu SAC to still yield high C_2H_4 activity rather than a more generic catalyst-support interaction. We expand on this hypothesis in the main text. Although we conclude that this Ti/MXene-based catalyst system goes against many conventional wisdoms, its uniqueness also makes it difficult to meaningfully compare to other Cu/Ti systems described in this work besides observing that it (again) consists of 2D nanosheets. This observation is also further addressed in the main text. In addition, although this singular Ti-based MXene source with high performance is promising, we would like to advocate cautious optimism. Namely, Zhao *et al.* report on a (seemingly) highly similar Cu SAC/Ti3C2Tx system, wherein they find MeOH as the dominant product and no C_2H_4 at all.[486] Although the reactants differ between the two studies (CO_2 vs. CO), we cannot identify any significant differences between the catalyst systems. Hence, we are unsure as to which is the truth and choose to be optimistic rather than pessimistic by assuming in our discussion that CORR on Cu-SAC/Ti3C2Tx indeed yields high C_2H_4 activity.

Table S18. Ti-based Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	Single atom Cu supported on ultrathin Ti3C2Tx nanosheets, on carbon paper	Single atom	Cu, C, Ti	Nafion	(Solution-phase reactant, supplied in front)	1.0 M KOH (pH 14)	Nafion 117	CO	-0.70 V vs. RHE	-23 mA/cm^2	71	[483]
2	Electroplated Cu on metallic Ti nanotube-functionalized Ti foil	A-supports-B	Cu, Ti	-	(Solution-phase reactant, supplied in front)	0.5 M KCl	"Nafion"	CO_2	-1.6 V vs. Ag/AgCl	-12 mA/cm^2	55	[487]
3	TiO2/sustainion toplayer on a Cu-sputtered PTFE GDL	Overlayer, Mixed-phase/Janus	Cu, Ti, O	Sustainion	(Gas-phase reactant, supplied from behind)	1 M KOH	-	CO_2	-3.00 V vs. ANODE	-261 mA/cm^2	48	[489]
4	Cu nanoclusters encapsulated in Ti-based MOF, on a GDL	Mixed-phase/Janus	Cu, Ti, O	?	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	-	CO_2	-1.0 V vs. RHE	-400 mA/cm^2	48	[490]
5	TiO2 NP overlayer on top of Cu-sputtered PTFE GDL	Overlayer, Mixed-phase/Janus	Cu, Ti, O	Nafion	(Gas-phase reactant, supplied from behind)	? 0.5 M KHCO3 + 0.5 M KCl	Nafion 117	CO_2	-0.91 V -iR vs. RHE	?	46	[491]
6	Cu NPs (40 wt%) supported on Magnéli phase Ti4O7 nanoflakes, on a GDL	Mixed-phase/Janus, A-supports-B	Cu, Ti, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-130	CO	-0.7 V -iR vs. RHE	-178 mA/cm^2	31	[492]
7	Cu NPs (20 wt%) supported on TiO2 NPs, on a GDL	Mixed-phase/Janus, A-supports-B	Cu, Ti, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-130	CO	-0.70 V -iR vs. RHE	-116 mA/cm^2	29	[492]
8	TiO2 overlayer on Cu-sputtered PTFE GDL	Overlayer, Mixed-phase/Janus	Cu, Ti, O	-	(Gas-phase reactant, supplied from behind)	1 M KOH	FAA-3-PK-130	CO_2	?	?	15	[395]

2.4.3. Si/Cu

A summary of best-performing Cu/Si bi-elemental catalysts for C_2H_4 production is given in Table S19. The Cu/Si catalyst dataset is derived from 15 unique publications and comprises a total of 19 catalyst systems, with 2 using CO as a reactant and 5 having been identified as alkaline CO_2 systems. A total of 3 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55 %, all of which were measured under alkaline CO2RR conditions. The top-most catalyst yields 82% C_2H_4 and concerns an alkaline CO2RR system.[493] The highest non-alkaline system yields 54% C_2H_4 and uses CO_2 as the reactant.[494]

Two primary types of catalyst systems can be identified for Si/Cu systems: i) mixed-phase/janus-type systems and ii) core/shell-type systems. High silicon contents in general are unfavorable for C_2H_4 performance[495], and overall we observe that morphological effects and the local environment seem equally – if not more – important than the presence of Si.[493,496,497] For both mixed-phase/janus-type and core/shell-type systems, the Cu/Si boundary region is often put forward as one of the main reasons for improved catalytic performance. Especially the continued existence of Cuδ+ sites during CO_2 reduction governed by the presence of these boundary regions is a popular hypothesis for explaining observed results.[498,499] Maximum FEs for C_2H_4 formation typically fall in the 40-50% range for these mixed-phase/janus-type and core/shell-type Si/Cu systems. However, the SiO_2 component is also generally reported as being unstable *in-operando* and dissolving into the electrolyte, with the high (local) alkalinity typically being put forward as the reason for this.[499,500] This effect is quite concerning for industrial application of Cu/Si systems for electrochemical C_2H_4 formation, at least in our opinion.

Interestingly, a single work reports improved performance for CORR vs. CO2RR for a core/shell-type system[501], although therein the C_2H_4 performance is was poor with a maximum C_2H_4 FE of 35%. Finally, a recent publication describing a catalyst consisting of porous, zeolite-like ordered CuO coated with a $CuSiO_3$ layer reports significantly improved performance relative to the other Si/Cu sources described thus far.[493] Specifically, a maximum C_2H_4 FE of 82% is reported therein for CO2RR in an alkaline environment (vs. 53% in an H-cell with 0.1 M KHCO3 catholyte). Likely, both the presence of Si and the enhanced mass transport due to the intricate morphology together play a role in the substantially enhanced catalytic activity – i.e., a partial nanoconfinement argument. We have seen similar behavior in, and made a similar confinement argument for, select Cu/Ni[363], a Cu/Co[143] and Cu/Zr[476,479] systems.

Table S19. Si-based Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	CuSiO3 coated on ordered porous CuO prepared from mesoporous SiO2 molecular sieve starting material, supported on carbon, on "GDE"	Core/shell, atomically mixed/crystalline	Cu, Si, O, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-PK-130	CO_2	-1.18 V vs. RHE	-400 mA/cm^2	82	493
2	Homogeneously dispersed Si(II)Ox clusters with Cu NPs, on Cu-sputtered PTFE GDL	Mixed-phase/Janus	Cu, Si, O	Aquivion	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-50 Grade RT	CO_2	-4.1 V vs. ANODE	-331 mA/cm^2	65	502
3	Cu2O octahedral NPs (800 nm) with a mesoporous SiO2 shell (25 nm), on carbon paper	Core/shell	Cu, Si, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-1.5 V vs. RHE	-380 mA/cm^2	56	503
4	Core/shell system comprising Cu2O NPs (ca. 200 nm) with an SiO2 shell (15 nm), on a GDL	Core/shell	Cu, Si	Nafion	(Gas-phase reactant, supplied from behind)	3.0 M KCl + 0.05 M H2SO4	Nafion 117	CO_2	-1.45 V - iR vs. RHE	-828 mA/cm^2	54	494
5	Cu NPs supported in/on fibrous SiO2 nanospheres (500 nm), on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Si, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	-	CO_2	-1.2 V vs. RHE	-19 mA/cm^2	53	497
6	CuSiO3 coated on ordered porous CuO prepared from mesoporous SiO2 molecular sieve starting material, supported on carbon, on carbon paper	Core/shell, atomically mixed/crystalline	Cu, Si, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.2 V vs. RHE	-40 mA/cm^2	53	493
7	Small CuO NPs (<5 nm) dispersed on (amorphous) CuSiO3 lamella, mixed with Vulcan XC-72R, on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, Si, C, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 115	CO_2	-1.1 V vs. RHE	-20 mA/cm^2	52	498
8	SiO2 NPs supported on Cu2O NCs through physical mixing (10:2 mL basis), on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, Si, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.4 V - iR vs. RHE	-25 mA/cm^2	47	499
9	Branched/'spikey', amorphous sub-micron SiOx particles decorated with amorphous CuO NPs (18.52 wt%), on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, Si, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.4 V vs. RHE	-23 mA/cm^2	46	504
10	Commercial Cu NPs with a hydrophobic polymer coating consisting of 3-methacryloxypropyltrimethoxysilane (MAPTMS), 2,2,2-trifluoroethyl methacrylate (TFEMA) and 2,2-azobis (2-methylpropionitrile) (AIBN), on GDL	Core/shell	Cu, Si	Nafion, 3-methacryloxypropyltrimethoxysilane (MAPTMS), 2,2,2-trifluoroethyl methacrylate (TFEMA) and 2,2-azobis (2-methylpropionitrile) (AIBN)	(Gas-phase reactant, supplied from behind)	-	X37-Grade 50 RT	CO_2	-3.81 V vs. ANODE	-450 mA/cm^2	42	505
11	CuSiO3 nanotube-assembled hollow spheres, on carbon fiber paper	Mixed-phase/Janus	Cu, Si, O	Nafion	(Solution-phase reactant, supplied in front)	?	Nafion 117	CO_2	-1.8 V vs. Ag/AgCl	?	41	496
12	Carbon/graphite toplayer on Cu2O dodecahedron NPs with a NH2-functionalized SiO2 shell supported on carbon midlayer, on Cu-sputtered PTFE GDL	Core/shell	Cu, Si, O, N, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KCl	Nafion 211	CO_2	-1.7 V vs. RHE	-292 mA/cm^2	40	500
13	SiO2 NPs with thin Cu/Si shell prepared via H2 atmosphere annealing of CuSiO3@SiO2, on Toray carbon paper	Core/shell	Cu, Si, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M CsBr	Nafion 117	CO_2	-1.1 V vs. RHE	-13 mA/cm^2	38	501
14	Cu2O octahedral NPs (800 nm) with a mesoporous SiO2 shell (25 nm), on carbon paper	Core/shell	Cu, Si, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO	-1.5 V vs. RHE	?	38	503
15	H2-annealed Cu-doped SiOx NPs (thermal treatment results in Cu aggregation), on glassy carbon	Mixed-phase/Janus	Cu, Si, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.4 V vs. RHE	?	37	506
16	SiO2 NPs with thin Cu/Si shell prepared via H2 atmosphere annealing of CuSiO3@SiO2, on Toray carbon paper	Core/shell	Cu, Si, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KOH	Nafion 117	CO	-0.6 V vs. RHE	?	35	501
17	Ultrathin hydrophobic SiO2 shell (3.4 nm) around Cu NP core (<90 nm) (1% Si), on GDL	Core/Shell	Cu, Si	Nafion	(Gas-phase reactant, supplied from behind)	3.0 M KCl + 0.05 M H2SO4	"Nafion"	CO_2	-2.2 V vs. RHE	-900 mA/cm^2	35	495
18	CuSiO3 long nanotubes, on carbon fiber paper	Mixed-phase/Janus	Cu, Si, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO_2	-1.8 V vs. Ag/AgCl	-19 mA/cm^2	30	496
19	CuOx impregnated in mesoporous SiO2 template (KIT-6) mixed with PTFE, on a GDL	Mixed-phase/Janus	Cu, Si	Nafion, PTFE	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Fuma FAA-PK-13	CO_2	-1.5 V vs. RHE	-100 mA/cm^2	28	507

2.4.4. Lanthanides: Ce, La, Pr, Nd, Eu, Sm, Gd, Er, Tb/Cu

Much like Zr & Hf, we will discuss the lanthanides together on account of their similar chemical properties. Much of the information will be derived from Cu/Ce systems (Table S20) on account of their abundance in literature relative to the other lanthanides (La, Pr, Nd, Eu, Sm, Gd, Er, Tb, Table S21). The Cu/Ce catalyst dataset is derived from 31 unique publications and comprises a total of 33 catalyst systems, with 1 using CO as a reactant and 12 having been identified as alkaline CO_2 systems. A total of 5 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55 %, though 3 of those were measured under alkaline CO2RR conditions. The top-most catalyst yields 78% C_2H_4 and concerns an alkaline CO2RR system.[508] The highest non-alkaline system yields 70% C_2H_4 and uses CO_2 as the reactant.[508] The other lanthanides that we are aware of to make appreciable amounts of C_2H_4 (La, Pr, Nd, Eu, Sm, Gd, Er, Tb) were grouped together (denoted as Cu/Ln) on account of the low number of publications. The Cu/Ln catalyst dataset is derived from 12 unique publications and comprises a total of 18 catalyst systems, with 0 (none) using CO as a reactant and 7 having been identified as alkaline CO_2 systems. A total of 2 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55 % (yielding 59%[509] and 60%[510] C_2H_4), both comprising Cu/La systems and both having been measured under non-alkaline CO2RR conditions. Cu/Ce systems have the propensity to phase-separate, resulting in mostly mixed-phase/janus-type systems, core/shell-type systems and overlayer-type systems being reported. However, few publications also exist on alloyed/doped-type systems containing (relatively) low quantities of either Ce[511] or Cu[512,513].

Contrary to other bi-elemental catalysts, the C_2H_4 performance spectrum for Cu/Ce systems is relatively consistent across different research groups. We ascribe this to the strong similarities between especially mixed-phase/janus-type catalyst systems (comprising ca. 50% of the total publications), all yielding maximum C_2H_4 FEs between 40%-55%. The other types of catalyst systems (overlayer-type, core/shell-type and alloyed/doped-type) exhibit more variability in their performance but generally exhibit relatively poorer C_2H_4 performance with FEs <45%. A notable outlier in terms of activity is a mixed-phase/janus-type catalyst reported by Tan *et al.,* who reported 70-78% FE for C_2H_4 for a Cu/Ce catalyst system with a unique hollow-fiber morphology under electrolyte-optimized conditions.[508] The morphology here seems to be the biggest differentiating factor. From our perspective, the hollow nature of these nanotubes with their high length-to-width ratio makes for a strongly confining environment, even though this morphology is different from other systems where we made this argument (typically consisting of nanoporous materials). Still, we feel, and hypothesize (as discussed in the main text), that nanoconfinement might play a driving role in the exceptional performance of this catalyst system as opposed to the combination of Cu and Ce as an active catalyst material. This would place it in the same sub-category as the previously described Cu/Ni[363], Cu/Co[143], Cu/Zr[476,479] and Cu/Si[493] systems.

Regarding why Cu/Ce (Cu/Ln) catalyst systems show the performances they do, most authors hypothesize that the presence of lanthanides help to stabilize the Cu^{1+} state at the Cu/Ce[514-517] (Cu/Ln[518-520]) interface, therewith yielding improved catalytic activity and, sometimes, stability.[519,521] Typically, this improved C_2H_4 performance is accompanied by suppressed HER activity, allowing for higher carbon product selectivity even if the product spectrum itself is otherwise unchanged. In addition, an optimum is typically observed for C_2H_4 performance when the Ce (Ln) content is varied, mostly when the Ce[512,514,522] (Ln[519,521]) content is relatively low (< 5%) though outliers exist[516,520,523]. Most authors interpret this as needing to find a balance between Cu/Ce interfacial sites, conductivity, and NP size (i.e., active area). Overall, the combination of lanthanides and Cu is not that promising for substantially improving

C_2H_4 performance (notwithstanding a single outlier[508] that we hypothesize is related to morphology rather than the combination of Cu and Ce). Rather, stability might be improved through the presence of such non-reducible oxides and could be of industrial importance for these types of bi-elemental systems.

As a final consideration, we would like to highlight a paper by Yang *et al.*, who found that for CeO_2 nanorods with a thin Cu shell, EtOH formation could be entirely suppressed during CO reduction, although this was accompanied by an increase in acetate formation and relatively poor C_2H_4 performance (ca. 30 % FE max).[524] Generally, for non-alkaline systems, we observe that C_2H_4 and EtOH are formed concomitantly in roughly equimolar proportion. Being able to shut down the ethanol pathway without severely inhibiting ethylene formation could be of substantial importance for novel catalyst design with improved C_2H_4 performance.

	Table S20. Ce-based Cu											
#	**Electromaterial description**	**Catalyst type**	**Main elements**	**Polymeric / organic & inorganic additives**	**Reactant delivery mode**	**Catholyte**	**Membrane**	**Reactant**	**E**	**j**	**C_2H_4 FE**	**Reference**
1	Hollow Cu/CeO2 nanotubes composed of aggregated nanoparticles, on carbon paper - prepared by decorating electrospun polyacrilonitrile (PAN) fibres with metal and burning away the PAN	Mixed-phase/Janus	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	1 M KOH	FAA-3-PK-130	CO$_2$	-0.7 V vs. RHE	-110 mA/cm^2	78	508
2	Hollow Cu/CeO2 nanotubes composed of aggregated nanoparticles, on carbon paper - prepared by decorating electrospun polyacrilonitrile (PAN) fibres with metal and burning away the PAN	Mixed-phase/Janus	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M K2SO4	Nafion 117	CO$_2$	-1.1 V vs. RHE	-25 mA/cm^2	70	508
3	CeO2 NPs supported on CuO NSs (Cu:Ce ratio of 7:1), on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Ce, O, C	?	(Gas-phase reactant, supplied from behind)	1 M KOH (pH 14)	?	CO$_2$	?	-600 mA/cm^2	64	525
4	CeO2 NPs supported on CuO NSs, on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KCl	-	CO$_2$	-1.25 V vs. RHE	-8 mA/cm^2	58	526
5	CuO NPs supported on Cu-doped CeO2 NRs, on GDL	Alloyed/Doped, Mixed-phase/Janus, A-supports-B	Cu, Ce, O	Nafion	(Gas-phase reactant, supplied from behind)	1 M KOH	"Sustainion membrane"	CO$_2$	-0.85 V -iR vs. RHE	-200 mA/cm^2	55	513
6	Mixed-phase CuOx/CeO2 NPs, on carbon paper	Mixed-phase/Janus	Cu, Ce, O	Nafion	(Gas-phase reactant, supplied from behind)	1 M KOH	FAA-3-PK-130	CO$_2$	-0.68 V vs. RHE	-150 mA/cm^2	53	527
7	Cu NPs supported on CeO2 nanorods, on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, Ce, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.6 V vs. RHE	-17 mA/cm^2	52	517
8	CuOx overlayer on CeO2 nanorods, on carbon paper	Core/shell	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M CsI	Nafion 117	CO$_2$	-1.16 V vs. RHE	-18 mA/cm^2	51	528
9	CuOx/CeOx mixed-phase supported on carbon black, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Ce, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.1 V vs. RHE	-8 mA/cm^2	50	516
10	CeO2 quantum dots (3 nm) supported on irregularly shaped CuO NPs (200 nm), on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Ce, O	Nafion	(Gas-phase reactant, supplied from behind)	1 M KOH	-	CO$_2$	?	-400 mA/cm^2	50	529
11	Mixed CuO/CeO2 NPs, on glassy carbon	Mixed-phase/Janus	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M CsHCO3	Selemion AMV	CO$_2$	-1.08 V -iR vs. RHE	-4 mA/cm^2	50	530
12	Cu-doped CeOx nanorods, on glassy carbon - prepared via deposition-precipitation method and subsequent annealing step	Alloyed/Doped	Ce, O, Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 115	CO$_2$	-1.1 V vs. RHE	-5 mA/cm^2	48	512
13	CeO2 NPs (5 nm) supported on CuO NPs, on PTFE GDL	Mixed-phase/Janus, A-supports-B	Cu, Ce, O	Nafion	(Gas-phase reactant, supplied from behind)	1 M KOH	FAA-3-PK-130	CO$_2$	-1.12 V -iR vs. RHE	-1214 mA/cm^2	48	515
14	Cu NSs supported on CeO2 nanorods, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.27 V vs. RHE	-27 mA/cm^2	45	531
15	Cu2O nanocubes with a tensile-strained CeO2/Cu shell, on GDL	Core/shell, mixed-phase/Janus	Cu, Ce, O	Nafion	(Gas-phase reactant, supplied from behind)	4 M KOH	?	CO$_2$	-0.43 V -iR vs. RHE	?	45	532
16	Ultrafine (<10 nm) CuOx/CeOx composite NPs, on a GDL	Mixed-phase/Janus	Cu, Ce, O	PVDF	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	"Nafion"	CO$_2$	-1.7 V -iR vs. RHE	-450 mA/cm^2	44	533
17	Mixed-phase CeO2/CuOx NPs, on carbon paper	Mixed-phase/Janus	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M CsI	Nafion 117	CO$_2$	-1.0 V vs. RHE	-17 mA/cm^2	43	534
18	Small Cu NPs supported on Cu-doped CeOx NRs, mixed with CNPs, on a GDL	Mixed-phase/Janus, A-supports-B, Alloyed/doped	Cu, Ce, O, C	Nafion	(Gas-phase reactant, supplied from behind)	1 M KOH (pH 14)	?	CO$_2$	-1.2 V vs. RHE	-610 mA/cm^2	40	535
19	Ce(OH)x overlayer on Cu-sputtered PTFE GDL	Overlayer, Mixed-phase/Janus	Cu, Ce, O	-	(Gas-phase reactant, supplied from behind)	1 M KOH	FAA-3-PK-130	CO$_2$	-0.64 V -iR vs. RHE	-200 mA/cm^2	39	395
20	Cu NPs (5 nm) supported on rod-shaped CeO2 particles, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.05 V vs. RHE	-7 mA/cm^2	39	536
21	CeO2 NPs overlayer interfaced with CuOx layer, on Cu foil - prepared via drop-casting and drying at 110 C	Overlayer	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.05 V vs. RHE	-14 mA/cm^2	38	522
22	Cu NPs supported on CeO2 nanorods on glassy carbon - prepared via galvanic displacement of lithiated CeO2 rods	Mixed-phase/Janus, A-supports-B	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	QAPPT	CO$_2$	-1.3 V vs. RHE	-13 mA/cm^2	38	537
23	CuO NPs supported on "3D spherical CeO2" with many oxygen	Mixed-phase/Janus,	Cu,	Nafion	(Solution-phase reactant,	0.1 M	?	CO$_2$	-1.2 V	-20	37	538

	vacancies (Cu:Ce of 7:3), on carbon paper	A-supports-B	Ce, O, C		supplied in front)	KHCO3 (pH 6.8)			vs. RHE	mA/cm^2		
24	r-GO overlayer on top of CNP overlayer on top of ultrafine highly dispersed Cu2S-CeOx nanocomposites supported on reduced graphene oxide, on Cu-sputtered PTFE	Overlayer, Mixed-phase/Janus, A-supports-B	Cu, Ce, S, O, C	Nafion	(Gas-phase reactant, supplied from behind)	2 M KOH	FAA-3-PK-130	CO_2	-0.9 V vs. RHE	-230[†_Cu-Ce,2] mA/cm^2	32	[539]
25	Cu/CeOx bi-phasic heterodimers (24 nm), on glassy carbon	Mixed-phase/Janus	Cu, Ce, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV	CO_2	-1.1 V vs. RHE	-1 mA/cm^2	31	[514]
26	Few-atom thick Cu shell on CeO2 NRs, on GDL	Core/shell	Cu, Ce, O	?	(Gas-phase reactant, supplied from behind)	1 M KOH (pH 14)	?	CO	?	-100 mA/cm^2	31	[524]
27	CuO NPs (30 nm) supported on CeO2 NCs (230 nm), on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	-	CO_2	-1.4 V vs. RHE	-5 mA/cm^2	31	[540]
28	r-GO overlayer on top of CNP overlayer on top of ultrafine highly dispersed Cu-CeOx nanocomposites supported on reduced graphene oxide, on Cu-sputtered PTFE	Overlayer, Mixed-phase/Janus, A-supports-B	Cu, Ce, O, C	Nafion	(Gas-phase reactant, supplied from behind)	2 M KOH	FAA-3-PK-130	CO_2	-0.9 V vs. RHE	-161[†_Cu-Ce,2] mA/cm^2	30	[539]
29	(Single atomic) Cu-doped ("4%") CeO2 nanorods, on carbon paper	Single atom, A-supports-B	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	?	CO_2	-1.4 V vs. RHE	-29 mA/cm^2	30	[484]
30	Cu/CeOx NPs with oxygen vacancies prepared via N2H4 as a reducing agent, on carbon paper	Mixed-phase/Janus	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.5 V -iR vs. RHE	? -16 mA/cm^2	29	[541]
31	Ce4+- (ion, not oxide) doped CuO NPs (100 nm), on carbon paper	Alloyed/Doped	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.3 V vs. RHE	-32 mA/cm^2	25[†_Cu-Ce,1]	[511]
32	Cu NPs supported on hollow CeO2 NCs (CeO2:Cu = 1:4), on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Ce, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-1.06 V vs. RHE	?	25	[542]
33	CuOx NPs supported on CeO2 NRs, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, Ce, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.3 V vs. RHE	-15 mA/cm^2	25	[543]
	[†_Cu-Ce,1] Conflicting information (main text vs. figure) in document, report here number given in main text											
	[†_Cu-Ce,2] Text and figure information does not match, report here the numbers provided in the text											

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	La2CuO4 perovskite nanobamboo fibers with abundant grain boundaries, on glassy carbon	Atomically mixed	Cu, La, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.0 V vs. Ag/AgCl	-3 mA/cm^2	60	[510]
2	In-situ decomposed La2CuO4 NPs, mixed with CNPs, on glassy carbon	Core/shell, mixed-phase/janus	Cu, La, C, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.3 V vs. RHE	-8 mA/cm^2	59	[509]
3	Mixed-phase Cu2NdOx NPs , on carbon paper	Mixed-phase/Janus	Cu, Nd	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KCl	Nafion 115	CO_2	-1.2 V vs. RHE	-28 mA/cm^2	54	[520]
4	"Cu10La1" (wt%/at.% not reported) co-catalyst electroplated on carbon paper	Alloyed/Doped	Cu, La	-	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO_2	-1.4 V vs. RHE	-46 mA/cm^2	51	[225]
5	CuO/Sm2O3 mixed phase NPs (8.2:1 at. Ratio Cu:Sm), on GDL	Mixed-phase/Janus	Cu, Sm, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	"ion exchange membrane"	CO_2	-1.1 V - iR vs. RHE	-700 mA/cm^2	48	[521]
6	CuO/Pr2O3 mixed phase NPs (ca. 9:1 at. Ratio Cu:Pr), on GDL	Mixed-phase/Janus	Cu, Pr, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	"ion exchange membrane"	CO_2	?	-700 mA/cm^2	46	[521]
7	La-doped Cu2O hollow sphere NPs, on a GDL	Alloyed/Doped	Cu, La, O	NafionD-521 dispersion	(Gas-phase reactant, supplied from behind)	3.0 M KCl + 0.05 M H2SO4	Nafion 117	CO_2	?	-800 mA/cm^2	43	[544]
8	Gd-doped (6.5 %, ICP) CuO NCs (60 nm), on carbon paper	Alloyed/Doped, single atom	Cu, Gd, O	Nafion	(Gas-phase reactant, supplied from behind)	2.0 M KOH	FAA-3-PK-130	CO_2	-0.8 V -iR vs. RHE	-546 mA/cm^2	42	[519]
9	La(OH)3 nanosheets supported on CuO nanosheets mixed with Ketjen Black, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, La, C, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Sustainion X37-50RT	CO_2	-1.25 V - iR vs. RHE	-1000 mA/cm^2	41	[523]
10	La2CuO4 calcined at 1000 °C, on glassy carbon	Mixed-phase/Janus	Cu, La, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M NaHCO3	-	CO_2	-1.0 V vs. Ag/AgCl	-1 mA/cm^2	40	[518]
11	CuO/Eu2O3 mixed phase NPs (ca. 9:1 at. Ratio Cu:Eu), on GDL	Mixed-phase/Janus	Cu, Eu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	"ion exchange membrane"	CO_2	?	-700 mA/cm^2	38	[521]
12	Fragmented Cu NPs derived from CO_2-induced electrochemically La-leached La2CuO4 NPs (La content ultra-low, near detection limit of equipment), on GDL	Alloyed/Doped, atomically mixed/crystalline	Cu, La, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KCl	Nafion 117	CO_2	-2.41 V - iR vs. NHE	-600 mA/cm^2	36[†_Cu-La,1]	[545]
13	CuO/La2O3 mixed phase NPs (ca. 9:1 at. Ratio Cu:La), on GDL	Mixed-phase/Janus	Cu, La, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	"ion exchange membrane"	CO_2	?	-700 mA/cm^2	33	[521]
14	Er-doped Cu2O hollow sphere NPs, on a GDL	Alloyed/Doped	Cu, Er, O	NafionD-521 dispersion	(Gas-phase reactant, supplied from behind)	3.0 M KCl + 0.05 M H2SO4	Nafion 117	CO_2	?	-900 mA/cm^2	30	[544]
15	La2-xCuO4-δ NPs with moderate oxygen vacancy content (x=0.01), on GDL	Atomically mixed	Cu, La, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	"X37-50 anion"	CO_2	-1.53 V vs. RHE	-160 mA/cm^2	28	[546]
16	Tb-doped Cu2O hollow sphere NPs, on a GDL	Alloyed/Doped	Cu, Tb, O	NafionD-521 dispersion	(Gas-phase reactant, supplied from behind)	3.0 M KCl + 0.05 M H2SO4	Nafion 117	CO_2	?	-900 mA/cm^2	28	[544]
17	Pr-doped Cu2O hollow sphere NPs, on a GDL	Alloyed/Doped	Cu, Pr, O	NafionD-521 dispersion	(Gas-phase reactant, supplied from behind)	3.0 M KCl + 0.05 M H2SO4	Nafion 117	CO_2	?	-900 mA/cm^2	26	[544]
18	Sm-doped Cu2O NCs, on Toray carbon paper	Alloyed/Doped	Cu, Sm, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.2 V vs. RHE	-40 mA/cm^2	26	[547]
	[†_Cu-La,1] SI is missing from publisher website, obtained via personal communication with author (provided as SI document for the current manuscript)											

2.5. Various forms of carbon and carbon-derivatives

A somewhat special case of bi-elemental Cu catalysts are the Cu/C catalysts, because of the rich chemistry of carbon making these systems extremely heterogeneous. Partially, this is on account of our decision to consider all morphologies and chemical states of carbon to be a single category. This includes e.g., nanoparticles, fibers, multiwalled nanotubes, graphene, graphene oxide, graphite, carbon nitride (C_3N_4), carbon nanodots etc. We even went a step further, and included copper-based transition metal complexes (TMCs), copper-containing metal organic frameworks (MOFs) and copper-containing covalent organic frameworks (COFs) in the Cu/C category on account of their propensity to decompose into carbon-rich copper ensembles.[548,549] It is important to note that in many instances the carbon component is added solely to support/disperse the 'active' catalyst, or possibly to serve as a (presumed catalytically inert) conductivity-enhancing agent. Although the Cu/C catalysts are quite different from the other bi-elemental catalyst systems discussed herein, we consider their inclusion vital on account of the industrial relevance of catalyst supports. Namely, supports can perform various functions within a catalytic system such as optimizing e.g., mass transport properties, heat management, catalyst stability, catalyst loading, and (for electrocatalytic purposes) electric conductivity. In addition, there might exist catalyst-support interactions which could influence binding strengths and therewith tune the inherent properties of the catalytically active sites.[550]

A summary of best-performing Cu/C catalyst systems is provided in Table S22. Due our broad definition, the Cu/C catalyst dataset is derived from 116 unique publications and comprises a total of 132 catalyst systems, with 9 using CO as a reactant and 39 having been identified as alkaline CO_2 systems. A total of 34 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55%, though 14 of those are reported under alkaline CO_2 reduction reaction (CO2RR) conditions. In our analysis, we will exclude such alkaline CO2RR systems, resulting in a final sample size of 93 catalysts. The top two most-selective catalysts yield 71%[551] and 81%[552] C_2H_4 and both concern non-alkaline CO2RR systems. Overall, we find that we can assign Cu/C catalysts to one of two categories: being of the core/shell-type, or of the supported-type. Here, the core/shell-type systems consist of copper catalysts modified with a surface layer of (potentially hetero-atom functionalized) carbon, whereas the following systems were categorized as being of the supported-type: i) copper particles grown on carbon, ii) copper particles physically mixed with carbon, iii) single-atom copper catalysts (SACs) on carbon-containing supports, and iv) Cu-based TMCs, MOFs and COFs. The various complexed forms of copper (be it as frameworks or individual homogeneous catalysts) were included through reasoning that they can be viewed as either a form of single-atom copper sites 'supported' by a hetero-atom doped carbon environment, or as unstable systems that decompose into (potentially) hetero-atom doped, carbon-rich aggregates that act as a 'support' for the copper particles that form *in-situ*.

Analyzing the various supported-type publications, we find C_2H_4 FEs in the 50%-70% range at the top-end of the spectrum. Simultaneously, we observe that virtually none of those systems have been tested under industrially relevant current densities, with only 4 catalysts having been tested at $\geq|-180|$ mA/cm^2.[363,553-555] Although this is a direct consequence of us ignoring alkaline CO2RR systems in our analysis, we still find this a worrying observation considering that one of the main reasons behind employing a supporting material is to increase catalyst area and therewith allow for higher reaction rates (higher current densities). In addition, this observation goes to show that relying too much on alkaline CO2RR results may paint a wrong picture of what is achievable in industrial systems. Focusing on the top-performing supported-type catalysts, we find that most of these consist of chemically modified carbon supports, e.g., through the presence of hetero atom-containing ligands[556], or in the form of hetero atom-functionalization.[306,552,557] It is only once we start to look at relatively poorer performing catalysts systems (C_2H_4 FEs <55%) that we begin to observe reports of (oxide-derived) copper NPs supported on more traditional, unmodified forms of carbon particles (e.g., Ketjen Black[558] and Vulcan XC-72[183]) though a single outlier exists in the form of a Cu-based MOF pre-catalyst mixed with Ketjen black (yielding 70% C_2H_4).[559] In that outlier, they show that the presence of supporting carbon helps limiting the size of the Cu NPs that form upon decomposition of the Cu MOF, making the presence of a carbon support a morphology-directing vector during the *in-situ* reconstruction of the unstable pre-catalyst particles.

To continue, we find that TMC-, COF- and MOF-derived supported catalysts are observed across the entirety of the activity spectrum, with C_2H_4 performance varying from very poor (≤35% C_2H_4)[560-562] to relatively high (ca. 70% C_2H_4).[559,563] We hypothesize that, in many instances, this is related to the morphology and size of the active catalyst that is formed during the decomposition of these materials, being highly dependent on i) the starting material, ii) the reaction environment and iii) the initial process conditions during the reduction (electrochemical decomposition) stage. This hypothesis is substantiated by the outlier we just discussed, wherein they showed that the addition of supporting carbon helped to direct the final size of the Cu NPs that were formed *in-situ*.[559] Although therein they show that the Cu NPs in the absence of a carbon support grow to be too large, Cu NPs are known to go through a 'size optimum' with respect to C_2H_4 performance.[64] With the starting conditions and materials dictating which active phase is formed, it is logical that a strong variation in such conditions and materials yields catalyst particles with a wide range of sizes and morphologies, thus resulting in the large spread in performance that we observe.

Besides supported-type Cu/C catalysts, we have also identified a small number of core/shell-type Cu/C catalyst systems (totaling 6). However, the highest-performing samples of this type, consisting of N-functionalized[294] (and B-functionalized[294], Table S4) carbon shells – yielding ca. 70% C_2H_4 – are alkaline CO2RR systems. Non-alkaline conditions typically result in substantially lower performance, with maximum C_2H_4 FEs ranging between 40%-55%.[564-566] The most important observation, in our opinion, is the fact that CO_2 reduction can still take place even if a carbon shell is present. In addition, a similar doping effect as previously discussed for supported-type catalysts is observed considering that the majority (5/6 for full dataset, 3/3 for non-alkaline systems) of the core/shell-type catalysts have hetero atom-doped carbon shells. For more in-depth information regarding such core/shell-type structures, the reader is referred to a review on specifically these structures.[567]

Although good C_2H_4 performance can be achieved under specific circumstances with Cu/C systems, most of these systems have only yielded current densities <|-50| mA/cm^2. As such, we fail the see one of the key benefits that introducing a support brings: higher reaction rates. It is actually the CORR systems where we observe higher overall reaction rates, though the C_2H_4 performance of those systems is considerably poorer (maximum C_2H_4 FEs ≤50%)[568] than the top-performing non-alkaline CO2RR systems.

	Table S22. C-based Cu											
#	**Electromaterial description**	**Catalyst type**	**Main elements**	**Polymeric / organic & inorganic additives**	**Reactant delivery mode**	**Catholyte**	**Membrane**	**Reactant**	**E**	**j**	**C$_2$H$_4$ FE**	**Reference**
1	Cu NPs supported on Cu/SAC-graphitic carbon nitride (g-C3N4), on carbon paper	SAC, supported	Cu, C	-	(Gas-phase reactant, supplied from behind)	0.1 M KHCO3 (pH 6.8)	Fumasep FAA-3-PK-130	CO$_2$	-1.28 V vs. RHE	-45$^{\dagger\text{\_Cu-C-supported},8}$ mA/cm^2	81	[552]
2	Cu2O NPs supported on CNTs modified with Cu-based COF, on glassy carbon	COF, supported	Cu, C, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO$_2$	-1.1 V vs. RHE	-44 mA/cm^2	71	[551]
3	Thin quasi-graphitic carbon-shell functionalized, N-doped Cu NPs supported on carbon fibers, on GDL	Core/shell	Cu, C, N	Nafion, quasi-graphitic carbon shell	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Sustanion X37-50	CO$_2$	-0.69 V -iR vs. RHE	-400 mA/cm^2	71	[294]
4	Cu3(2,3,6,7,10,11-hexaiminotriphenylene)2 MOF supported on Ketjen Black, on glassy carbon	MOF, supported	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion	CO$_2$	-1.37 V - iR vs. RHE	-38 mA/cm^2	70	[559]
5	In-situ formed Cu2O ultra-small NPs derived from CO$_2$RR/KCl electro-activated Cu(Pyrazole)2 MOF, on carbon paper	MOF, supported	Cu, O, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion	CO$_2$	-1.03 V - iR vs. RHE	-18 mA/cm^2	70	[549]
6	Cu NPs supported on XC-72R, on home-made GDL	Supported	Cu, C	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	-	CO$_2$	-3 V vs. Ag/AgCl	-400 mA/cm^2	69	[93]
7	Solution-phase Cu phenanthroline complex with carbon paper cathode	TMC, supported	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	"Hangzhou Huamo Technology Co., Ltd"	CO$_2$	-1.3 V vs. RHE	-7 mA/cm^2	69	[563]
8	Water-etched Cu MOF ([Cu2(benzene-1,3,5-tricarboxylic acid,)(OH)(H2O)]n·2nH2O), on glassy carbon	MOF, supported	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 + 0.1 M KCl (pH 6.8)	Nafion 117	CO$_2$	-1.40 V vs. RHE	-23 mA/cm^2	67	[569]
9	Water-etched Cu MOF ([Cu2(benzene-1,3,5-tricarboxylic acid,)(OH)(H2O)]n·2nH2O), on a GDL	MOF, supported	Cu	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAB-PK-130	CO$_2$	-0.73 V - iR vs. RHE	-350 mA/cm^2	65	[569]
10	Impregnation-derived Cu NPs supported on N-functionalized carbon, on carbon paper (ill-defined carbon support derived from biological source)	Supported	Cu, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3/CO (pH 8.3)	Nafion 115	CO$_2$	-1.0 V vs. RHE	-50 mA/cm^2	64	[557]
11	Pre-reduced CuOx NPs supported on sheet-like tannic acid substrate, on GDL	Supported	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Nafion 117	CO$_2$	-0.7 V - iR vs. RHE	-500 mA/cm^2	64	[570]
12	Cu-MOF calcination derived grainboundary-rich CuOx NPs supported on Ketjen Black, on glassy carbon	MOF, supported	Cu, O, C	Nafion (top-coat)	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.01 V - iR vs. RHE	-11 mA/cm^2	63	[571]
13	Cu NPs supported on N-doped CNTs, on GDL	Supported	Cu, C, N	Nafion	(Gas-phase reactant, supplied from behind)	5.0 M KOH	"Sustainion"	CO$_2$	-0.57 V - iR vs. RHE	-500 mA/cm^2	62	[572]
14	In-situ generated Cu NPs from 3-(2-Pyridyl)-5-phenyl-1,2,4-triazole-based Cu-TMC, on Cu-sputtered PTFE	TMC, supported	Cu	Nafion	(Gas-phase reactant, supplied from behind)	0.05 M H2SO4 + 2.5 M KCl	Nafion 117	CO$_2$	-1.64 V - iR vs. RHE	-200 mA/cm^2	62	[555]
15	Cu2O NPs electroplated on Cu-CuTCPP MOF nanosheets, on GDL	MOF, supported	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 211	CO$_2$	-1.3 V vs. RHE	-15 mA/cm^2	62	[573]
16	Polyvinylpyrrolidone-assisted ("P2") self-assembled Cu-based supramolecular polymer MPs, on glassy carbon	Supramolecular	Cu	? Nafion	(Solution-phase reactant, supplied in front)	1.0 M KOH (pH 14)	FAB-PK-130	CO$_2$	-1.4 V vs. RHE	-128 mA/cm^2	62	[574]
17	(100)-rich Cu NPs derived from reconstruction of Cu-tannic acid NSs, on GDL	TMC, supported	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-130	CO$_2$	-2.16 V vs. RHE	-700 mA/cm^2	61	[211]
18	Ultrafine Cu NPs supported on N-functionalized carbon, on carbon paper	Supported	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-PK-130	CO$_2$	-1.05 V vs. RHE	-208 mA/cm^2	61	[575]
19	Cu NPs supported on vacuum-calcined (1800 C) UD-90 nanodiamonds from NanoBlox,Inc., on glassy carbon	Supported	Cu, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3/CO (pH 8.3)	-	CO$_2$	-1.8 V vs. RHE	-6 mA/cm^2	60	[576]
20	Honeycomb-like CuO supported on amorphous carbon annealed at 600 °C, on carbon paper	Supported	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.2 V vs. RHE	-18 mA/cm^2	60	[577]
21	Cu-SAC (<1 wt%) on hetero-atom (S) doped C3N4 lamellae, on carbon paper	SAC, supported	Cu, C, N, S	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	"ion exchange membrane"	CO$_2$	-0.9 V vs. RHE	-20 mA/cm^2	60	[306]
22	Sulfur-doped Cu-MOF Cu3(benzene-1,3,5-tricarboxylate)2·xH2O, on glassy carbon	MOF, supported	Cu, O, S	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.32 V - iR vs. RHE	-19 mA/cm^2	60	[556]
23	Polyvinylpyrrolidone-assisted ("P2") self-assembled Cu-based supramolecular polymer MPs, on glassy carbon	Supramolecular	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO$_2$	-1.4 V vs. RHE	-29 mA/cm^2	60	[574]
24	CuO NPs supported on NH2 modified carbon dots, on glassy carbon (possibly carbon paper - unclear)	Supported	Cu, O, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 212	CO$_2$	-1.4 V vs. RHE	-41 mA/cm^2	57	[578]
25	Sulfur-doped Cu-MOF Cu3(benzene-1,3,5-tricarboxylate)2·xH2O, on Cu-sputtered PTFE GDL	MOF, supported	Cu, O, S	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO$_2$	-1.09 V - iR vs. RHE	-400 mA/cm^2	57	[556]
26	1D chains of Cu transition metal complex [Cu(4-"H-pyrazole")2]n·solvent, on carbon paper	TMC, supported	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO$_2$	-1.0 V - iR vs. RHE	-346 mA/cm^2	56$^{\dagger\text{\_Cu-C-supported},1}$	[579]
27	Cu NPs supported on N-doped CNTs, on Cu-sputtered PTFE GDL	Supported	Cu, C, N	Nafion	(Gas-phase reactant, supplied from behind)	5.0 M KOH	"Sustainion"	CO$_2$	-2.6 vs. Hg/HgO	-200 mA/cm^2	56	[572]
28	CuO NSs supported on Ketjen EC-300 J, on a GDL	Supported	Cu, O, C	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FABPK-130	CO$_2$	-0.87 V - iR vs. RHE	-304 mA/cm^2	56	[580]
29	Cu2O NPs supported on pyridinic-N-rich graphitic carbon nitride (C3N4), on carbon paper	Supported	Cu, O, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.2 V vs. RHE	-23 mA/cm^2	56	[581]
30	Copper-tetracyanoquinodimethane (TCNQ)-derived Cu NPs, on glassy carbon	TMC, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO$_2$	-1.3 V vs. RHE	-12 mA/cm^2	56	[582]
31	Anionic Cu-MOF (a-HKUST1) NPs, on a GDL	MOF, supported	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAB-PK-130	CO$_2$	-0.70 V vs. RHE	-150 mA/cm^2	56	[583]
32	Cu transition metal complex with oxygen coordination center; ((Cu3(m3-OH)(mpz)3(Im)3)2+)2+ with Br- anion, on carbon paper	TMC, supported	Cu, O,	Nafion	(Gas-phase reactant, supplied from behind)	0.5 M KOH (pH	Fumasep, FAA-3-PK-130	CO$_2$	-0.70 V - iR vs. RHE	-130 mA/cm^2	55	[584]

			Br			13.7)						
33	Conductive dinuclear Cu-based TMC ([Cu2(ophen)2] (Cuophen) with ophen = 1H-[1,10]phenanthrolin-2-one), on GDL	TMC, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	?	CO$_2$	-1.4 V vs. RHE	-52 mA/cm^2	55	585
34	Cu-based MOF NPs (109 nm) with many grain boundaries, on glassy carbon	MOF	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 212	CO$_2$	-1.15 V - iR vs. SHE	-13 mA/cm^2	55	586
35	Cu layered double hydroxide (Cu5Al-CO3)-derived CuOx NPs supported on reduced graphene oxide, on carbon cloth (also referred to as "carbon paper" [sic] in text)[†–Cu-C-supported,5]	Supported	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	-	CO$_2$	-1.2 V vs. RHE	-12 mA/cm^2	54[†–Cu-C-supported,6]	587
36	C-doped ("6%") CuOX NPs, on a GDL	Alloyed/Doped	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-130	CO$_2$	-0.72 V -iR vs. RHE	-1250 mA/cm^2	54	588
37	Quasi-1D Cu MOF (Cu(OH)[1,2,3-benzotriazolate]) nanowires, on GDL	MOF, supported	Cu	Nafion	(Gas-phase reactant, supplied from behind)	-	Sustainion x37-50-grade-60	CO$_2$	-3.8 V vs. ANODE	-240 mA/cm^2	54	589
38	Reductively calcined (350 C) dopamine-derived N-functionalized carbon-shell functionalized Cu NPs, on glassy carbon	Core/shell	Cu, C, N	Nafion, carbon shell	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion	CO$_2$	-1.4 V vs. RHE	-15 mA/cm^2	54	566
39	Cu2O-derived bimodal Cu catalyst supported on Ketjen black, on glassy carbon	Supported	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.15 V - iR vs. RHE	-40 mA/cm^2	53	558
40	Cu3(2,3,6,7,10,11-hexaiminotriphenylene)2 MOF supported on Ketjen Black, on GDL	MOF, supported	Cu, O, C	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAB-PK-130	CO$_2$	-0.82 V - iR vs. RHE	-500 mA/cm^2	53	559
41	Tetraminobenzo-quinone/Cu2+ based hydrogen-bonded network, on GDL (carbon paper modified with PTFE-coated carbon spheres)	COF, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	1.0 M KOH (pH 14)	Fumasep FAA-3-PK-130	CO$_2$	-1.17 V - iR vs. RHE	-423 mA/cm^2	53	590
42	Triazolate-based Cu MOF, on glassy carbon	MOF, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	-	CO$_2$	-1.2 V vs. RHE	-6 mA/cm^2	53	591
43	High loading electrosprayed CuO particles on carbon paper/fibers (Toray, TGP-H-120)	Supported	Cu, O, C	-	(Solution-phase reactant, supplied in front)	0.1 M CsHCO3 (pH 6.8)	Selemion AMV	CO$_2$	-1.09 V - iR vs. RHE	-40 mA/cm^2	52	592
44	CuOx NPs prepared through thermal reduction of Cu(acac)2-oleylamine complex, on GDL	TMC, supported	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	"Nafion"	CO$_2$	-1.0 V - iR vs. RHE	-360 mA/cm^2	52	593
45	Dual-site single atom copper on N-doped carbon derived from pyrolysis of Cu-impregnated MOF, on a GDL	MOF, supported	Cu, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	? Nafion 117	CO$_2$	-1.4 V vs. RHE	-180 mA/cm^2	52	554
46	Cu-MOF [azolate] / Cu(I) 3,5-dialkyl-1,2,4-triazolate, on glassy carbon	MOF, supported	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion	CO$_2$	-1.3 V vs. RHE	-11 mA/cm^2	52	594
47	Ultrathin 'wavy' Cu-MOF based nanosheets, on glassy carbon	MOF, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	-	CO$_2$	-1.3 V vs. RHE	-12 mA/cm^2	52	595
48	CuOx NPs with hydrophobic porous carbon shell, on Cu-sputtered PTFE GDL	Core/shell	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	"Sustainion"	CO$_2$	?	-300 mA/cm^2	52	596
49	Polystyrene template-assisted interconnected mesoporous Cu2O NPs supported on Vulcan XC-72, on glassy carbon	Supported	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.4 V vs. RHE	-18 mA/cm^2	51	183
50	Cu NPs encapsulated in cub mesoporous carbon (CMK-8), on GDL	Supported	Cu, C, N	-	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	"Fuel Cell Store"	CO$_2$	-1.1 V -iR vs. RHE	-250 mA/cm^2	51	363
51	Calcined (265 C) Cu-MOF [HKUST-1] (C18H6Cu3O12, Cu3(benzene-1,3,5-tricarboxylate)2·xH2O)-derived CuOx/C, on glassy carbon (?)	MOF, supported	Cu, O, C	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.57 V vs. RHE	?	51	597
52	Cu-based MOF with dual-Cu sites, on a GDL (XGL 29bc)	MOF, supported	Cu	? Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAA-3-50	CO$_2$	-1.6 V vs. RHE	-920 mA/cm^2	51	598
53	Metallic Cu overlayer sputtered on commercial Cu NPs (25 nm, Sigma Aldrich) supported on Ketjen Black mixed with poly(methyl methacrylate) electrosprayed on a GDL	Supported	Cu	Poly(methyl methacrylate)	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FABPK-130	CO	-0.56 V - iR vs. RHE	-60 mA/cm^2	50	568
54	Cu-based TMC (terephthalate), on glassy carbon (?)	TMC, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO$_2$	-1.1 V vs. RHE	-12 mA/cm^2	50	599
55	Calcined (265 C) Cu-MOF [HKUST-1] (C18H6Cu3O12, Cu3(benzene-1,3,5-tricarboxylate)2·xH2O)-derived CuOx/C, on GDL	MOF, supported	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	1.0 M KOH (pH 14)	Fumasep FAA-3-PK-130	CO$_2$	?	-320 mA/cm^2	50	597
56	Exfoiliated 2D MOF obtained from combining copper(II) acetylacetonate with (2,3,9,10,16,17,23,24-octahydroxyphthalo-cyaninato)copper(II), on glassy carbon	MOF, supported	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.2 V vs. RHE	-7 mA/cm^2	50	600
57	Cu MOF ([Cu3(μ3-OH)(μ3-trz)3(OH)2(H2O)4]·xH2O)-derived CuOx NPs, on GDL	MOF, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	1.0 M KHCO3	Nafion 117	CO$_2$	-0.8 V vs. RHE	-250 mA/cm^2	50	553
58	Ultrafine CuO NPs supported on 2D copper 1,4-dicarboxybenzene (1,4-BDC) MOF, on carbon paper	MOF, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.1 V vs. RHE	-14 mA/cm^2	50	601
59	Magnetic-assisted catalysis on spin ordered/disordered Cu-based MOF (HKUST) via partial-H2O replacement with TEMPOL, on carbon paper	MOF, supported	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	?	CO$_2$	-1.8 V vs. Ag/AgCl	-10 mA/cm^2	50	602
60	Cu NCs with N/C shell obtained via in-situ reconstruction of Cu-based MOF (2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine), on Cu foil substrate	Core/shell	Cu, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.15 V vs. RHE	-27 mA/cm^2	50	603
61	Ultrafine Cu NPs on fibrous pyrenyl-graphdiyne, supported on Cu foil	Supported	Cu, C	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.5 V vs. RHE	-12 mA/cm^2	49	604
62	Cu NPs embedded in carbon matrix derived from pyrolysis of benzoxazine, mixed with PTFE (25 wt%), on GDL	Supported	Cu, C	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-75	CO$_2$	-0.58 V -iR vs. RHE	-200 mA/cm^2	49	605
63	Cu MOF ([Cu2(L1)2(L2)(H2O)2]·SO4·2H2O)-functionalized Cu plate	MOF, supported	Cu	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.11 V - iR vs. RHE	-17 mA/cm^2	49	606
64	Commercial Cu NPs (10-30 nm, Macklin) supported on Ketjen Black, on GDL	Supported	Cu, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion	CO$_2$	-1.56 V - iR vs. RHE	-60 mA/cm^2	48	559
65	2D Cu-phenylalanine nanoflakes supported on carbon powder, on GDL	MOF, supported	Cu, O, C	Nafion	(Gas-phase reactant, supplied from behind)	0.5 M KHCO3	Nafion 117	CO$_2$	-0.8 V vs. RHE	-88 mA/cm^2	48	607
66	CuO NSs supported on phenol formaldehyde resin carbon (PFRC), on GDL	Supported	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Nafion 117	CO$_2$	-0.64 V vs. RHE	-1268 mA/cm^2	47	608
67	Individual Cu NPs supported on/embedded in an amorphous CuOx phase obtained through tannic acid-assisted synthesis, on a GDL	Supported [on Cu]	Cu, O	Nafion	(Gas-phase reactant, supplied from behind)	3.0 M KCl	Nafion 117	CO$_2$	-0.9 V - iR vs. RHE	-400 mA/cm^2	46	609
68	CuOx NPs supported on Vulcan XC-72, on GDL	Supported	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	FAB-PK-130	CO$_2$	-1.65 V vs. RHE	-200 mA/cm^2	46	610
69	N-doped carbon quantum dots supported on CuOx NRs, on a "PTFE membrane"	Supported	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-130	CO$_2$	-1.5 V -iR vs. RHE	?	46	268

70	Cu-MOF calcination derived grainboundary-rich CuOx NPs supported on Ketjen Black, on carbon paper	MOF, supported	Cu, O, C	Nafion (top-coat)	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Nafion 117	CO_2	-0.56 V - iR vs. RHE	-200 mA/cm^2	46	571
71	Self-assembling Cu-TMC (Bis(triphenylphosphine) Cu(I) nitrate) nanorods supported on XC-72R, on glassy carbon	TMC, supported	Cu, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	?	CO_2	-0.96 V vs. RHE	-2 mA/cm^2	45	611
72	Calcination-distorted Cu-MOF [HKUST-1] (C18H6Cu3O12, Cu3(benzene-1,3,5-tricarboxylate)2·xH2O), on GDL	MOF, supported	Cu, O, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-1.07 V - iR vs. RHE	-262 mA/cm^2	45	612
73	CuO nanosheets derived from calcining CuII/adeninato/carboxylato-MOFs, on glassy carbon	MOF, supported	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.4 V vs. RHE	-9 mA/cm^2	45	613
74	In-situ reduced air-annealed commercial µm sized Cu particles supported on multi-walled carbon nanotubes, on GDL	Supported	Cu, O, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumatech FAA-3	CO	-0.72 V - iR vs. RHE	-1050 mA/cm^2	44	614
75	CuO NSs supported on VXC-72r, on GDL	Supported	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Nafion 117	CO_2	-0.66 V vs. RHE	?	44	608
76	Cubic Cu2O microparticles (1 µm) supported on carbon black, on glassy carbon	Supported	Cu, C, O	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.1 V vs. RHE	-18 mA/cm^2	44	341
77	[Cu3(HBtz = benzotriazole)3(Btz)Cl2] based, π-π stacking-driven network, on glassy carbon	COF, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 + 0.1 M KCl (pH 6.8)	Nafion 117	CO_2	-1.3 V vs. RHE	-8 mA/cm^2	44	615
78	Thermally decomposed Cu TMC (copper phthalocyanine) supported on Ketjen Black EC600 JD, on copper foil (unclear if it remains as a supported catalyst after final heat treatment)	TMC, supported	Cu, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 115	80/20 CO_2/O2	-0.4 V vs. RHE	-8 mA/cm^2	43	616
79	CuBaCO3 NPs supported on MWCNTs, on Cu-sputtered PTFE GDL	Supported	Cu, Ba, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO_2	-0.7 V vs. RHE	-500 mA/cm^2	43	236
80	Cu NPs with nitrogen-doped carbon shell prepared with a mass ratio of Cu to 7, 7, 8, 8-tetracyanoquinodimethane of 20:4 and calcined at 350 °C, on glassy carbon	Core/shell	Cu, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	QAPPT	CO_2	-1.1 V vs. RHE	-19 mA/cm^2	43	565
81	Dimeric Cu transition metal complex [Cu2(tris(2-benzimidazolylmethyl)amine)2Cl2]Cl2 immobilized on nafion-coated mesoporous carbon, on carbon paper	TMC, supported	Cu, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO_2	-1.28 V vs. RHE	-9 mA/cm^2	42	617
82	CuO nanoplates mixed with MWCNTs, on GDL	Supported	Cu, O, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumatech FAA	CO	-0.69 V -iR vs. RHE	-500 mA/cm^2	42	618
83	Binuclear Cu phenanthroline TMC mixed with graphite powder, on carbon paper	TMC, supported	Cu, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M CsHCO3 (pH 6.8)	Glass frit	CO_2	-1.25 V vs. RHE	-6 mA/cm^2	42	619
84	(111)-rich 6 nm Cu NPs supported on Cu-tetrahydroxy-1,4-quinone (THQ) MOF, on glassy carbon	MOF, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 + 0.1 M KCl (pH 6.8)	Nafion 117	CO_2	-1.4 V vs. RHE	-14 mA/cm^2	42	620
85	CuOx NPs with carbon nitride shell, on carbon paper	Core/shell	Cu, O, C, N	C3N4	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.2 V vs. RHE	-40 mA/cm^2	42	564
86	Cu-TMC (Copper(II) meso -tetra(4-carboxyphenyl)porphine) NSs, on glassy carbon	TMC, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 211	CO_2	-1.2 V vs. RHE	-8 mA/cm^2	41	621
87	Ultrafine Cu NPs supported on graphdiyne, on GDL	Supported	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	0.1 M KOH (pH 13)	Fumatech FAA–3	CO	-1.0 V vs. RHE	-24 mA/cm^2	40	622
88	Eleborate electrospun fiber-network, eventually yielding conductive CNT/PTFE fibers with half-exposed porous µm-sized CuO particles, on carbon paper	Supported	Cu, O, C	PTFE	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.4 V vs. RHE	-121 mA/cm^2	40	623
89	Cu NPs with carbon shell, supported on mesoporous carbon nanofibers, on a GDL†$_{Cu-C-core/shell,1}$	Core/shell	Cu, C	?	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-75	CO_2	-1.27 V - iR vs. RHE	-500 mA/cm^2	40	624
90	"Cu catalyst" supported on mixed carbon powder (Lonza KS-44) with a Cu/C ratio of 0.5, made into a GDE	Supported	Cu, C	Dibutyle phtalate	?	0.3 M KHCO3	Nafion 417	CO_2	-3.5 V vs. SCE	?	38	625
91	CuO 'nanospindles' (resembles plates) supported on C60/fullerene, on GDL	Supported	Cu, O, C	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Nafion 117	CO_2	-1.8 V - iR vs. RHE	-563†$_{Cu-C-supported,2}$ mA/cm^2	37	626
92	CuOX NPs supported on graphite phase carbon nitride (C3N4), on carbon paper	Supported	Cu, O, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.0 V - iR vs. RHE	-14 mA/cm^2	37	627
93	Air-calcined Cu NPs supported on N-doped carbon formed at 700 °C, on carbon paper	Supported	Cu, O, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.1 M NaHCO3 (pH 6.8)	Nafion 117	CO_2	-1.25 V - iR vs. RHE	-11 mA/cm^2	36	628
94	Crystalline copper(II) Phthalocyanine supported on Vulcan XC-72R, on glassy carbon	Supported	Cu, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KCl	Nafion 424	CO_2	-1.7 V vs. RHE	-35 mA/cm^2	35	629
95	Pre-reduction of Cu TMC (cuprous 7,7,8,8-tetracyanoquinodimethane)-derived Cu NPs, on GDL	TMC, supported	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	"Membrane"	CO	-0.61 V - iR vs. RHE	-330 mA/cm^2	35	630
96	Pre-reduced dual atom Cu SAC supported on N-doped carbon, on carbon paper	Supported, SAC	Cu, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.23 V vs. RHE	-35 mA/cm^2	35	631
97	CuO NPs supported on N-doped C, on GDL	Supported	Cu, C, N	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	Sustainion X37 50	CO_2	-0.72 V -iR vs. RHE	-400 mA/cm^2	35	376
98	Cu NPs supported on a Cu COF ("4.8%"), on carbon paper	COF, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.3 M KCl	Nafion 115	CO	-1.5 V - iR vs. SHE	?	35	632
99	Post-annealed, electrodeposited Cu2O MPs "supported on" roughened N-doped graphite paper	Supported	Cu, O	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-0.9 V vs. RHE	-24 mA/cm^2	35	633
100	N-doped graphene quantum dots supported on CuOx NRs, on a "PTFE membrane"	Supported	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-130	CO_2	-1.3 V -iR vs. RHE	-348 mA/cm^2	35	268
101	Imidazolium-functionalized cationic covalent triazine framework-stabilized Cu NPs supported on Ketjen Black, on glassy carbon	COF, supported	Cu, C	Nafion, imidazolium-functionalized cationic covalent triazine framework	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 + 0.1 M KCl (pH 6.8)	Nafion 117	CO_2	-1.3 V vs. RHE	-12 mA/cm^2	35	562
102	Cu NPs supported on a Cu COF ("4.8%"), on carbon paper	COF, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.3 M KCl	Nafion 115	CO	-1.5 V - iR vs. SHE	?	35	632
103	Metallic 50 nm Cu NWs supported on Ketjen EC300J, on carbon paper	Supported	Cu, C	Polyvinylidene fluoride	(Solution-phase reactant, supplied in front)	0.1 M KHCO3/CO (pH 8.3)	Nafion 212	CO	-1.1 V vs. RHE	-84 mA/cm^2	34	634
104	"Activated" Cu NPs embedded in self-assembled coordination polyer ([Cu2(µ-Br)2(PPh3)2(µ-DPB)]n), on carbon paper (C2H4 activity increases with time)	TMC, supported	Cu	[Cu2(µ-Br)2(PPh3)2(µ-DPB)]n	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Astom Co. ASE	CO_2	-1.34 V vs. RHE	-35 mA/cm^2	34	635
105	Powdered electroplated (40 °C/14 V/60 min) CuOx particles supported on graphene oxide, pressure sprayed on carbon fiber paper	Supported	Cu, O, C	-	(Solution-phase reactant, supplied in front)	0.2 M KHCO3	Nafion 117	CO_2	-0.99 V - iR vs. RHE	-41 mA/cm^2	34	636
106	Pre-reduced CuOx NPs supported on polymer-derived N-doped	Supported	Cu,	Nafion	(Solution-phase reactant,	0.1 M	Nafion 117	CO_2	-1.2 V	-12	34†–	637

	carbon fibers prepared via electrospinning and calcination (400 °C/Ar), on glassy carbon		O, C, N		supplied in front)	KHCO3 (pH 6.8)			vs. RHE	mA/cm^2	[Cu-C-supported,7]	
107	Cu2O NPs mixed with N-doped graphene (Figure S20), on a GDL	Supported	Cu, O, C, N	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	-	CO$_2$	-1.9 V vs. RHE	-200 mA/cm^2	34	638
108	Cu NCs anchored/immobilized on N-doped graphene oxide, unknown substrate	Supported	Cu, C	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	?	CO$_2$	-1.0 V vs. RHE	-11 mA/cm^2	33	639
109	Cu2O NCs supported on graphitic carbon nitride (g-C3N4), on carbon paper	Supported	Cu, C, N	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.1 V vs. RHE	-13 mA/cm^2	32	640
110	Cu-based TMC (Cu(N,N’-bis-(salicylidene)-o-phenylenediamine) supported on carbon black, on a GDL	TMC, supported	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAA-130	CO$_2$	-1.1 V vs. RHE	-303 mA/cm^2	32	560
111	Cu2O NPs supported on a Cu MOF (CU-BDC / terephthalic acid), on carbon paper	MOF, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KBr	Nafion 117	CO$_2$	-1.19 V vs. RHE	-7 mA/cm^2	32	641
112	Cu NPs (20 wt%) supported on thermally annealed (800 C) polypyrrole-derived N-functionalized porous carbon, on graphite	Supported	Cu, C, N	-	(Solution-phase reactant, supplied in front)	0.2 M KHCO3	Nafion 212	CO$_2$	-1.05 V - iR vs. RHE	-11 mA/cm^2	31	642
113	4 nm Cu NPs supported on "moderate" density Cu-SAC/carbon, on GDL	SAC, supported	Cu, C	Nafion D-521	(Gas-phase reactant, supplied from behind)	5.0 M KOH	FAA-3-PK-130	CO$_2$	-0.6 V - iR vs. RHE	-383 mA/cm^2	31	643
114	High loading 72 nm Cu2O NCs supported on ionic liquid-functionalized graphite sheets, on glassy carbon	Supported	Cu, O, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.15 V vs. RHE	-8 mA/cm^2	31	644
115	Cu NPs supported on a Cu COF ("4.8%"), on carbon paper	COF, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.3 M KCl	Nafion 115	CO$_2$	-1.47 V - iR vs. SHE	-28 mA/cm^2	31	632
116	Cu NPs supported on a Cu MOF ([perylene tetracarboxylic di-(propyl imidazole)-Cu-Cl2(H2O)2]n), on a GDL	MOF, supported	Cu	Nafion, perylene tetracarboxylic di-(propyl imidazole)	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO$_2$	-1.9 V vs. RHE	-73 mA/cm^2	31	561
117	Cu NPs supported on a Cu COF ("4.8%"), on carbon paper	COF, supported	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.3 M KCl	Nafion 115	CO$_2$	-1.47 V - iR vs. SHE	-28 mA/cm^2	31	632
118	Phosphate-buffered saline-treated CuO NPs-turned-nanoshees supported on Vulcan XC-72R, on carbon paper	Supported	Cu, O, C, P	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	-	CO$_2$	-1.4 V vs. RHE	-25 mA/cm^2	30	645
119	Few (~4) atom Cu SACs prepared with a cyclohexene:Cu ratio of 60 supported on CNTs, on Toray carbon paper	SAC, supported	Cu, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	-	CO$_2$	-1.4 V vs. RHE	-21 mA/cm^2	29	485
120	Cu-MOF derived, CuOx NPs with carbon shell (2 nm), on a GDL	Core/shell, MOF	Cu, O, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	"Anionic membrane"	CO$_2$	-0.88 V -iR vs. RHE	-560 mA/cm^2	29	646
121	Hydrogen annealed, Cu-MOF derived Cu NPs with carbon shell (2 nm), on a GDL	Core/shell, MOF	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	"Anionic membrane"	CO$_2$	-0.98 V -iR vs. RHE	-339 mA/cm^2	28	646
122	Cu2O NCs supported on N-doped carbon "shells" (involving ZnO NP templating - may be a trace contaminant), on glassy carbon	Supported	Cu, O, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.3 V vs. RHE	-10 mA/cm^2	25	647
123	MOF-derived high loading Cu SAC supported on N-doped carbon nanosheet calcined at 800 °C, on carbon paper	Supported, MOF	Cu, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.4 V vs. RHE	-28 mA/cm^2	25	648
124	Electroreduced Cu MOF (Cu3(1,3,5-benzenetricarboxylate)2)-derived CuOx NPs supported on N-doped graphene, on carbon paper (ambiguously reported)	Supported, MOF	Cu, O, C, N	Nafion	(Gas-phase reactant, supplied from behind)	0.2 M KI	Nafion 117	CO$_2$	-1.9 V vs. RHE	-15 mA/cm^2	24	649
125	CuOx NCs supported (23 wt%) on Vulcan XC-27R, on glassy carbon	Supported	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 212	CO$_2$	-0.97 V - iR vs. RHE	-14 mA/cm^2	22	650
126	Cu NPs supported on N-doped (0.17 at.%) carbon, on GDL	Supported	Cu, C, N	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAB-PK-130	CO	-0.91 V -iR vs. RHE	-580 mA/cm^2	22	651
127	Cu2O NCs supported on N-doped reduced graphene oxide, on glassy carbon	Supported	Cu, O, C, N	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.4 V vs. RHE	-12 mA/cm^2	20	652
128	7nm Cu NPs supported on pyridinic-N rich graphene, on carbon paper	Supported	Cu, C, N	Polyvinylidene fluoride	?	0.5 M KHCO3	Nafion 212	CO$_2$	-0.9 V vs. RHE	-311[†_Cu-C-supported,4] mA/cm^2	19	653
129	Oleylamine-stabilized Cu-NWs supported on CNPs, on glassy carbon, cleaned (ligand removal) via photonic curing method	Supported	Cu, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO$_2$	-1.2 V - iR vs. RHE	?	19	135
130	CuOx NCs supported on Vulcan XC-27R, on GDL	Supported	Cu, O, C	Nafion	(Solution-phase reactant, supplied in front)	1 M KHCO3	Selemion AMV	CO$_2$	-1.38 V - iR vs. RHE	-600 mA/cm^2	15	650
131	Cu NPs supported on ENSACO-350 G, on glassy carbon	Supported	Cu, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO$_2$	-1.08 V -iR vs. RHE	-4 mA/cm^2	15	380
132	Cu NPs supported on Vulcan XC72, on glassy carbon	Supported	Cu, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO$_2$	-1.1 V -iR vs. RHE	-4 mA/cm^2	12	380
	[†_Cu-C-supported,1] Value given in main text and in tabular form in SI is different - took tabular value											
	[†_Cu-C-supported,2] This has been calculated from the C2+ FE, the roughness factor extracted from the double layer capacity and specified reference charging value, and the ESCA current density plot in SI											
	[†_Cu-C-supported,4] Unclear: calculated from C2H4 mass activity, C2H4 FE, catalyst loading, Cu % in catalyst and reported electrode area by assuming that the mass activity is specifically for C2H4 and not total mass activity (otherwise, it's 19% of the tabulated value)											
	[†_Cu-C-supported,5] Text also discusses glassy carbon as an electrode material, but it is unclear to us how this can be combined with other sections and discussed procedures in the text so we cite what we believe to be the most logical electrode											
	[†_Cu-C-supported,6] Main text and SI give different numbers, we report the number in the main text											
	[†_Cu-C-supported,7] Total FE only computes to ca. 59 % - furthermore, SI states 34 % (reported herein) whilst text states 37 % FE C2H4											
	[†_Cu-C-supported,8] SI erroneously reports partial jC2H4@80.73 % C2H4 as 60.15, report here image-extracted jtotal											
	[†_Cu-C-core/shell,1] Electrode manufacturing unspecified, but must be on a GDL considering the reported current density											

2.6. Bi-metallics with too limited data: Pt, Sb, Bi, Sr, Se, [Mo, Mn, Ru, Rh, Sc, Ge, In, W]

All these bi-elemental catalyst systems share the same primary concern, namely that insufficient literature is available for making reasonable inferences. However, considering that information on bi-elemental catalysts that make C_2H_4 is relatively scarce, we do not want to disregard the information either. As such, we provide here a brief description of the publications for these elements, trying to lean on the knowledge we have obtained from other bi-elemental works. Overall results for these bi-elemental systems with limited available sources are summarized in Table S23. The assorted catalyst dataset is derived from 26 unique publications and comprises a total of 33 catalyst systems, with 4 using CO as a reactant and 16 having been identified as alkaline CO_2 systems. A total of 1 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55% (being 55%[654]), having been measured under non-alkaline CO2RR conditions with a Cu/Se catalyst. It should be noted that the small quantity of available sources is not necessarily related to the absence of publications describing these particular Cu/M catalyst systems in general, but rather that these systems seem to exhibit poor overall C_2H_4 performance.

2.6.1. Pt/Cu

The only sources known to us concerning Cu/Pt systems comprise either core/shell particles or alloyed/doped-type particles, all having relatively low Pt contents (0.25 – 5 at. %).[110,343] The optimum for ethylene formation seems to lie at the lower end of the reported regime (< 1 at. % Pt), which is in line with what is observed for most bi-elemental systems. The product spectrum is found to shift in the direction of ethanol rather than ethylene, though moderate amounts of C_2H_4 are still generated (between 25%[343] and 39%[110]) when the Pt content is sufficiently low. The enhancement of EtOH formation is also observed for certain Cu/Pd systems[343,348], which is a logical partner to compare with on account of the strong similarities between the catalytic properties of Pt and Pd, respectively. Possibly interesting is the observation that pure Pt has also been reported to be able to reduce CO into C_2H_4, albeit at elevated pressures and with low FE.[655] However, we are not aware of any researchers having reproduced this particular result. Although we wish to be careful and not overanalyze the results, currently available information is not promising regarding the combination of Cu and Pt for making C_2H_4 electrochemically with Pt doping being detrimental instead by favoring the formation of EtOH.

2.6.2. Sb/Cu

Although the sample size is small (4 works total), there are some recurring themes for Cu/Sb catalysts. Firstly, most of the reported Cu/Sb systems that make appreciable amounts of C_2H_4 do so at moderate Sb contents (< 10%).[337,656,657] Additionally, two works report on increased quantities of oxygen vacancies upon Sb doping (Cuδ+ argument), and posit this is what accounts for the observed shift in catalytic activity.[337,658] Maximum C_2H_4 FEs are reported in the 40-50% range. However, oftentimes Cu/Sb is not the main topic of study, making details and discussion scarce.

2.6.3. Bi/Cu

Cu/Bi systems that make C_2H_4 are uncommon, with only two references available to our knowledge. Both have relatively low Bi content: 0.5 at.%[337] and 1.15 at.%[659], and both happen to yield a maximum C_2H_4 FE of 48%.[337,659] Upon Bi addition, the hydrogen evolution reaction is reported to be suppressed. Changes in catalytic activity are attributed to an increase in the number of oxygen vacancies (V_o) upon bismuth doping, or *"… p-d orbital hybridization to modulate the electronic structure of catalyst*", respectively. We observe that bismuth- and tin-based copper bi-elemental catalysts exhibit relatively similar behaviors and explanations, though the limited amount of data is insufficient to substantiate this finding.

2.6.4. Sr/Cu

Little information is available for Cu/Sr catalysts, though at least some C_2H_4 performance is observed for such systems.[105,660] Strontium is found to leach into the electrolyte, but supposedly not in its entirety.[660] Changes in conductivity could play a role in changes in performance, with the better-performing catalyst (out of 2…) being the one that was mixed with carbon nanoparticles. Overall, Sr seems not too promising as a dopant on account of its poor stability (leaching) and poor C_2H_4 performance (C_2H_4 FE max of 37%).

2.6.5. Se/Cu

Selenium is another uncommon component for bi-elemental Cu-based catalyst systems. We are aware of only two sources that reports on a Cu/Se system that makes appreciable amounts of C_2H_4.[654,661] Out of these, Mi *et al.* observe substantially higher C_2H_4 selectivity than Li *et al.* (35% vs. 55%). However, the catalytic activity in Mi's work is convoluted with pressure effects considering that the maximum C_2H_4 FE increases from 41% to 55% when the CO_2 pressure is increased from atmospheric pressure to 10 atm. Additionally, this system is seemingly highly sensitive to Se content, with $Cu_{1.81}Se$ yielding 55% C_2H_4 at 10 atm, but Cu_2Se only yielding 35% C_2H_4 (as reported in the same manuscript). Importantly, these relatively promising results are in direct conflict with another work[662], wherein they report that Cu2Se makes no C_2H_4 whatsoever at atmospheric CO_2 pressures – although it can still form C-C bonds, yielding EtOH as a product instead. This increase in EtOH is similarly reported by Li *et al.*, who attribute it to the presence of vacancies resulting from the leaching of selenium over time.[661]

2.6.6. Mo, Mn, Ru, Rh, Sc, Ge, In, W/Cu

All these bi-elemental systems share the same characteristic of having a very limited (1-2) number of publications with many of them actually originating from a singular source: a work by Lai *et al.* reporting on a high throughput screening methodology for studying the (alkaline) CO2RR.[657] Furthermore, most of the catalysts in this group exhibit poor C_2H_4 performance (<30% C_2H_4). However, there do exist some outliers in this group. Namely, a Cu/In alloy catalyst with single atom In sites has been reported to yield a decent 49% C_2H_4 albeit experimental details were scarcely provided. Such moderate C_2H_4 performance for low levels of doping yielding single-atom catalyst sites has also been reported for e.g., Cu/Bi (48% C_2H_4)[659], Cu/Pd (45% C_2H_4)[345], Cu/Gd (42% C_2H_4)[519], Cu/Zn (35% C_2H_4)[331] and Cu/Fe (31% C2H4)[397] systems.

Similar moderate C_2H_4 performance has been reported for Cu/Ge (C_2H_4 FE max of 47%)[277] and Cu/W (C_2H_4 FE max of 42%)[663] systems, with the addition of tungsten being reported to result in suppressed EtOH activity.[663] Such suppression of EtOH formation could be industrially beneficial considering that currently existing membranes are typically poorly compatible with alcohols.

	Table 23. W/Sr/Se/Sc/Sb/Ru/Rh/Pt/Mo/Mn/In/Ge/Bi-based Cu											
#	**Electromaterial description**	**Catalyst type**	**Main elements**	**Polymeric / organic & inorganic additives**	**Reactant delivery mode**	**Catholyte**	**Membrane**	**Reactant**	**E**	**j**	**C_2H_4 FE**	**Reference**
1	Selenized Cu NWs (Cu/Se ratio of 1.8:1) supported on Cu foam	Atomically mixed/Crystalline	Cu, Se	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 115	CO_2	-1.1 V vs. RHE	-15 mA/cm^2	55	654
2	Cu10Sb1 NPs, on carbon paper - prepared via co-precipitation	Alloyed/Doped	Cu, Sb	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO_2	-1.19 V vs. RHE	-29 mA/cm^2	50	656
3	Cu/In alloy prepared via co-electrodeposition with single-atom In sites, on carbon fiber	Alloyed/Doped	Cu, In	-	(Solution-phase reactant, supplied in front)	0.1 M CsI	Nafion 117	CO_2	-1.3 V vs. RHE	-53 mA/cm^2	49	664
4	Bi-doped oxygen vacancy-rich CuO nanoribbons, on carbon paper	Alloyed/Doped	Cu, Bi, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.05 V -iR vs. RHE	-9 mA/cm^2	48	337
5	Bi-doped Cu (3.7 wt% > 1.15 at. % Bi) derived from Bi-CuS precursor, on GDL	Alloyed/Doped	Cu, Bi	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	-0.75 V -iR vs. RHE	-450 mA/cm^2	48	659
6	Ge-doped CuOx NCs ("CuGe-II"), on Toray GDL	Alloyed/Doped	Cu, Ge, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	?	-900 mA/cm^2	47	277
7	Oxygen vacancy-rich CuOx NPs with atomically dispersed Sb atoms, on glassy carbon	Single atom	Cu, Sb, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.1 V vs. RHE	-8 mA/cm^2	46	658
8	Bi-doped Cu (3.7 wt% > 1.15 at. % Bi) derived from Bi-CuS precursor, on glassy carbon	Alloyed/Doped	Cu, Bi	-	(Gas-phase reactant, supplied from behind)	0.1 M KHCO3	Nafion 117	CO_2	-1.15 V -iR vs. RHE	-25 mA/cm^2	43	659
9	Core/shell NPs with Cu shell and Cu4W10 core, supported on carbon black, on GDL	Core/shell, A-supports-B	Cu, W, C	Nafion	(Gas-phase reactant, supplied from behind)	5.0 M KOH	?	CO_2	-1.0 V vs. RHE	-200 mA/cm^2	42	663
10	Selenized Cu NWs (Cu/Se ratio of 1.8:1) supported on Cu foam	Atomically mixed/Crystalline	Cu, Se	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 115	CO_2	-1.1 V vs. RHE	-13 mA/cm^2	41	654
11	F-doped CuInOx (In/Cu = 0.06) NPs, on carbon paper	Alloyed/Doped	Cu, In, F	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	-0.7 V -iR vs. RHE	-216 mA/cm^2	41	665
12	Sb-doped oxygen vacancy-rich CuO nanoribbons, on carbon paper	Alloyed/Doped	Cu, Sb, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	?	-5 mA/cm^2	40	337
13	CuPtx NPs prepared via ultrasonic-assisted galvanic replacement (atomic ratio not reported, likely Cu1Pt0.008) of commercial Cu NPs (100 nm), on GDL	Core/shell	Cu, Pt	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-PK-130	CO	-0.63 V - iR vs. RHE	-709 mA/cm^2	39	110
14	SrCuO2 pre-catalyst supported on vulcan, on GDL	Atomically mixed/Crystalline	Cu, Sr, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA_3-PK-130	CO_2	-0.83 V -iR vs. RHE	-200 mA/cm^2	37	660
15	Se/Cu NPs (54 nm) distributed on porous carbon, derived from calcination (450 °C) of Se-doped Cu MOF	Alloyed/Doped	Cu, Se	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB–PK–130	CO_2	-0.83 V - iR vs. RHE	-239 mA/cm^2	35	661
16	Ultralow (single atom, 1.1 wt%) surface Pt-doped Cu NPs, on a GDL	Alloyed/Doped, SAC	Cu, Pt	-	(Gas-phase reactant, supplied from behind)	0.5 M KHCO3	"Sustanion"	CO_2	-1.1 V vs. RHE	-220 mA/cm^2	35	350
17	Dilute (atomically isolated) Pt-doped (2.2 wt%) Cu2O NCs, on a GDL	Alloyed/Doped	Cu, Pt, O	Nafion	(Gas-phase reactant, supplied from behind)	3.0 M KOH	Fumasep FAB-PK-130	CO_2	-1.2 V vs. RHE	-828 mA/cm^2	34	666
18	Ru-doped (1 at%) CuOx NWs derived from annealing Cu(OH)2 NW functionalized Cu-sputtered GDL	Alloyed/Doped	Cu, O, Ru	-	(Gas-phase reactant, supplied from behind)	-	PiperION (or Sustainion?)	CO	-2.28 V vs. ANODE	-200 mA/cm^2	33	129
19	Sc/Cu alloy layer (5% Sc) (400 nm) sputtered on a GDL	Alloyed/doped	Cu, Sc	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-50	CO_2	-0.65 V - iR vs. RHE	-200 mA/cm^2	31	139
20	Atomically dispersed Rh-doped Cu2O (Rh:Cu = 0.004) MPs (ca. 1 µm) with rhombic dodecahedral shape , on carbon paper	Alloyed/Doped	Cu, Rh	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO_2	-1.0 V vs. RHE	-12 mA/cm^2	27	667
21	Atomically dispersed Rh-doped Cu2O (Rh:Cu = 0.004) MPs (ca. 1 µm) with rhombic dodecahedral shape , on GDL	Alloyed/Doped	Cu, Rh	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	-0.65 V - iR vs. RHE	-178 mA/cm^2	26	667
22	Thermodynamically unstable Cu9In1 NPs prepared via thermal shock, on carbon nanotubes	Alloyed/Doped, A-supports-B	Cu, In	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3	CO	-0.70 V -iR vs. RHE	-50 mA/cm^2	26	334
23	Ru-doped (1 at%) CuOx NWs derived from annealing Cu(OH)2 NW functionalized Cu-sputtered GDL	Alloyed/Doped	Cu, O, Ru	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-130	CO	-0.7 V vs. RHE	-107 mA/cm^2	25	129
24	CuPt NPs (1:0.00797 at. ratio) prepared via galvanic replacement of Cu NPs (100 nm), on SGL 29BC GDL	Core/shell	Cu, Pt	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAA-3-PK-130	CO_2	?	-500 mA/cm^2	25$^{\dagger\_\text{Cu-Pt,1}}$	343
25	Mn(OH)x overlayer on Cu-sputtered PTFE GDL	Overlayer, Mixed-phase/Janus	Cu, Mn, O	-	(Gas-phase reactant, supplied from behind)	1 M KOH	FAA-3-PK-130	CO_2	?	?	23	395
26	Alloy/mixed metal Sr/Cu (1:3 ratio) microparticles, on GDL - obtained via reduction of mixed nitrate salt with NaBH4 over 12h period	Alloyed/Doped	Cu, Sr	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	NEOSEPTA, AHA	CO_2	-0.8 V vs. RHE	-173 mA/cm^2	21	105
27	Mn/Cu alloy (9.7 at. % Mn) NPs, on GDL	Alloyed/Doped	Cu, Mn	Nafion	(Gas-phase reactant, supplied from behind)	1 M KOH	X37-50 Grade T	CO_2	-0.8 V vs. RHE	-136 mA/cm^2	21	668
28	Cu/Sb (2 at. % Sb) thin film on Si wafer prepared via DC sputtering	Alloyed/Doped	Cu, Sb	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	"Selemion"	CO_2	-1.15 V vs. RHE	?	20	657
29	Commercial Cu NPs with Ru shell prepared through galvanic displacement, on Cu foil	Core/shell	Cu, Ru	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Selemion AMV	CO_2	-1.55 V vs. RHE	-8 mA/cm^2	19	669
30	Alloy/mixed metal Sc/Cu (1:3 ratio) microparticles, on GDL - obtained via reduction of mixed nitrate salt with NaBH4 over 12h period	Alloyed/Doped	Cu, Sc	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	NEOSEPTA, AHA	CO_2	-0.8 V vs. RHE	-204 mA/cm^2	18	105
31	Partial Mo overlayer (forming aggregates) sputter-deposited on (100)-oriented Cu-modified Si(100) substrate	Mixed-phase/Janus	Cu, Mo	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Selemion® AMV	CO_2	-1.0 V - iR vs. RHE	-8 mA/cm^2	16	670
32	Alloy/mixed metal W/Cu (1:3 ratio) microparticles, on GDL - obtained via reduction of mixed nitrate salt with NaBH4 over 12h period	Alloyed/Doped	Cu, W	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	NEOSEPTA, AHA	CO_2	-0.6 V vs. RHE	-104 mA/cm^2	14	105
33	Mn-doped Cu(OH)2 NWs with a PTFE shell, on a GDL	Alloyed/Doped, Core/shell (in-)organic	Cu, Mn, O	PTFE	(Gas-phase reactant, supplied from behind)	-	X37-50 grade RT	CO_2	-3.6 V vs. ANODE	-200 mA/cm^2	10	311
	$^{\dagger_\text{Cu-Pt,1}}$SI of publication did not provide per-product FEs for Cu/Pt catalyst, obtained deconvoluted FEs through a personal communication with the authors (provided as SI for this manuscript)											

2.7. Multi-elemental systems (3+)

This final section pertaining to the elemental composition of C_2H_4 forming catalyst systems is on the topic of multi-elemental catalysts that consist of at least 3 constituents. However, the discussion will be more generic than previous sections on account of the increased heterogeneity of this subset of catalyst systems. Please note that we do not count any of the 'oxidic' elements as defined in the main text (X = Li, Na, K, Rb, Cs, N, O, P, S, F, Cl, Br and/or I) as a valid element for the 3+ elemental count in this category.

A summary of multi-elemental Cu/∑M catalyst systems for C_2H_4 production is given in Table S24. The Cu/∑M catalyst dataset is derived from 25 unique publications and comprises a total of 41 catalyst systems, with 4 using CO as a reactant and 10 having been identified as alkaline CO_2 systems. A total of 11 of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55%, with 2 having been measured under alkaline CO2RR conditions. The top-most selective catalyst concerns vanadium-copper layered double hydroxide (LDH) particles supported on TiO_2 NPs, yielding up to 84% C_2H_4 under non-alkaline CO2RR conditions. The second-highest catalyst system concerns a Cu/Ag/Au composite material that yields 77% C_2H_4 under alkaline CO2RR conditions.[671]

Overall, we find that multi-elemental systems serve to fulfil mostly the same functions as we identified for bi-elemental systems (discussed in the main text). For example, Cu NPs supported on exfoliated Mg/Al LDHs yielded improved performance at increased current densities on account of the supporting effect of the nanosheets.[672] We also observe the benefits that the presence of nanoconfinement morphologies bring about[479,673], with further information on this topic provided in an excellent review.[674] To continue, we identified various multi-elemental systems that behave similarly as oxide-derived systems on account of their reconstruction under reaction conditions[225], possibly with morphology-directing effects.[675] Maybe most importantly, we do start seeing an additional function that is not often observed for bi-elemental systems. Specifically, systems start emerging where the addition of extra components is hypothesized to result in improved stability.[304,353,468,673]

Overall, including additional elements to improve performance provides more options, at least in theory. However, it also adds additional complexity to the catalyst system, with currently seemingly little benefit considering the small portion of reported multi-elemental systems that make ≥55% C_2H_4. In the end, we could only identify two truly top-tier multi-elemental catalyst systems. And, looking at the morphology of those specific catalyst systems, a nanoconfinement effect could reasonably be hypothesized to be present for both. The third- and fourth-best systems 'only' yield 72%[676] and 71%[479] C_2H_4, which barely qualifies them for a spot in amongst the top-ranking catalysts provided in the main paper which has a cut-off value of ≥70%.

Thus, the question naturally arises if adding more elements is beneficial compared to simpler, bi-elemental systems. As for answering this question, we are of the opinion that the additional elements themselves might not be that important, but rather that their presence can be used to facilitate in the creation of conditions that are favorable for C_2H_4 performance as identified during our discussion of bi-elemental systems in both the main text and the supporting information. Namely, their presence can aid in e.g., i) the formation and stabilization of copper-based 2D nanosheet morphologies[675], ii) the formation (and stabilization) of nanopores[673], iii) creating reactive pre-cursor catalyst species that reconstruct into specific morphologies *in-situ*[677], or iv) increase electrical conductivity and aid in catalyst dispersion through acting as conductive but electrochemically inert supports.[672] Importantly, the function of stabilizing the active phase without influencing catalytic activity is something that is difficult to achieve with bi-elemental systems.[304,353,468,673]

Table S24. Multi-elemental Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C$_2$H$_4$ FE	Reference
1	TiO2 NPs supported on V/Cu-based layered double hydroxide, on carbon paper	Mixed-phase/Janus, A-supports-B	Cu, V, Ti, O	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO$_2$	-0.4 V vs. RHE	-7 mA/cm^2	84	678
2	Ag/Au (3:1 ratio) alloy, highly defective, cubic wireframe NPs (59 nm) post-modified with epitaxially deposited Cu 'overlayer', on GDL	A-supports-B, alloyed/doped	Ag, Au, Cu	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAB-PK-130	CO$_2$	-0.65 V - iR vs. RHE	- 305 mA/cm^2	77	671
3	Ag-doped La2-xAgxCuO4-δ NPs (x=0.2) with oxygen vacancies, on Toray carbon paper	Atomically mixed/Crystalline, alloyed/doped	Cu, Ag, La	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion	CO$_2$	-1.1 V vs. RHE	-28 mA/cm^2	72	676
4	Single atom Cu sites enclosed in an Ir-containing Zr-based MOF framework with rod-like morphology, on carbon cloth	Single atom, Atomically mixed/Crystalline	Cu, Ir, Zr	Nafion	(Solution-phase reactant, supplied in front)	1.0 M phosphate buffer saline	Nafion 212	CO$_2$	-1.0 V vs. RHE	-28 mA/cm^2	71	479
5	Ag/Au (3:1 ratio) alloy, highly defective, cubic wireframe NPs (59 nm) post-modified with epitaxially deposited Cu 'overlayer', on glassy carbon	A-supports-B, alloyed/doped	Ag, Au, Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	"Nafion"	CO$_2$	-1.2 V vs. RHE	-13 mA/cm^2	69	671
6	Single atom Cu sites enclosed in an Ir-containing Zr-based MOF framework with rod-like morphology, on GDL	Single atom, Atomically mixed/Crystalline	Cu, Ir, Zr	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M phosphate buffer saline	Nafion 212	CO$_2$	-1.0 V vs. RHE	$-80^{\dagger\text{\_Cu-multi\_element,1}}$ mA/cm^2	67	479
7	Cu2O microcubes (1 µm) decorated with small Pd/Ag NPs (20-50 nm, 0.49 and 0.39 wt%, respectively), prepared via galvanic displacement, mixed with carbon black, on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, Ag, Pd, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Nafion 117	CO$_2$	-1.2 V vs. RHE	-31 mA/cm^2	63	353
8	Cu8Zn6Mn alloy (89.3:1.53:3.92 at. %) NPs, on GDL	Alloyed/Doped	Cu, Mn, Zn	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	X37-50 Grade T	CO$_2$	-1.4 V vs. RHE	-758 mA/cm^2	58	668
9	Trimetallic Cu10La1Cs1 (mol ratio: 10:0.16:0.14) prepared via co-electroplating, on carbon paper	Mixed-phase/Janus	Cu, La, Cs	-	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO$_2$	-1.2 V vs. RHE	-37 mA/cm^2	57	225
10	Cu/Pd mixed NPs supported on 2D Bi2S3 nanosheets, on copper foam	Mixed-phase/Janus, A-supports-B	Cu, Pd, Bi, S	Nafion	(Gas-phase reactant, forced through surface)	0.1 M KHCO3	Nafion	CO$_2$	-0.4 V vs. RHE	-2 mA/cm^2	57	679
11	Exfoliated Mg/Al LDH nanosheets spraycoated onto a Cu-sputtered GDL	Overlayer	Cu, Mg, Al	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	AMVN	CO$_2$	-2.8 V vs. RHE	-300 mA/cm^2	55	680
12	Au nanoneedle-impregnated inside of the channels of Zr-based MOF with Cu-TMC sites mixed with CNPs, on glassy carbon	Mixed-phase/Janus, Atomically mixed/Crystalline	Cu, Zr, Au	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 115	CO$_2$	-1.2 V vs. RHE	-12 mA/cm^2	53	673
13	B/Mg-doped CuOX NPs ("Cu5(B0.02 M)Mg1"), on a GDL	Alloyed/Doped, Mixed-phase/Janus	Cu, Mg, B, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH	?	CO$_2$	-1.57 V vs. RHE	-293 mA/cm^2	50	307
14	Trimetallic Cu10Zn1Cs1 prepared via co-electroplating, on carbon paper	Mixed-phase/Janus	Cu, Zn, Cs	-	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO$_2$	-1.2 V vs. RHE	-33 mA/cm^2	48	225
15	Cu and Bi co-impregnated into a Zr-based MOF (UiO-66), on carbon paper	Alloyed/Doped	Cu, Bi, Zr	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO$_2$	-1.2 V vs. RHE	-51 mA/cm^2	47	482
16	Commercial CuOx NPs (5.8 mg/cm2!) supported on scaffold of exfoliated Mg/Al LDH, on GDL	Mixed-phase/Janus, A-supports-B	Cu, Mg, Al, O	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	SELEMION AMV	CO	-0.7 V -iR vs. RHE	-1773 mA/cm^2	46	672
17	Simultaneous galvanic displacement of Zn substrate with Cu and Pb, with traces of Zn present after reaction (0.6-1.1 %), mixed with carbon black, on glassy carbon	Alloyed/Doped, atomically mixed/crystalline	Cu, Pb, Zn, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO$_2$	-1.2 V -iR vs. RHE	?	45	451
18	Trimetallic Cu10La1Zn1 prepared via co-electroplating, on carbon paper	Mixed-phase/Janus	Cu, La, Zn	-	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO$_2$	-1.2 V vs. RHE	-30 mA/cm^2	43	225
19	Cu and Bi co-impregnated (ca 1:1 atomic ratio) into a Zr-based MOF (UiO-66), on GDL	Alloyed/Doped	Cu, Bi, Zr	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	Nafion 117	CO$_2$	-0.9 V vs. RHE	-100 mA/cm^2	42	482
20	B-doped Cu (1.4 at. % B; NaBH4 as reductant and Boron source) NPs (0.5 mg/cm2) mixed with Zn NSs (0.01 mg/cm2) and PTFE, on GDL	Alloyed/Doped	Cu, B, Zn	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH	FAB-PK-75	CO$_2$	-0.5 V -iR vs. RHE	-200 mA/cm^2	40	304
21	Trimetallic Cu10Zn1Co1 prepared via co-electroplating, on carbon paper	Mixed-phase/Janus	Cu, Zn, Co	-	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO$_2$	-1.2 V vs. RHE	-26 mA/cm^2	38	225
22	Consecutive galvanic replacement-prepared Ag/Ru-doped (4% and 1 %, XPS) CuOx NPs, on Cu-sputtered PTFE GDL	Alloyed/Doped	Cu, Ag, Ru	Nafion	(Gas-phase reactant, supplied from behind)	-	"Sustainion"	CO	?	-600 mA/cm^2	38	447
23	CNP and graphite layers on top of CuZnO/CuZnAl2O4 catalyst prepared via co-precipitation and calcination (800 °C) midlayer , on Cu-sputtered PTFE GDL	Atomically mixed/Crystalline, A-supports-B, Alloyed/Doped	Cu, Zn, Al, O, C	Nafion	(Gas-phase reactant, supplied from behind)	2.0 M KOH	FAA-3-PK-130	CO$_2$	-1.1 V vs. RHE	-400 mA/cm^2	36	290
24	Pd-doped, agglomerated defective Ag/CuOx nanosheets derived from CuOx NPs with Au seed ("Pd0.7Cu40.0Ag59.3"), on a GDL	Mixed-phase/Janus	Cu, Pd, Ag, Au	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Nafion 117	CO$_2$	-1.0 V vs. RHE	-502 mA/cm^2	35	675
25	Consecutive galvanic replacement-prepared Ag/Au-doped CuOx NPs, on Cu-sputtered PTFE GDL	Alloyed/Doped	Cu, Ag, Au	Nafion	(Gas-phase reactant, supplied from behind)	-	"Sustainion"	CO	?	-400 mA/cm^2	34	447
26	Consecutive galvanic replacement-prepared Ag/Pd-doped CuOx NPs, on Cu-sputtered PTFE GDL	Alloyed/Doped	Cu, Ag, Pd	Nafion	(Gas-phase reactant, supplied from behind)	-	"Sustainion"	CO	?	-600 mA/cm^2	34	447
27	Simultaneous galvanic displacement of Zn substrate with Cu and Sn (Cu/Sn wt of ca. 40), with traces of Zn present after reaction (0.6-1.1 %), mixed with carbon black, on glassy carbon	Alloyed/Doped, atomically mixed/crystalline	Cu, Sn, Zn,	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO$_2$	-1.3 V -iR vs. RHE	-19 mA/cm^2	33	451

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28	Simultaneous galvanic displacement of Zn substrate with Cu and Ag, with traces of Zn present after reaction (0.6-1.1 %), mixed with carbon black, on glassy carbon	Alloyed/Doped, atomically mixed/crystalline	Cu, Ag, Zn, C	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO_2	-1.1 V -iR vs. RHE	?	33	[451]
29	Trimetallic Cu10Ag1Zn1 prepared via co-electroplating, on carbon paper	Mixed-phase/Janus	Cu, Ag, Zn	-	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO_2	-1.2 V vs. RHE	-26 mA/cm^2	31	[225]
30	Cu NCs with a non-equilibrium Cu/Ag/Pd alloy shell (Cu79Ag16Pd5), on a GDL	Alloyed/Doped, core/shell	Cu, Ag, Pd	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	"Nafion"	CO_2	-1.1 V -iR vs. RHE	?	31	[468]
31	High entrypy AuAgPtPdCu NPs (16 +- 10 nm) with single atom Cu sites, on glassy carbon	Atomically mixed/Crystalline, alloyed/doped	Au, Ag, Pt, Pd, Cu	Nafion	(Solution-phase reactant, supplied in front)	0.5 M K2SO4	?	CO_2	-0.3 V vs. RHE	-14 mA/cm^2	30	[465]
32	Trimetallic Cu10La1Ag1 prepared via co-electroplating, on carbon paper	Mixed-phase/Janus	Cu, La, Ag	-	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO_2	-1.2 V vs. RHE	-18 mA/cm^2	28	[225]
33	Trimetallic Cu10Ag1Au1 prepared via co-electroplating, on carbon paper	Mixed-phase/Janus	Cu, Ag, Au	-	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO_2	-1.2 V vs. RHE	-26 mA/cm^2	27	[225]
34	Au NPs ("small") supported on Cu2O octahedra (ca. 200 nm) through galvanic displacement mixed with Ni-SAC, on a GDL	Mixed-phase/Janus, A-supports-B	Cu, Au, Ni, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	"Selemion"	CO_2	-0.94 V -iR vs. RHE	-500 mA/cm^2	25	[377]
35	Chemically dealloyed (5 M NaOH, 50 °C) Al90Cu7.5Ce2.5 ribbons, with remaining traces of Al (2.2 at %), on GDL	Mixed-phase/Janus	Cu, Ce, Al	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAS-50	CO_2	-0.7 V - iR vs. RHE	- 98 mA/cm^2	23	[677]
36	Trimetallic Cu10Ag1Co1 prepared via co-electroplating, on carbon paper	Mixed-phase/Janus	Cu, Ag, Co	-	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO_2	-1.2 V vs. RHE	-18 mA/cm^2	22	[225]
37	Exfoliated B/Cu-based MOF ("BIF-104(Cu)") nanosheets decorated with ultrasmall AgOx NPs mixed with carbon black, on glassy carbon	Mixed-phase/Janus, A-supports-B	Cu, B, Ag, C	Nafion	(Solution-phase reactant, supplied in front)	0.5 M KHCO3 + 0.5 M KCl	Nafion 117	CO_2	-1.2 V vs. RHE	-4 mA/cm^2	21	[681]
38	Tensile strained Cu overlayer (32 nm) on NiTi sheet	Overlayer	Cu, Ti, Ni	-	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.1 V -iR vs. RHE	-11 mA/cm^2	20	[682]
39	La0.9Sr0.1CuO3 particles, on GDE (little information provided)	Atomically mixed/Crystalline	Cu, La, Sr	?	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Nafion 417	CO_2	?	-120 mA/cm^2	20	[683]
40	Gd0.9Sr0.1CuO3 particles, on GDE (little information provided)	Atomically mixed/Crystalline	Cu, Gd, Sr	?	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Nafion 417	CO_2	?	-240 mA/cm^2	20	[683]
41	Pr0.9Sr0.1CuO3 particles, on GDE (little information provided)	Atomically mixed/Crystalline	Cu, Pr, Sr	?	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Nafion 417	CO_2	?	-240 mA/cm^2	17	[683]
	[†_Cu-multi_element,1]Used value from LSV, rather than text value											

2.8. (In-)organic polymer modification through core/shell & overlayer structures

We already hinted at the potential of inorganic layers as a means to improve C_2H_4 performance during our discussions of various bi-elemental, such as for an e.g., Cu/Ag system where a Cu NP/Nafion layer was deposited on top of an Ag foil, [413,414] and for a Cu/Zn catalyst modified with a Nafion/PVDF coating[312], and for a Cu/Pb catalyst supported on a polyaniline-modified carbon substrate.[359] However the effect can also be observed to exist for pristine and oxide-derived copper systems. To this end, we have compiled the final two summary tables. Table S25describes metallic copper and oxide-derived copper catalysts where each NP is coated by a layer of an organic and/or inorganic component, best described as a core/shell-type morphology comprising an organic/inorganic-based shell. In Table S26, metallic copper and oxide-derived copper catalysts which have been post-modified by an organic and/or inorganic toplayer are summarized, being best described as overlayer-type systems. Examples of organic/inorganic (over-)layers include e.g., polymeric coatings, addition of ionic liquids to the catalyst layer, thiol-bound surface modifying agents, PTFE coatings, cross-linked ionomer overlayers and carbon-derived overlayers. Although morphologically distinct, we believe that the presence of an organic/inorganic component either as an overlayer or as a core/shell-type of structure has similar effects on catalysis. As such, we discuss them together as if they were one.

The first observation is the high number of catalysts belonging to the organic/inorganic-modified category of copper catalysts, totaling 58 unique publications comprising 70 catalyst systems. A total of 11 use CO as the reactant and 29 have been identified as alkaline CO_2 systems. A remarkable total of 31 (i.e., 44%!) of these catalyst systems exhibit maximum C_2H_4 FEs of ≥55%, with 14 having been measured under alkaline CO2RR conditions. A total of 4+9 = 13 (out of 70) of these systems even yield ≥70% C_2H_4. This makes this category of catalysts the highest performing in the entirety of the dataset, with oxide-derived catalysts (generally presumed best-in-class) 'only' having 20 catalyst systems that yield ≥70% C_2H_4, but the sample size being ca. 2.2x (70 vs. 157) larger. However, this difference becomes smaller if we remove alkaline CO2RR conditions from the equation with 6/13 catalyst systems remaining for (in-)organic component systems and 11/20 catalyst systems remaining for oxide-derived systems. In addition to high C_2H_4 performance, we also find that several manuscripts report on the combination of high current densities (e.g., ≥150 mA/cm^2) and high C_2H_4 FEs (e.g., 65-86% C_2H_4) under non-alkaline conditions[491,684-687] for these organic/inorganic-modified catalyst systems, demonstrating the industrial viability of organic/inorganic (over-)layers as modifiers.

However, besides a high-level overview we cannot say much about this category of systems on account of their high heterogeneity. For more detailed information, we refer the reader to other sources more suited to investigating this topic in more depth.[688-693] Irrespectively, just from a high-level perspective it is already evident that the presence of an organic/inorganic (over-)layer has a positive effect on C_2H_4 performance, which matches with our observations for those select bi-elemental systems discussed previously. Importantly, we see few hypothetical issues with combining a bi-elemental strategy to improve intrinsic catalytic performance with an organic/inorganic modification strategy to bring about further improvements. Especially as currently existing systems still tend to suffer from poor stability and low current densities even if industrially relevant FEs has been demonstrated for a relatively large (and diverse) number of catalysts. One can envision a case where intrinsic catalytic activity is optimized in a bi-elemental system, possibly with addition of a third element for stability purposes. Then, an organic/inorganic (over-)layer can be added to further tune the microenvironment to allow for increased current densities without significantly compromising stability and/or C_2H_4 selectivity. Although for the time being, this is much more a dream than it is reality.

Table S25. (In-) organic core/shell-Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	Electroplated Cu modified via grafting an aryl diazonium-based polymeric coating (without Nafion toplayer), on GDL	Core/shell (in-)organic	Cu, O	Aryl diazonium-based polymer	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-50	CO	-2.5 V vs. ANODE	-179 mA/cm^2	86	684
2	CuO NPs coated with 1-dodecanethiol, on GDL	Core/shell (in-)organic	Cu, O	Nafion, 1-dodecanethiol	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-1.2 V vs. RHE	-304 mA/cm^2	80	694
3	Ionic liquid-coated Cu-MOF (Cu3(1,3,5-Benzenetricarboxylic acid)2), on glassy carbon	Core/shell (in-)organic	Cu	Nafion, 1,3,5-Benzenetricarboxylic acid (BTC), 1-Butyl-3-methylimidazolium nitrate (BmimNO3)	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.49 V vs. RHE	-34 mA/cm^2	77	695
4	CuOx NPs (large size distribution) mixed with PTFE, on carbon paper	Core/shell (in-)organic	Cu, O	Nafion, PTFE	(Solution-phase reactant, supplied in front)	0.5 M KCl + 50 mM benzyl alcohol	FKB PK 130	CO_2	-1.38 V vs. RHE	-88 mA/cm^2	72	696
5	Hydrophobic Cu NPs electroplated from a PTFE-containing solution, on carbon paper	Core/shell (in-)organic	Cu	PTFE	(Solution-phase reactant, supplied in front)	0.1 M CsI	Nafion 117	CO_2	-1.25 V vs. RHE	-35 mA/cm^2	67	697
6	Cu2O NPs coated with a carboxylic-acid terminated C12 alkyl chain, on carbon paper	Core/shell (in-)organic	Cu, O	Nafion, HOOC-(CHy)n-COOH	(Solution-phase reactant, supplied in front)	? 0.1 M KHCO3 (pH 6.8)	? Nafion	CO_2	-1.2 V vs. RHE	-7 mA/cm^2	63	698
7	Polystyrene vinylbenzyl imidazolium chloride (PSMIM, 0.25 wt%) coated CuO NSs, on carbon paper	Core/shell (in-)organic	Cu, O	Polystyrene vinylbenzyl imidazolium chloride (PSMIM)	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	X37-50 Grade T	CO_2	-1.05 V vs. RHE	-119 mA/cm^2	62	699
8	Core/shell-type particles comprising a carbon core with a CuOx shell coated with a PTFE layer, on carbon paper	Core/shell (in-)organic	Cu, C, O	PTFE, nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAB-PK-130	CO_2	-0.92 V - iR vs. RHE	-230 mA/cm^2	62	700
9	Water-insoluble organosuperbase-modified Cu2O NCs, on GDL	Core/shell (in-)organic	Cu	Nafion, 1,8-bis(dimethylamino) naphthalene	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	Nafion 117	CO_2	?	-300 mA/cm^2	60	701
10	Commercial Cu NPs (25 nm) coated with a 4,5-dicyanoimidazole shell, on a GDL	Core/shell (in-)organic	Cu	4,5-dicyanoimidazole, Nafion	(Gas-phase reactant, supplied from behind)	3 M KCl + x M HCl (pH 1)	"Nafion"	CO_2	-2.08 V vs. RHE	-200 mA/cm^2	58	702
11	Water-insoluble organosuperbase-modified Cu NPs, on GDL	Core/shell (in-)organic	Cu	Nafion, 1,8-bis(dimethylamino) naphthalene	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	Nafion 117	CO_2	-1.0 V -iR vs. RHE	-200 mA/cm^2	52	701
12	Partially PVP-capped Cu NPs grown from Au seed, supported on Vulcan XC-72, on GDL	Core/shell (in-)organic	Cu	Nafion, PVP capping	(Gas-phase reactant, supplied from behind)	0.5 M KOH	Fumapem FAA-3-PK-130	CO_2	-0.85 V - iR vs. RHE	-200 mA/cm^2	52	208
13	Pyroglutamic acid-modified ("Pyr1.0") Cu2O NPs (reconstructing into nanoneedles), grown on carbon paper	Core/shell (in-)organic	Cu, O	Pyroglutami acid		1.0 M KHCO3 ("CO_2-saturated 1.0 M KOH")	?	CO_2	-1.0 V vs. RHE	-510 mA/cm^2	52	703
14	Cationic tetrabutylammonium-coated electroplated CuO dendrites (1.75 mg/cm2), on 121 Wet Proofing-modified GDL	Core/shell (in-)organic	Cu, O, N	Nafion, Tetrabutylammonium	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Selemion AMV	CO	-0.60 V vs. RHE	-1223 mA/cm^2	50	704
15	Poly-ionic liquid-coated Cu NPs mixed with CuCl, on GDL	Core/shell (in-)organic	Cu	Imidazolium, bipyridinium-based ionic liquid	(Gas-phase reactant, supplied from behind)	3.0 M KCl + 0.005 M H2SO4 (pH 2)	Nafion 117	CO_2	?	-100 mA/cm^2	47	705
16	CuO NPs coated with hexaethynylbenzene layer, on GDL	Core/shell (in-)organic	Cu, O	Hexaethynylbenzene	(Gas-phase reactant, supplied from behind)	-	"Sustainion"	CO_2	-4 V vs. ANODE	-400 mA/cm^2	44	706
17	Mesoporous Cu(OH)2 NRs mixed with large quantity of Nafion (28.4 wt%), supported on CNTs, on carbon paper	Core/shell (in-)organic, A-supports-B	Cu, O, C	Nafion or Sustainion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-0.76 V - iR vs. RHE	-300 mA/cm^2	44	707
18	CuO NPs coated with hexaethynylbenzene layer, on GDL	Core/shell (in-)organic	Cu, O	Hexaethynylbenzene	(Gas-phase reactant, supplied from behind)	1.0 M KCl	"N117"	CO_2	-1.1 V - iR vs. RHE	-350 mA/cm^2	43	706

Table S26. (In-) organic overlayer Cu

#	Electromaterial description	Catalyst type	Main elements	Polymeric / organic & inorganic additives	Reactant delivery mode	Catholyte	Membrane	Reactant	E	j	C_2H_4 FE	Reference
1	50 µm Cu-exchanged stannosilicate UZAR-S3 'mixed matrix membrane' toplayer, on a PVA/Chitosan midlayer, on a commercial 70 nm Cu NPs with chitosan bio-based polymeric binder underlayer, on Toray TGP-H-60 GDL (exact conditions ambiguously reported)	Overlayer	Cu	Chitosan, Cu exchanged stannosilicate UZAR-S3, polyvinylalcohol	(Gas-phase reactant, supplied from behind)	-	Sustainion X-37 50 grade	CO_2	-0.87 V vs. RHE	-10 mA/cm^2	98	97
2	Nafion overlayer covering a catalyst layer comprised of electroplated Cu modified via grafting an aryl diazonium-based polymeric coating, on GDL	Overlayer	Cu, O	Nafion, Aryl diazonium-based polymer	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-50	CO_2	-3.85 V vs. ANODE	-602 mA/cm^2	89	684
3	Poly-N-(6-aminohexyl)acrylamide-coated electrodeposited Cu dendrites on GDL	Overlayer	Cu	Poly-N-(6-aminohexyl)acrylamide	(Gas-phase reactant, supplied from behind)	10 M KOH	?	CO_2	-0.47 V -iR vs. RHE	?	87	708
4	N1-/N3-substituted imidazolium-based overlayer on Cu plate	Overlayer	Cu	N1-substituted (1,10-phenanthrolinyl) and N3-substituted (n-butyl) imidazolium	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	"Hangzhou Huamo Technology Co., Ltd"	CO_2	-1.24 V vs. RHE	-6 mA/cm^2	73	709
5	N-arylpyridinium electrodeposition-modified Cu-sputtered PTFE GDL	Overlayer	Cu	N,N′-(1,4-phenylene) bispyridinium salt	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	Fumapem FAA-3-PK-130	CO_2	-0.83 V -iR vs. RHE	-325 mA/cm^2	72	685
6	Poly-N-(6-aminohexyl)acrylamide-coated electrodeposited Cu dendrites on GDL	Overlayer	Cu	Poly-N-(6-aminohexyl)acrylamide	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO_2	-0.97 V -iR vs. RHE	-433 mA/cm^2	72	708

7	Sputtered Cu with Carbon NP midlayer and graphite toplayer, on PTFE GDL	Overlayer	Cu, C	CNPs, Graphite	(Gas-phase reactant, supplied from behind)	7.0 M KOH (pH 14.7)	Fumasep FAB-PK-130	CO$_2$	-0.57 V - iR vs. RHE	-100 mA/cm^2	70	101
8	Electroplated Cu (60 s @ 400 mA/cm^2) from CuBr2/tartrate/1 M KOH-containing bath with active CO$_2$ flow (though CO also seems to work), with Carbon NP midlayer and graphite toplayer, on Cu-sputtered PTFE GDL (ambiguously reported)	Overlayer	Cu, C	CNPs/Nafion, Graphite/Nafion	(Gas-phase reactant, supplied from behind)	7.0 M KOH (pH 14.7)	Fumapem FAA-3-PK-130	CO$_2$	-0.67 V - iR vs. RHE	-280 mA/cm^2	70	710
9	Carbon black NP (XC72R) overlayer on top of Cu-sputtered PTFE GDL	Overlayer	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	0.5 M KHCO3 + 0.5 M KCl	Nafion 117	CO$_2$	-0.89 V -iR vs. RHE	-500 mA/cm^2	70	491
10	Aquivion toplayer on N,N'-ethylene-phenanthrolinium electrodeposition-modified Cu-sputtered PTFE GDL	Overlayer	Cu	Aquivion D79-25BS, N,N'-ethylene-phenanthrolinium dibromide	(Gas-phase reactant, supplied from behind)	0.1 M KHCO3 (pH 6.8)	Sustainion X37-50	CO$_2$	-4.4 V vs. ANODE	-330 mA/cm^2	69	686
11	Electroplated Cu (90 s @ 400 mA/cm^2) from CuBr2/tartrate/1 M KOH-containing bath with active CO$_2$ flow (though CO also seems to work[insert ref]), with N-tolyl substituted tetrahydro-bipyridine (Py) midlayer and hydrophobic (C4HF7O4S.C2F4)x short sidechain (SSC) ionomer toplayer, on Cu-sputtered PTFE GDL	Overlayer	Cu	N-tolyl substituted tetrahydro-bipyridine, (C4HF7O4S.C2F4)x	(Gas-phase reactant, supplied from behind)	-	Sustainion X37–50 grade 60	CO	-2.5 V vs. ANODE	-164 mA/cm^2	65	687
12	Commercial 25 nm Cu NPs with Hex-Aza COF-based overlayer, on GDL	Overlayer	Cu	Hexaketocyclohexane, 2,3,6,7-tetraamino-phenazine hydrochloride	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-50	CO$_2$	-3.85 V vs. ANODE	-316 mA/cm^2	62	711
13	Electroplated Cu (60 s @ 400 mA/cm^2) from CuBr2/tartrate/1 M KOH-containing bath with active CO$_2$ flow (though CO also seems to work), with Carbon NP midlayer and graphite toplayer, on Cu-sputtered PTFE GDL (ambiguously reported)	Overlayer	Cu, C	CNPs/Nafion, Graphite/Nafion	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-50 grade 60	CO$_2$	-3.7 V vs. ANODE	-330 mA/cm^2	60	710
14	25 nm Cu NPs/nafion mix sprayed on top of nafion pre-covered Cu-sputtered PTFE nanowires	Overlayer	Cu	Nafion	(Gas-phase reactant, supplied from behind)	7.0 M KOH (pH 14.7)	Fumasep FAB-PK-130	CO$_2$	-1.3 V -iR vs. RHE	-800 mA/cm^2	60	712
15	Electrodeposited Cu(OH)x dendrites (-200 mA/cm^2 for 10 min from 0.05 M H2SO4/2.5 M KCl/7 mM CuSO4 bath with poly(Lys, Phe), with active CO$_2$ flow), on Cu-sputtered PTFE GDL	Overlayer	Cu, O	poly(Lys, Phe)	(Gas-phase reactant, supplied from behind)	0.05 M H2SO4 + 2.5 M KCl	Nafion 117	CO$_2$	-2.3 V vs. Ag/AgCl	-200 mA/cm^2	60	204
16	Electroplated Cu on top of polyaniline pre-functionalized carbon paper	Overlayer	Cu	Polyaniline	(Solution-phase reactant, supplied in front)	0.1 M KCl	Nafion 117	CO$_2$	-1.2 V -iR vs. RHE	-30 mA/cm^2	59	713
17	Carbon black (Vulcan XC 72) layer on top of Cu2O NCs mixed with PVP/amine-containing microgel spheres midlayer, on PTFE GDL	Overlayer	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-50	CO$_2$	-4 V vs. ANODE	-358 mA/cm^2	58	714
18	1-octadecanethiol-modified electroplated Cu dendrites, on Cu plate	Overlayer	Cu	1-octadecanethiol	(Solution-phase reactant, supplied in front)	0.1 M CsHCO3	Nafion 115	CO$_2$	-1.5 V -iR vs. RHE	-30 mA/cm^2	56	715
19	Spin-coated tricomponent ionic liquid polymer-modified Cu plate	Overlayer	Cu	Various ionic liquids	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV	CO$_2$	-1.08 V -iR vs. RHE	-5 mA/cm^2	56	716
20	Polypyrrole nanowires-modified Cu NPs, on GDL	Overlayer	Cu	Nafion, Polypyrrole	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumatech FAB-PK-130	CO	-0.58 V vs. RHE	-33 mA/cm^2	56†–Cu-inorganic_overlayer,1 (69)	717
21	Carbon black (Vulcan XC 72) layer on top of Cu2O NCs mixed with PVP/amine-containing microgel spheres midlayer, on PTFE GDL	Overlayer	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-130	CO$_2$	-1.15 V -iR vs. RHE	-700 mA/cm^2	56	714
22	Carbon NP/nafion toplayer on a sputtered Cu midlayer with a MOF/nafion-derived underlayer, on a PTFE GDL	Overlayer	Cu, C	Nafion, Cu3(benzene-1,3,5-tricarboxylate)2·xH2O	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-50	CO$_2$	-3.8 V vs. ANODE	-255 mA/cm^2	54	718
23	Aquivion toplayer on N,N'-ethylene-phenanthrolinium electrodeposition-modified Cu-sputtered PTFE GDL	Overlayer	Cu	Aquivion D79-25BS, N,N'-ethylene-phenanthrolinium dibromide	(Gas-phase reactant, supplied from behind)	0.1 M KHCO3 (pH 6.8)	Sustainion X37-50	CO	-2.5 V vs. ANODE	-84 mA/cm^2	52	686
24	Polydopamine-coated rod-like Cu-MOF, on glassy carbon	Overlayer	Cu	Nafion, polydopamine	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO$_2$	-1.2 V -iR vs. RHE	-5 mA/cm^2	51	719
25	Carbon NP/nafion toplayer on a sputtered Cu midlayer with a calcined MOF-derived/nafion underlayer, on a PTFE GDL	Overlayer	Cu, C	Nafion, Cu3(benzene-1,3,5-tricarboxylate)2·xH2O	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAA-3-PK-130	CO$_2$	-4.1 V (?) vs. ANODE	-525 mA/cm^2	51	718
26	Cs-exchanged Nafion overlayer (0.7 µm) on Cu sputtered PTFE GDL	Overlayer	Cu	Nafion (Cs)	(Gas-phase reactant, supplied from behind)	-	-	CO	-2.3 V vs. ANODE	-50 mA/cm^2	51	125
27	Polyaniline-coated Cu NPs on glassy carbon	Overlayer	Cu	Nafion, Polyaniline	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Quaternary ammonia poly(N-methylpiperidine-co-p-terphenyl)	CO$_2$	-1.13 V -iR vs. RHE	-35 mA/cm^2	49	720
28	Commercial 25 nm Cu NPs with Hex-Aza COF-based overlayer, on GDL	Overlayer	Cu	Hexaketocyclohexane, 2,3,6,7-tetraamino-phenazine hydrochloride	(Gas-phase reactant, supplied from behind)	-	Fumasep FAA-3-50	CO	-2.51 V vs. ANODE	-500 mA/cm^2	49	711
29	0.01 mg/cm2 microporous polymer (combination of ethanoanthracene (EA) and Troger's base (TB) monomers)-coated Cu-sputtered GDL	Overlayer	Cu	Ethanoanthracene, Troger's base	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	?	CO$_2$	-0.63 V vs. RHE	-39 mA/cm^2	48	721
30	Metallic Cu NPs with nafion toplayer, on GDL	Overlayer	Cu	Nafion	(Gas-phase reactant, supplied from behind)	1.0 M NaOH (pH 14)	Nafion 117	CO	-1.46 V vs. RHE	-72 mA/cm^2	48	722
31	QAPEEK' overlayer on 1 µm-thick Cu layer with nanoscale roughness, sputtered on a GDL	Overlayer	Cu	QAPEEK (quaternary ammonia poly(ether ether ketone))	(Gas-phase reactant, supplied from behind)	-	QAPPT	CO$_2$	-3.46 V vs. ANODE	-600 mA/cm^2	48	281
32	Surface S-doped 'coral-like' CuO MPs, on carbon paper	Overlayer	Cu, S, O	Nafion, thioacetamide	(Solution-phase reactant, supplied in front)	0.1 M KHCO3	Nafion 117	CO$_2$	-1.3 V vs. RHE	-32 mA/cm^2	48	723
33	Sputtered Cu with Carbon NP midlayer and graphite toplayer, on PTFE GDL	Overlayer	Cu, C	CNPs, Graphite	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-50	CO$_2$	-4.1 V vs. ANODE	-182 mA/cm^2	48	724
34	Tip-exposed PTFE-coated electrochemically grown Cu nanoneedles scraped off and deposited on a PTFE GDL	Overlayer	Cu	Nafion, PTFE	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	Fumasep FAB-PK-130	CO$_2$	-0.76 V -iR vs. RHE	-300 mA/cm^2	45	725
35	Cu plate with in-situ electrodeposited N-functionalized aryl moiety (10 mM)	Overlayer	Cu	N,N'-ethylene-phenanthrolinium-Br2	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV	CO$_2$	-1.07 V -iR vs. RHE	-4 mA/cm^2	45	156
36	Amorphous N-functionalized (34% N)) carbon overlayer on top of Cu-sputtered PTFE GDL	Overlayer	Cu, C, N	-	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAB-PK-130	CO$_2$	-0.59 V -iR vs. RHE	-200 mA/cm^2	45	726
37	Pre-reduced gluconic acid-capped (800 mg) OH-rich Cu2O NPs, on	Overlayer	Cu,	Nafion, Gluconic acid	(Gas-phase reactant,	1.0 M	"Sustainion"	CO$_2$	-0.94 V -iR	-350	44	727

	GDL		O		supplied from behind)	KHCO3 (pH 7.8)			vs. RHE	mA/cm^2		
38	Electrolyte-soaked 60 µm-thick porous (0.44 µm pore size) PTFE support overlayer on top of commercial 25 nm Cu NPs, on GDL	Overlayer	Cu	Nafion	(Gas-phase reactant, supplied from behind)	0.5M K2SO4	Home-made BPM with TiO2 NP interlayer	CO_2	-5.35 V vs. ANODE	-300 mA/cm^2	44	[728]
39	Electroplated Cu (60 s @ 400 mA/cm^2) from CuBr2/tartrate/1 M KOH-containing bath with active CO_2 flow (though CO also seems to work), with Carbon NP midlayer and graphite toplayer, on Cu-sputtered PTFE GDL (ambiguously reported)	Overlayer	Cu, C	CNPs/Nafion, Graphite/Nafion	(Gas-phase reactant, supplied from behind)	1.0 M KHCO3	Fumapem FAA-3-PK-130	CO_2	-1.1 V - iR vs. RHE	n/a	42	[710]
40	Hydrophobic pention D18 overlayer on Cu-sputtered PTFE GDL	Overlayer	Cu	Pention D18	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-50, grade 60	CO_2	-2.58 V -iR vs. Au/QRE	-200 mA/cm^2	42	[729]
41	Carbon black NP (XC72R) overlayer on top of Cu-sputtered PTFE GDL	Overlayer	Cu, C	Nafion	(Gas-phase reactant, supplied from behind)	0.5 M K2SO4 + x M H2SO4 (pH 2)	Nafion 117	CO	-0.74 V -iR vs. RHE	?	42	[491]
42	Carbon NP/nafion toplayer with a MOF/nafion-derived midlayer on a Cu-sputtered PTFE GDL	Overlayer	Cu, C	Nafion, Cu3(benzene-1,3,5-tricarboxylate)2·xH2O	(Gas-phase reactant, supplied from behind)	-	Sustainion X37-50	CO	-2.7 V vs. ANODE	-295 mA/cm^2	41	[718]
43	Electrocycled (CVs in 0.3 M KCl) Cu plate with benzimidazole overlayer	Overlayer	Cu	Benzimidazole	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	?	CO_2	-1.07 V vs. RHE	-26 mA/cm^2	41	[730]
44	Polymerized a-ethyl cyanoacrylate overlayer on top of Cu foil	Overlayer	Cu	a-ethyl cyanoacrylate	(Solution-phase reactant, supplied in front)	0.5 M KCl	Nafion 117	CO_2	-1.1 V -iR vs. RHE	-22 mA/cm^2	41	[731]
45	Polymerized a-ethyl cyanoacrylate overlayer on top of commercial Cu NPs on GDL	Overlayer	Cu	a-ethyl cyanoacrylate, nafion	(Gas-phase reactant, supplied from behind)	1.0 M KOH (pH 14)	FAA-3-PK-130	CO_2	-0.9 V -iR vs. RHE	-190 mA/cm^2	41	[731]
46	PVDF overlayer on top of CuO NPs on carbon paper	Overlayer	Cu, O	PVDF	(Solution-phase reactant, supplied in front)	0.5 M KHCO3	Glass frit	CO_2	-1.22 V vs. RHE	-15 mA/cm^2	41	[732]
47	1-methyl-benzimidazolium-functionalized paraterphenyl-trifluoroheptan-2-one polymer on top of on Cu NPs, on carbon paper	Overlayer	Cu	1-methyl-benzimidazolium, paraterphenyl-trifluoroheptan-2-one	(Gas-phase reactant, supplied from behind)	-	QAPPT (?)	CO_2	-3.44 V vs. ANODE	-500 mA/cm^2	40	[690]
48	Diphenyliodonium salt-derived electrografted overlayer on Cu-sputtered PTFE GDL	Overlayer	Cu	Diphenyliodonium salt	(Solution-phase reactant, supplied in front)	1.0 M H3PO4 + 1.0 M KCl (pH ≈ 1)	Selemion AMV	CO_2	?	-100 mA/cm^2	39	[733]
49	Commercial spherical Cu microparticles with native CuOx film and nafion toplayer, on GDL	Overlayer	Cu	Nafion	(Solution-phase reactant, supplied in front)	0.1 M KOH (pH 13)	Selemion AMV	CO	-0.78 V -iR vs. RHE	-21 mA/cm^2	38	[734]
50	Electropolymerized N-tolyl pyridinium-based overlayer on Cu foil	Overlayer	Cu	N-tolyl pyridinium	(Solution-phase reactant, supplied in front)	H3PO4/0.1 M KOH (pH 2)	Selemion AMV	CO_2	-1.41 V -iR vs. RHE	-1 mA/cm^2	34	[735]
51	Glycine overlayer on top Cu plate	Overlayer	Cu	Glycine	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Nafion 117	CO_2	-1.9 V vs. RHE	- mA/cm^2	24	[736]
52	Electropolymerized ethynyl and azide-based overlayer with in-situ generated distrubted Cu NPs, on Cu substrate	Overlayer	Cu	Ethynyl-precursor, azide-precursor	(Solution-phase reactant, supplied in front)	0.1 M KHCO3 (pH 6.8)	Selemion AMV	CO_2	-1.3 V vs. RHE	-25 mA/cm^2	20	[737]
	[†_Cu-inorganic_overlayer,1]Many of the total FE values in the publication were shown to be ca. 110 % - thus we report here the highest C2H4 value with a total FE close to 100% (being 56 % as opposed to 69 %)											

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