Supporting information

Electrochemical oxidation of a highly soluble redox mediator in aqueous solution for energy conversion

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(8 pages; Figure S1-S4; Table S1)

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Table S1 Equilibrium constants for (a) Fe-HEDTA, (b) Fe-EDTA, (c) Fe_{aq} and (d) HEDTA and EDTA.

(a)

Metal ion	Metal chelate	Formulation	Log β	Reference
Fe^{3+}	FeL	$[FeL]/[Fe^{3+}][L^{3-}]$	19.8	1
	$Fe(OH)L^{-}$	$[Fe(OH)L^{-}][H^{+}]/[Fe^{3+}][L^{3-}][H_2O]$	15.7	2
	$Fe(OH)_2L^{2-}$	$[Fe(OH)_2L^{-}][H^{+}]^2/[Fe^{3+}][L^{3-}][H_2O]^2$	7.0	2
	$Fe(OH)_3L^{3-}$	$[Fe(OH)_3L^{-}][H^{+}]^3/[Fe^{3+}][L^{3-}][H_2O]^3$	-3.2	3
	$(FeL)_2O^{2-}$	$[(FeL)_2O^{2-}][H^{+}]^2/[Fe^{3+}]^2[L^{3-}]^2[H_2O]$	33.8	2
Fe^{2+}	FeHL	$[FeHL^{-}]/[Fe^{2+}][L^{3-}][H^{+}]$	14.9	3
	FeL^{-}	$[FeL^{-}]/[Fe^{2+}][L^{3-}]$	12.2	1
	$Fe(OH)L^{2-}$	$[Fe(OH)L^{2-}][H^{+}]/[Fe^{2+}][L^{3-}][H_2O]$	3.2	3
	$Fe(OH)_2L^{3-}$	$[Fe(OH)_2L^{2-}][H^{+}]^2/[Fe^{2+}][L^{3-}][H_2O]^2$	-6.8	3

(b)

Metal ion	Metal chelate	Formulation	Log β	Reference
Fe^{3+}	FeHL	$[FeHL]/[Fe^{3+}][L^{4-}][H^{+}]$	26.4	4
	FeL^{-}	$[FeL^{-}]/[Fe^{3+}][L^{4-}]$	25.1	4
	$Fe(OH)L^{2-}$	$[Fe(OH)L^{2-}][H^{+}]/[Fe^{3+}][L^{4-}][H_2O]$	17.6	4
	$(FeL)_2O^{4-}$	$[(FeL)_2O^{4-}][H^{+}]^2/[Fe^{3+}]^2[L^{4-}]^2[H_2O]$	38.2	2
	$Fe(OH)_2L^{3-}$	$[Fe(OH)_2L^{3-}][H^{+}]^2/[Fe^{3+}][L^{4-}][H_2O]^2$	8.2	4
Fe^{2+}	FeH_2L	$[FeH_2L]/[Fe^{2+}][L^{4-}][H^{+}]^2$	19.5	4
	$FeHL^{-}$	$[FeHL^{-}]/[Fe^{2+}][L^{4-}][H^{+}]$	17.1	4
	FeL^{2-}	$[FeL^{2-}]/[Fe^{2+}][L^{4-}]$	14.3	4
	$Fe(OH)L^{3-}$	$[Fe(OH)L^{3-}][H^{+}]/[Fe^{2+}][L^{4-}][H_2O]$	5.3	4
	$Fe(OH)_2L^{4-}$	$[Fe(OH)_2L^{4-}][H^{+}]^2/[Fe^{2+}][L^{4-}][H_2O]^2$	-4.6	4

(c)

Metal ion	Metal chelate	Formulation	Log β	Reference
Fe^{3+}	$FeOH^{2+}$	$[Fe(OH)^{2+}][H^+]/[Fe^{3+}][H_2O]$	−2.7	5
	$Fe(OH)_2^+$	$[Fe(OH)_2^+][H^+]^2/[Fe^{3+}][H_2O]^2$	−7.0	5
	$Fe(OH)_3$	$[Fe(OH)_3][H^+]^3/[Fe^{3+}][H_2O]^3$	−12.5	5
	$Fe(OH)_4^-$	$[Fe(OH)_4^-][H^+]^4/[Fe^{3+}][H_2O]^4$	−20.6	5
	$Fe_2(OH)_2^{4+}$	$[Fe_2(OH)_2^{4+}][H^+]^2/[Fe^{3+}]^2[H_2O]^2$	−3.2	6
	$Fe_3(OH)_4^{5+}$	$[Fe_3(OH)_4^{5+}][H^+]^4/[Fe^{3+}]^3[H_2O]^4$	−7.0	6
	$Fe(OH)_3(s)$	$[Fe(OH)_3(s)][H^+]^3/[Fe^{3+}][H_2O]^3$	−4.8	7
Fe^{2+}	$FeOH^+$	$[Fe(OH)^+][H^+]/[Fe^{2+}][H_2O]$	−9.3	4
	$Fe(OH)_2$	$[Fe(OH)_2][H^+]^2/[Fe^{2+}][H_2O]^2$	−20.3	4
	$Fe(OH)_3^-$	$[Fe(OH)_3^-][H^+]^3/[Fe^{2+}][H_2O]^3$	−31.3	4
	$Fe(OH)_4^{2-}$	$[Fe(OH)_4^{2-}][H^+]^4/[Fe^{2+}][H_2O]^4$	−45.5	4
	$Fe(OH)_2(s)$	$[Fe(OH)_2(s)][H^+]^2/[Fe^{2+}][H_2O]^2$	−13.3	7

(d)

Ligand = L	Protonated ligand	Formulation	Log β	Reference
$EDTA^{4-}$	H_6L^{2+}	$[H_6L^{2+}]/[L^{4-}][H^+]^6$	22.5	4
	H_5L^+	$[H_5L^+]/[L^{4-}][H^+]^5$	22.5	4
	H_4L	$[H_4L]/[L^{4-}][H^+]^4$	21.0	4
	H_3L^-	$[H_3L^-]/[L^{4-}][H^+]^3$	19.0	4
	H_2L^{2-}	$[H_2L^{2-}]/[L^{4-}][H^+]^2$	16.3	4
	HL^{3-}	$[HL^{3-}]/[L^{4-}][H^+]$	10.2	4
$HEDTA^{3-}$	H_3L	$[H_3L]/[L^{3-}][H^+]^3$	17.7	3
	H_2L^-	$[H_2L^-]/[L^{3-}][H^+]^2$	15.1	3
	HL^{2-}	$[HL^{2-}]/[L^{3-}][H^+]$	9.7	3

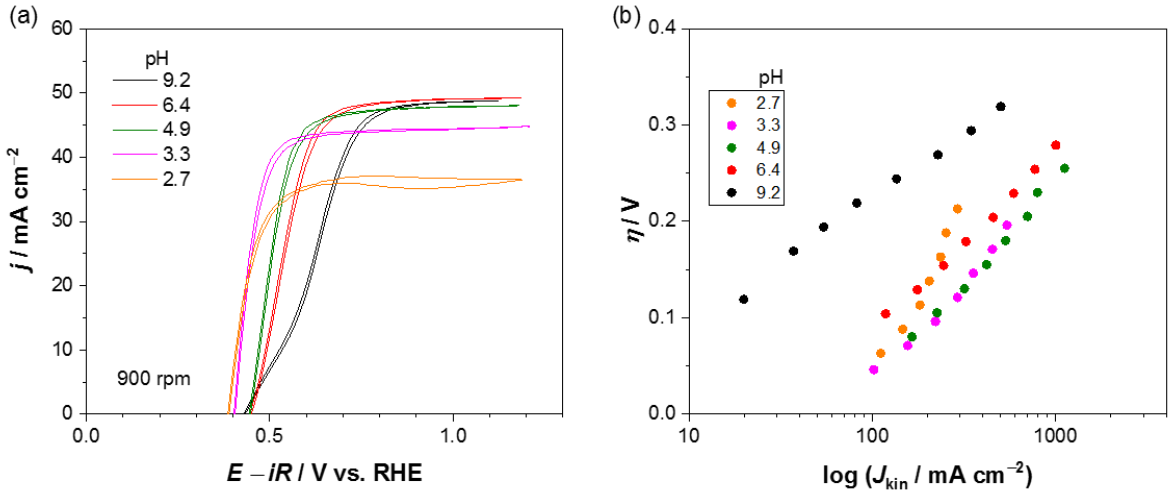

Figure S1.(a) Cyclic voltammograms measured by a platinum rotating disk electrode in the solution containing total 1.0 mol kg^{-1} Fe-HEDTA with 0.5 mol kg^{-1} of HEDTA. Redox solutions have 50% of reduced species and 50% oxidized species. (b) Tafel plot of kinetic current density after Koutecký -Levich analysis**.**

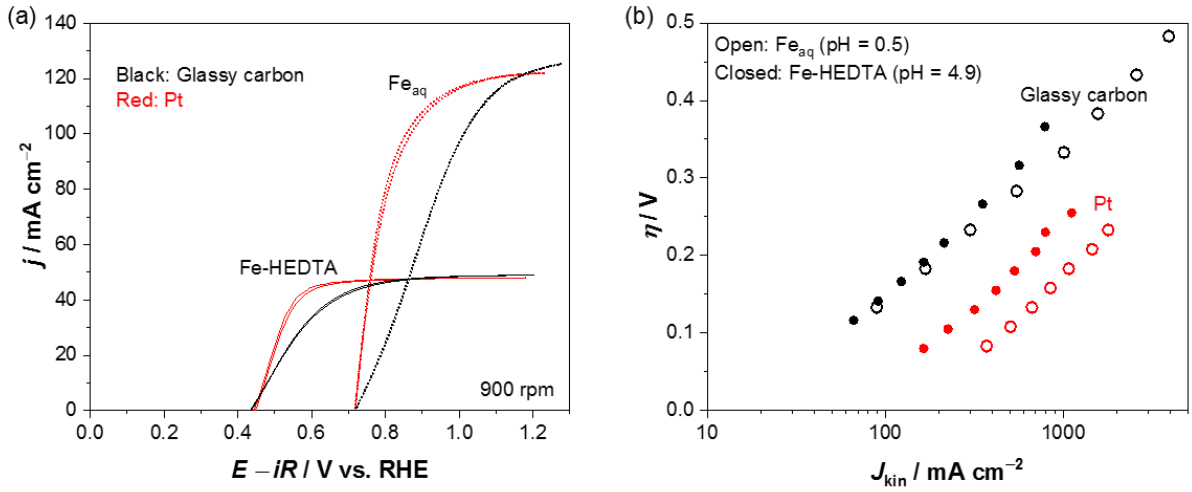

Figure S2. (a) Cyclic voltammograms measured by a glassy carbon and a platinum rotating disk electrode in the solution containing total 1.0 mol kg^{-1} $Fe^{2+/3+}_{aq}$ in 0.5 mol L^{-1} of H_2SO_4 or total 1.0 mol kg^{-1} Fe-HEDTA in 0.5 mol kg^{-1} of excess HEDTA. Redox solutions have 50% of reduced species and 50% oxidized species. (b) corresponding Tafel plot after Koutecký -Levich analysis.

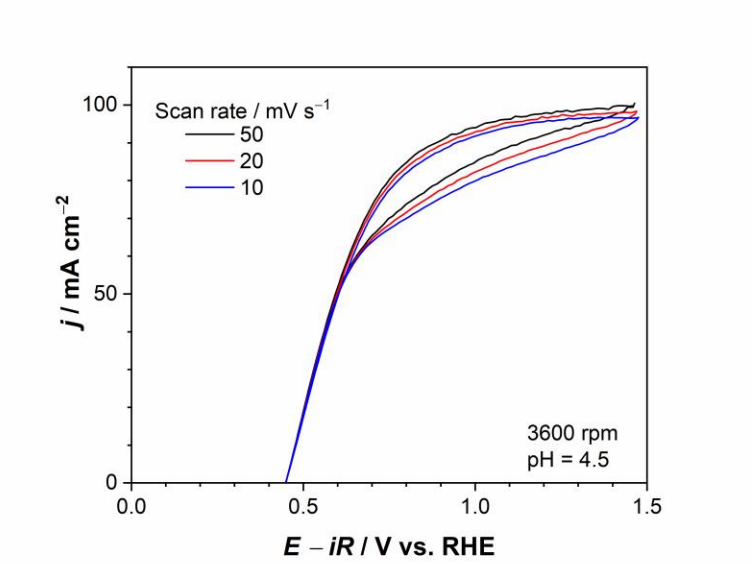

Figure S3. Cyclic voltammograms measured by a glassy carbon rotating disk electrode in the solution containing total 1.0 mol kg^{-1} Fe-HEDTA without buffer at different scan rates. Redox solutions have 50% of reduced species and 50% oxidized species. (3600 rpm, 298 K).

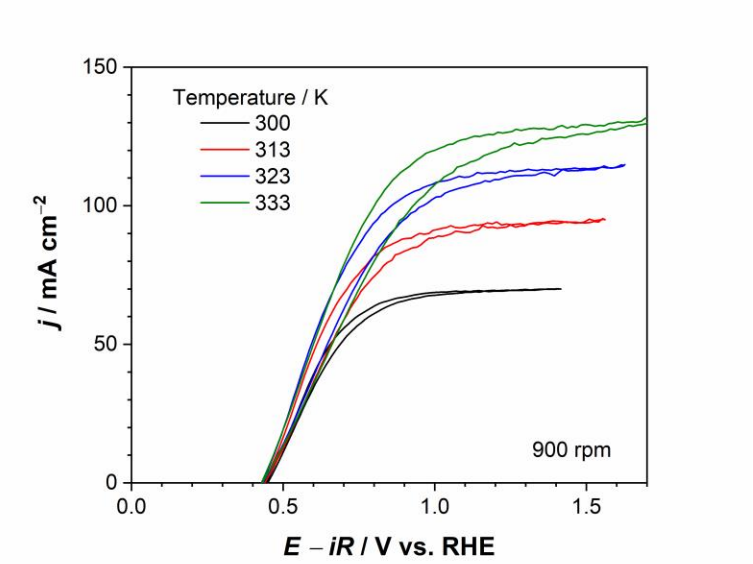

Figure S4. Cyclic voltammograms measured by a glassy carbon rotating disk electrode in the solution containing total 1.0 mol kg^{-1} Fe-HEDTA with 0.5 mol kg^{-1} malonate buffer at different temperatures. Redox solutions have 50% of reduced species and 50% oxidized species. (50 mV s^{-1}, 900 rpm).

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