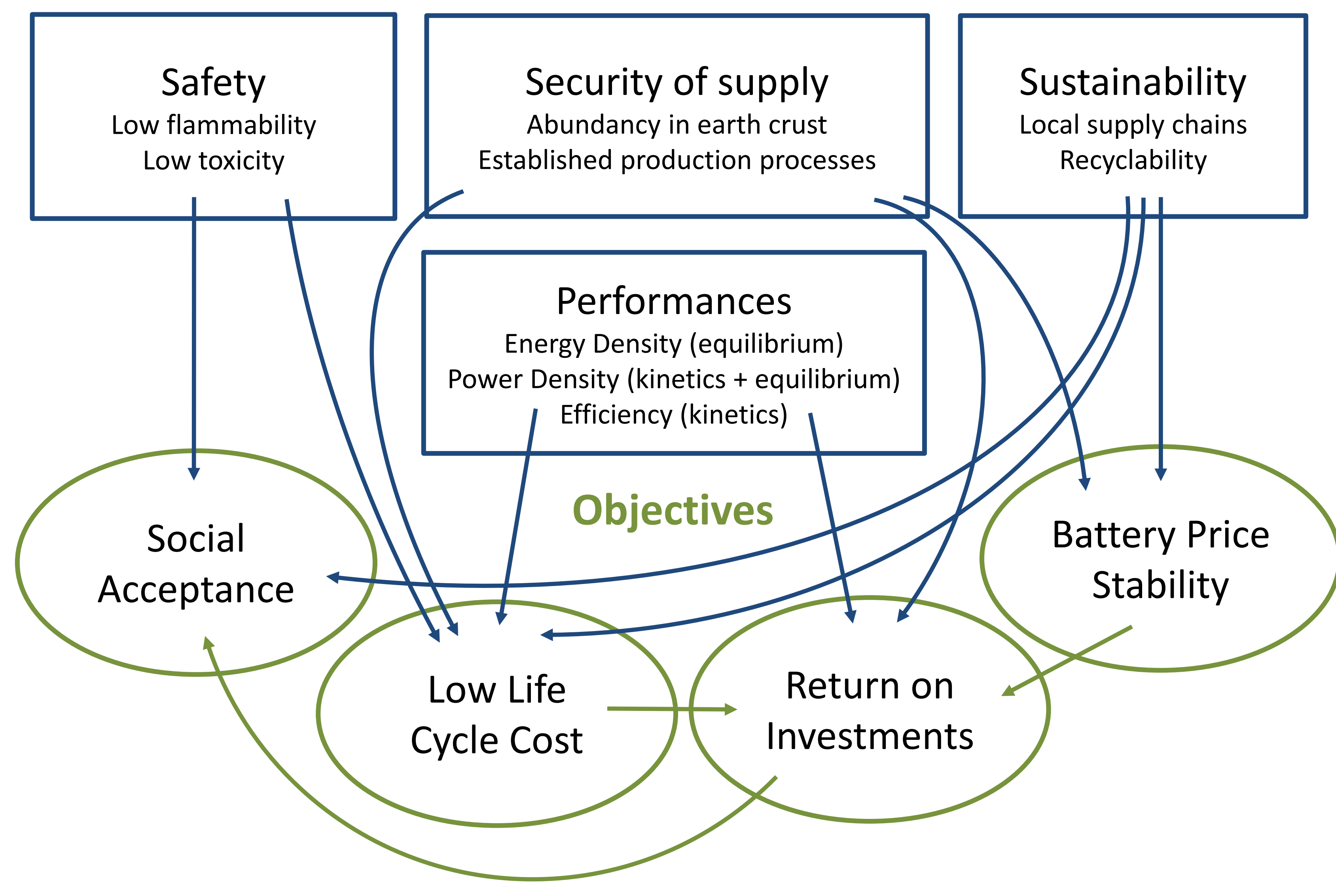


Mattia Duranti ^(1,*), William Gomes De Moraes ⁽¹⁾, Emanuele Maria Groiss ^(1,2), Edoardo Gino Macchi ⁽¹⁾

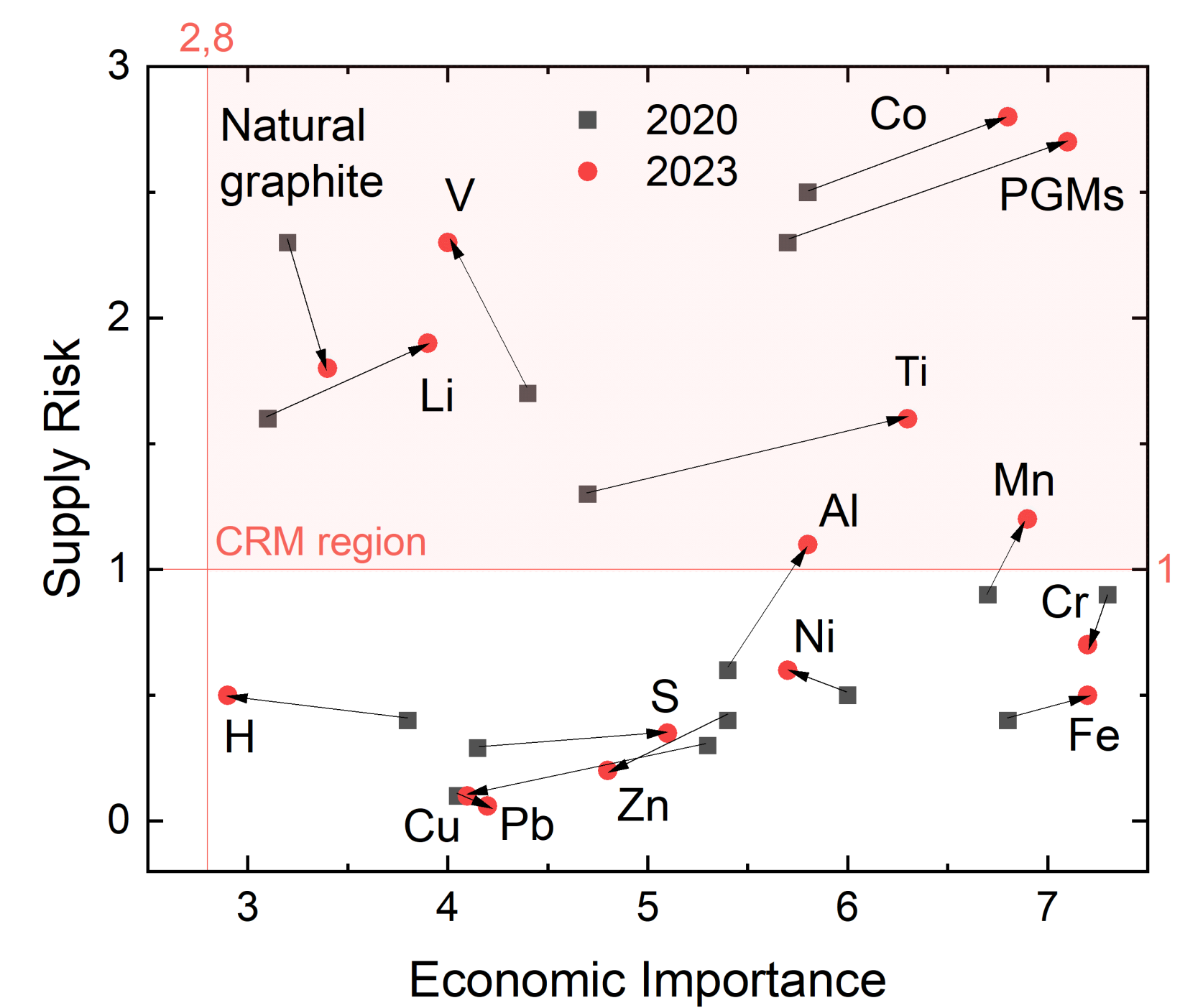
⁽¹⁾ Center for Sustainable Energy, Fondazione Bruno Kessler, Via Sommarive 18, 38123 Trento
⁽²⁾ Industrial Engineering Department, University of Trento, Via Sommarive 9, 38123 Trento

Electrolytes for Next-generation Redox Flow Batteries

Requisites



EU report on Critical Raw Materials

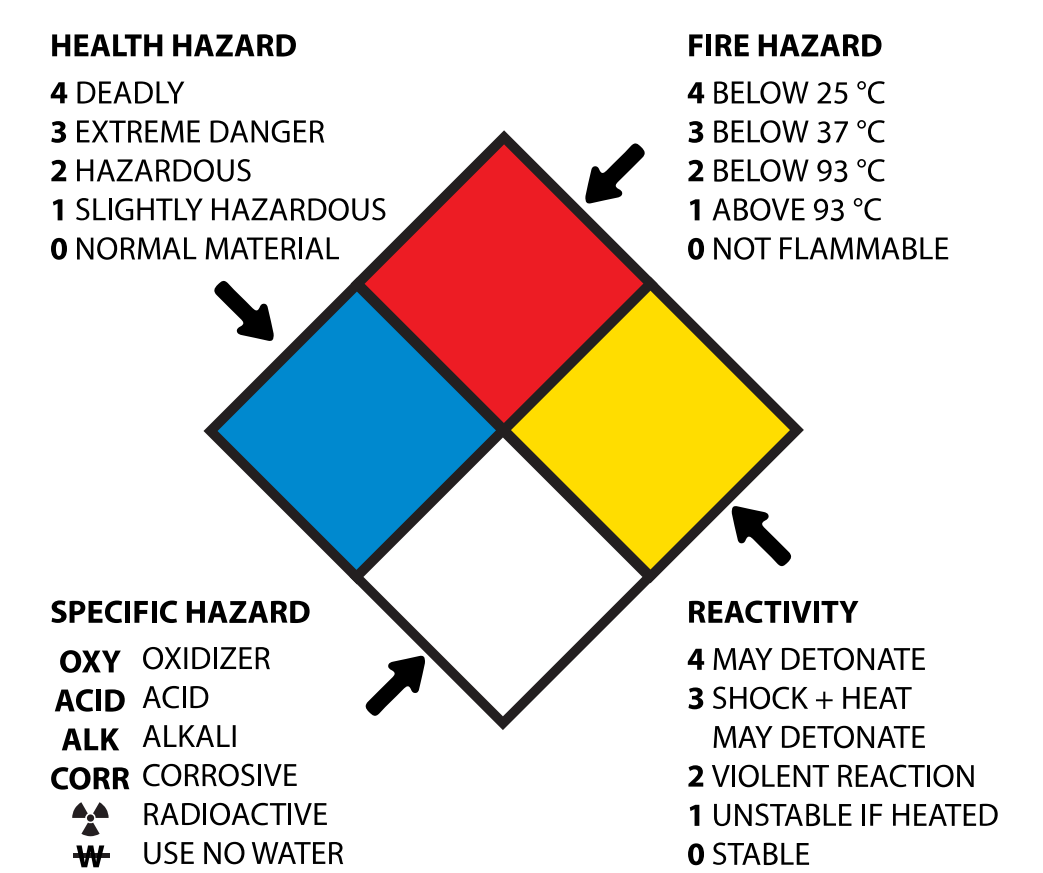


Transition Metals

Cycling stability → Poor/Good
Energy density → Good
Solubility → Poor/Good
Production processes → Established

Organic

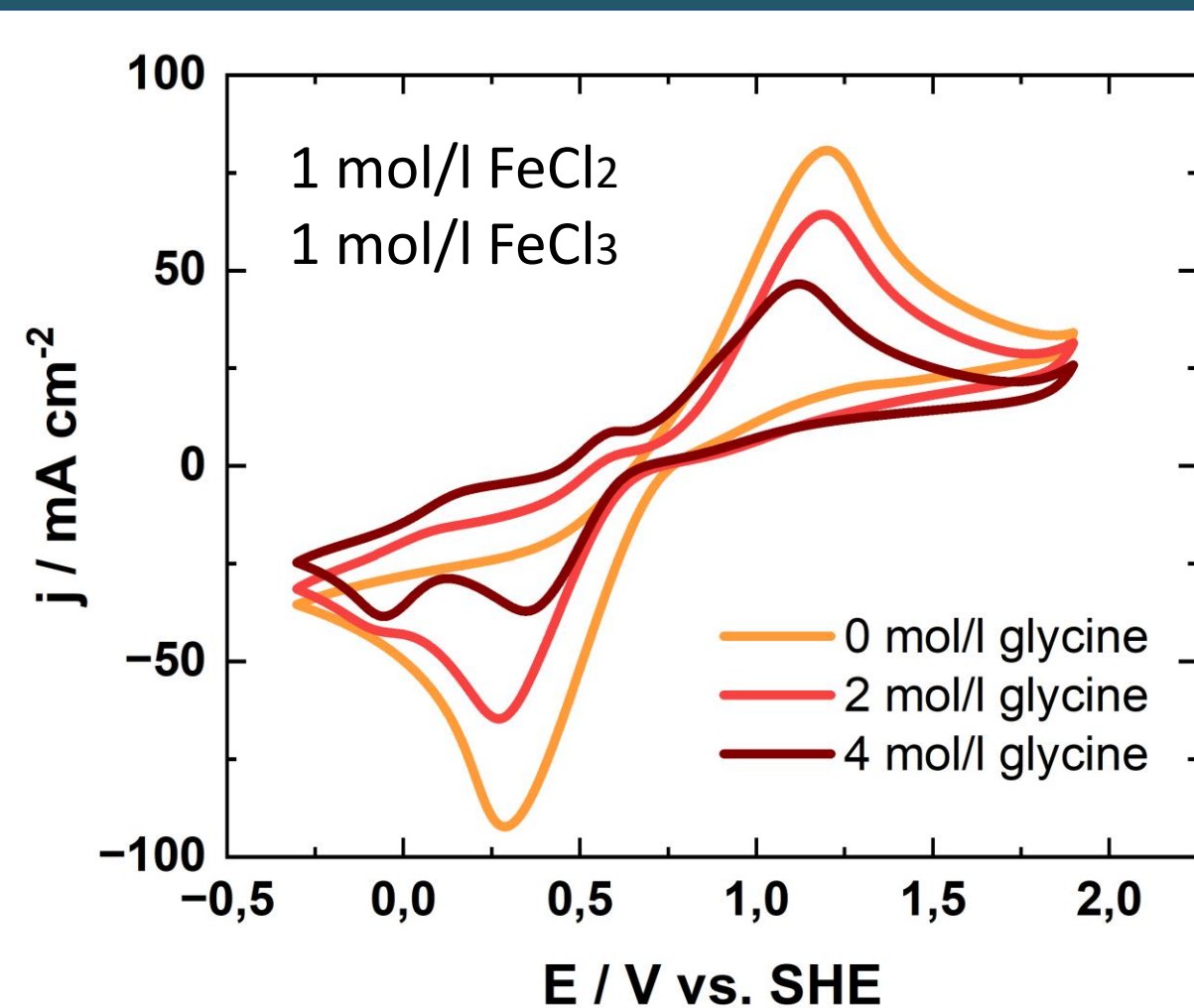
Cycling stability → Poor
Energy density → Low
Solubility → Poor/Good
Production processes → Expensive



Transition Metals for Redox flow batteries

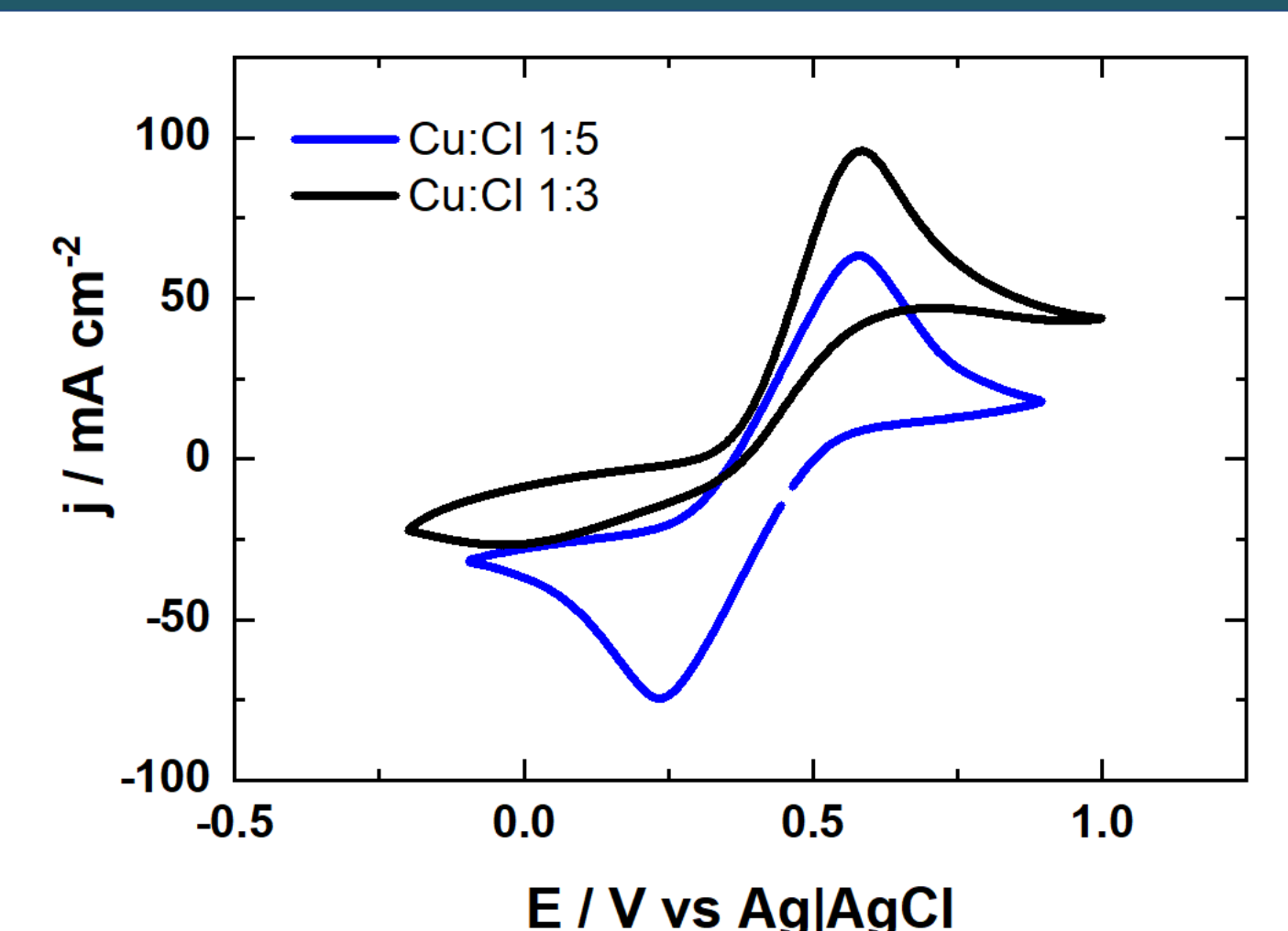
Oxidation reaction	E_0 / E_{eq} vs SHE	Possible additives	Supporting	Membranes	Problems	K_p at GC (cm/s)	Diffusion Coefficient M (cm ² /s)	Diffusion Coefficient M ⁿ (cm ² /s)	Practical concentration of active ions (total molarity)	Conductivity (mS/cm)	Viscosity (mm ² /s)	pH	Azardousness (NFPA 704)	Metal Supply Risk (EU)	Economic importance (EU)	EU 2023 CRM report	References
Zn (s) ↔ Zn ²⁺ + 2 e ⁻	-0.762 V	DMSO, metallic (Pb+, Cr+, etc.), polymeric (PEG, PEO, etc.)	HCl, HBr, H ₂ SO ₄ , KOH	CEM, Daramic, PBI, porous polyolefine/PEG composite	Dendrites, HER, SEI formation	n.a. good kinetics	-	~ 1.5E-6	~ 1-3 M	~ 50-500	~ 0.5-4	acid / neutral / alkaline	3 0 0	0.2	4.8	-	Ashok et al. 2024, Wang et al. 2021
Fe (s) ↔ Fe ²⁺ + 2 e ⁻	-0.44 V	Bi (HER)	H ₂ SO ₄ , HCl, HCN, KOH	AEM, co-polymeric membrane	Hydrolysis, Fe oxides precipitation at non-acidic pH	n.a. good kinetics	-	~ 2.5E-6	~ 2 M	~ 200	~ 0.5-5*	acid / alkaline	3 0 0	0.5	7.2	-	Hawth. et al. 2014, Belon. et al. 2023
Cr ²⁺ ↔ Cr ³⁺ + e ⁻	-0.410 V (eq. down to -0.50 V)	Bi+3 (HER), EDTA, PDTA, LICI	HCl ~3M	CEM, microporous	HER, electrolytes imbalance	~ 2.5E-3	~ 6E-6	~ 6E-6	~ 1M	~ 550	0.85	Acid (pH=9 with PDTA)	3 0 0	0.7	7.2	-	Wang et al. 2020, Kocigit et al. 2021
V ²⁺ ↔ V ³⁺ + e ⁻	-0.255 V	-	H ₂ SO ₄ , HCl, HBr	CEM, nanofiltration	Oxidation of V(II) to V(III), Sulphates precipitation at T<10°C, need for catalyist	~ 1.4E-4 (1E-3 in CP)	~ 7E-8	~ 1E-6	~ 1.5 M	~ 230	~ 5	Acid	3 0 0	2.3	3.9	CRM/SRM	Lour. et al. 2019, Wu et al. 2011
Ti ³⁺ ↔ TiO ²⁺ + e ⁻	0.100 V	Sulfonic acid (HER) + Bi ₂ (SO ₄) ₃ catalyis	H ₂ SO ₄ , HCl, HNO ₃ , H ₃ PO ₄	CEM, SPEEK	Hydrolysis, HER, precipitation of TiO ₂ at high pH	~ 2.0E-5	~ 4E-9	~ 4E-9	~ 1.0 M	n.a.	2.5-4.0	Acid (pH<1.5)	4 0 0	0.5	5.4	-	Ahmed et al. 2022, Quiao te al. 2022
Cu ²⁺ ↔ Cu ²⁺ + e ⁻	0.161 V	Bi ₂ O ₃ catalyis	CaCl ₂ , HCl	AEM (FAP-330, AR-118), CEM (FS-990), Porous (Daramic-CL, Amersil S10)	Cu+ instable, disproportionation	n.a.	~ 4E-6	~ 4E-6	~ 2-3 M	~ 200*	~ 1.9*	pH ~ 0	3 0 1	0.1	4	SRM	Ashok et al. 2024, Lac. et al. 2021
Cu (s) ↔ Cu ²⁺ + 2 e ⁻	0.337 V	Bi ₂ O ₃ catalyis	CaCl ₂ , HCl	AEM (FAP-330, AR-118), CEM (FS-990), Porous (Daramic-CL, Amersil S10)	Unstable copper deposition or uneven copper stripping	n.a. good kinetics	-	~ 8E-6	~ 2-3 M	~ 200*	~ 1.9*	pH ~ 0	2 0 1	0.1	4	SRM	Ashok et al. 2024, Lac. et al. 2021
V ³⁺ ↔ VO ²⁺ + e ⁻	0.337 V	-	H ₂ SO ₄ , HCl	CEM, nanofiltration	Sulphates precipitation at t<20°C	-	~ 1E-7	~ 3E-7	~ 1.5 M	~ 230	~ 5	Acid	2 0 0	2.3	3.9	CRM/SRM	Lour. et al. 2019, Xiao et al. 2016
Cu (s) ↔ Cu ⁺ + e ⁻	0.518 V	Bi ₂ O ₃ catalyis	CaCl ₂ , HCl	AEM (FAP-330, AR-118), CEM (FS-990), Porous (Daramic-CL, Amersil S10)	Cu+ instable, disproportionation	~ 5E-4 (with Bi)	-	~ 4E-6	~ 1-2M	~ 300*	~ 1.3*	Acid	3 0 1	0.1	4	SRM	Ashok et al. 2024, Lac. et al. 2021
Fe ²⁺ ↔ Fe ³⁺ + e ⁻	0.770 V	BMImCl, Glycine, DMSO, DTPA, Malic acid, Malonic acid, choline chloride	H ₂ SO ₄ , HCl, HCN, KOH	Microporous separator, CEM (Nafion, Fumasep)	Hydrolysis, Fe oxides precipitation at low pH	~ 1E-3 (up 8.6E-2 if TT)	~ 2.5E-6	~ 2.5E-6	~ 2 M (1.3 with DTPA)	~ 200*	~ 3-5*	Acid	3 0 0	0.5	7.2	-	Wang et al., 2020, Hawth. et al. 2014
VO ²⁺ ↔ VO ₂ ⁺ + e ⁻	1.000 V	-	H ₂ SO ₄ ~ 4.2 M (> 2M)	CEM, nanofiltration	V(V) oxide precipitation at T>40°C	~ 7.5E-4 (1E-3 in CP)	~ 3E-7	~ 1E-6	~ 1.5 M	~ 330	~ 5	Acid	4 0 0	2.3	3.9	CRM/SRM	Lour. et al. 2019, Wu et al. 2011
Mn ²⁺ ↔ MnO ₂ + 2 e ⁻	1.230 V	Glycine, Acetic acid	H ₂ SO ₄ , HCl	Perfluorosulfonic Acid	OER, CIER, MnO ₂ insoluble (possible use as powder suspension)	n.a.	~ 2E-7	-	~ 2 M*	~ 150*	~ 2*	Acid	2 1 2	1.2	6.9	CRM/SRM	Liu et al. 2023, Xue et al. 2008
Ce ³⁺ ↔ Ce ⁴⁺ + e ⁻	1.610 V (eq. up to 1.920 V)	EDTA, DTPA, Sulfosalicylic acid, Phthalic anhydride	H ₂ SO ₄ , CH ₃ SO ₃ H, HNO ₃	CEM	OER, precipitation at T>40°C	~ 3E-4	~ 6E-6	~ 6E-6	~ 1 M	~ 150	n.a.	Acid	2 0 1	4.0	4.9	Rare earth (available in EU)	Xie, et al. 2013, Kocigit et al. 2021
Mn ²⁺ ↔ Mn ³⁺ + e ⁻	1.560 V	EDTA, TiO ²⁺ , V ⁵⁺ , CH ₃ SO ₃ H	H ₂ SO ₄ , HCl	Perfluorosulfonic Acid	OER, CIER, Mn ³⁺ instable	~ 4E-8	~ 2E-7	n.a.	~ 2 M*	~ 150*	~ 2*	Acid	2 0 1	1.2	6.9	CRM/SRM	Naresh et al. 2023, Reyn. et al. 2020

Iron-based electrolyte



- Glycine prevents the precipitation of insoluble iron hydroxides in highly concentrated iron chloride sol.
- Too much Glycine is detrimental as it reduces the kinetics of the Fe(II)/Fe(III) couple and it decreases the OCV. The rich Gly-Fe chemistry causes the degeneration of the reduction peaks.
- 1 mol/l Glycine is found to be the optimal value to preserve the original bare iron properties preventing the precipitation of a solid phase.

Copper-based electrolyte



- At low chloride concentrations, the peak for the reduction of Cu(II) to Cu(I) cannot be clearly identified.
- This suggests that a direct transition from Cu(II) to Cu(0) is more favorable under these conditions.
- Effective stabilization of cuprous ions by chloro-complexes is observed to occur at a Cu:Cl ratio ≥ 1:5.