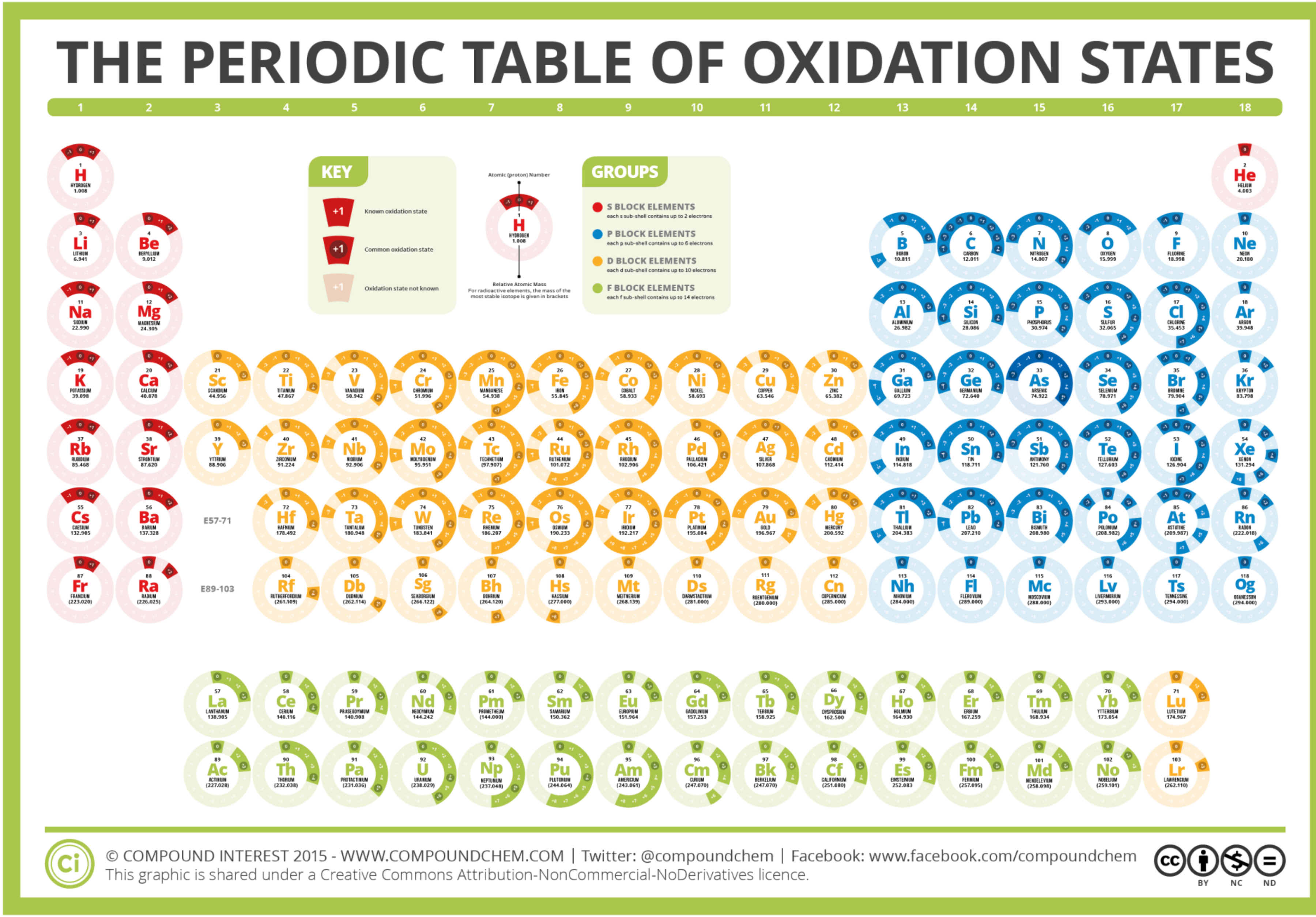
2 – Pourbaix diagrams

What materials can be electrodeposited?



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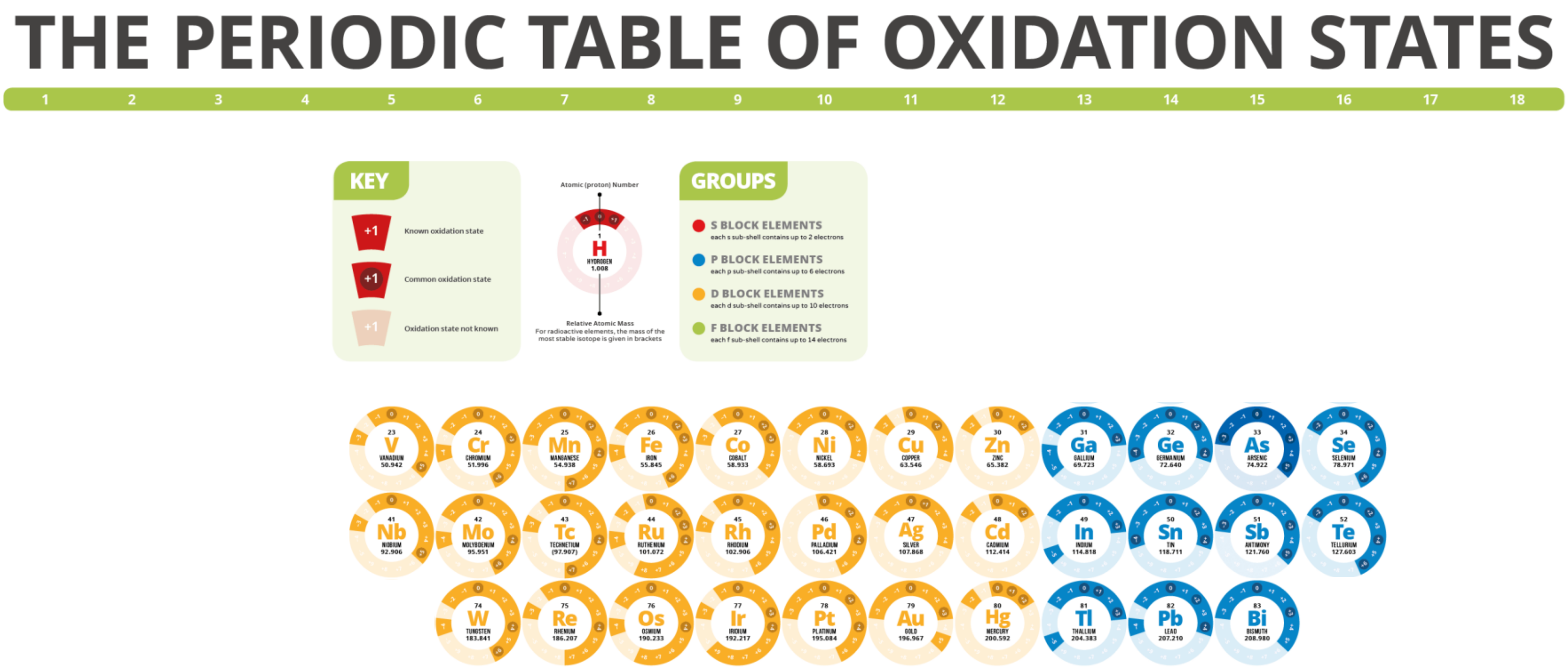
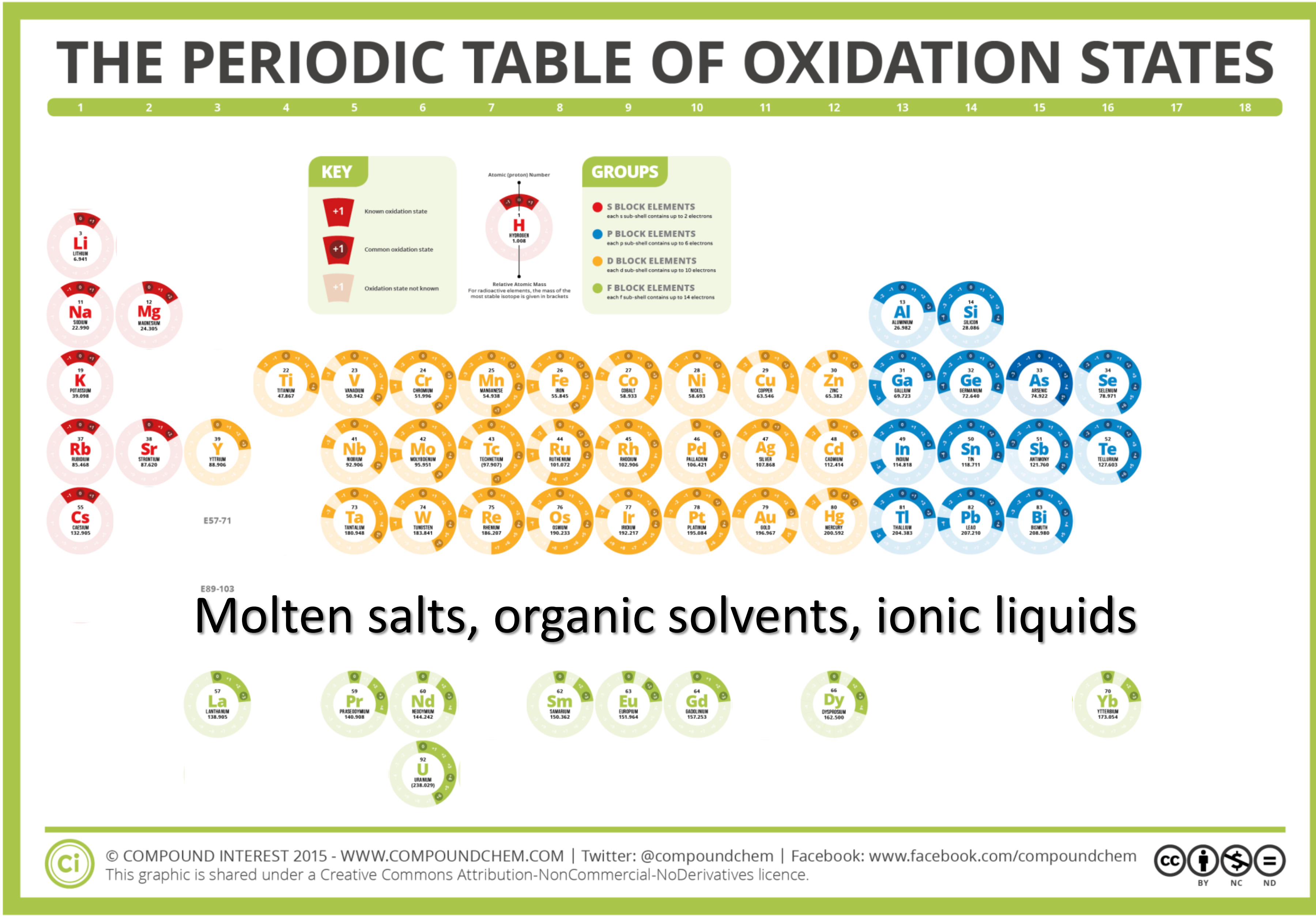


Electrodeposited from aqueous electrolytes

Transition metals, metals, semi-metals and metalloids

What materials can be electrodeposited?



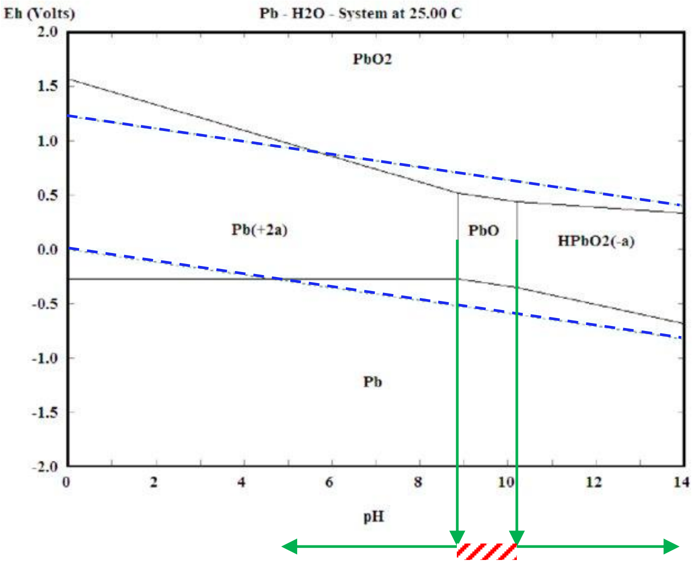
Molten salts, organic solvents, ionic liquids

What materials can be electrodeposited?

In aqueous electrolytes, one can refer to Pourbaix diagrams:

Thermodynamically stable phases = f(E, pH)

Example of Lead



pH < 8.8 or pH > 10.2

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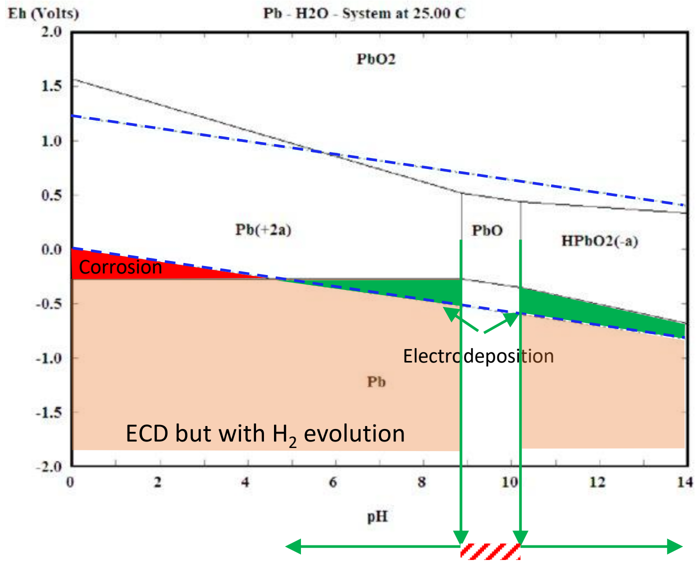

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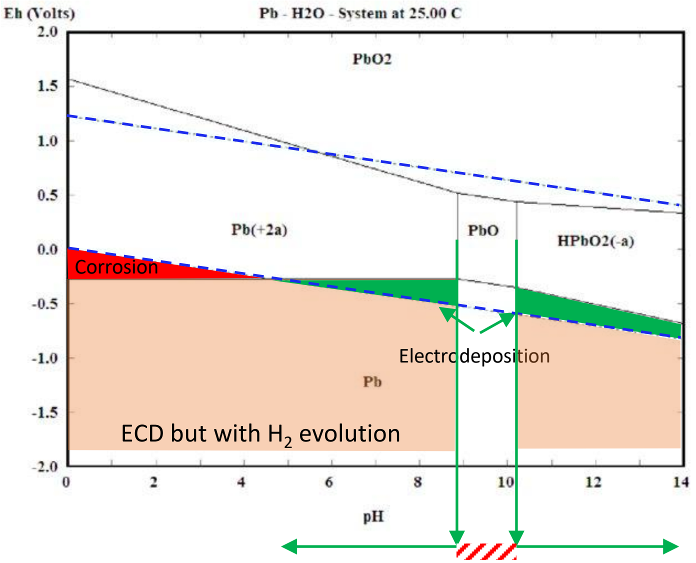
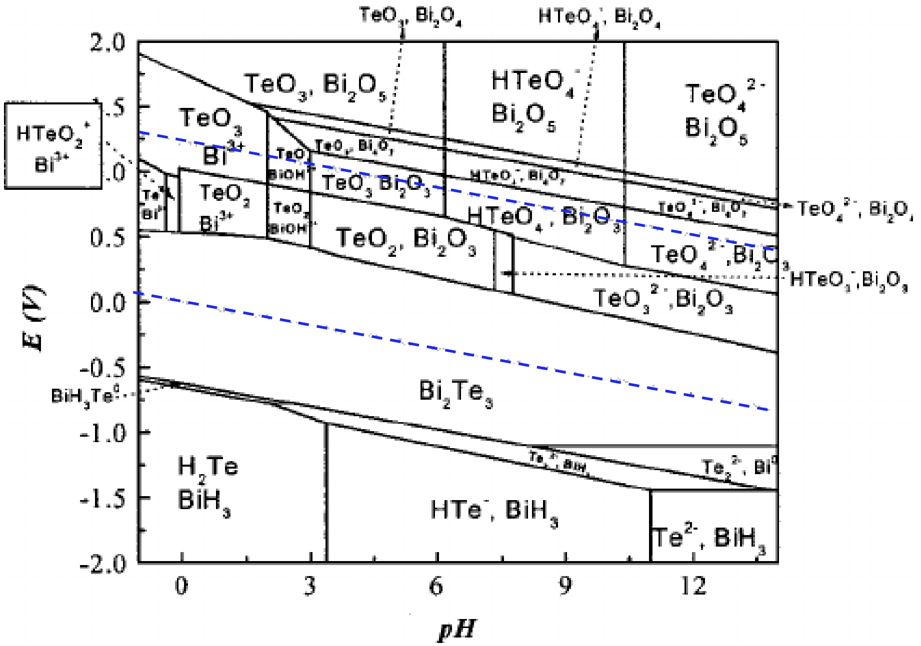


pH < 8.8 or pH > 10.2

Binary diagram – case of Bi_2Te_3



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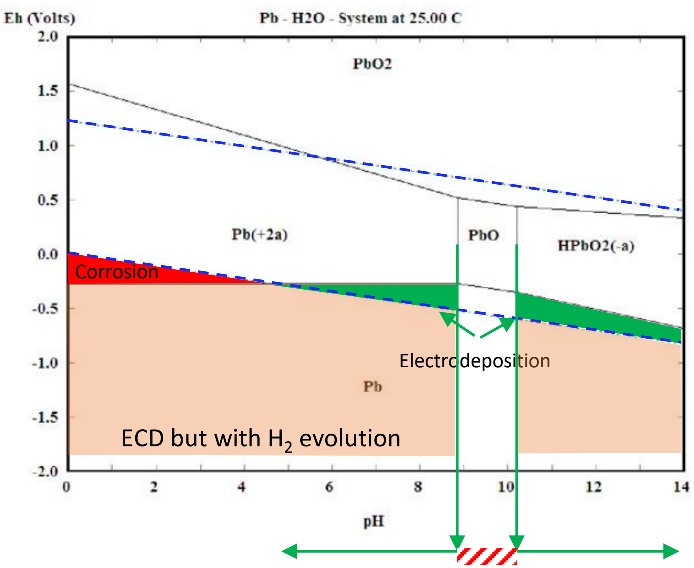
Example of Lead



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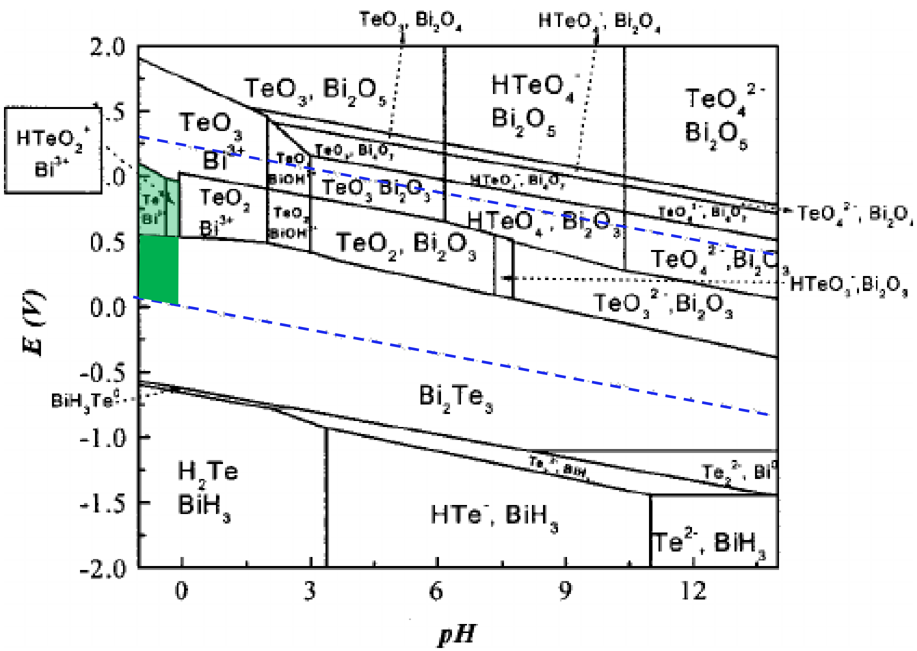
Binary diagram – case of Bi_2Te_3



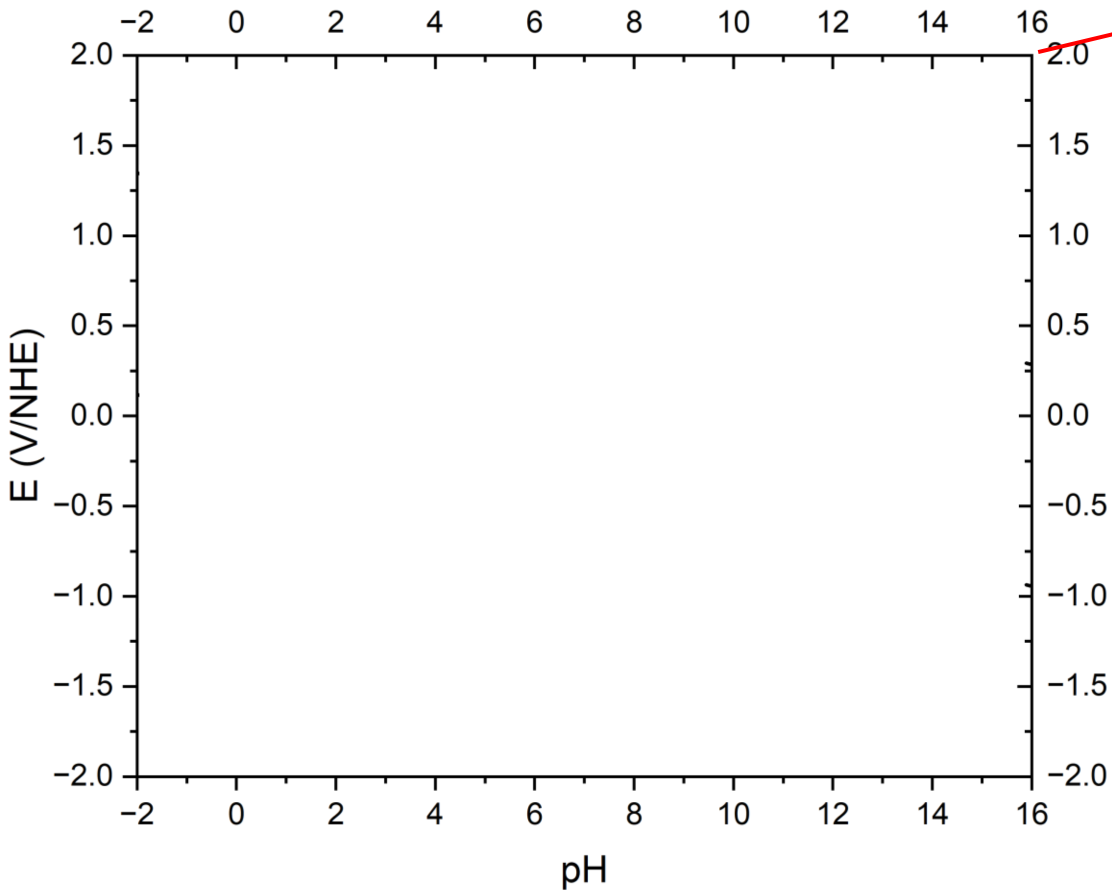
The more the elements the more the complexity
→ ECD window narrows

Building a Pourbaix diagram (E-pH)

$$xM^{2y+} + yH_2O \rightleftharpoons M_xO_y + 2yH^+$$

$$K_a = \frac{[M_xO_y][H^+]^{2y}}{[M^{2y+}]^x} \Rightarrow pK_a = -log\frac{[M_xO_y]}{[M^{2y+}]^x} + 2y\,pH$$

Acidity constants



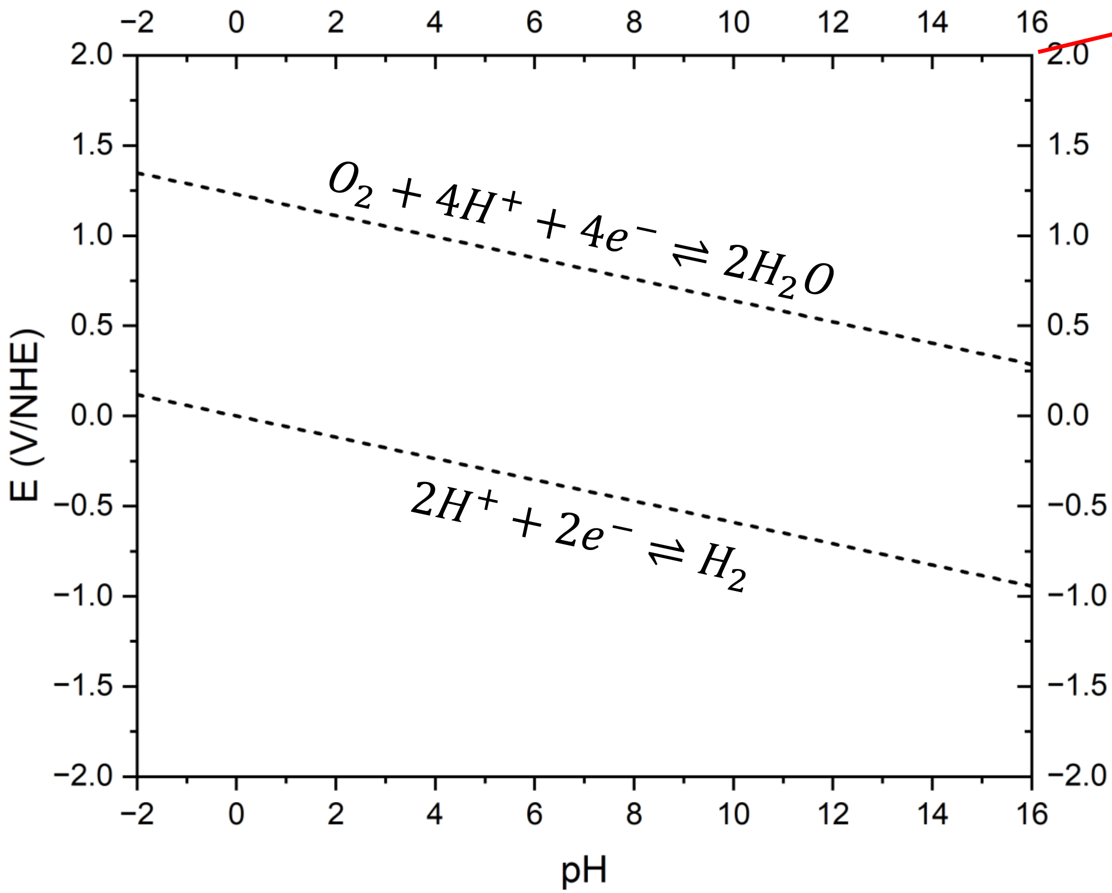
Nernst Potentials

$$E^{eq} = E^0 - 2.303\frac{RT}{nF}log\frac{{a_{Red}}^{\alpha}}{{a_{Ox}}^{\beta}}$$

At 25 °C, $2.303\frac{RT}{F} \approx 0.059\ V$

Building a Pourbaix diagram (E-pH)

Acidity constants



Nernst Potentials

$$E = E^0 - 2.303\frac{RT}{nF}log\frac{{a_{Red}}^{\alpha}}{{a_{Ox}}^{\beta}}$$

$$E = 1.23 - 0.059 * \frac{4}{4} * pH$$

Electrochemical window of water

$$E = 0 - 0.059 * \frac{2}{2} * pH$$

At 25 °C, $2.303\frac{RT}{F} \approx 0.059\ V$

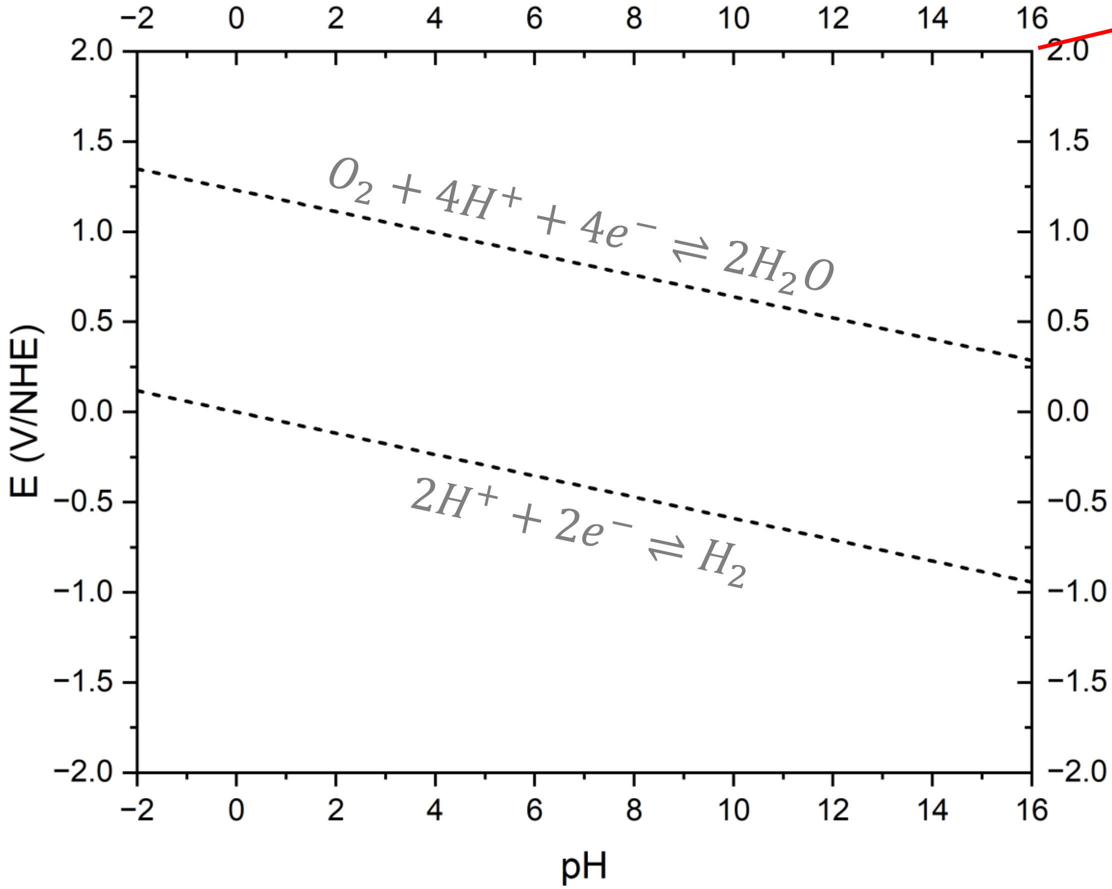
Building a Pourbaix diagram (E-pH)

Acid-base equilibria

$$Cu^{2+} \rightleftharpoons CuO \rightleftharpoons {CuO_2}^{2-}$$

$$Cu^{+} \rightleftharpoons Cu_2O$$

Acidity constants



Nernst Potentials

Redox

$$Cu^{+II}: Cu^{2+} \rightleftharpoons CuO \rightleftharpoons {CuO_2}^{2-}$$

$$\rightleftharpoons$$

$$Cu^{+I}: Cu^{+} \rightleftharpoons Cu_2O$$

$$\rightleftharpoons$$

$$Cu^0$$

At 25 °C, $2.303\frac{RT}{F} \approx 0.059\ V$

Building a Pourbaix diagram (E-pH)

Acid-base equilibria

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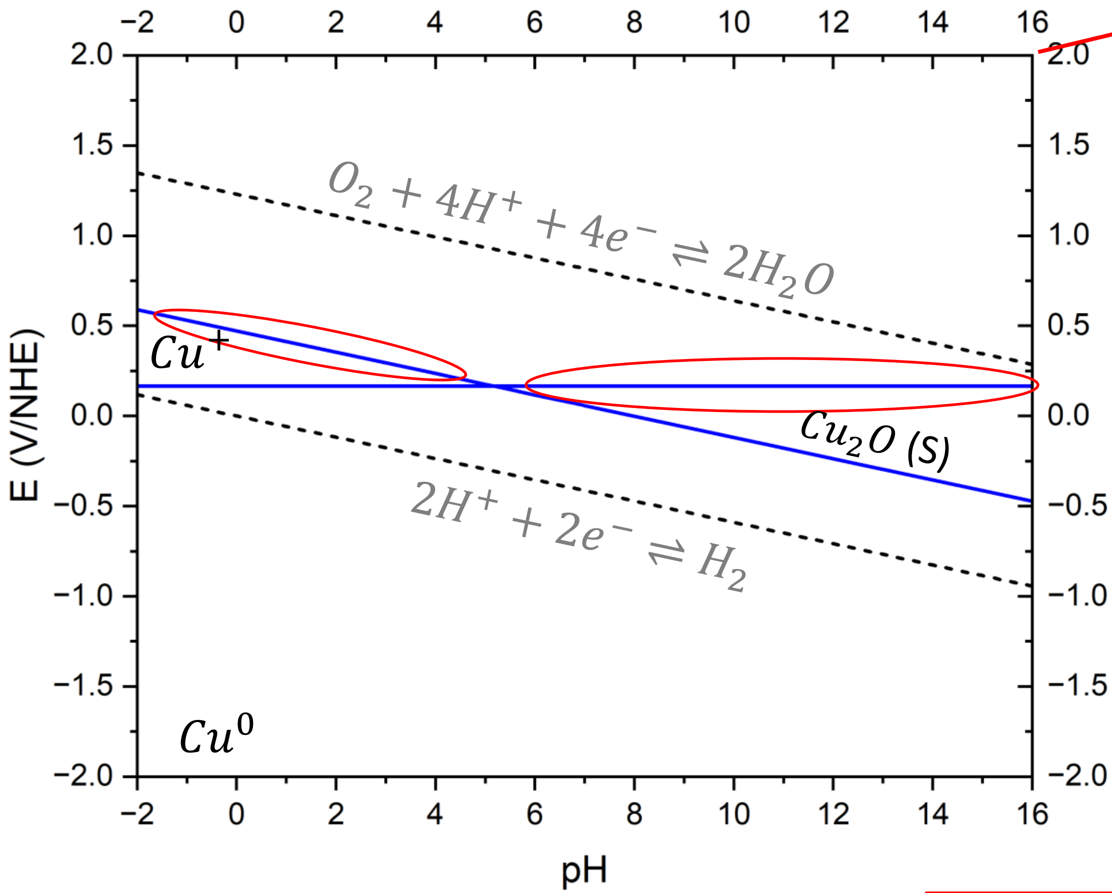


Nernst Potentials

Redox Cu+I/Cu0

$$Cu^+ + e^- \rightleftharpoons Cu$$

$$E_{Cu^+/Cu} = 0.520 + 0.059\log[Cu^+]$$

$$\mathbf{E_{Cu^+/Cu} = 0.166\ V/NHE}$$

$$Cu_2O + 2e^- + 2H^+ \rightleftharpoons 2Cu + H_2O$$

$$E_{Cu_2O/Cu} = 0.471 - \frac{0.059}{2}\log\frac{1}{[H^+]^2}$$

$$\mathbf{E_{Cu_2O/Cu} = 0.471 - 0.059\ pH}$$

At 25 °C, $2.303\frac{RT}{F} \approx 0.059\ V$ [Cu]=10^{-6} mol/L

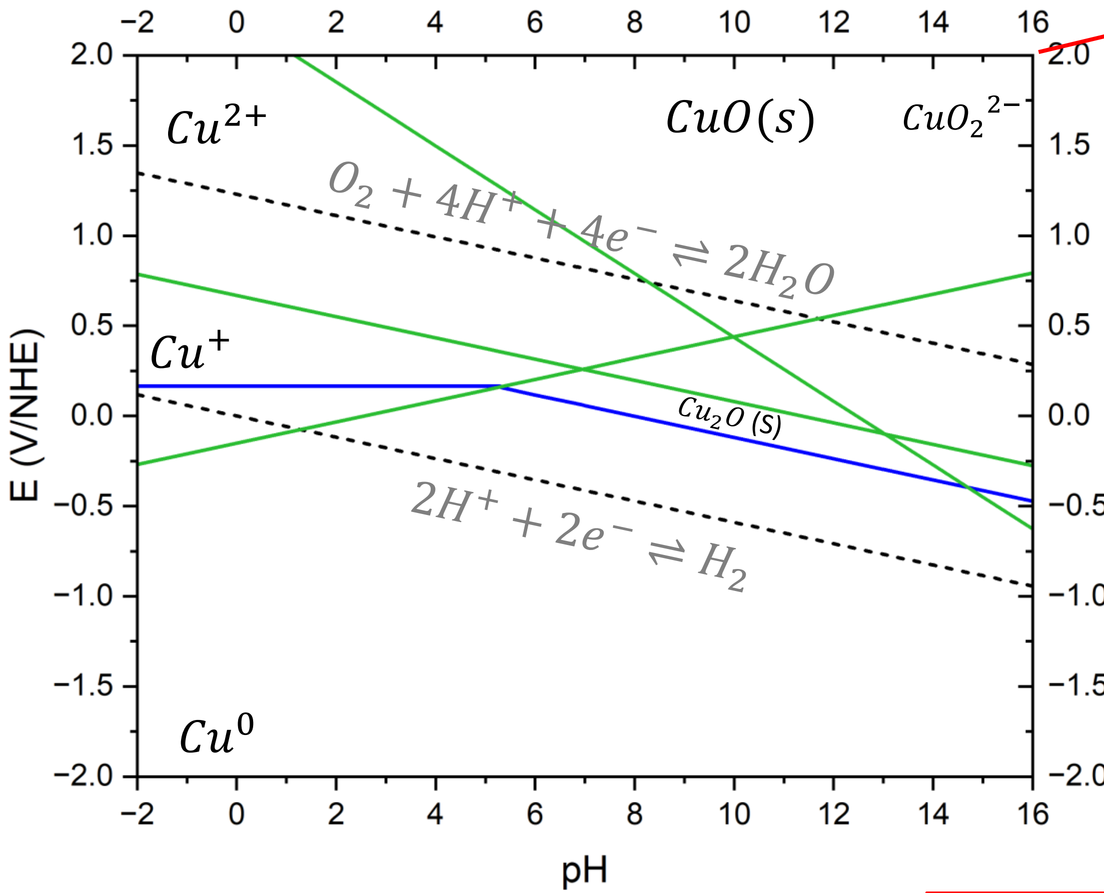
Building a Pourbaix diagram (E-pH)

Acid-base equilibria

$$Cu^{2+} \rightleftharpoons CuO \rightleftharpoons {CuO_2}^{2-}$$

$$Cu^{+} \rightleftharpoons Cu_2O$$

Acidity constants



Nernst Potentials

Redox Cu[+II]/Cu[+I]

$$2Cu^{2+} + 2e^- + H_2O \rightleftharpoons Cu_2O + 2H^+$$

$$E_{Cu^{2+}/Cu_2O} = 0.203 + 0.059\ \mathrm{pH} + 0.059\log[Cu^{2+}]$$

$$2CuO + 2e^- + 2H^+ \rightleftharpoons Cu_2O + H_2O$$

$$E_{CuO/Cu_2O} = 0.669 - 0.059\ \mathrm{pH}$$

$$2{CuO_2}^{2-} + 2e^- + 6H^+ \rightleftharpoons Cu_2O + 3H_2O$$

$$E_{{CuO_2}^{2-}/Cu_2O} = 2.560 + 0.177\ \mathrm{pH} + 0.059\log[{CuO_2}^{2-}]$$

At 25 °C, $2.303\frac{RT}{F} \approx 0.059\ V$ [Cu]=10^{-6} mol/L

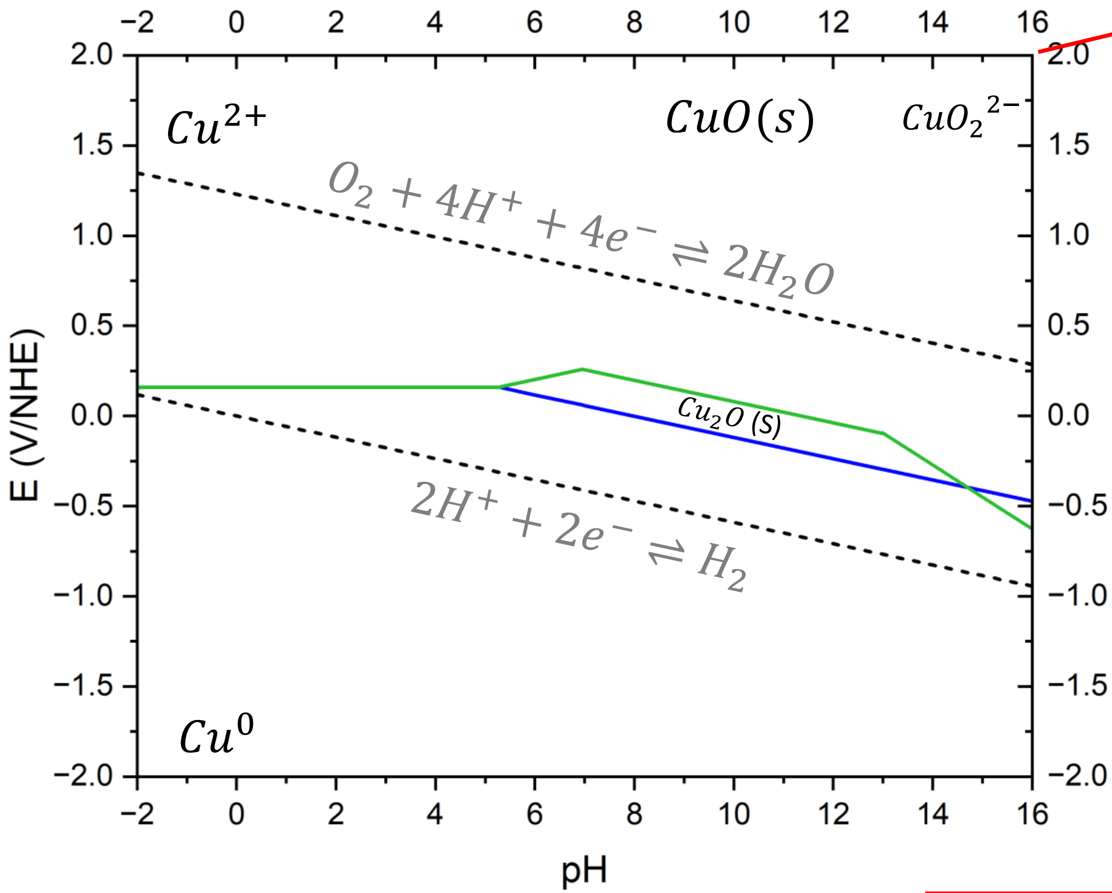
Building a Pourbaix diagram (E-pH)

Acid-base equilibria

$$Cu^{2+} \rightleftharpoons CuO \rightleftharpoons {CuO_2}^{2-}$$

$$Cu^{+} \rightleftharpoons Cu_2O$$

Acidity constants



Nernst Potentials

Redox Cu^{+II}/Cu^0

$$Cu^{2+} + 2e^- \rightleftharpoons Cu$$

$$E_{Cu^{2+}/Cu} = 0.337 + \frac{0.059}{2}\log[Cu^{2+}]$$

$$\mathbf{E_{Cu^{2+}/Cu} = 0.160\ V/NHE} < \mathbf{E_{Cu^{+}/Cu}}$$

Disproportionation

$$2Cu^{+} \rightleftharpoons Cu^{2+} + Cu$$

At 25 °C, $2.303\frac{RT}{F} \approx 0.059\ V$ [Cu]=10^{-6} mol/L

Building a Pourbaix diagram (E-pH)

Acid-base equilibria

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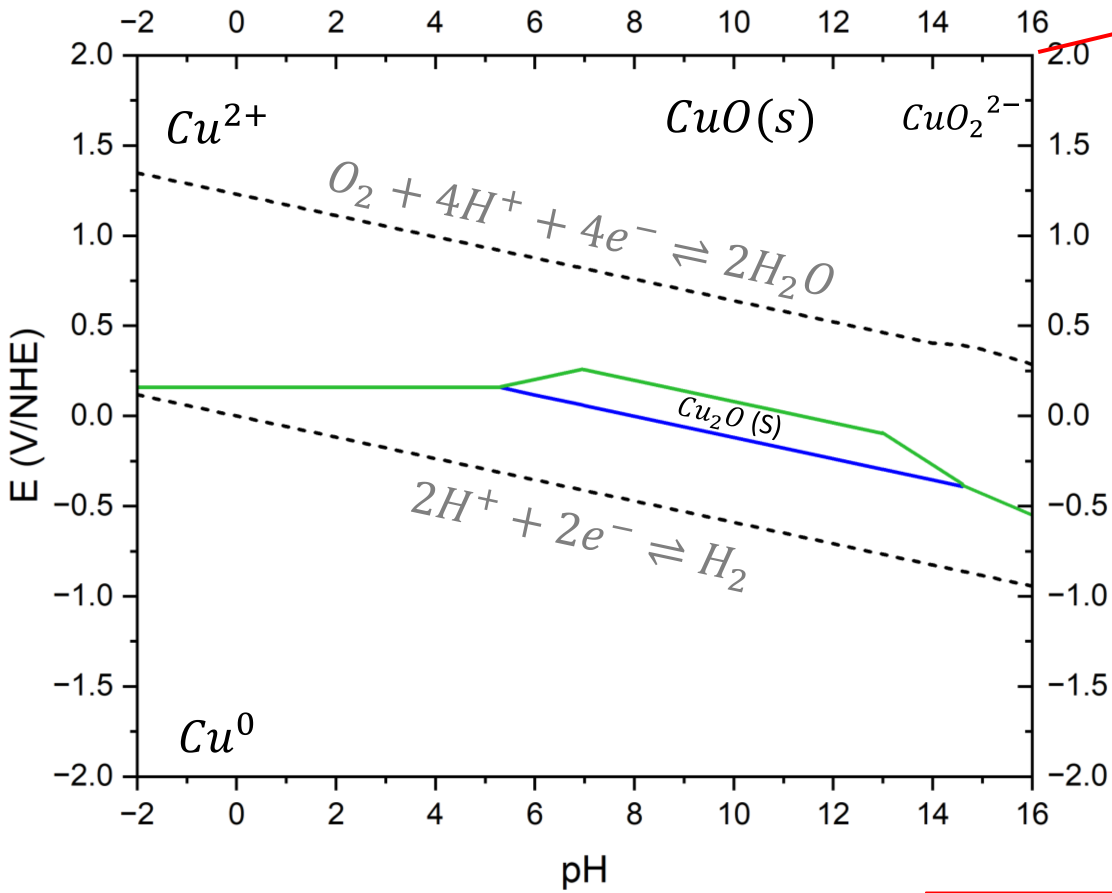

Nernst Potentials

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$$Cu^{2+} + 2e^- \rightleftharpoons Cu$$

$$E_{Cu^{2+}/Cu} = 0.337 + \frac{0.059}{2}\log[Cu^{2+}]$$

$$\mathbf{E_{Cu^{2+}/Cu} = 0.160\ V/NHE}$$

$${CuO_2}^{2-} + 2e^- + 4H^+ \rightleftharpoons Cu + 2H_2O$$

$$E_{{CuO_2}^{2-}/Cu} = 1.515 + 0.118\ \mathrm{pH} + 0.0295\log[{CuO_2}^{2-}]$$

At 25 °C, $2.303\frac{RT}{F} \approx 0.059\ V$ [Cu]=10^{-6} mol/L

Building a Pourbaix diagram (E-pH)

Acid-base equilibria

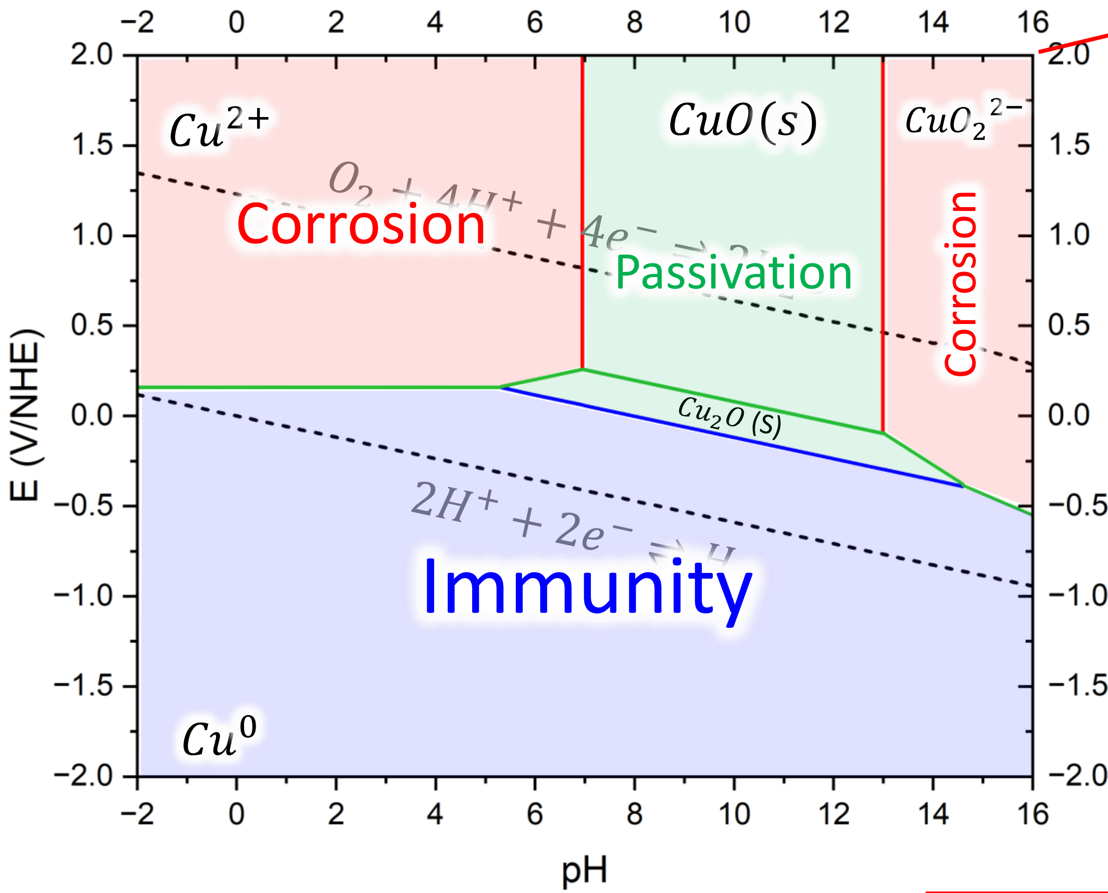
$Cu^{2+} + H_2O \rightleftharpoons CuO + 2H^+ \quad \Rightarrow 2pH = pKa + \log[Cu^{2+}]$

$\Rightarrow \boldsymbol{pH = 6.945}$

$CuO + H_2O \rightleftharpoons {CuO_2}^{2-} + 2H^+ \quad \Rightarrow 2pH = pKa - \log[{CuO_2}^{2-}]$

$\Rightarrow \boldsymbol{pH = 12.99}$

Acidity constants



Nernst Potentials

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Cu^0

At 25 °C, $2.303\frac{RT}{F} \approx 0.059\ V$ [Cu]=10^{-6} mol/L

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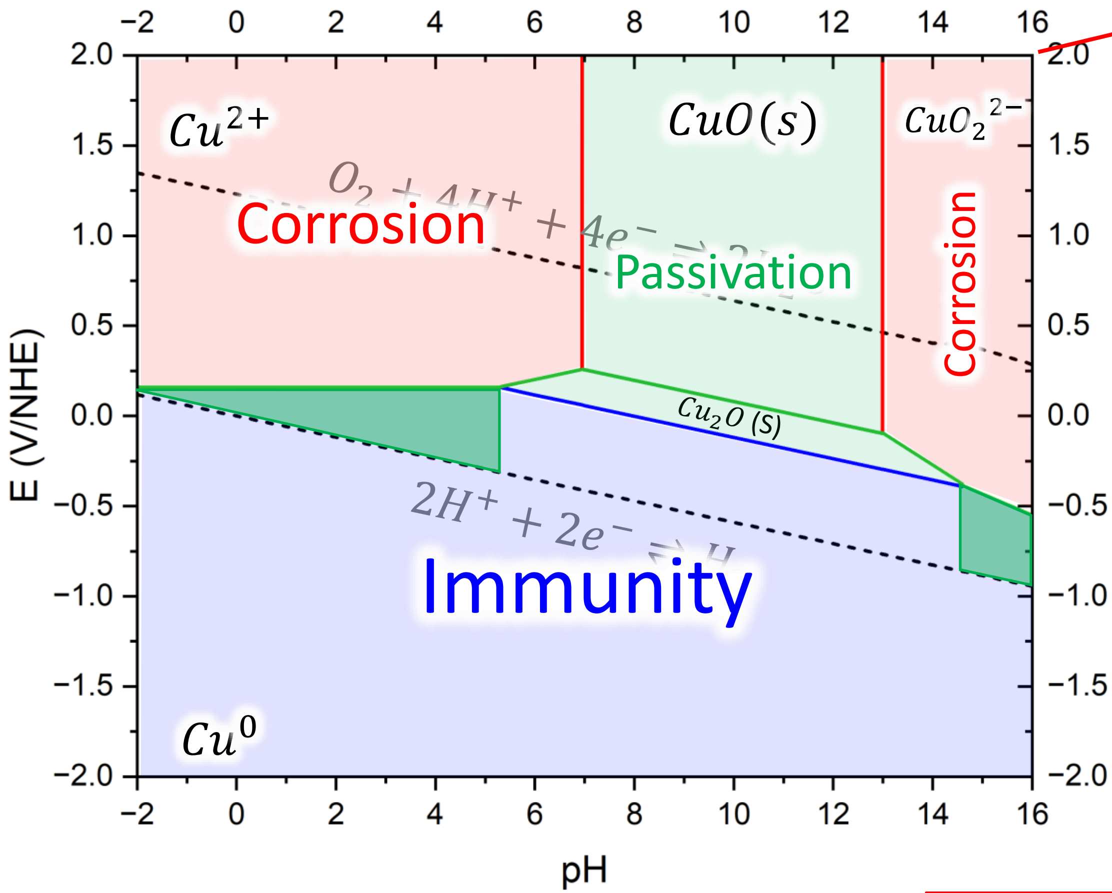
Acidity constants

Nernst Potentials



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$\rightleftharpoons$

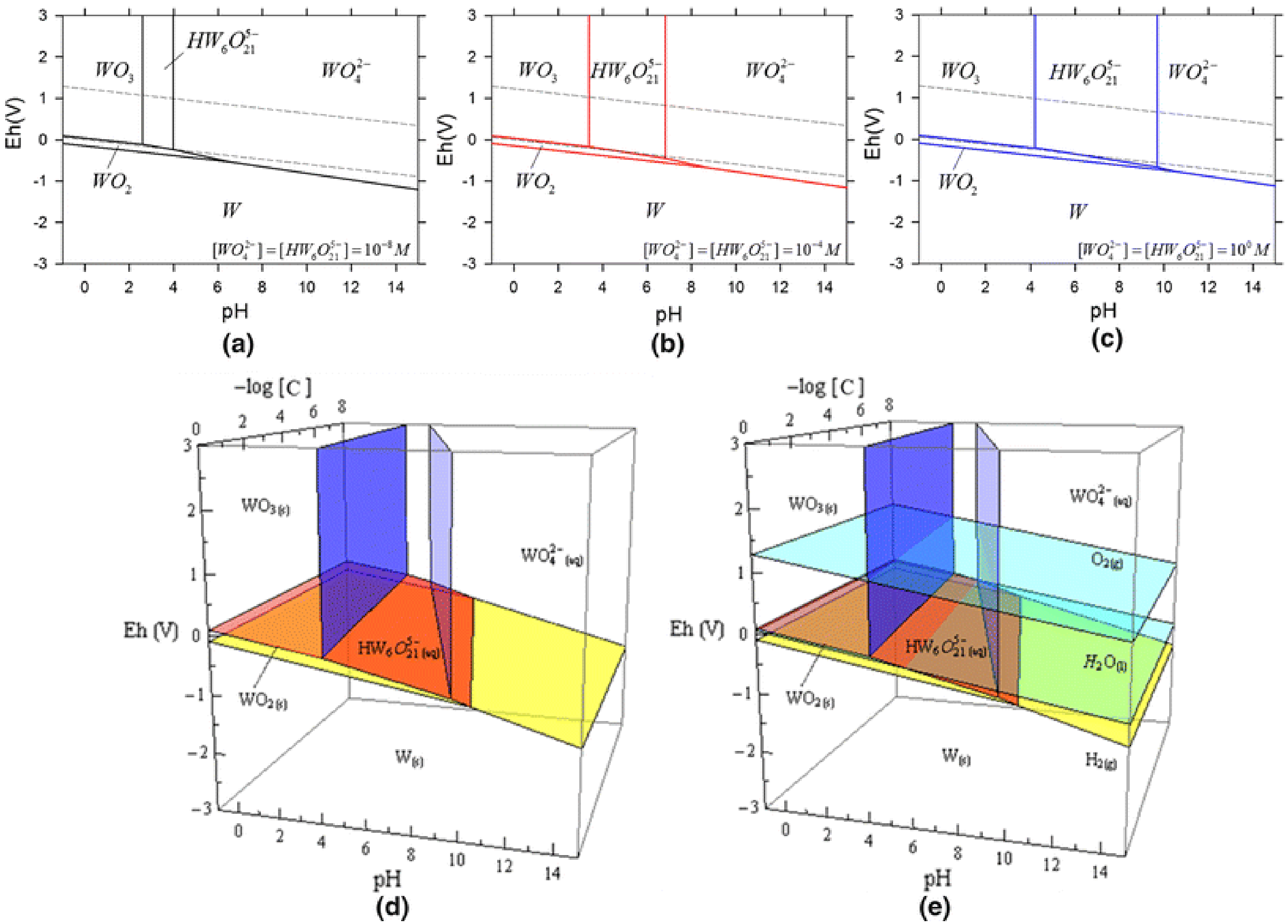
Cu^0

At 25 °C, $2.303\,\frac{RT}{F} \approx 0.059\ V$ [Cu]=10^{-6} mol/L

3D Pourbaix diagram (E-pH-M and E-pH-X)

Nernst potential depends on concentrations:

$$E = E^0 - 2.303\,\frac{RT}{nF}\,log\,\frac{{a_{Red}}^{\alpha}}{{a_{Ox}}^{\beta}}$$



3D Pourbaix diagram (E-pH-X)

Nernst potential for metalorganic complex $[ML_x]^{z+}$

1) $[ML_x]^{n+} \rightarrow M^{z+} + xL^{m-}$ complexation constant independent of the potential

2) $M^{z+} + ze^{-} \rightarrow M^0$ the slower process defines the reaction kinetics

Can you express the new Nernst potential $E^{eq}(ML_x^{n+}/M^0, xL^{m-})$ as a function of:

$E^0(M^{z+}/M^0)$ the standard potential for the metal M

pK_d = -log K_d the complex dissociation constant $K_d = \frac{[M^{z+}][L^{m-}]^x}{[ML_x^{n+}]}$

and the concentrations $[\boldsymbol{ML_x^{n+}}]$ and $[\boldsymbol{L^{m-}}]$

3D Pourbaix diagram (E-pH-X)

Nernst potential for metalorganic complex $[ML_x]^{z+}$

1) $[ML_x]^{n+} \rightarrow M^{z+} + xL^{m-}$ complexation constant independent of the potential

2) $M^{z+} + ze^- \rightarrow M^0$ the slower process defines the reaction kinetics

$$E^{eq} = E^0(M^{z+}/M^0) + \frac{RT}{zF}\ln[M^{z+}]$$

$$K_d = \frac{[M^{z+}][L^{m-}]^x}{[ML_x^{n+}]} \quad \rightarrow \quad [M^{z+}] = K_d \frac{[ML_x^{n+}]}{[L^{m-}]^x}$$

$$E^{eq} = E^0(M^{z+}/M^0) + \frac{RT}{zF}\ln\left(K_d \frac{[ML_x^{n+}]}{[L^{m-}]^x}\right)$$

$$E^{eq} = E^0 + 2.303\frac{RT}{zF}\{\log[ML_x^{n+}] - \text{x}.\log[L^{m-}] - pK_d\}$$

$E^{eq}(ML_x^{n+}/M^0, xL^{m-}) < E^{eq}(M^{z+}/M^0)$