

Electronic Supplementary information for:

**Interplay between Halides in Electrolyte and Chemical States of
Cu in Cu-based Electrode Determines Selectivity of the C₂
Product**

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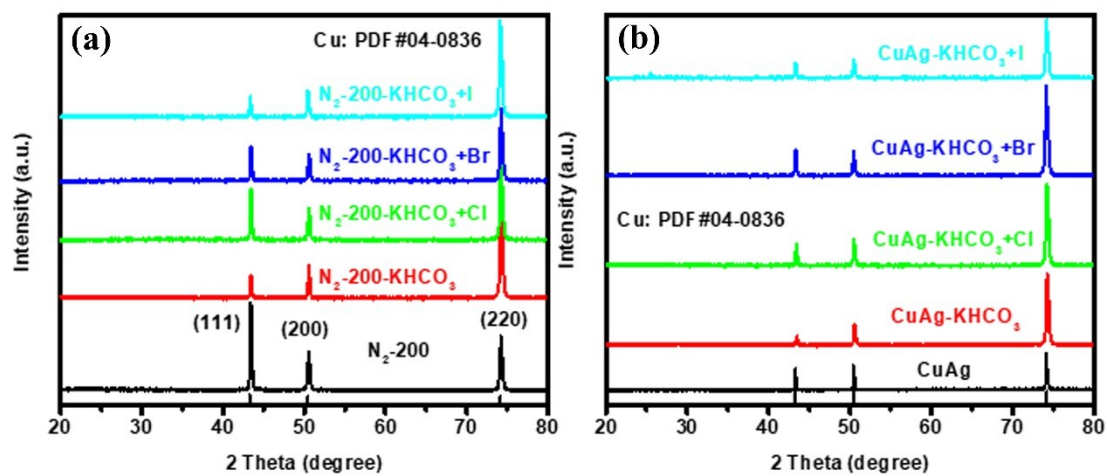


Fig. S1 The XRD spectra of (a) N₂-200 and (b) CuAg alloy before and after reaction in 0.1 M KHCO₃, 0.1 M KHCO₃ + 0.1 M KCl, 0.1 M KHCO₃ + 0.1 M KBr and 0.1 M KHCO₃ + 0.1 M KI electrolyte at -1.7 V versus (vs.) RHE.

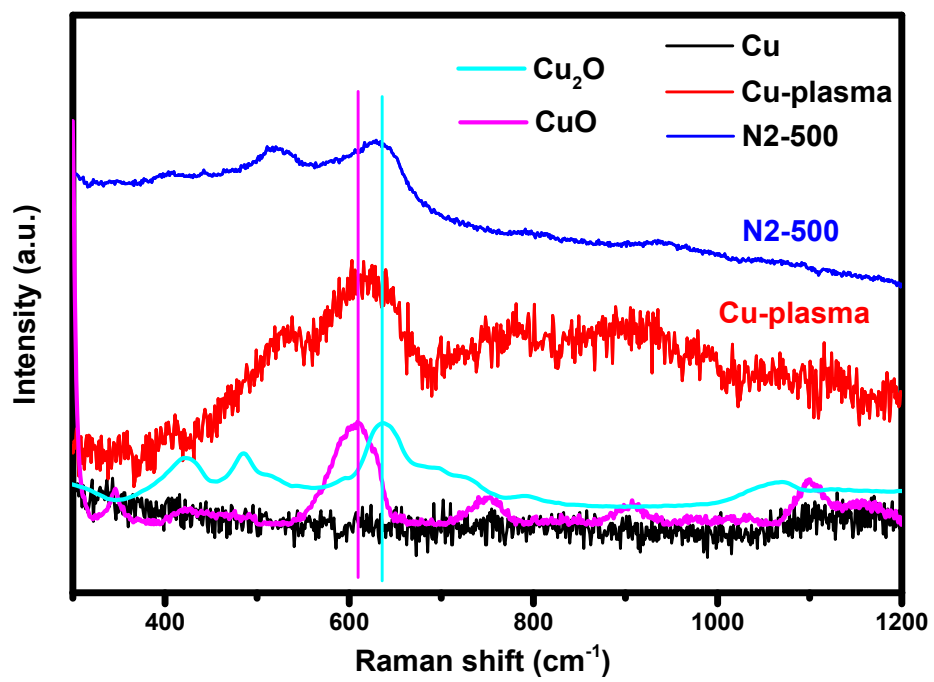


Fig. S2 Raman spectra of Cu, N2-500 and Cu-plasma.

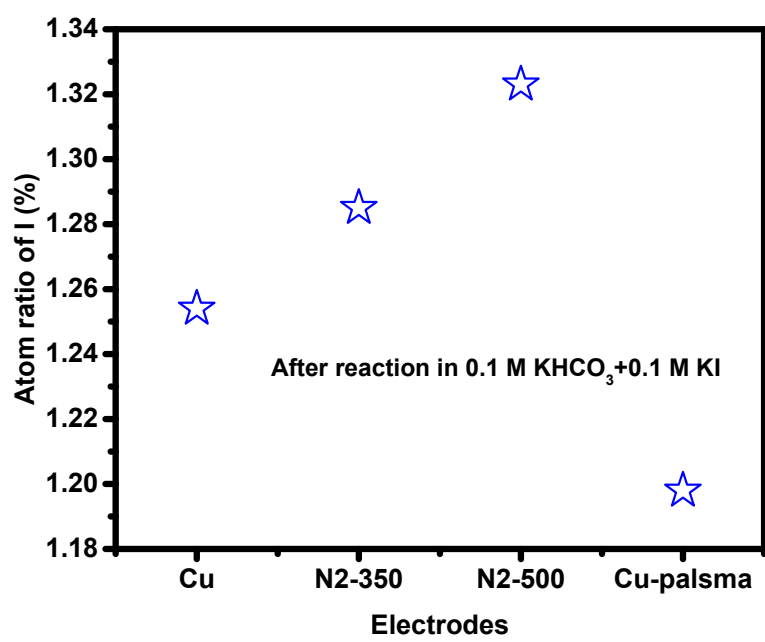


Fig. S3 Atomic percentage of I element on electrodes surface detected by XPS.

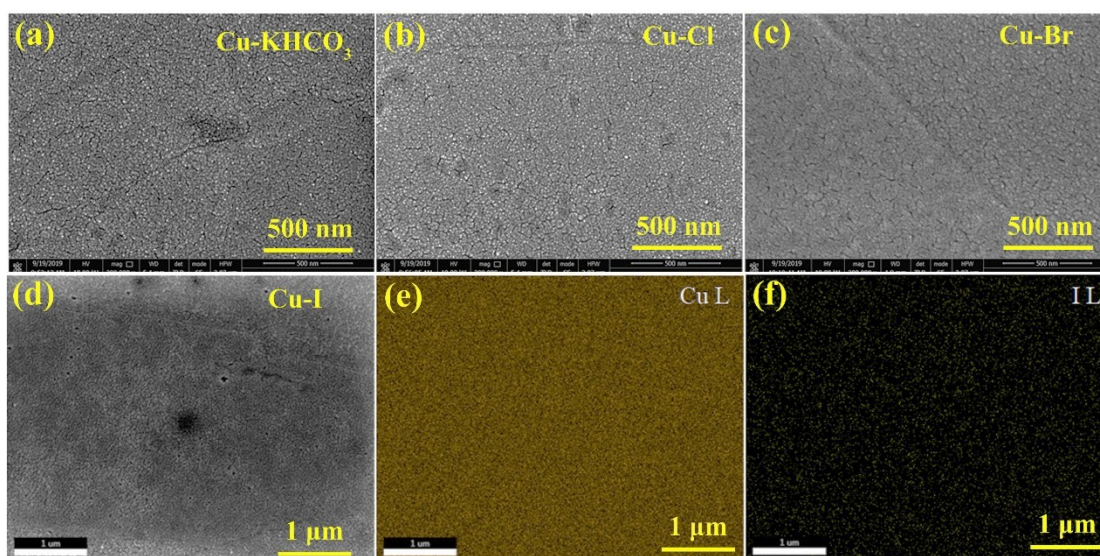


Fig. S4 SEM images of Cu electrode after reaction in (a) 0.1 M KHCO₃, (b) 0.1 M KHCO₃ + 0.1 M KCl, (c) 0.1 M KHCO₃ + 0.1 M KI at -1.7 V vs. RHE. EDX mapping of (e) Cu and (f) I element distribution in (d).

Table S1. Elemental composition (atomic and weight percentage) as determined by EDX of Cu electrode after reaction in 0.1 M KHCO₃ + 0.1 M KI electrolyte at -1.7 V vs. RHE.

Element	Weight (%)	Atomic (%)
Cu L	98.3	98.9
I L	0.02	0.018
O K	1.67	1.1

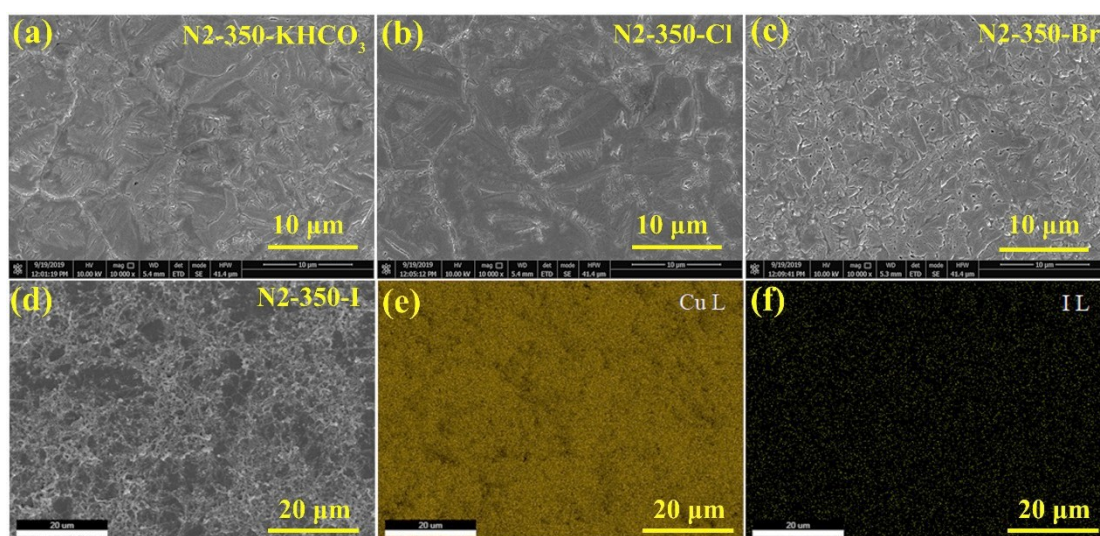


Fig. S5 SEM images of N2-350 electrode after reaction in (a) 0.1 M KHCO_3 , (b) 0.1 M $\text{KHCO}_3 + 0.1 \text{ M KCl}$, (c) 0.1 M $\text{KHCO}_3 + 0.1 \text{ M KCl}$, (d) 0.1 M $\text{KHCO}_3 + 0.1 \text{ M KI}$. EDX mapping of (e) Cu and (f) I element distribution in (d) at -1.7 V vs. RHE.

Table S2. Elemental composition (atomic and weight percentage) as determined by EDX of N2-350 electrode after reaction in 0.1 M $\text{KHCO}_3 + 0.1 \text{ M KI}$ electrolyte at -1.7 V vs. RHE.

Element	Weight (%)	Atomic (%)
Cu L	96.15	89.99
I L	1.33	0.62
O K	2.53	9.39

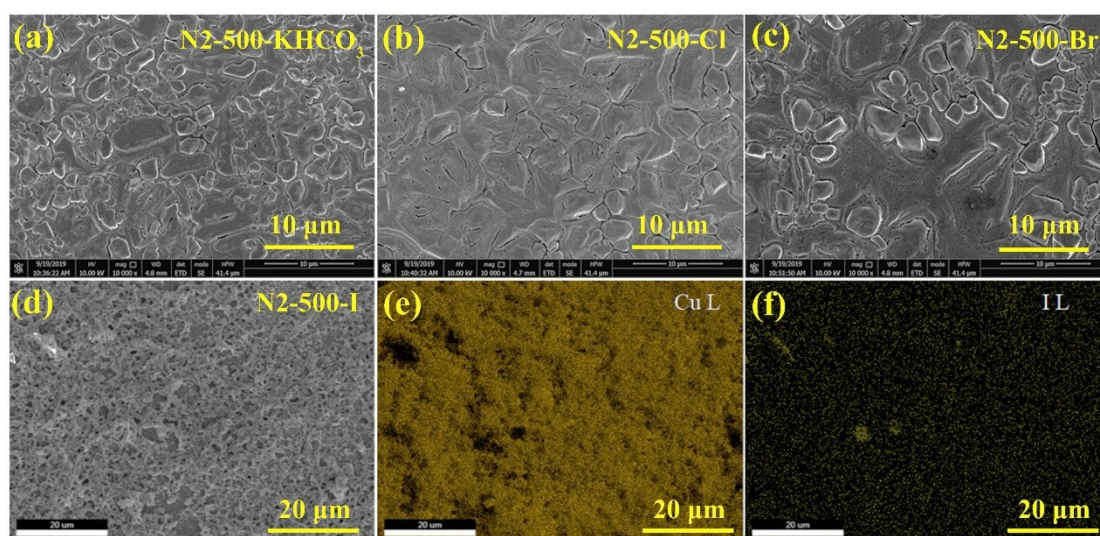


Fig. S6 SEM images of N2-500 electrode after reaction in (a) 0.1 M KHCO₃, (b) 0.1 M KHCO₃ + 0.1 M KCl, (c) 0.1 M KHCO₃ + 0.1 M KI, (d) 0.1 M KHCO₃ + 0.1 M KI. EDX mapping of (e) Cu and (f) I element distribution in (d) at -1.7 V vs. RHE.

Table S3. Elemental composition (atomic and weight percentage) as determined by EDX of N2-500 electrode after reaction in 0.1 M KHCO₃ + 0.1 M KI electrolyte at -1.7 V vs. RHE.

Element	Weight (%)	Atomic (%)
Cu L	87.9	71.66
I L	3.8	1.55
O K	8.3	26.78

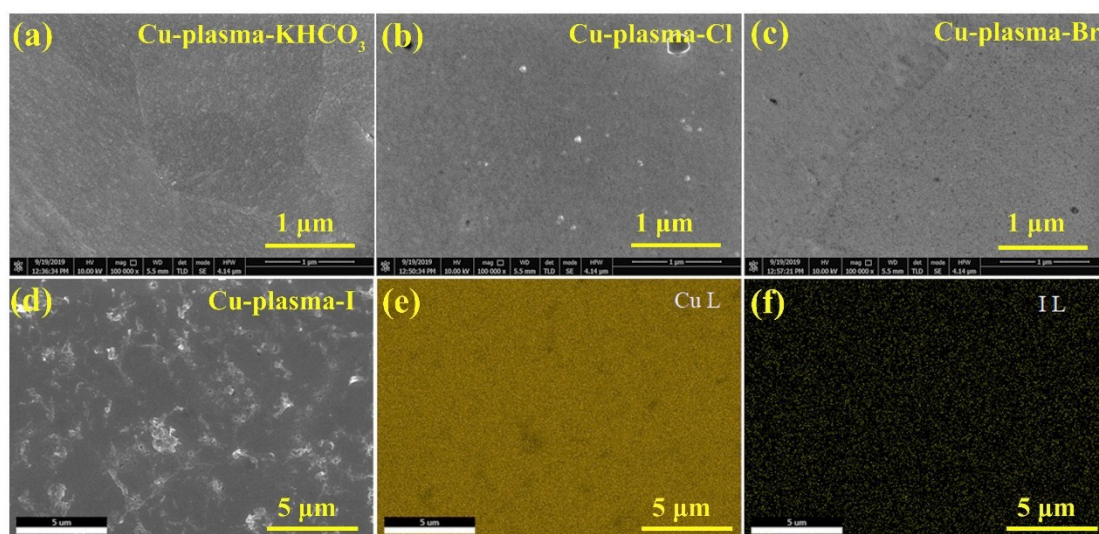


Fig.S7 SEM images of Cu-plasma electrode after reaction in (a) 0.1 M KHCO₃, (b) 0.1 M KHCO₃ + 0.1 M KCl, (c) 0.1 M KHCO₃ + 0.1 M KBr, (d) 0.1 M KHCO₃ + 0.1 M KI. EDX mapping of (e) Cu and (f) I element distribution in (d) at -1.7 V vs. RHE.

Table S4. Elemental composition (atomic and weight percentage) as determined by EDX of Cu-plasma electrode after reaction in 0.1 M KHCO₃ + 0.1 M KI electrolyte at -1.7 V vs. RHE.

Element	Weight (%)	Atomic (%)
Cu L	98.39	94.8
I L	0.28	0.14
O K	1.32	5.06

Table S5. Faradaic efficiencies of products on Cu electrode in KHCO₃ electrolyte at potential range -1.2 V – -1.9 V vs. RHE.

Potential V vs. RHE	Current density (mA/cm ²)	Faradaic efficiency (%)				
		H ₂	CO	CH ₄	C ₂ H ₄	HCOO ⁻
-1.2	6.1	21	1	9	6	18
-1.4	12.2	24	0.3	19	9	3
-1.6	13.3	25	0.7	16	9	7
-1.7	18.3	29	0.5	17	10	9
-1.9	23.9	31	0.5	21	13	5

Table S6. Faradaic efficiencies of products on N2-200 electrode in KHCO₃ electrolyte at potential range -1.2 V – -1.9 V vs. RHE.

Potential V vs. RHE	Current density (mA/cm ²)	Faradaic efficiency (%)				
		H ₂	CO	CH ₄	C ₂ H ₄	HCOO ⁻
-1.2	9.9	23	0.8	12	9	9
-1.4	15.3	44	0.7	18	12	9
-1.6	20	32	0.5	17	11	4
-1.7	21.1	36	0.3	15	9	14
-1.9	23.6	38	0.4	14	15	4

Table S7. Faradaic efficiencies of products on N2-350 electrode in KHCO₃ electrolyte at potential range -1.2 V – -1.9 V vs. RHE.

Potential V vs. RHE	Current density (mA/cm ²)	Faradaic efficiency (%)				
		H ₂	CO	CH ₄	C ₂ H ₄	HCOO ⁻
-1.2	8.7	27	3.1	5	9.7	15.1
-1.4	13.6	33	0.8	4	5.9	9.5
-1.6	15.6	33	0.4	9	8.3	8.5
-1.7	18.3	35	0.5	7	20	15
-1.9	20.8	36	0.3	11	11	4.2

Table S8. Faradaic efficiencies of products on N2-500 electrode in KHCO₃ electrolyte at potential range -1.2 V – -1.9 V vs. RHE.

Potential V vs. RHE	Current density (mA/cm ²)	Faradaic efficiency (%)				
		H ₂	CO	CH ₄	C ₂ H ₄	HCOO ⁻
-1.2	9.4	28	1.6	1	9	21
-1.4	12.1	33	1.6	3	9	17
-1.6	19.8	37	1.4	6	20	13
-1.7	22.4	32	0.8	2	24	16
-1.9	21.1	36	1.9	5	26	12

Table S9. Faradaic efficiencies of products on Cu electrode at -1.7 V vs. RHE in 0.1 M KHCO₃ and 0.1 M KHCO₃ + 0.1 M KX (X = Cl, Br, I) electrolytes.

Electrolyte	Current density (mA/cm ²)	Faradaic efficiency (%)					
		H ₂	CO	CH ₄	C ₂ H ₄	HCOO ⁻	CH ₃ CH ₂ OH
KHCO₃	14.3	28.6		16.7	10.5	9	2.6
KHCO₃+KCl	19.9	30.5		36.2	14.6	2.3	7.5
KHCO₃+KBr	31.7	41		30	12.9	3.7	2.7
KHCO₃+KI	34.2	59		11.5	7.3	7.9	0.4

Table S10. Faradaic efficiencies of products on N2-200 electrode at -1.7 V vs. RHE in 0.1 M KHCO₃ and 0.1 M KHCO₃ + 0.1 M KX (X = Cl, Br, I) electrolytes.

Electrolyte	Current density (mA/cm ²)	Faradaic efficiency (%)						
		H ₂	CO	CH ₄	C ₂ H ₄	HCOO ⁻	CH ₃ CH ₂ OH	n-propanol
KHCO₃	21.1	36	0.3	14.3	5.5	14.8	N.D.	N.D.
KHCO₃+KCl	29.8	26	0.65	39.6	12.8	7.8	N.D.	N.D.
KHCO₃+KBr	29.8	40.5	0.5	26.8	9.1	8.1	N.D.	N.D.
KHCO₃+KI	30.7	54.5	0.45	9.5	13	19.9	N.D.	N.D.

Notes: N.D. present the product was not quantified by NMR.

Table S11. Faradaic efficiencies of products on N2-350 electrode at -1.7 V vs. RHE in 0.1 M KHCO₃ and 0.1 M KHCO₃ + 0.1 M KX (X = Cl, Br, I) electrolytes.

Electrolyte	Current density (mA/cm ²)	Faradaic efficiency (%)						
		H ₂	CO	CH ₄	C ₂ H ₄	HCOO ⁻	CH ₃ CH ₂ OH	n-propanol
KHCO₃	18.3	35	0.5	7	20	15	N.D.	N.D.
KHCO₃+KCl	35.6	38	0.5	21	28	7.6	N.D.	N.D.
KHCO₃+KBr	35.8	54.5	0.4	7.8	12.7	6	N.D.	N.D.
KHCO₃+KI	41.1	60	0.3	1.7	21.5	5.2	N.D.	N.D.

Notes: N.D. present the product was not quantified by NMR.

Table S12. Faradaic efficiencies of products on N2-500 electrode at -1.7 V vs. RHE in 0.1 M KHCO₃ and 0.1 M KHCO₃ + 0.1 M KX (X = Cl, Br, I) electrolytes.

Electrolyte	Current density (mA/cm ²)	Faradaic efficiency (%)						
		H ₂	CO	CH ₄	C ₂ H ₄	HCOO ⁻	CH ₃ CH ₂ OH	n-propanol
KHCO₃	22.4	32	0.7	1.3	24.2	15.6	7.3	7.6
KHCO₃+KCl	29.9	38.5	0.8	3.4	28.1	12	8.5	5.5
KHCO₃+KBr	32.2	41	0.9	2.1	25.7	13	6.7	4.1
KHCO₃+KI	33	40.5	0.5	0.1	37.2	8.6	8.6	1.2

Table S13. Faradaic efficiencies of products on Cu-plasma electrode at -1.7 V vs. RHE in 0.1 M KHCO₃ and 0.1 M KHCO₃ + 0.1 M KX (X = Cl, Br, I) electrolytes.

Electrolyte	Current density (mA/cm ²)	Faradaic efficiency (%)						
		H ₂	CO	CH ₄	C ₂ H ₄	HCOO ⁻	CH ₃ CH ₂ OH	n-propanol
KHCO₃	19.9	27	0.3	14.5	18.1	7.5	N.D.	N.D.
KHCO₃+KCl	32.6	30	0.2	29.5	14.1	2.7	N.D.	N.D.
KHCO₃+KBr	35.4	43.2	0.4	29	7	2.8	N.D.	N.D.
KHCO₃+KI	36.7	63.3	0.3	14.1	11.2	6.1	N.D.	N.D.

Table S14. Faradaic efficiencies of products on CuAg electrode at -1.7 V vs. RHE in 0.1 M KHCO₃ and 0.1 M KHCO₃ + 0.1 M KX (X = Cl, Br, I) electrolytes.

Electrolyte	Current density (mA/cm ²)	Faradaic efficiency (%)						
		H ₂	CO	CH ₄	C ₂ H ₄	HCOO ⁻	CH ₃ CH ₂ OH	n-propanol
KHCO₃	21.8	46	0.5	1.7	26.8	1	7.7	4.9
KHCO₃+KCl	41.3	47	0.5	2.1	28	1	-	-
KHCO₃+KBr	40.4	52.5	0.4	2.9	29.6	0.75	5.6	-.
KHCO₃+KI	41.3	67	0.5	0.9	20.3	5.65	5.2	-

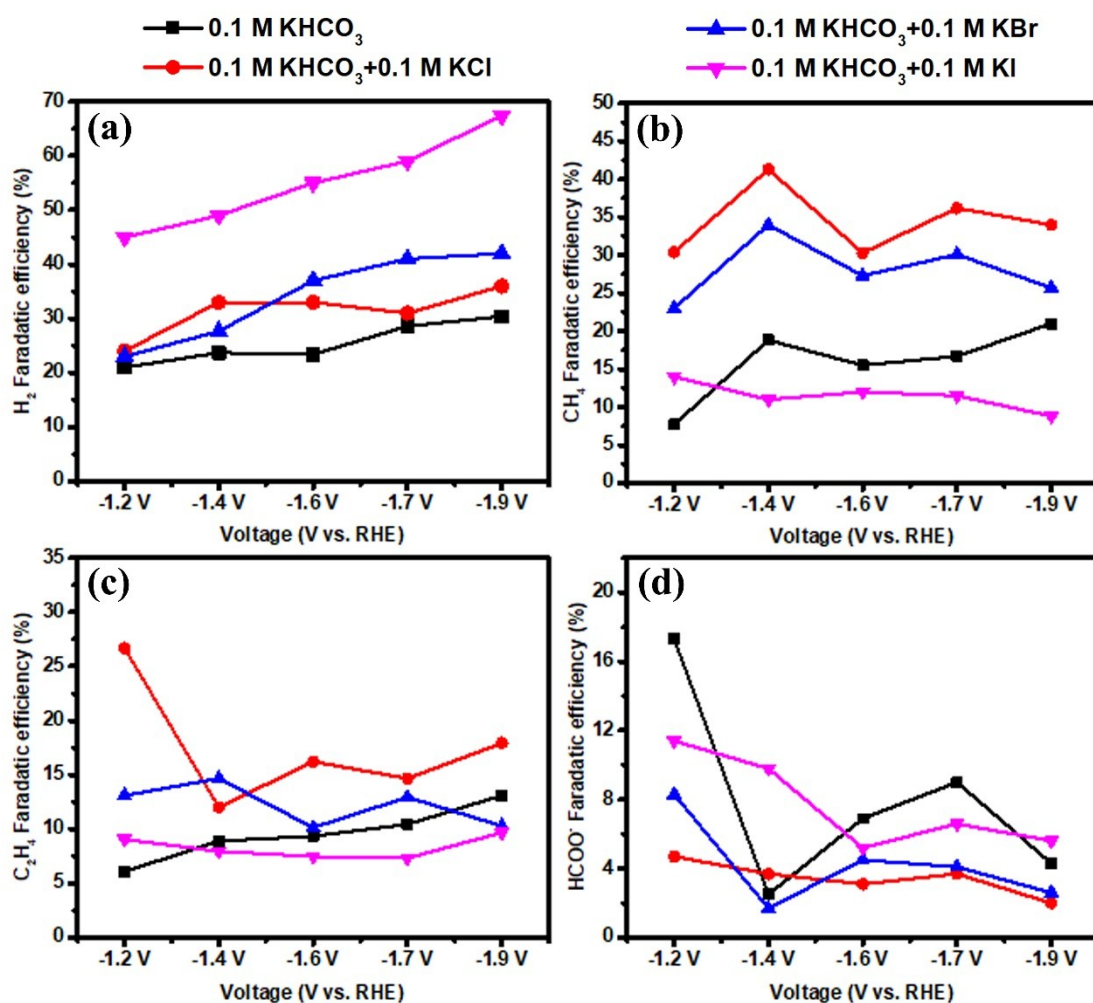


Fig. S8 Faradaic efficiencies of (a) H_2 , (b) CH_4 , (c) C_2H_4 and (d) HCOO^- on Cu electrode at -1.2 V – -1.9 V vs. RHE in various electrolytes.

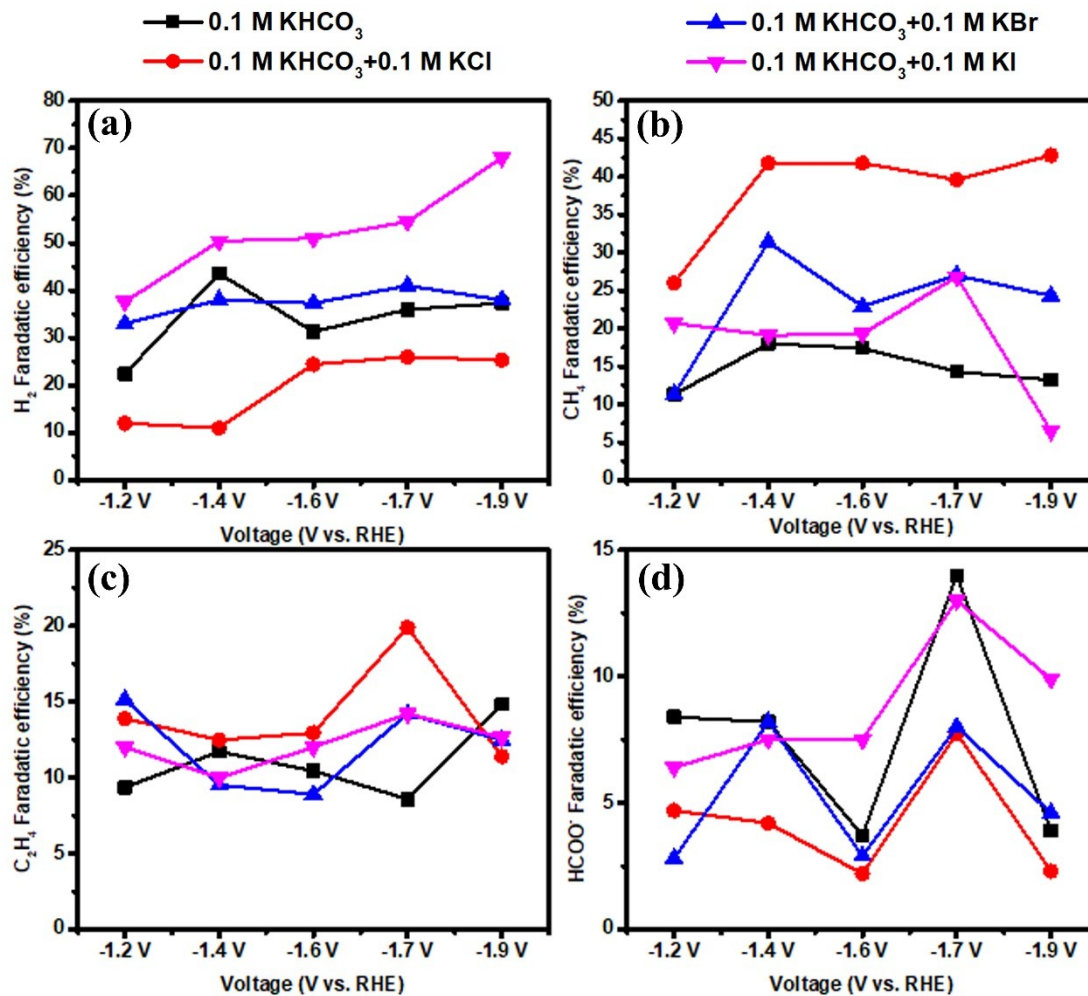


Fig. S9 Faradaic efficiencies of (a) H_2 , (b) CH_4 , (c) C_2H_4 and (d) HCOO^- on N2-200 electrode at -1.2 V – -1.9 V vs. RHE in various electrolytes.

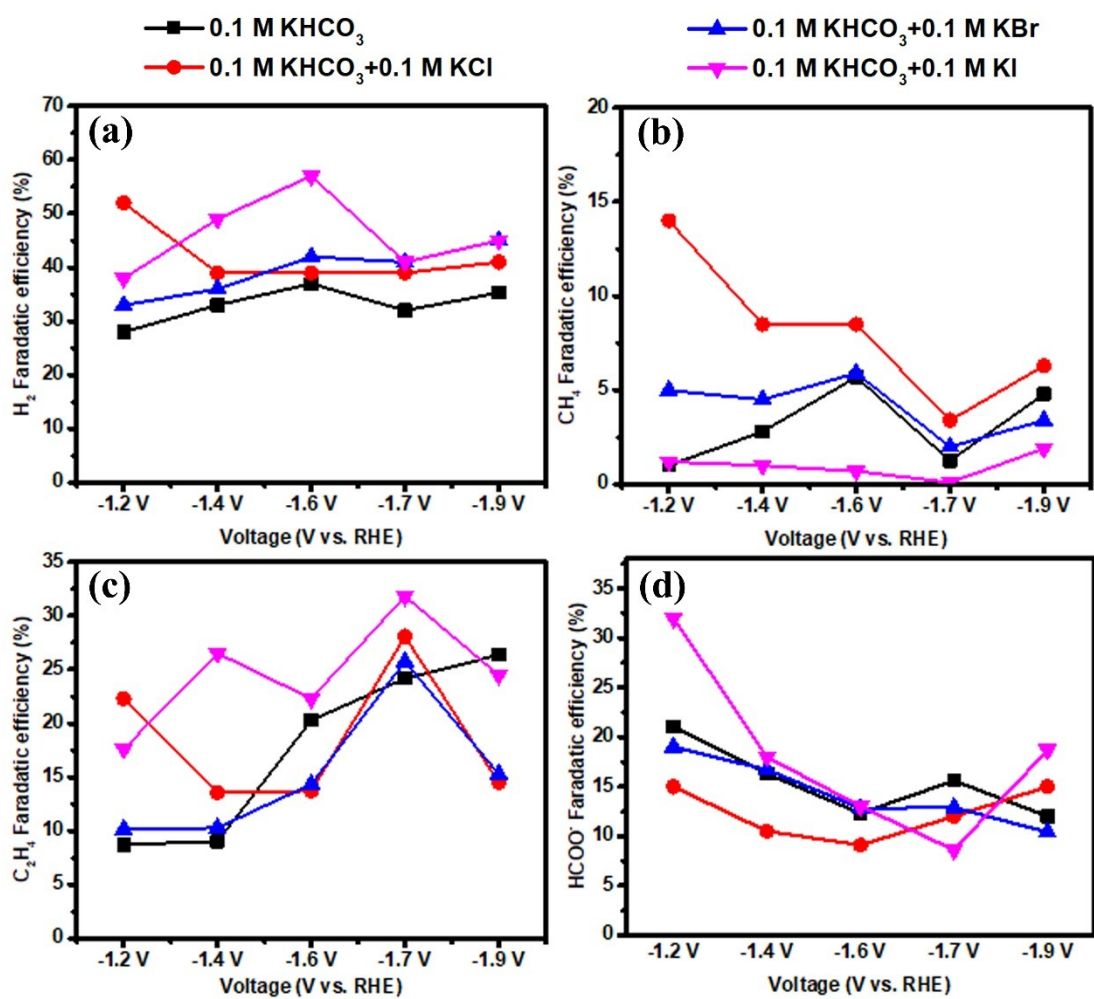


Fig. S10 Faradaic efficiencies of (a) H_2 , (b) CH_4 , (c) C_2H_4 and (d) HCOO^- on N2-500 electrode at -1.2 V – -1.9 V vs. RHE in various electrolytes.

Table S15. Faradaic efficiency ratio of C₂H₄/CH₄ at -1.7 V vs. RHE over Cu-based electrodes in different electrolytes.

C₂H₄/CH₄ Selectivity -1.7 V vs. RHE	0.1 M KHCO₃	0.1 M KHCO₃ + 0.1 M KCl	0.1 M KHCO₃ + 0.1 M KBr	0.1 M KHCO₃ + 0.1 M KI
Cu	0.63	0.40	0.43	0.64
N2-200	0.60	0.50	0.53	0.53
N2-350	2.86	1.33	1.63	13.03
N2-500	19.3	8.25	12.56	372.06
Cu-plasma	1.24	0.47	0.25	0.8
CuAg	15.78	13.37	10.4	22.53