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Materie prime critiche e Urban Mining

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XVII Edizione, La Terra: un sistema in trasformazione
Hotel Perla del Golfo, Terrasini (Pa), 25-29 luglio 2023

Critical Raw Materials

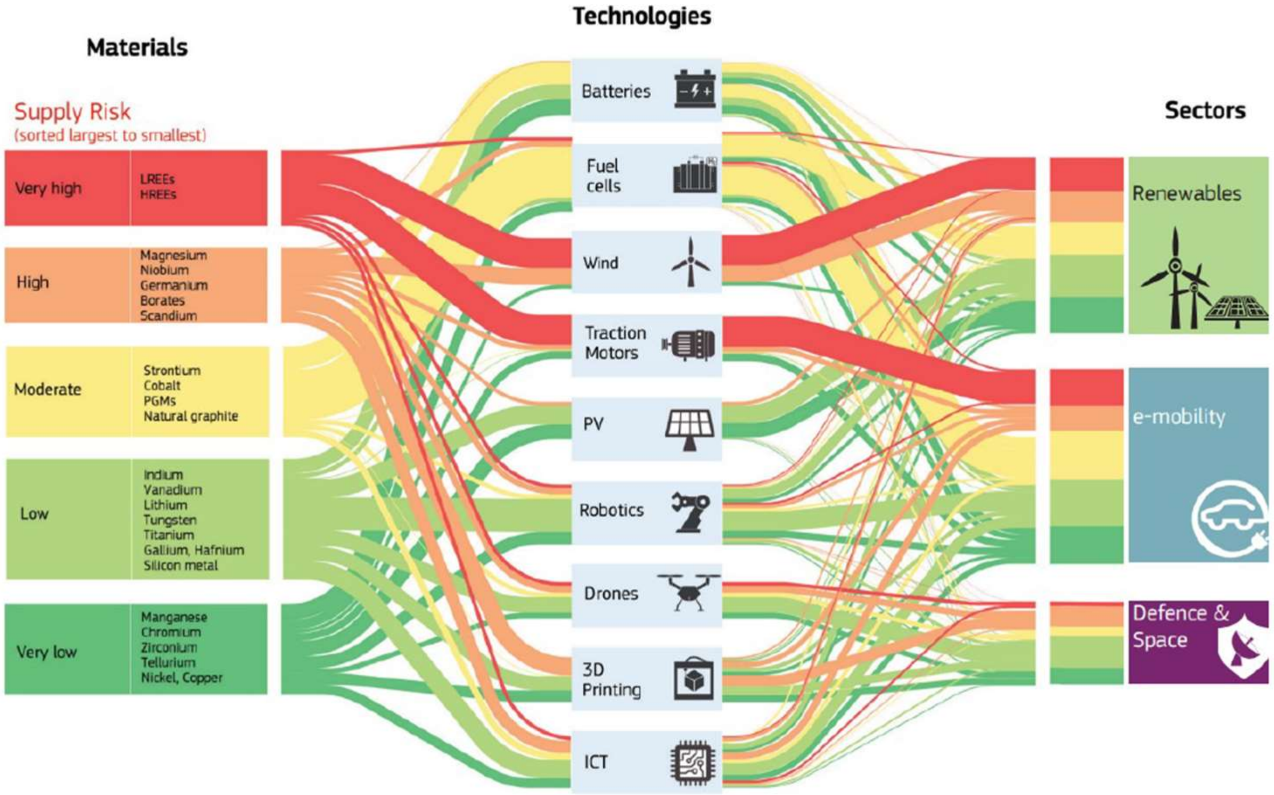
*“**CRMs** are considered to be those that have **high economic importance for the EU** (based on the value added of corresponding EU manufacturing sectors, corrected by a substitution index) **and a high supply risk** (based on supply concentration at global and EU levels weighted by a governance performance index, corrected by recycling and substitution parameters).“*

European Commission, Study on the Critical Raw Materials for the EU 2023 – Final Report

Critical Raw Materials

*"**CRMs** are considered to be those that have **high economic importance for the EU**…"*

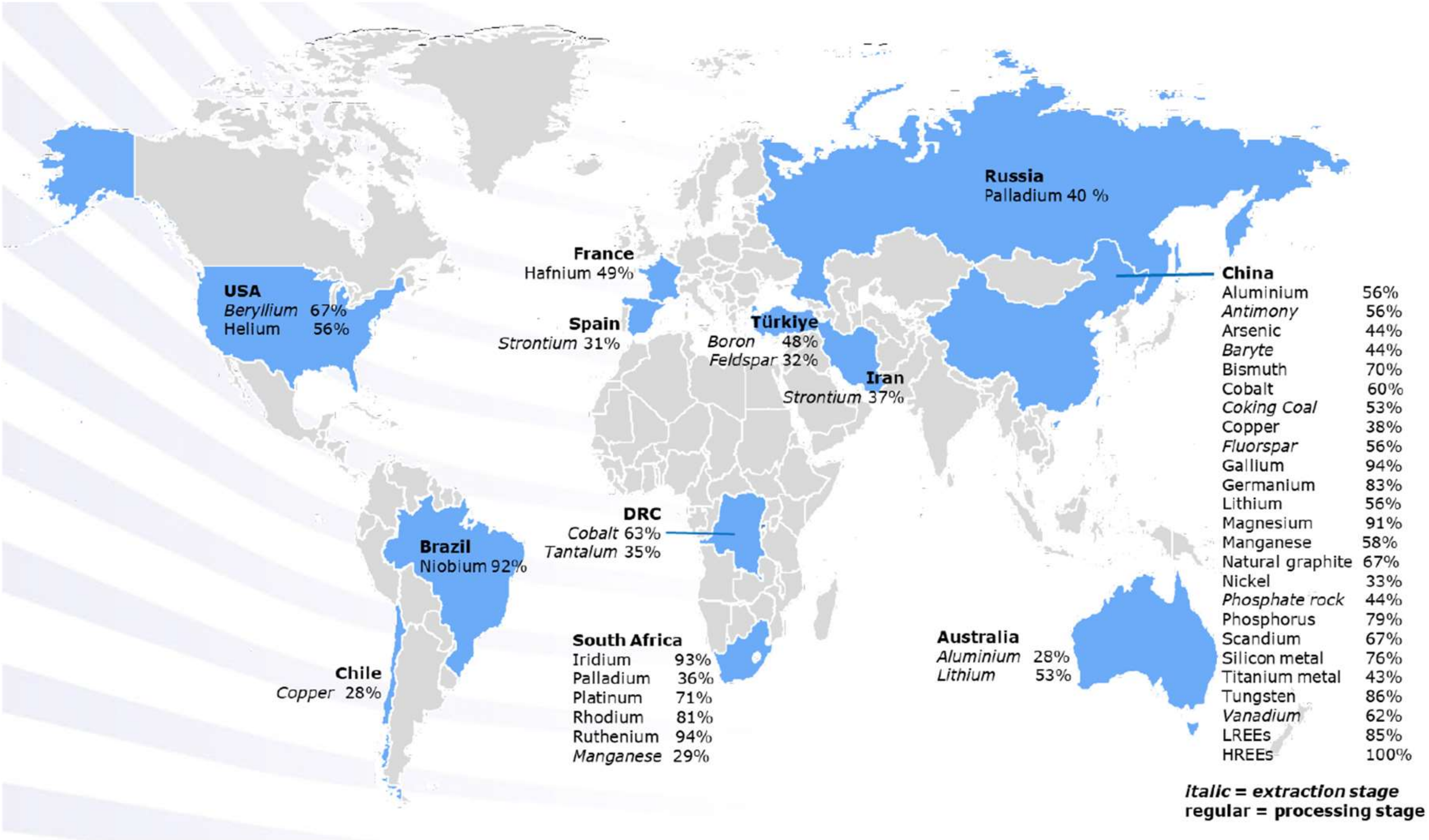
Figure 7 – Technologies and sectors competing for access to CRMs



Source: CRMs for Strategic Technologies and Sectors – A Foresight Study, Joint Research Centre, 2020.

Critical Raw Materials

*“**CRMs** are considered to be those that have **high supply risk**…”*



Critical Raw Materials

↓

Strategic Raw Materials

*"…the Act identifies a list of **strategic raw materials**, which are crucial to technologies important to Europe's green and digital ambitions and for defence and space applications, while being subject to potential supply risks in the future."*

European Critical Raw Materials Act, 2023

Critical Raw Materials

↓

Strategic Raw Materials

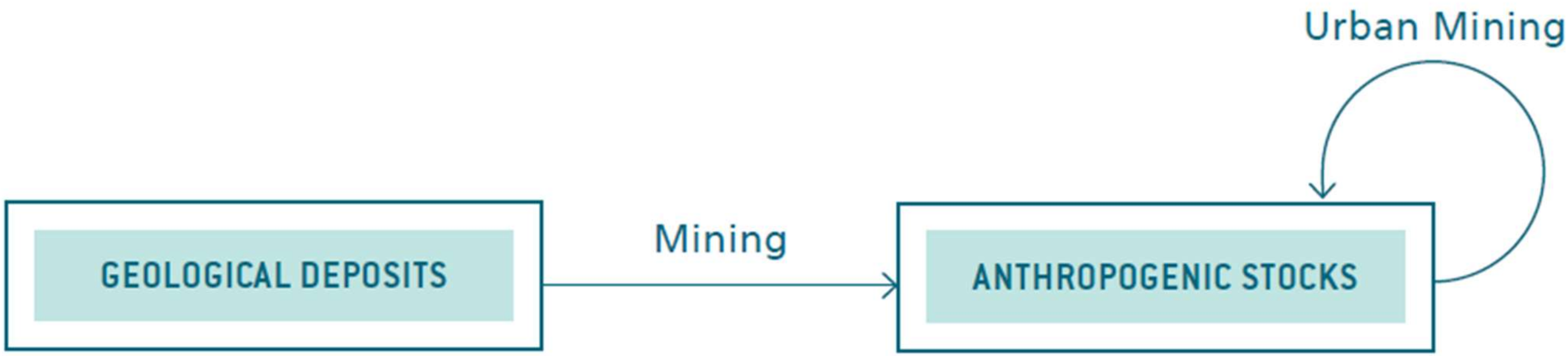
Table 1. Strategic and critical raw materials used in the technologies in scope.

Supply Risk	Raw material															
4.8	Gallium						•			•	•	•		•	•	•
4.1	Magnesium			•							•	•	•	•	•	•
4.0	REE (magnets)		•	•	•	•		•		•	•	•		•	•	•
3.8	Boron		•	•	•	•	•	•		•	•	•		•	•	•
2.7	PGM		•	•						•	•	•		•	•	•
1.9	Lithium	•								•		•		•	•	•
1.9	Bismuth									•	•	•				•
1.8	Germanium						•			•	•	•				•
1.8	Natural graphite	•	•	•					•	•		•		•	•	
1.7	Cobalt	•	•	•						•		•	•	•	•	•
1.6	Titanium metal											•	•	•	•	•
1.4	Silicon metal		•	•	•	•	•	•	•	•	•	•	•	•	•	•
1.2	Tungsten			•								•	•		•	•
1.2	Manganese	•	•	•	•			•	•	•	•	•	•	•	•	•
0.5	Nickel	•	•	•	•		•	•	•	•	•	•	•	•	•	•
0.1	Copper	•	•	•	•	•	•	•		•	•	•	•	•	•	•
5.3	HREE (rest)		•	•						•	•	•	•	•	•	•
4.4	Niobium			•	•					•			•		•	•
3.5	LREE (rest)		•	•						•		•		•	•	•
3.3	Phosphorus	•					•		•		•	•				•
2.6	Strontium		•	•						•		•				
2.4	Scandium			•							•		•			•
2.3	Vanadium		•	•					•	•			•	•	•	•
1.8	Antimony						•			•	•	•		•	•	•
1.8	Beryllium										•	•				•
1.6	Arsenic						•			•	•	•				•
1.5	Feldspar		•												•	
1.5	Hafnium										•		•		•	•
1.3	Baryte		•	•						•	•	•				•
1.3	Tantalum			•						•		•			•	•
1.2	Aluminium	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
1.2	Helium										•					•
1.1	Fluorspar	•					•	•		•		•		•	•	•
1.0	Phosphate rock									•						

Source: JRC analysis. Although it is a critical material, coking coal does not appear in the table as it is not used in any technology.

Urban Mining

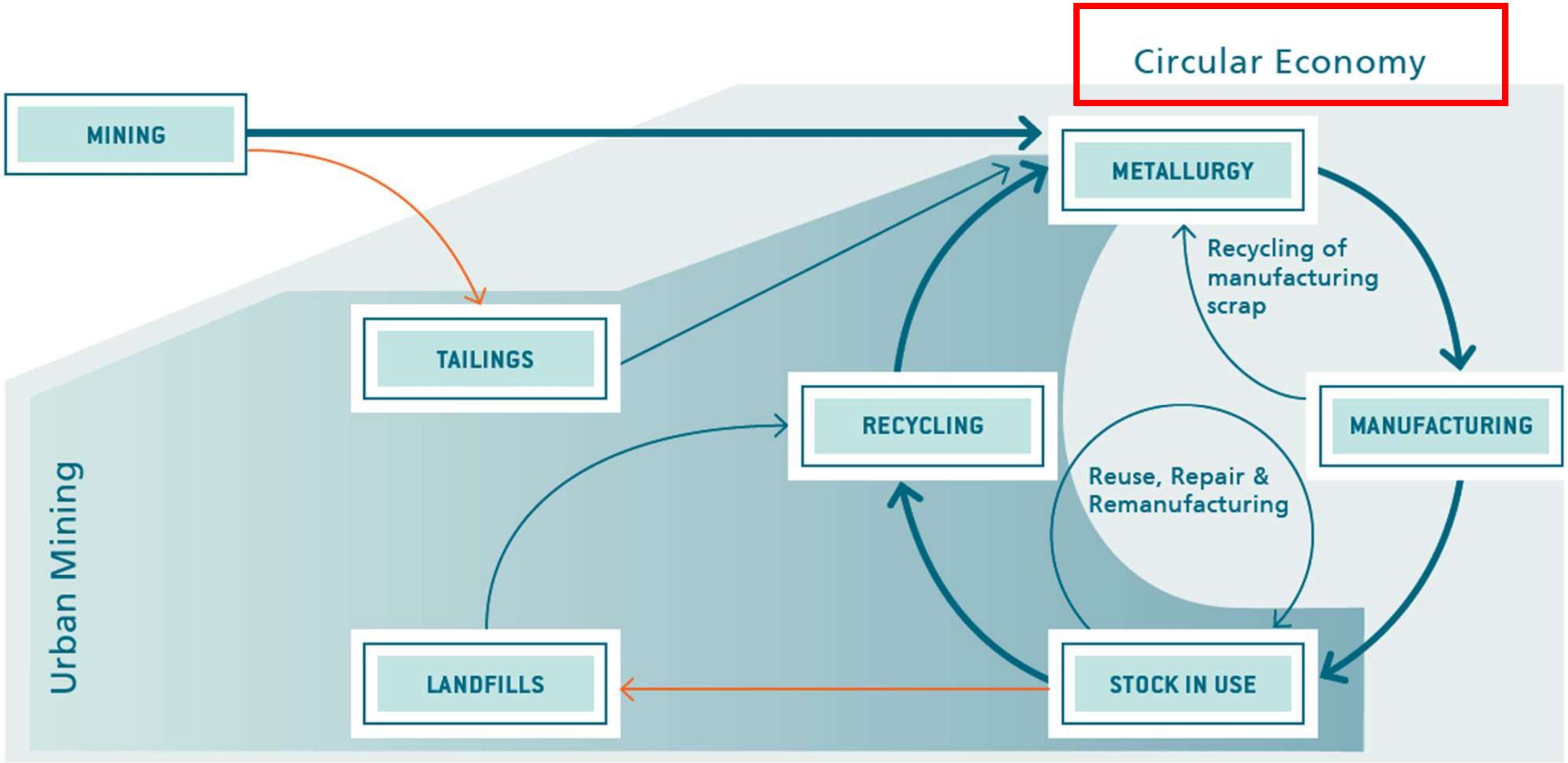
Urban Mining is the concept of using the materials present within the anthroposphere as a source for our raw material supply.



The potential of the Urban Mine – the anthropogenic stock – is the sum of all materials contained in products used or stored by society over a comparatively long time. This includes – among many others – buildings, electronic goods, waste and mine tailings.

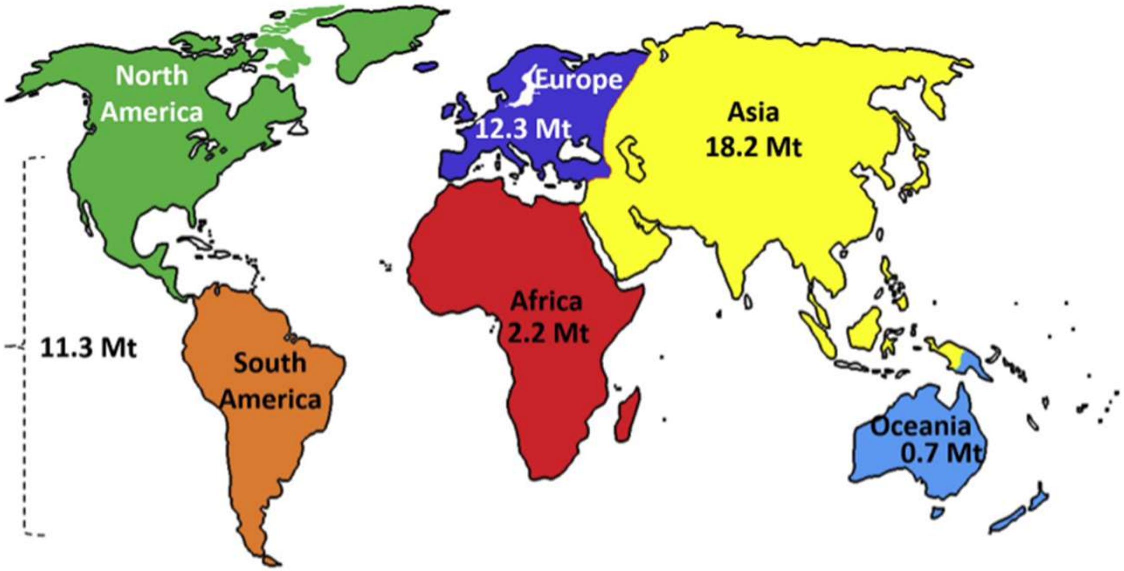
Urban Mining

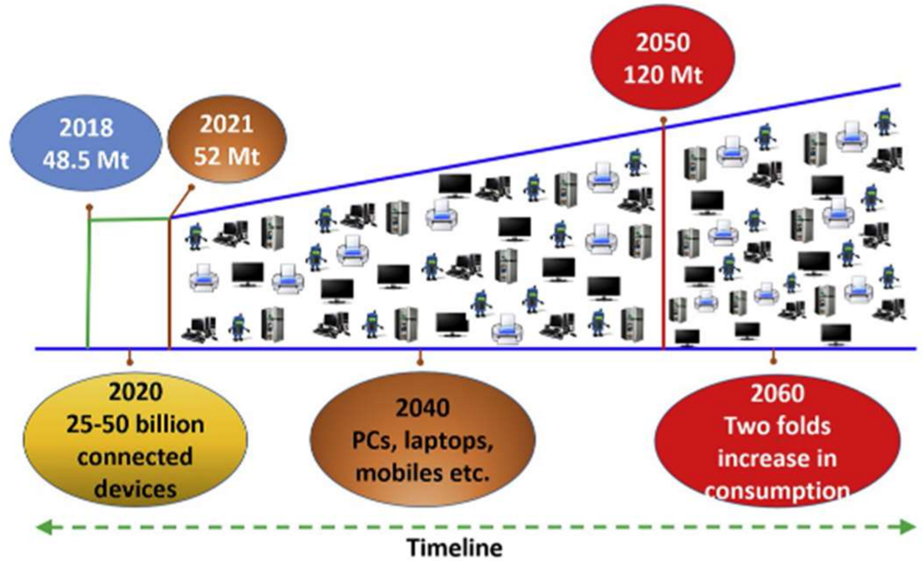
A more **Circular Economy** aims to keep the value of products and the materials they contain for as long as possible in the economy and to minimize waste generation



Urban Mining

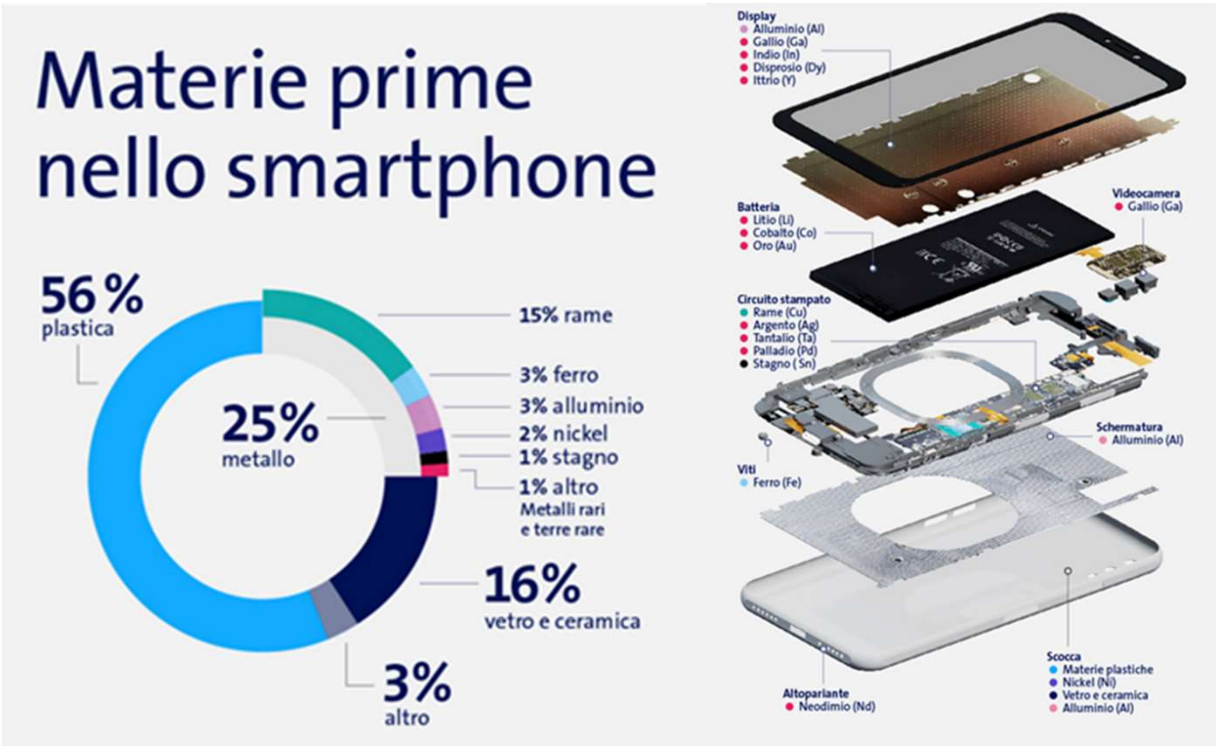
WEEE
(*RAEE: Rifiuti di Apparecchiature Elettriche e Elettroniche*)





Urban Mining

WEEE
(*RAEE: Rifiuti di Apparecchiature Elettriche e Elettroniche*)



Urban Mining

WEEE
(*RAEE: Rifiuti di Apparecchiature Elettriche e Elettroniche*)

Pyrometallurgical processes

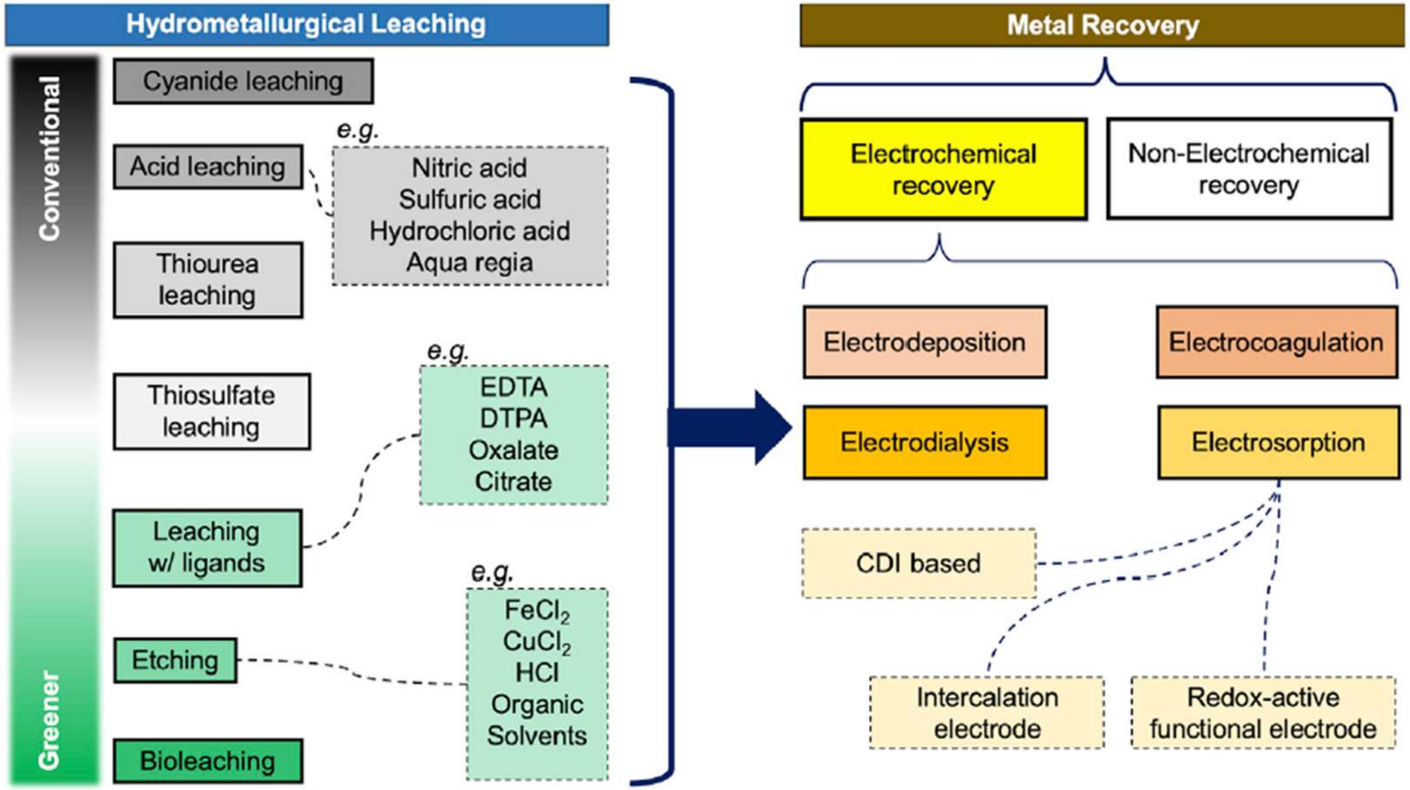
- ❑ Large energy input
- ❑ Environmental hazard
- ❑ Low selectivity
- ❑ High capital cost

Hydrometallurgical processes

- ❑ Aqueous environment
- ❑ Low temperature
- ❑ Cost effective
- ❑ Lower environmental impact

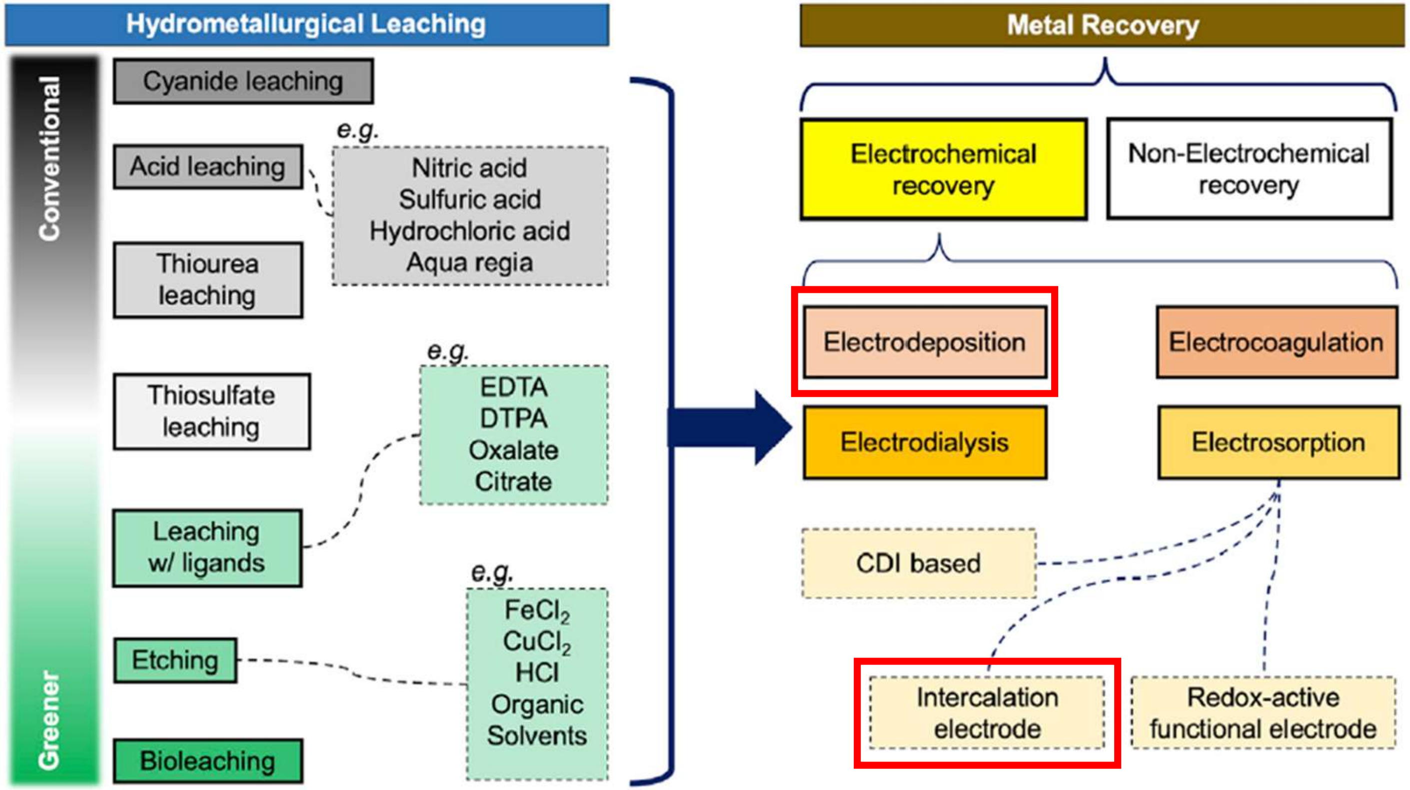
Urban Mining

Metal recovery from WEEE



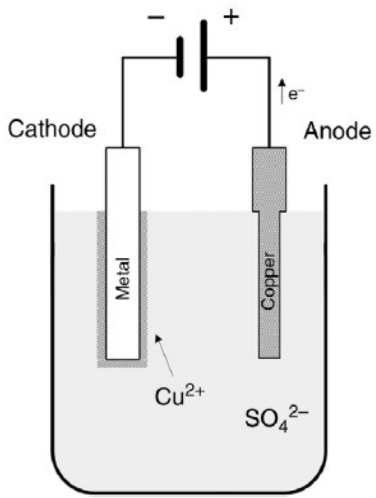
Urban Mining

Metal recovery from WEEE – Electrochemical processes



Urban Mining

Electrodeposition



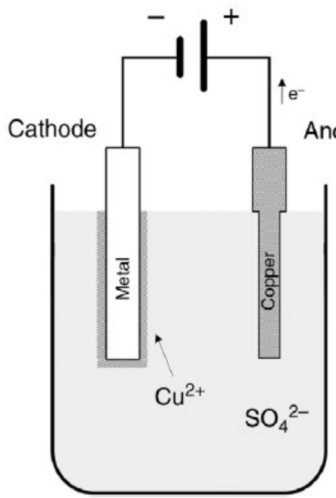
- The reduction and deposition of an electronically conductive species at the cathode of an electrochemical cell

- It's the shorten form of "electrolytic deposition"

- It's used for depositing metals on surfaces

Urban Mining

Electrodeposition



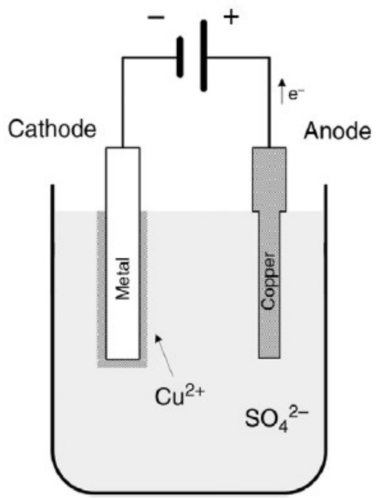
- **Electroplating** (electrochemical deposition of metals)

- **Electrowinning** (production of metals from ores by electrodeposition from a melt or a solution, e.g. Al production)

- **Electrorefining** (purify rather than recover a metal, e.g. Cu, Ni, Co, Sn)

Urban Mining

Electrodeposition

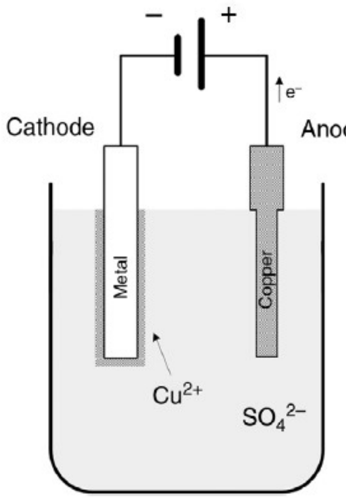


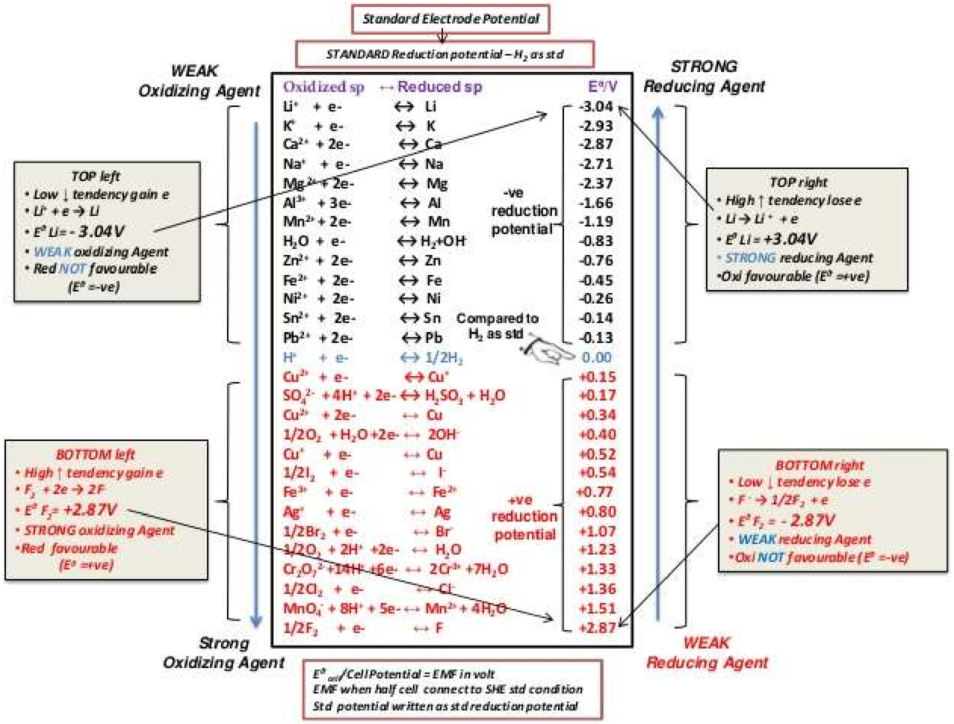
C) $M^{x+} + xe^- \rightarrow M$ Metal ions **reduction**

A) $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$ Water **oxidation** (OER)

Urban Mining

Electrodeposition





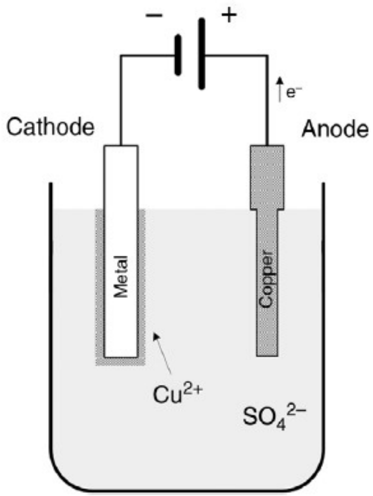
Standard Electrode Potentials series

C) $M^{x+} + xe^- \rightarrow M$ — Metal ions **reduction**

A) $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$ — Water **oxidation** (OER)

Urban Mining

Electrodeposition



Non Standard Conditions – Equilibrium Potential

$\nu M \rightarrow \psi M^{z+} + ze^-$

Standard potential
E° vs SHE

$$E_{eq} = E° + RT/zF \ln([Ox]^{\psi}/[Red]^{\nu})$$

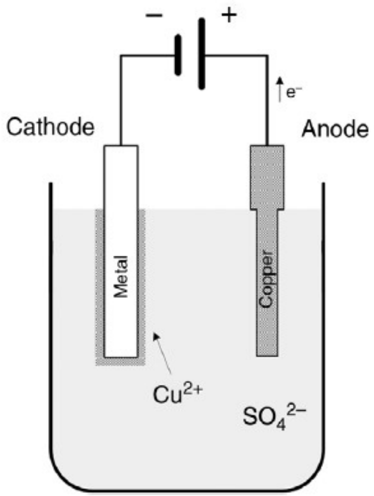
Nernst Equation

C) $M^{x+} + xe^- \rightarrow M$ — Metal ions **reduction**

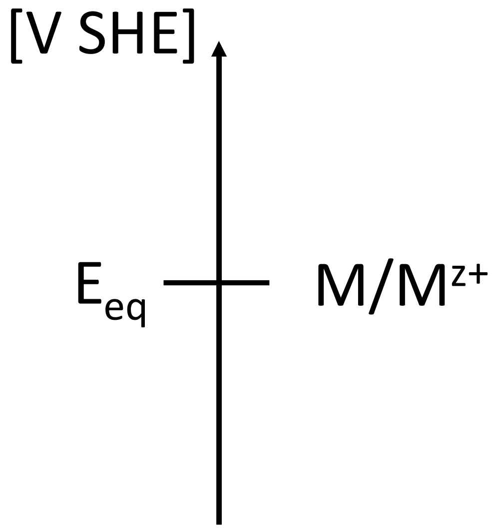
A) $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$ — Water **oxidation** (OER)

Urban Mining

Electrodeposition



equilibrium $M \leftrightarrow M^{z+} + ze^-$



$$\eta = E_{(i \neq 0)} - E_{eq}$$ **Overpotential**

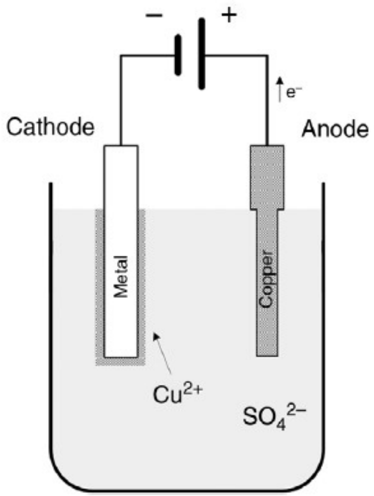
$(E_{eq} \rightarrow i = 0)$

C) $M^{x+} + xe^- \rightarrow M$ Metal ions **reduction**

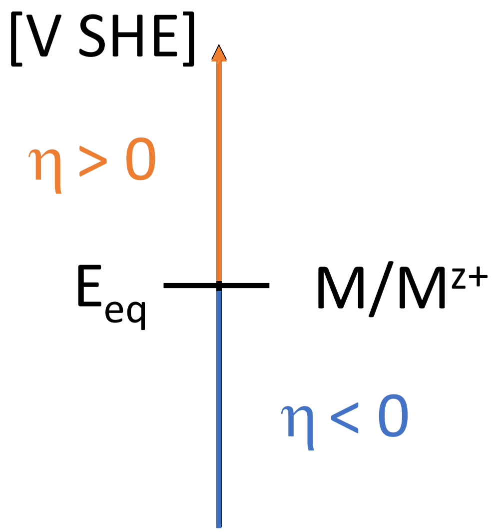
A) $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$ Water **oxidation** (OER)

Urban Mining

Electrodeposition



equilibrium $M \leftrightarrow M^{z+} + ze^-$



$$\eta = E_{(i \neq 0)} - E_{eq}$$

Overpotential

$(E_{eq} \rightarrow i = 0)$

$\eta > 0$ Anodic polarization

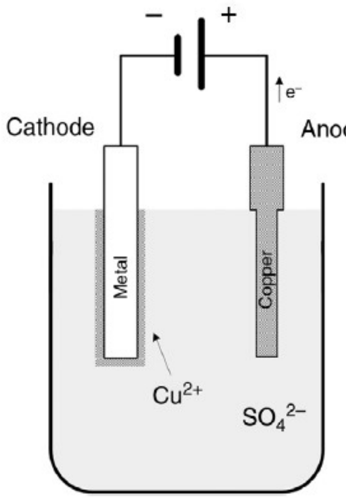
$\eta < 0$ Cathodic polarization

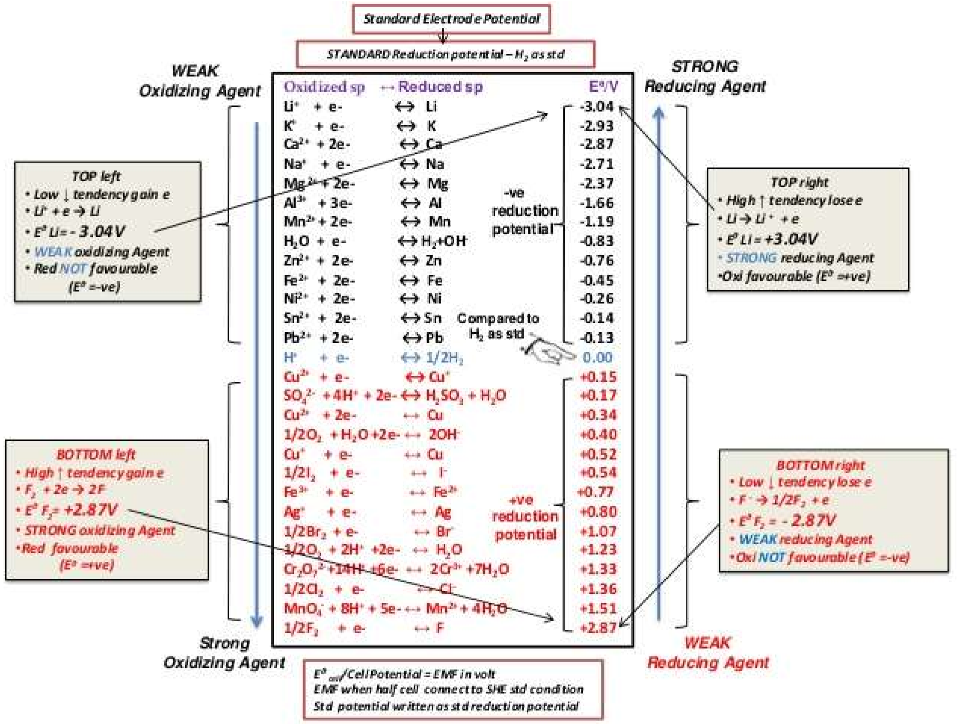
C) $M^{x+} + xe^- \rightarrow M$ Metal ions **reduction**

A) $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$ Water **oxidation** (OER)

Urban Mining

Electrodeposition





Standard Electrode Potentials series

C) $M^{x+} + xe^- \rightarrow M$ — Metal ions **reduction**

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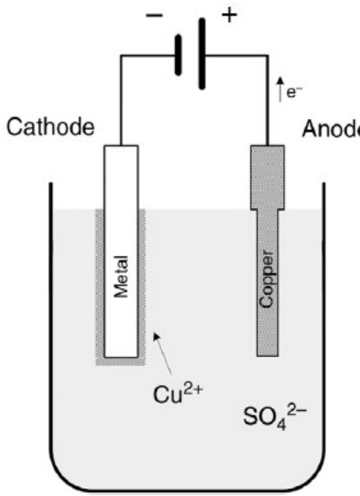
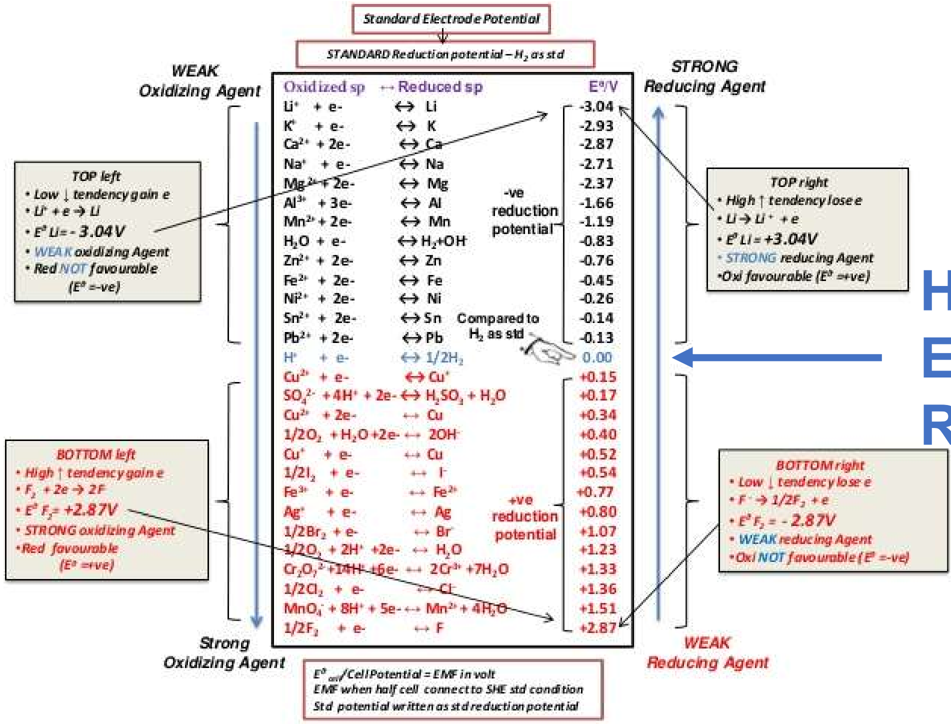
Urban Mining

Electrodeposition





Standard Electrode Potentials series

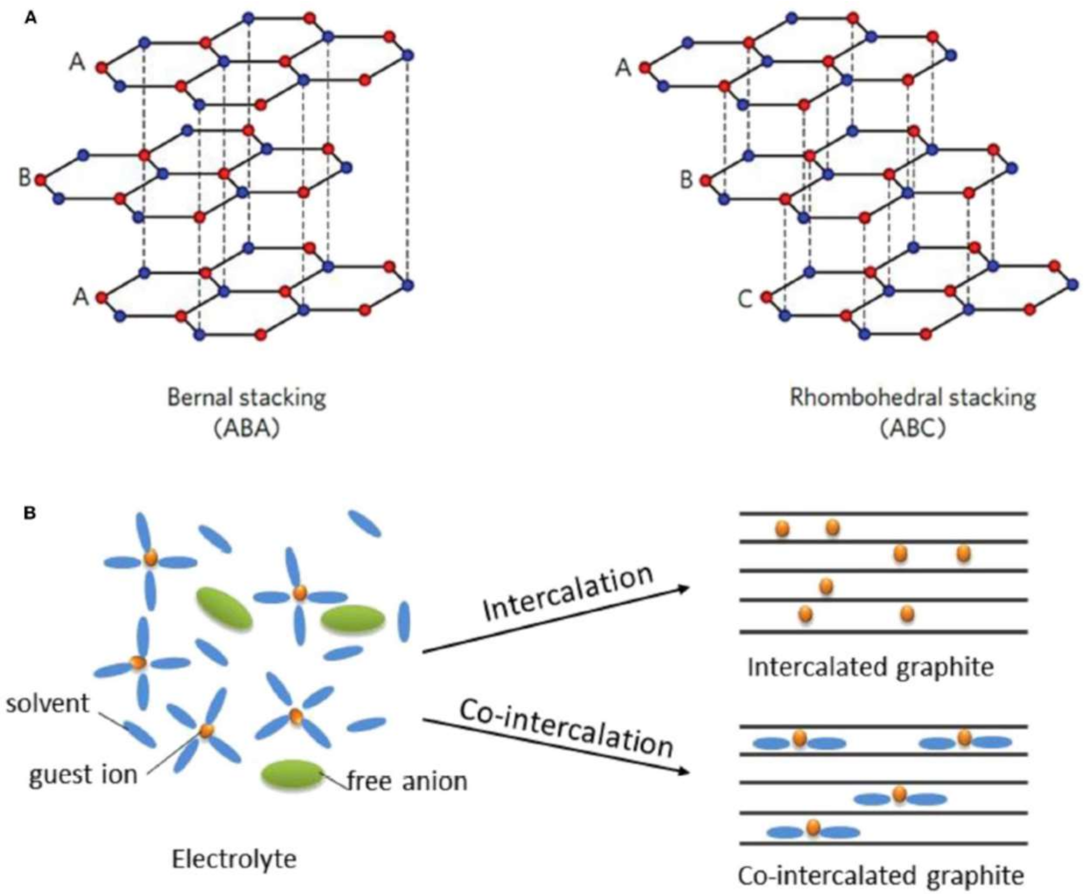
Hydrogen Evolution Reaction (HER)

C) $M^{x+} + xe^{-} \rightarrow M$ Metal ions **reduction**

A) $H_2O \rightarrow 1/2O_2 + 2H^{+} + 2e^{-}$ Water **oxidation** (OER)

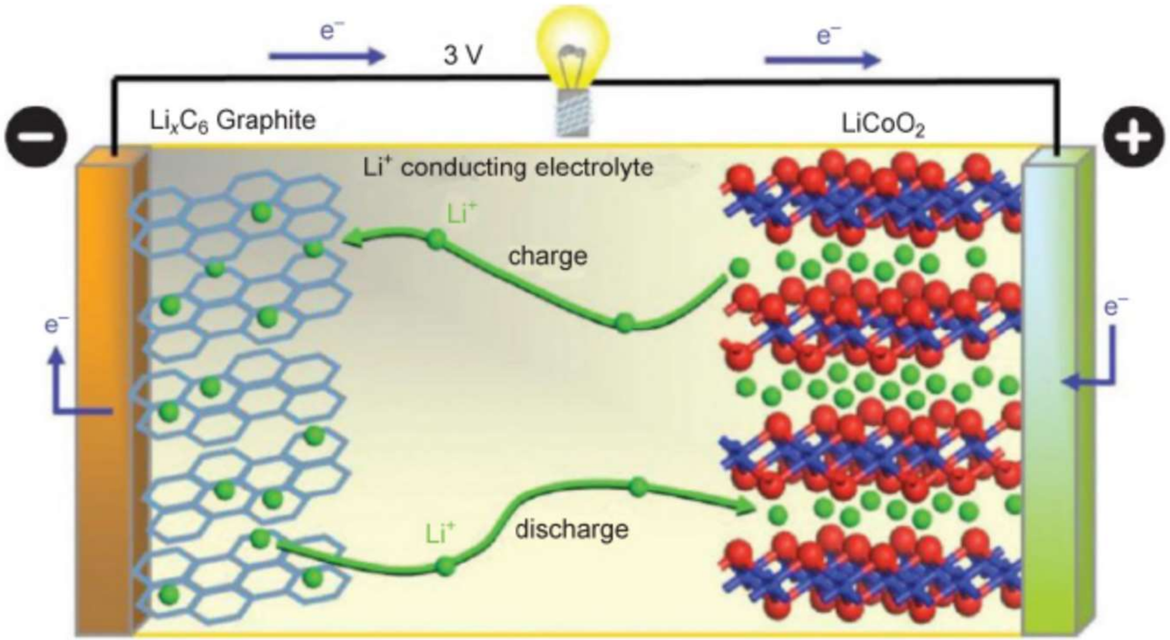
Urban Mining

Intercalation electrode



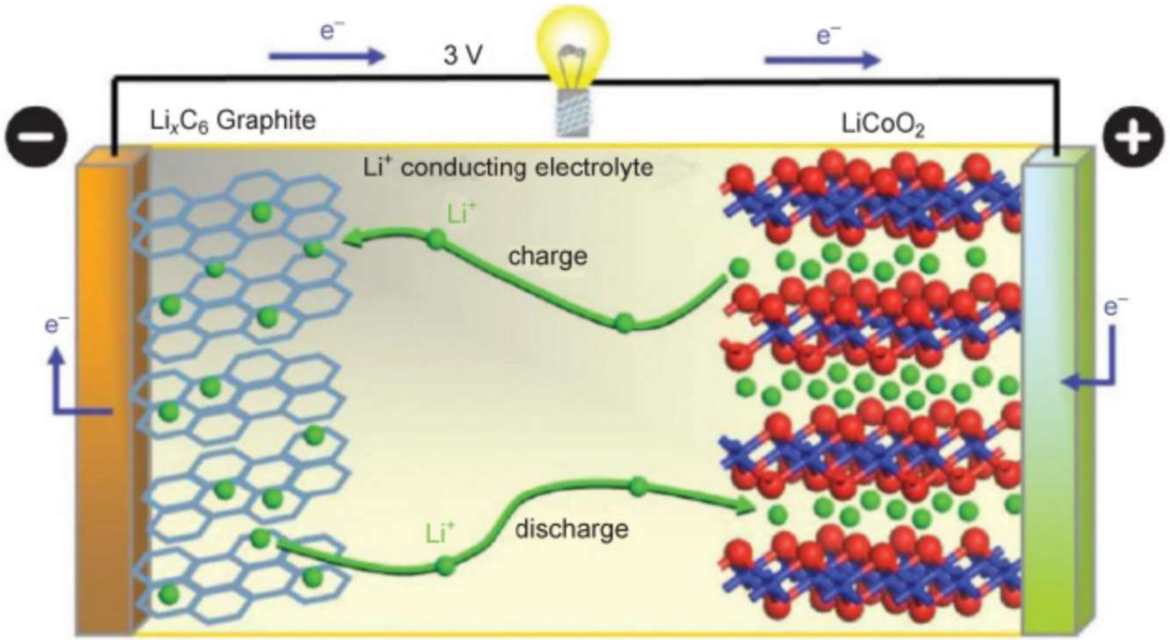
Urban Mining

Intercalation electrode – Li recovery



Urban Mining

Intercalation electrode – Li recovery



$$x\mathrm{Li}^+ + \mathrm{A}_z\mathrm{B}_y(\mathrm{s}) + x\mathrm{e} \rightleftharpoons \mathrm{Li}_x\mathrm{A}_z\mathrm{B}_y(\mathrm{s})$$

Urban Mining

Intercalation electrode – Li recovery

$$xLi^{+} + A_zB_y(s) + xe \rightleftharpoons Li_xA_zB_y(s)$$

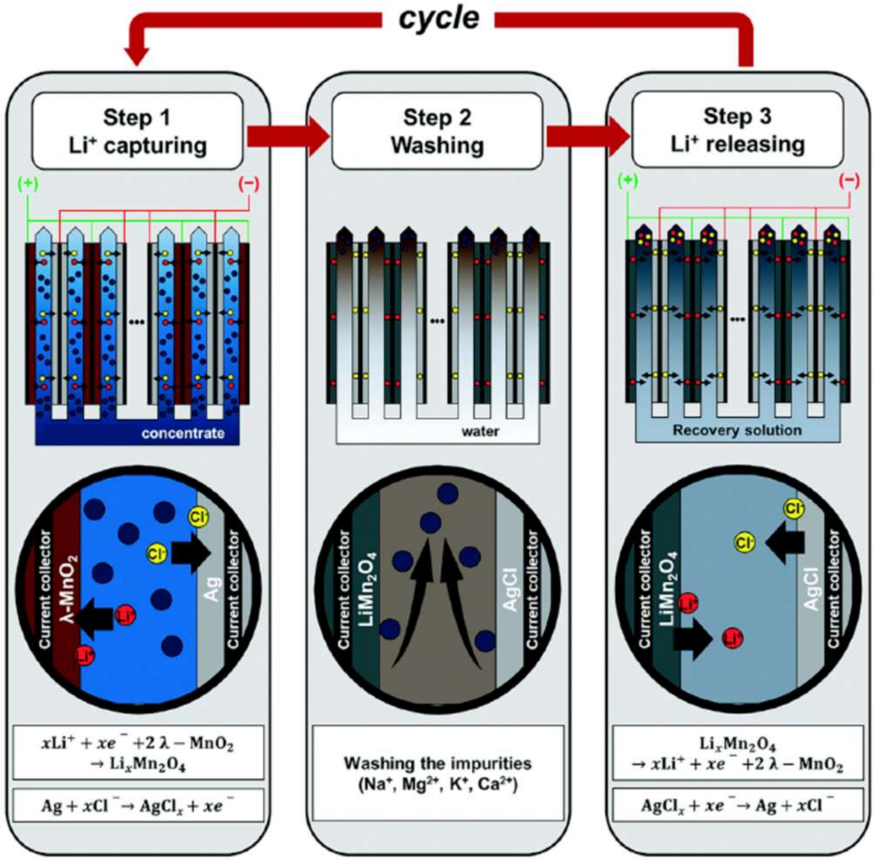
TABLE 1

Characteristics of representative intercalation cathode compounds; crystal structure, theoretical/experimental/commercial gravimetric and volumetric capacities, average potentials, and level of development.

Crystal structure	Compound	Specific capacity ($mAh\ g^{-1}$) (theoretical/experimental/typical in commercial cells)	Volumetric capacity ($mAh\ cm^{-3}$) (theoretical/typical in commercial cells)	Average voltage (V) [34]	Level of development
Layered	$LiTiS_2$	225/210 [35]	697	1.9	Commercialized
	$LiCoO_2$	274/148 [36]/145	1363/550	3.8	Commercialized
	$LiNiO_2$	275/150 [37]	1280	3.8	Research
	$LiMnO_2$	285/140 [38]	1148	3.3	Research
	$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$	280/160 [32]/170	1333/600	3.7	Commercialized
	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	279/199 [33]/200	1284/700	3.7	Commercialized
	Li_2MnO_3	458/180 [39]	1708	3.8	Research
Spinel	$LiMn_2O_4$	148/120 [40]	596	4.1	Commercialized
	$LiCo_2O_4$	142/84 [41]	704	4.0	Research
Olivine	$LiFePO_4$	170/165 [42]	589	3.4	Commercialized
	$LiMnPO_4$	171/168 [43]	567	3.8	Research
	$LiCoPO_4$	167/125 [44]	510	4.2	Research
Tavorite	$LiFeSO_4F$	151/120 [30]	487	3.7	Research
	$LiVPO_4F$	156/129 [45]	484	4.2	Research

Urban Mining

Intercalation electrode – Li recovery



Summary

- Critical Raw Materials
- Strategic Raw Materials
- Urban Mining: what and how in a circular economy system
- Metals recovery from WEEE
- **Electrodeposition**
- **Intercalation electrodes**

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