

Supplementary Information

Thermo-Kinetic diagrams: the Cu-H₂O-Acetate and the Cu-H₂O systems

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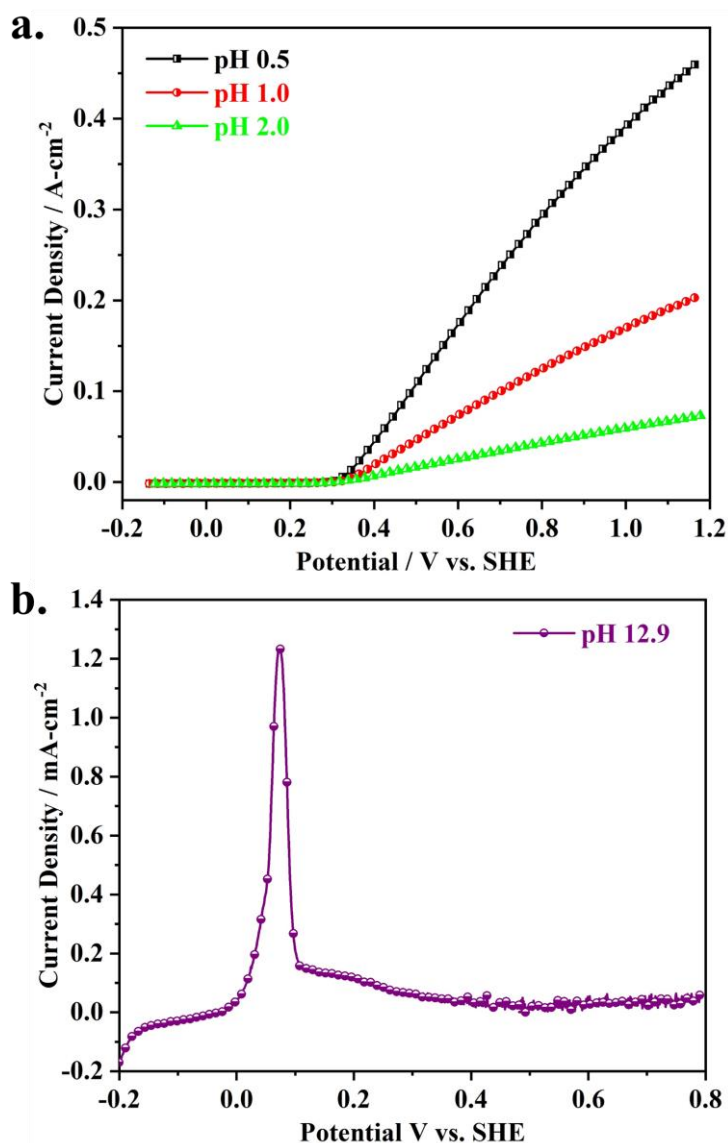


Figure S1: The LSV curves for the Cu-RDE obtained in solutions of (a) low pH (i.e. 0.5, 1.0 and 2.0) and high pH (12.9). The LSV scan were obtained at 0.1667 mV/s sweep rate, at a fixed 500 rpm rotation rate and constant solution temperature of 25 °C)

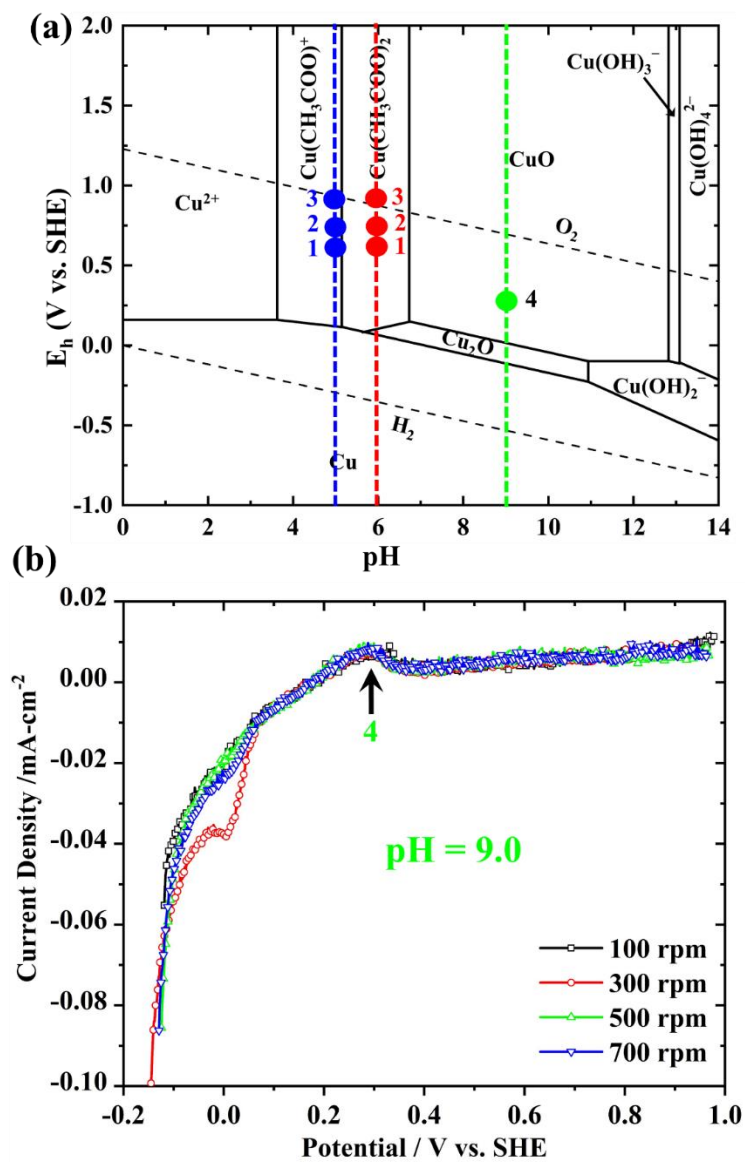


Figure S2: (a) E_h -pH diagram of the Cu-H₂O system indicating the peak potential at pH 5, 6 and 9 (b) LSV scans for the Cu-RDE obtained at different rotation rates at constant pH (9.0)

Table S1: The selected Cu species and their standard Gibbs free energy values used to construct the Cu–H₂O–Acetate Eh–pH diagram [1, 2]

Species	ΔG° (kJ/mol)
Cu	0
Cu ²⁺	65.04
Cu(CH ₃ COO) ⁺	-316.4
Cu(CH ₃ COO) ₂	-683.5
Cu ₂ O	-147.9
CuO	-128.29
Cu(OH) ²⁻	-333.05
Cu(OH) ³⁻	-494.98
Cu(OH) ₄ ²⁻	-657.48
H ₂ O	-237.19
CH ₃ COO ⁻	-369.3
CH ₃ COOH	-396.48
H ⁺	0

Table S2: Electrochemical reactions considered to develop the Eh – pH diagram of the Cu–H₂O–Acetate system using the data given in Table S2 and equations E1 and E2 (in the main text)

No.	Reactions considered	Equations
1	$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$	$\text{Eh} = 0.1596$
2	$\text{Cu}(\text{CH}_3\text{COO})^+ + \text{H}^+ + 2\text{e}^- = \text{Cu} + \text{CH}_3\text{COOH}$	$\text{Eh} = 0.267 - 0.02956\text{pH}$
3	$\text{Cu}(\text{CH}_3\text{COO})_2 + 2\text{H}^+ + 2\text{e}^- = \text{Cu} + 2\text{CH}_3\text{COOH}$	$\text{Eh} = 0.4193 - 0.0591\text{pH}$
4	$2\text{Cu}(\text{CH}_3\text{COO})_2 + \text{H}_2\text{O} + 2\text{e}^- = \text{Cu}_2\text{O} + 4\text{CH}_3\text{COO}^- + 2\text{H}^+$	$\text{Eh} = -0.246 + 0.0591\text{pH}$
5	$\text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{e}^- = 2\text{Cu} + \text{H}_2\text{O}$	$\text{Eh} = 0.419 - 0.0591\text{pH}$
6	$2\text{CuO} + 2\text{H}^+ + 2\text{e}^- = \text{Cu}_2\text{O} + \text{H}_2\text{O}$	$\text{Eh} = 0.547 - 0.0591\text{pH}$
7	$\text{Cu}(\text{OH})^{2-} + 2\text{H}^+ + \text{e}^- = \text{Cu} + 2\text{H}_2\text{O}$	$\text{Eh} = 1.11 - 0.0591\text{pH}$
8	$\text{CuO} + \text{H}_2\text{O} + \text{e}^- = \text{Cu}(\text{OH})^{2-}$	$\text{Eh} = -0.09955$
9	$\text{Cu}(\text{OH})^{3-} + \text{H}^+ + \text{e}^- = \text{Cu}(\text{OH})^{2-} + \text{H}_2\text{O}$	$\text{Eh} = 0.66 - 0.0591\text{pH}$
10	$\text{Cu}(\text{OH})_4^{2-} + 2\text{H}^+ + \text{e}^- = \text{Cu}(\text{OH})^{2-} + 2\text{H}_2\text{O}$	$\text{Eh} = 1.554 - 0.0591\text{pH}$
11	$\text{Cu}(\text{CH}_3\text{COO})^+ + \text{H}^+ = \text{Cu}^{2+} + \text{CH}_3\text{COOH}$	$\text{pH} = 3.63$
12	$\text{Cu}(\text{CH}_3\text{COO})_2 + \text{H}^+ = \text{Cu}(\text{CH}_3\text{COO})^+ + \text{CH}_3\text{COOH}$	$\text{pH} = 5.15$
13	$\text{CuO} + 2\text{CH}_3\text{COO}^- + 2\text{H}^+ = \text{Cu}(\text{CH}_3\text{COO})_2 + \text{H}_2\text{O}$	$\text{pH} = 6.73$
14	$\text{Cu}(\text{OH})^{3-} + \text{H}^+ = \text{CuO} + 2\text{H}_2\text{O}$	$\text{pH} = 12.82$
15	$\text{Cu}(\text{OH})_4^{2-} + \text{H}^+ = \text{Cu}(\text{OH})^{3-} + \text{H}_2\text{O}$	$\text{pH} = 13.08$
16	$2\text{Cu}(\text{OH})^{2-} + 2\text{H}^+ = \text{Cu}_2\text{O} + 3\text{H}_2\text{O}$	$\text{pH} = 10.94$
17	$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	$\text{Eh} = -0.0592\text{pH}$
18	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$	$\text{Eh} = 1.228 - 0.0591\text{pH}$

Table S3: Differentiating the current domains based on the dissolution rate as designated in the TK-diagram

Current Density (A/cm ²)	Dissolution Rate (gm/cm ² -h)	Loss in thickness (mm/y)	Domains
$< 10^{-5}$	$< 1.2 \times 10^{-5}$	< 0.116	Passive/slow dissolution
$10^{-5} - 10^{-3}$	$1.2 \times 10^{-5} - 0.0012$	$0.116 - 11.6$	Intermediate dissolution
$> 10^{-3}$	> 0.0012	> 11.6	Aggressive dissolution

References

- [1] H.-P. Hermansson, Copper Thermodynamics in the Repository Environment up to 130 deg C, Sweden, 2010, p. 60.
- [2] E.L. Shock, C.M. Koretsky, Metal-organic complexes in geochemical processes: Calculation of standard partial molal thermodynamic properties of aqueous acetate complexes at high pressures and temperatures, *Geochimica et Cosmochimica Acta* 57(20) (1993) 4899-4922.