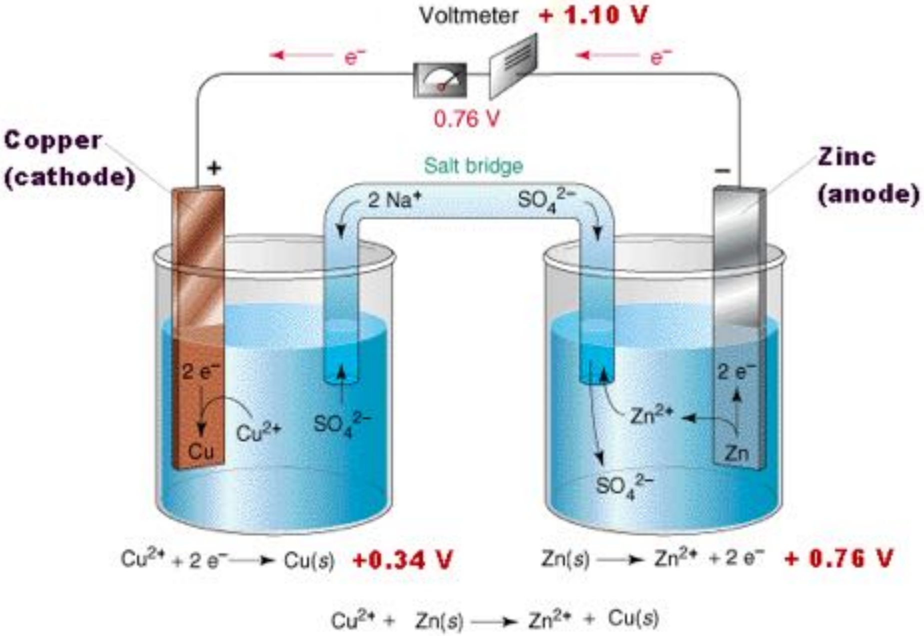
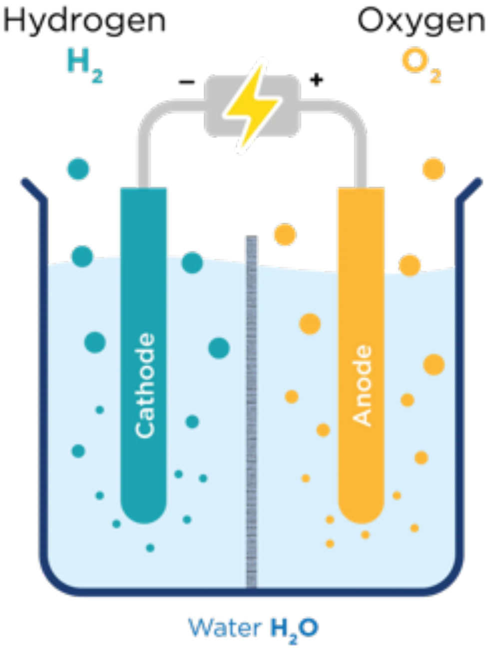
Fundamentals of Electrochemistry and Electrochemical Cells

Galvanic cell



Electrolytic cell



Redox-reaction

$$\Delta G_{\mathrm{r}} = \Delta G_{\mathrm{r}}{}^{0} + \mathrm{R}\cdot\mathrm{T}\cdot\ln(\mathrm{Q}) = -\mathrm{z}\cdot F\cdot\Delta E_{\mathrm{cell}}$$

Prof. Dr. Andreas ZÜTTEL

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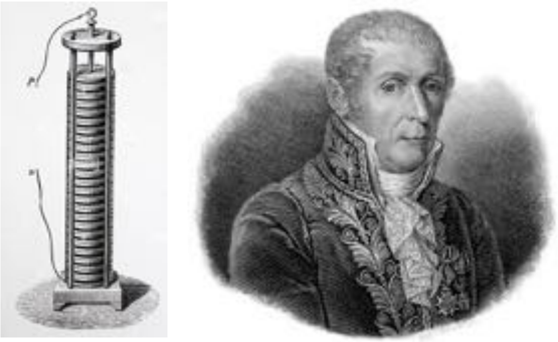
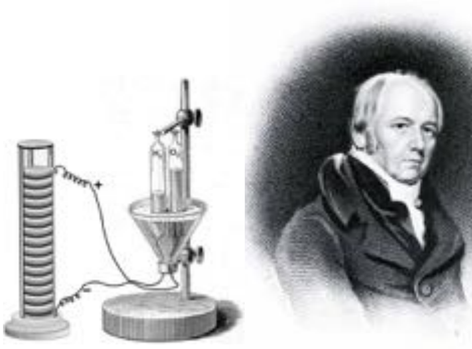
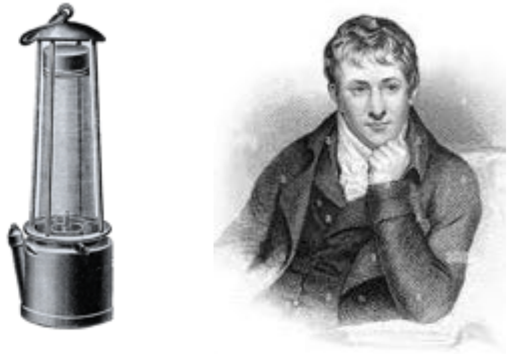
1. History of electrochemistry (first 100 years)



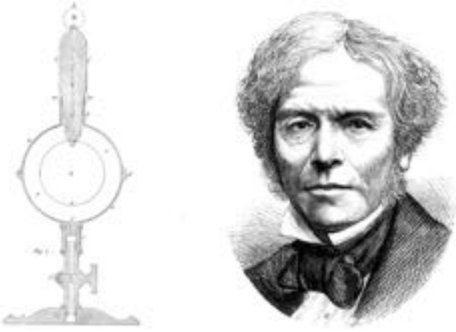
Voltaic cell Cu/Zn
1799, Alessandro VOLTA in Como (I)



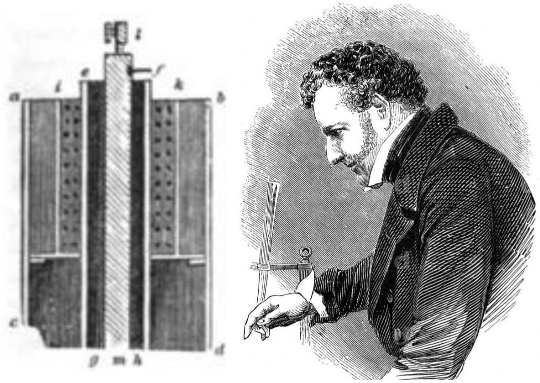
1st electrolysis of water
1800, William NICHELSON



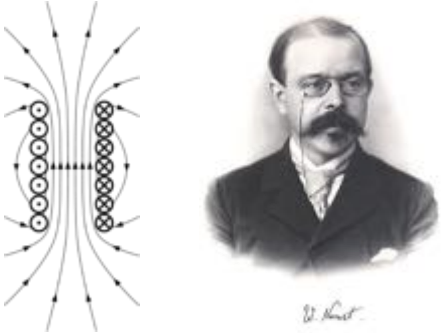
Electrical theory of chemical affinity
1806, Sir Humphry DAVY in London (GB)



Charge and mass
1832, Michael FARADAY in London (GB)

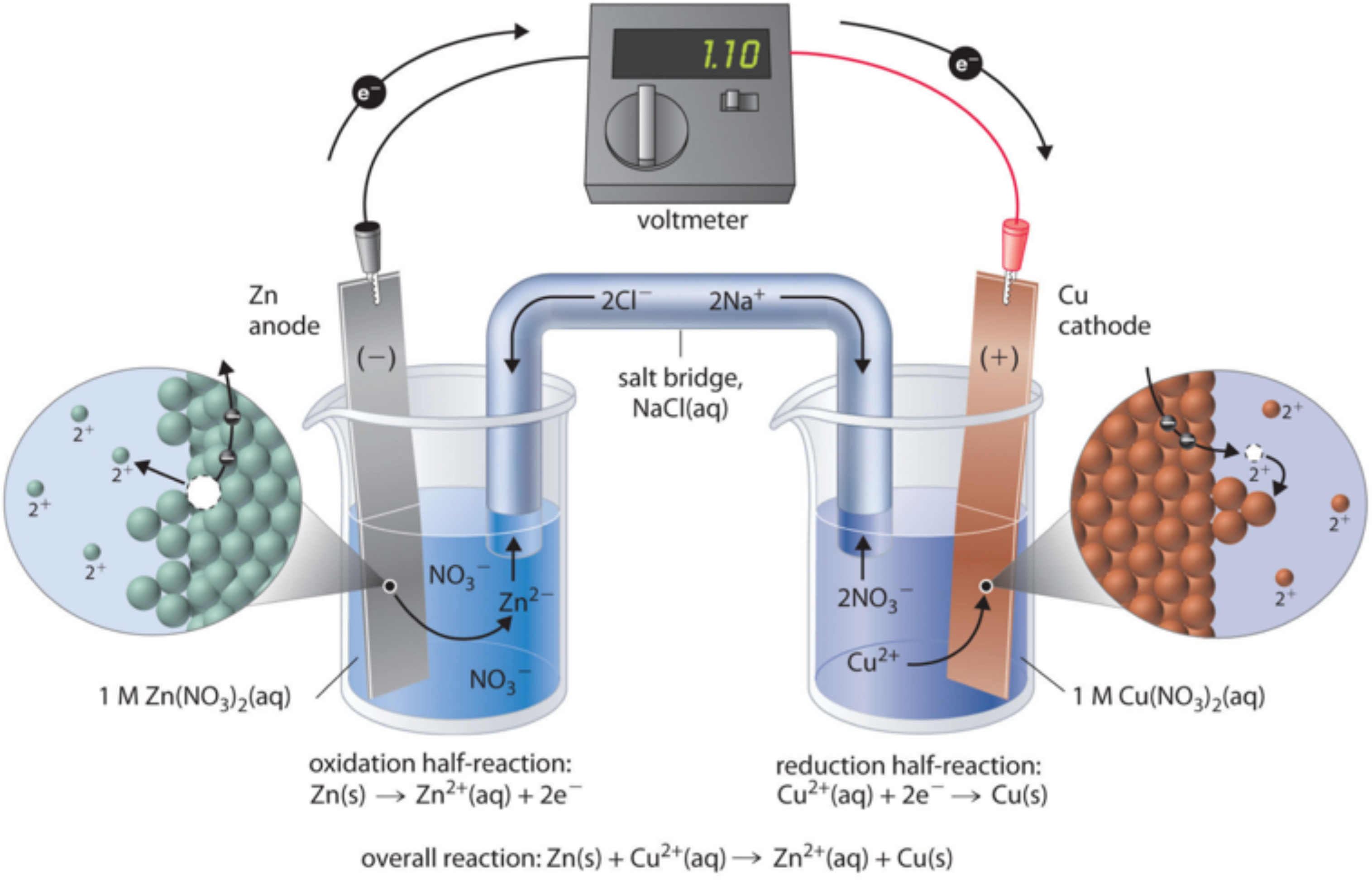


1st battery (Cu/Zn)
1836, John Frederic DANIELL



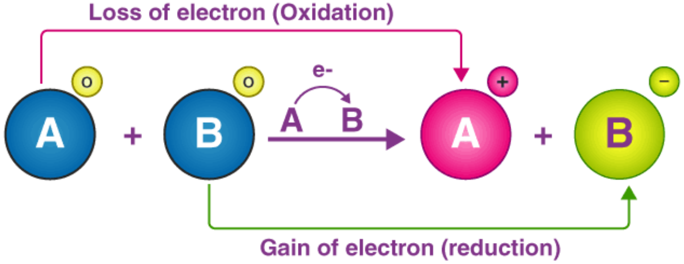
Electrodynamics
1889, Walther Hermann NERNST

1.1. Galvanic cell (Cu/Zn)



A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. The zinc electrode is spontaneously oxidized to Zn^{2+} ions (**anode**) in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (**cathode**).

1.2. Redox reaction



Reduction reaction: $M^{n+} + n{\cdot}e^{-} \rightarrow M$

the oxidation number of a specimen is reducing (+ e^{-})

Oxidation reaction: $M \rightarrow M^{n+} + n{\cdot}e^{-}$

the oxidation number of a specimen is increasing (- e^{-})

$$\Delta G^{0} = -z{\cdot}F{\cdot}\Delta E^{0}$$

Standard Gibbs free energy at 298K and 1 bar with the standard potential ΔE^0 and the Faraday constant

$F = 1.602{\cdot}10^{-19}$ A·s·$e^{-1}{\cdot}6.022{\cdot}10^{23}$ e·mol^{-1} = 96'485 A·s·mol^{-1}.
z stands for the charge.

The standard Gibbs free energy change (ΔG^0) is a thermodynamic quantity that determines the spontaneity of a reaction at constant temperature and pressure. It represents the maximum amount of non-expansion work that can be extracted from a process under standard conditions. The electrochemical potential (ΔE^0_{cell}), also known as cell potential, is the driving force for an electrochemical reaction and is related to the Gibbs free energy change.

1.3. Standard potential and equilibrium constant K

Standard Gibbs free energy of the reaction in equilibrium at 298K and 1 bar

$$\Delta G_{\mathrm{r}}^{0} = -R \cdot T \cdot ln(K) \quad and \quad \Delta G_{\mathrm{r}}^{0} = -\mathrm{z} \cdot F \cdot \Delta E^{0}$$

leads to the equilibrium constant

$$ln(K) = \frac{\boldsymbol{z} \cdot F}{R \cdot T} \cdot \Delta E^{0}$$

$R = 8.314\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$

Calculation of the equilibrium constant for the reaction

$\mathrm{Zn(s) + Cu^{2+}(aq) \rightleftarrows Zn^{2+}(aq) + Cu(s)}$

$\ln(K) = 2 \cdot 96485\ \mathrm{C/mol}/(8.314\ \mathrm{J/(mol \cdot K)} \cdot 298\mathrm{K}) \cdot 1.1\mathrm{V} = 85.6$

with $a(\mathrm{Zn(s)}) = a(\mathrm{Cu(s)}) = 1$ activity of solids in the electrolyte

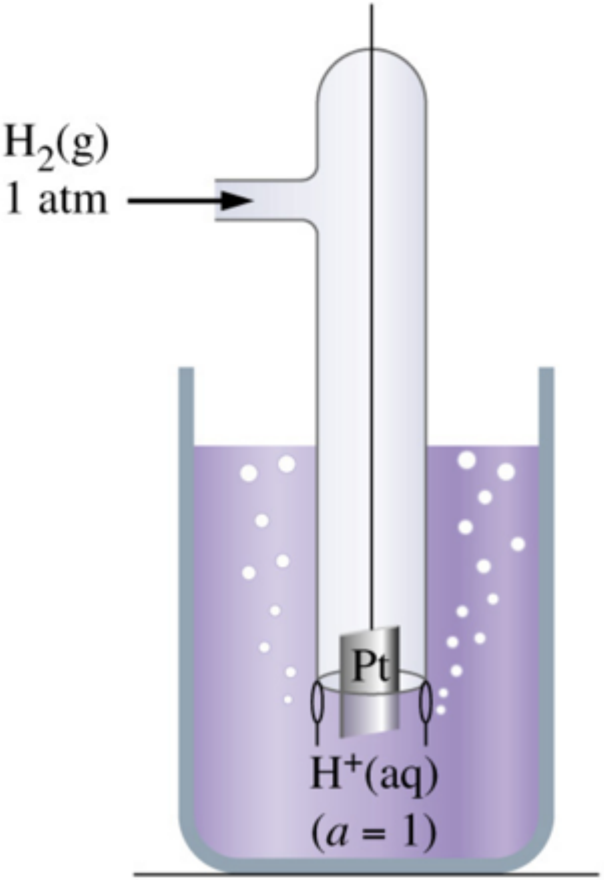
$K = a(\mathrm{Zn^{2+}})/a(\mathrm{Cu^{2+}}) = 1.6 \cdot 10^{37}$ the equilibrium is on the right hand side!

2. Standard potential of an electrode E^0

By convention, E^0 will be the electromotive force (ΔE^0) of the cell formed by the combination of the half-cell of the redox couple under consideration and a half-cell formed by the standard hydrogen electrode ($E^0 = 0$).

ΔE^0(galvanic cell) = E^0(cathode) – E^0(anode)

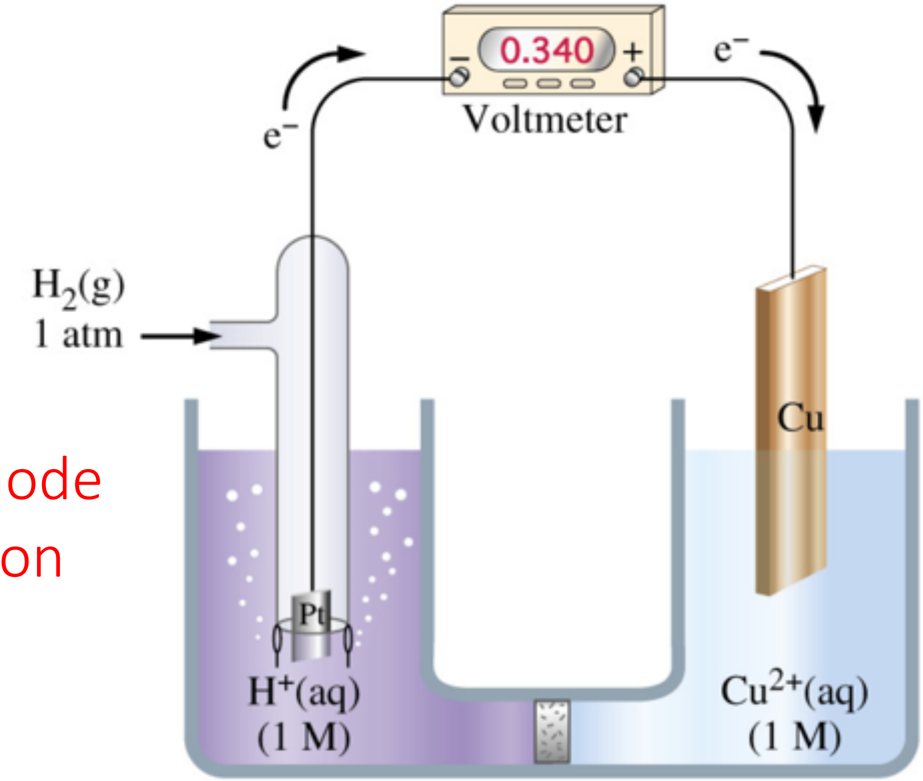
For a galvanic cell:
E^0(cathode), positive pole (+)
E^0(anode), negative pole (-)



Reaction: $2H^+(aq) + 2e^- \rightleftarrows H_2(g)$
Redox pair: H^+/H_2 the Pt electrode is inert

By definition: $E^0(H^+, H_2) = 0.00V$
at 1 bar (100 kPa) and all temperatures

2.1. Measuring the standard potential $E^0(Cu^{2+}/Cu)$



H^+/Pt anode oxidation

-

Cu cathode reduction

+

Reaction: $Cu^{2+}(aq) + H_2(g) \rightleftarrows Cu(s) + 2H^+(aq)$

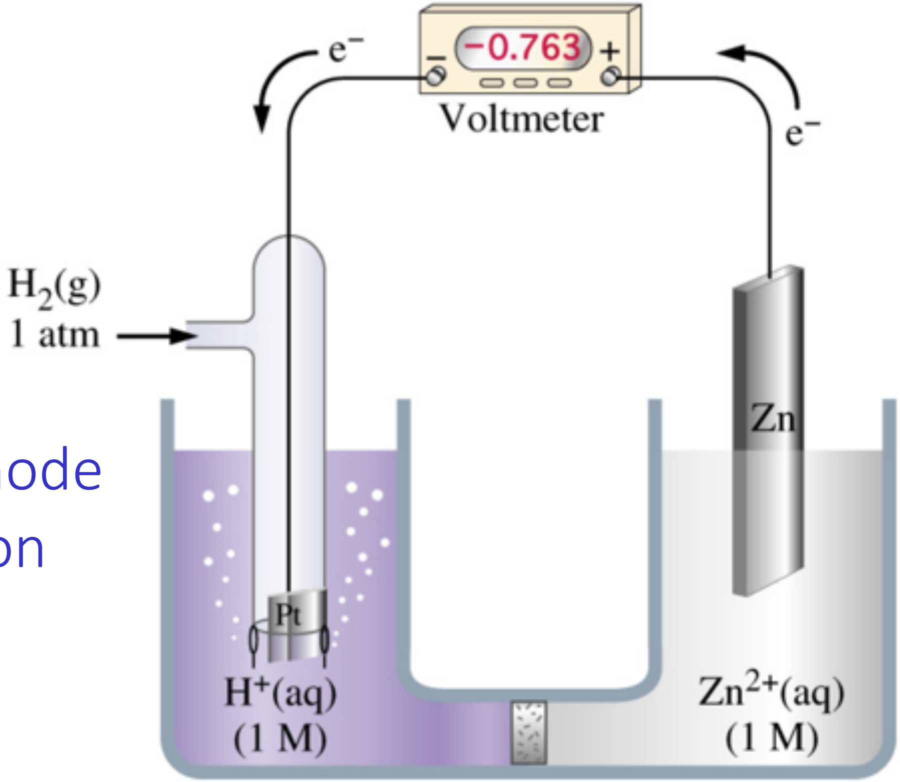
$Pt(s)\ |\ H_2(g)\ |\ H^+(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu(s)$

$\Delta E^0 = E^0(\text{cathode}) - E^0(\text{anode})$

$\Delta E^0 = E^0(Cu^{2+},Cu) - E^0(H^+,H_2) = 0.34V$ (current $I = 0$)

$E^0(Cu^{2+},Cu) = 0.34V$

2.2. Measuring the standard potential $E^0(Zn^{2+}/Zn)$



Pt/H⁺ cathode
reduction
+

Zn anode
oxidation
-

Reaction: $Zn(s) + 2H^+(aq) \rightleftarrows Zn^{2+}(aq) + H_2(g)$

$Zn^{2+}(aq) \mid Zn(s) \parallel H_2(g) \mid H^+(aq) \mid Pt(s)$

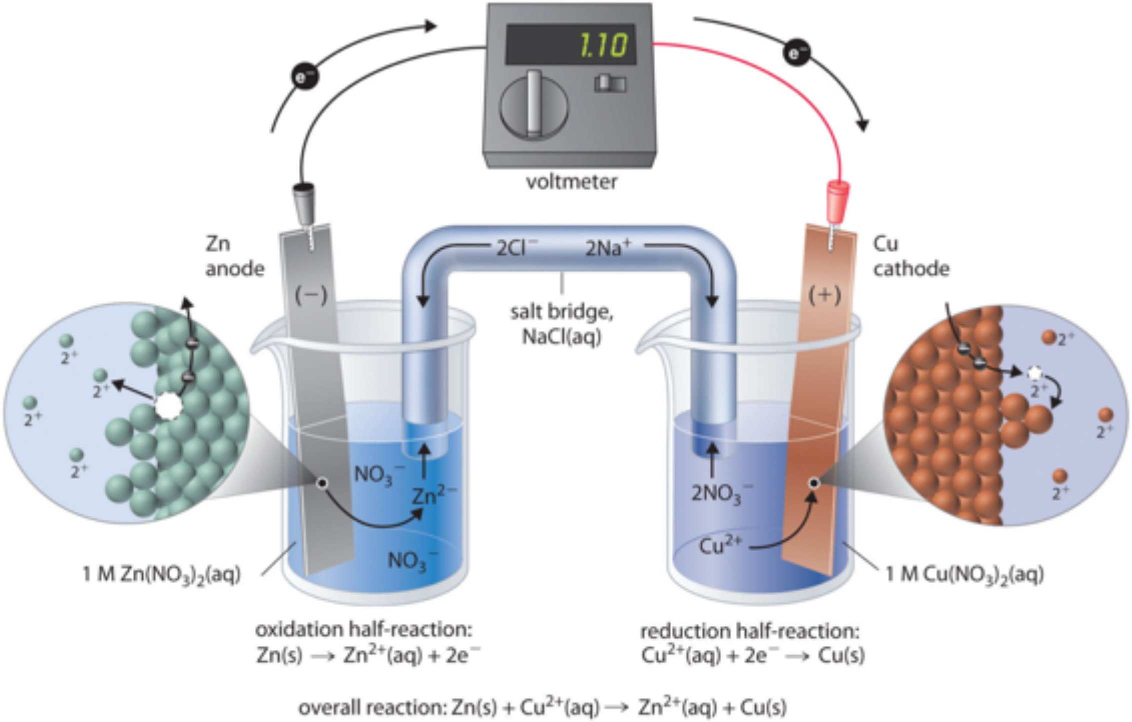
$\Delta E^0 = E^0(\text{cathode}) - E^0(\text{anode})$

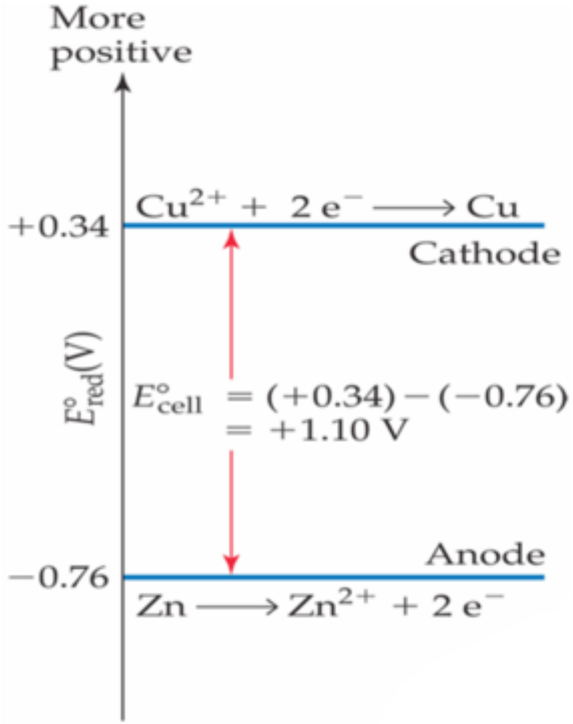
$\Delta E^0 = E^0(H^+,H_2) - E^0(Zn^{2+},Zn) = 0.76\text{V}$ (current I = 0)

$E^0(Zn^{2+},Zn) = -0.76\text{V}$

2.3. Standard potential of a galvanic cell (Cu/Zn)

$$\Delta E^0 = E^0(\text{cathode}) - E^0(\text{anode})$$





+ pole, cathode: $Cu^{2+}(aq) + 2e^- \rightleftarrows Cu(s)$ $E^0(Cu^{2+},Cu) = 0.34V$

- pole, anode: $Zn(s) \rightleftarrows Zn^{2+}(aq) + 2e^-$ $E^0(Zn^{2+},Zn) = -0.76V$

$$\Delta E^0 = E^0(Cu^{2+},Cu) - E^0(Zn^{2+},Zn) = 0.34V - (-0.76V) = +1.1V$$

2.4. Standard electrode potentials E^0

Half Reaction	Potential
$F_2 + 2e^- \rightarrow 2F^-$	+2.87 V
$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	+2.07 V
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+2.05 V
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	+1.69 V
$Au^+ + e^- \rightarrow Au$	+1.69 V
$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$	+1.67 V
$2\,HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$	+1.63 V
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61 V
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51 V
$Au^{3+} + 3e^- \rightarrow Au$	+1.40 V
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36 V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.33 V
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23 V
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+1.21 V
$Pt^{2+} + 2e^- \rightarrow Pt$	+1.20 V
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09 V
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	+0.92 V
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	+0.89 V
$Ag^+ + e^- \rightarrow Ag$	+0.80 V
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	+0.79 V
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77 V
$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$	+0.60 V
$I_2 + 2e^- \rightarrow 2I^-$	+0.54 V
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40 V
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34 V
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+0.27 V
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22 V
$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$	+0.01 V
$2H^+ + 2e^- \rightarrow H_2$	**0.000 V**

Half Reaction	Potential
$2H^+ + 2e^- \rightarrow H_2$	**0.000 V**
$Fe^{3+} + 3e^- \rightarrow Fe$	−0.04 V
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13 V
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14 V
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23 V
$V^{3+} + e^- \rightarrow V^{2+}$	−0.26 V
$Co^{2+} + 2e^- \rightarrow Co$	−0.28 V
$In^{3+} + 3e^- \rightarrow In$	−0.34 V
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.36 V
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40 V
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.41 V
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44 V
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76 V
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83 V
$Cr^{2+} + 2e^- \rightarrow Cr$	−0.91 V
$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18 V
$V^{2+} + 2e^- \rightarrow V$	−1.19 V
$ZnS + 2e^- \rightarrow Zn + S^{2-}$	−1.44 V
$Al^{3+} + 3e^- \rightarrow Al$	−1.66 V
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.36 V
$Na^+ + e^- \rightarrow Na$	−2.71 V
$K^+ + e^- \rightarrow K$	−2.92 V
$Li^+ + e^- \rightarrow Li$	−3.05 V

Note: all ions are aqueous (aq), many neutral species are solids (s), although some are liquids (l), gases (g), and even aqueous (aq). Use other sources for details on state. They were purposely left off here to save space and keep a cleaner looking table.

reactions written as reduction

$$O + z \cdot e^- \rightleftarrows R$$

E^0 is also called the standard reduction potential

$$\Delta E^0 = E^0_+ - E^0_-$$

$Cu^{2+} + 2e^- \rightarrow Cu$ $E^0 = +0.34V$
$Zn^{2+} + 2e^- \rightarrow Zn$ $E^0 = -0.76\ V$

$\Delta E^0 = +0.34 - -0.76V = \mathbf{+1.1V}$
$Zn \rightarrow Zn^{2+} + 2e^-$ $E^0 = +0.76\ V$

$Zn^{2+} + 2e^- \rightarrow Zn$ $E^0 = -0.76\ V$
$Cu^{2+} + 2e^- \rightarrow Cu$ $E^0 = +0.34V$

$\Delta E^0 = -0.76 - +0.34 = \mathbf{-1.1V}$
$Cu^{2+} + 2e^- \rightarrow Cu$ $E^0 = +0.34V$
$Zn \rightarrow Zn^{2+} + 2e^-$ $E^0 = +0.76\ V$

3. Galvanic cell potential ΔE from the Gibbs free energy

Gibbs free energy of the reduction reaction $O_1 + R_2 \rightleftarrows R_1 + O_2$

$$\Delta G_\mathrm{r} = \Delta G_\mathrm{r}{}^0 + R \cdot T \cdot ln(Q) \qquad and \qquad \Delta G_\mathrm{r} = -\mathrm{z} \cdot F \cdot \Delta E$$

with $$\mathrm{Q} = \left(\frac{a(R_1) \cdot a(O_2)}{a(O_1) \cdot a(R_{2)}} \right)$$

The cell potential ΔE is

$$\Delta E = \Delta E^0 - \frac{R \cdot T}{\boldsymbol{z} \cdot F} \cdot ln(Q)$$

in equilibrium $\Delta G_\mathrm{r} = 0$ and $Q = K$, therefore, $\Delta E = 0$

$$ln(K) = \frac{\boldsymbol{z} \cdot F}{R \cdot T} \cdot \Delta E^0$$

3.1. Galvanic cell potential from the standard electrode potentials

The two half cells are

$O_1 + n \cdot e^- \rightleftarrows R_1$ and $O_2 + n \cdot e^- \rightleftarrows R_2$

$$\Delta E_+ = \Delta E_+^0 - \frac{R \cdot T}{\boldsymbol{z} \cdot F} \cdot ln\left(\frac{a(R_1)}{a(O_1)}\right)$$

cathode (+)

$$\Delta E_- = \Delta E_-^0 - \frac{R \cdot T}{\boldsymbol{z} \cdot F} \cdot ln\left(\frac{a(R_2)}{a(O_2)}\right)$$

anode (-)

$\Delta E^0 = \Delta E^0_+ - \Delta E^0_-$

$\Delta E = \Delta E_+ - \Delta E_-$

$$\Delta E = \Delta E^0 - \frac{R \cdot T}{\boldsymbol{z} \cdot F} \cdot ln\left(\frac{a(R_1) \cdot \mathrm{a}(O_2)}{a(O_1) \cdot a(R_2)}\right)$$

NERNST equation

Walther Hermann NERNST (1864 – 1941)

3.2. Galvanic cell potential of the Daniell cell

The two half cells are

$Cu^{2+} + 2 \cdot e^- \rightleftarrows Cu$ and $Zn^{2+} + 2 \cdot e^- \rightleftarrows Zn$

$$\Delta E_+ = 0.34\text{V} - \frac{R \cdot T}{2 \cdot F} \cdot ln\left(\frac{a(Cu)}{a(Cu^{2+})}\right) \text{ cathode (+)}$$

$$\Delta E_- = -0.76\text{V} - \frac{R \cdot T}{2 \cdot F} \cdot ln\left(\frac{a(Zn)}{a(Zn^{2+})}\right) \text{ anode (-)}$$

$\Delta E^0 = \Delta E^0_+ - \Delta E^0_- = 1.1\text{V}$

$\Delta E = \Delta E_+ - \Delta E_-$

$$\Delta E = 1.1\text{V} - \frac{R \cdot T}{2 \cdot F} \cdot ln\left(\frac{a(Cu) \cdot a(Zn^{2+})}{a(Cu^{2+}) \cdot a(Zn)}\right)$$

$$\Delta E = 1.1\text{V} - \frac{R \cdot T}{2 \cdot F} \cdot ln\left(\frac{a(Zn^{2+})}{a(Cu^{2+})}\right)$$

$a(Zn^{2+})/a(Cu^{2+}) = 1000 \rightarrow 90\text{mV}$

12.8 mV at 298K $a(Cu) = 1$, $a(Zn) = 1$

3.3. Measuring the pH = -log(a(H^+))

The two half cells are

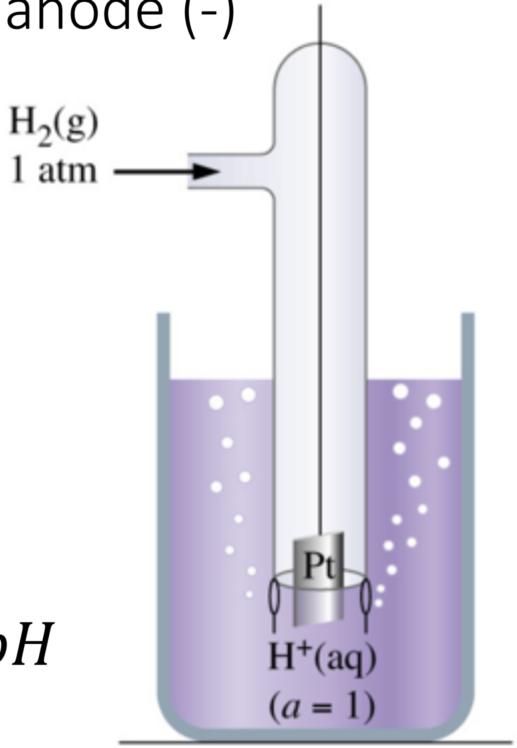
$H^+(1M) + e^- \rightleftarrows \frac{1}{2} H_2(g, 1\ bar)$ and $H^+(xM) + e^- \rightleftarrows \frac{1}{2} H_2(g, 1\ bar)$

$$\Delta E_+ = 0V - \frac{R \cdot T}{F} \cdot ln\left(\frac{a(H_2)}{a(H^+)}\right)$$

cathode (+)
a(H^+) = 1

$$\Delta E_- = 0V - \frac{R \cdot T}{F} \cdot ln\left(\frac{a(H_2)}{a(H^+)}\right)$$

anode (-)



$\Delta E^0 = \Delta E^0_+ - \Delta E^0_- = 0V$

$\Delta E = \Delta E_+ - \Delta E_-$

a(H_2) = 1

$$\Delta E = 0V - \frac{R \cdot T}{F} \cdot ln\left(\frac{a(H_2) \cdot a(H^+)}{a(H^+) \cdot a(H_2)}\right)$$

a(H^+) = 1 a(H_2) = 1

$$\Delta E = -\frac{R \cdot T}{F} \cdot ln\left(\frac{c(H^+)}{1M}\right) = 0.059V \cdot pH$$

25.6 mV at 298K

3.4. Half cell electrode potential E

The two half cells are

$H^+(1M) + e^- \rightleftarrows \frac{1}{2} H_2(g, 1\,bar)$ and $O_1 + n \cdot e^- \rightleftarrows R_1$

$$\Delta E_+ = \Delta E_+^0 - \frac{R \cdot T}{\boldsymbol{z} \cdot F} \cdot ln\left(\frac{a(R_1)}{a(O_1)}\right) \quad \text{cathode (+)}$$

$$\Delta E_- = 0\mathrm{V} - \frac{R \cdot T}{F} \cdot ln\left(\frac{a(H_2)}{a(H^+)}\right) \quad \text{anode (-)}$$

$E^0 = \Delta E^0_+ - 0$

$E = \Delta E_+ - 0$

$$E = E^0 - \frac{R \cdot T}{\boldsymbol{z} \cdot F} \cdot ln\left(\frac{a(R_1)}{a(O_1)}\right)$$

$$E = E^0 - \frac{0.059V}{\boldsymbol{z}} \cdot log\left(\frac{a(R_1)}{a(O_1)}\right)$$

4. Relationship between charge (Q) and quantity (m)

The mass of a substance (m) deposited or liberated at an electrode is directly proportional to the total electric charge (Q = I·t) passed as current I during the time t through the electrolyte.

$$\frac{m}{M} = \frac{Q}{z}$$

m is the mass
M is the molecular mass
z is the charge
Q is the charge
I is the current

$$m = \frac{Q}{z} \cdot M = \frac{I \cdot t}{z} M$$

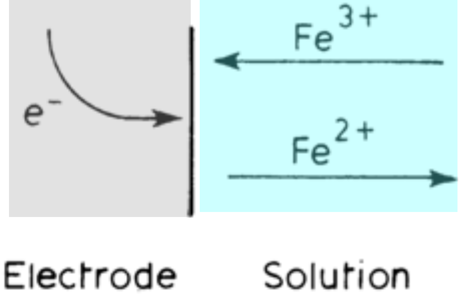
$$F = n \cdot Q_e = 6.022 \cdot 10^{23}\, mol^{-1} \cdot 1.602 \cdot 10^{-19}\, As$$

$$F = 96'485\, As \cdot mol^{-1}$$

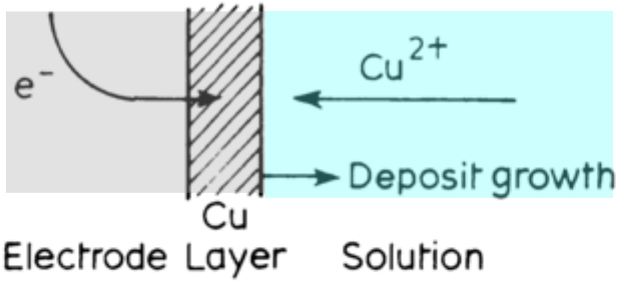
Faraday's laws of electrolysis establish the quantitative relationship between electric charge and the mass of substances involved in electrochemical reactions. These laws are fundamental in predicting the outcomes of electrolysis processes, such as electroplating or metal refining.

Michael Faraday
1791 - 1867

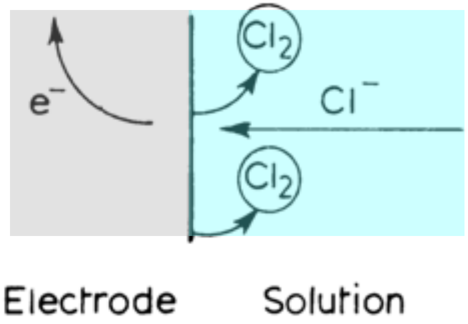
5. Electrode processes 1/2



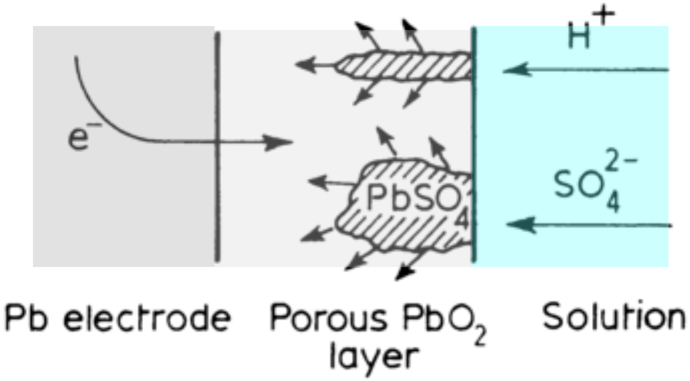
(a) Simple electron transfer,
e.g. $Fe^{3+} + e^- \rightarrow Fe^{2+}$



(b) Metal deposition
e.g. $Cu^{2+} + 2e^- \rightarrow Cu$



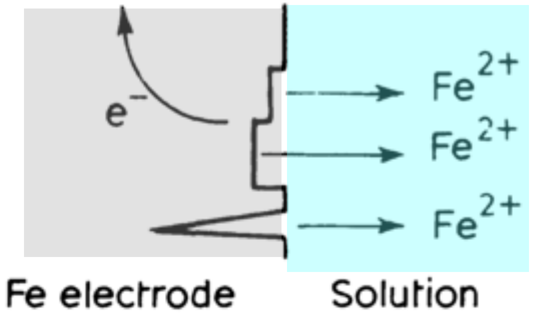
(c) Gas evolution,
e.g. $2Cl^- - 2e^- \rightarrow Cl_2$



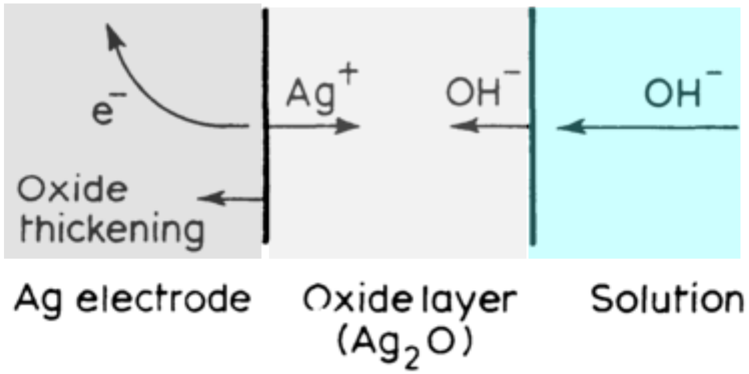
(d) Surface film transformation
e.g. $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

Ref.: Derek Pletcher, Frank C. Walsh, “Industrial Electrochemistry”, SECOND EDITION, Springer Science + Business Media, LLC, (1993).

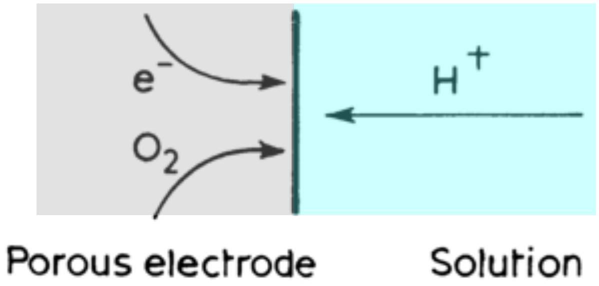
5.1. Electrode processes 2/2



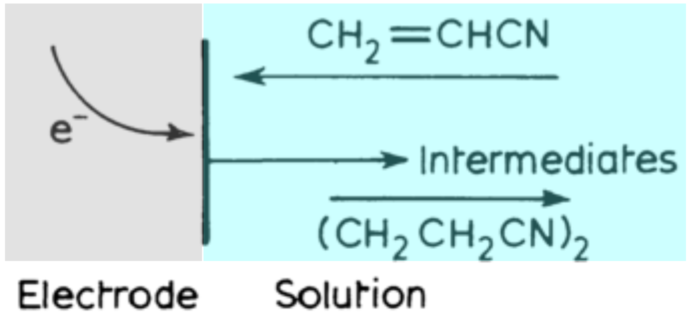
(e) Anodic dissolution
e.g. $Fe - 2e^- \rightarrow Fe^{2+}$



(f) Oxide formation
e.g. $2Ag - 2e^- + 2OH^- \rightarrow Ag_2O + H_2O$



(g) Gas reduction in porous gas diffusion electrode,
e.g. $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

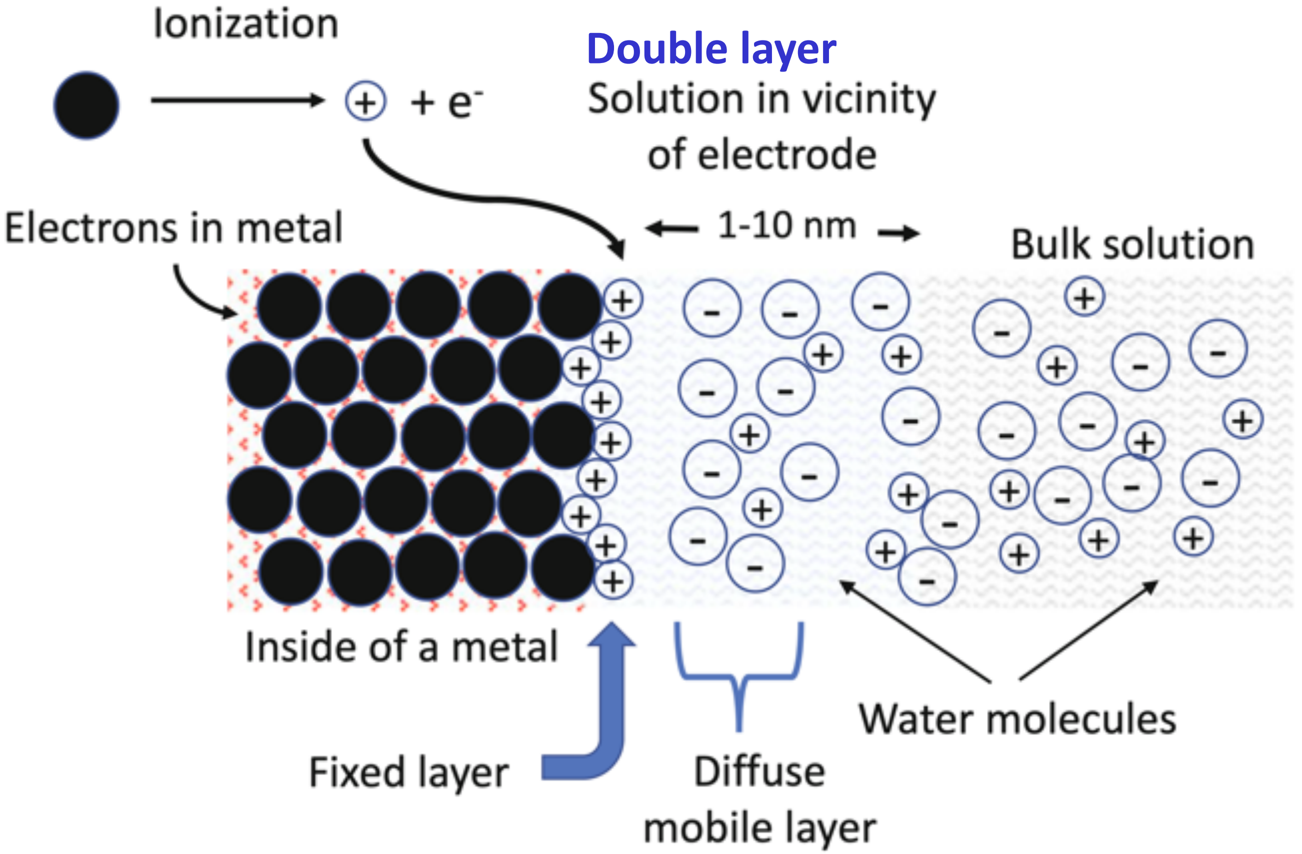


(h) Electron transfer with coupled chemistry,
e.g. $2CH_2{=}CHCN + 2H_2O + 2e^-$
$\rightarrow (CH_2CH_2CN)_2 + 2OH^-$

Ref.: Derek Pletcher, Frank C. Walsh, “Industrial Electrochemistry”, SECOND EDITION, Springer Science + Business Media, LLC, (1993).

6. Electrode/Electrolyte Interface (Double layer)

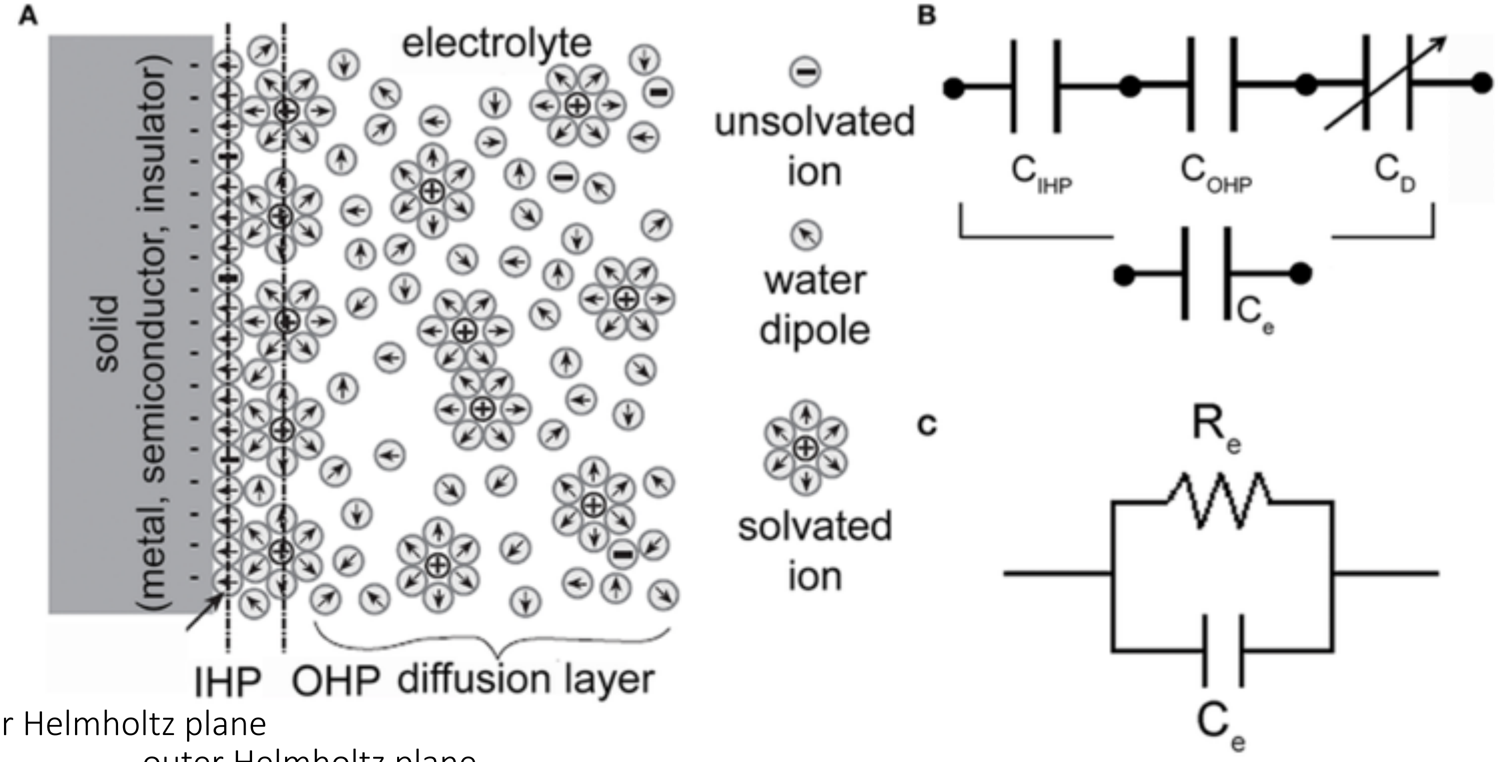
When a metal is immersed in a solution it undergoes ionization, which results in the formation of a positive charge adsorbed at the surface (in the case of moderate ionization), e.g. Zn^{2+}, Fe^{2+}, or Al^{3+}.



The complete cell, comprised of electrode and solution, is electrically neutral, but it contains positive and negative ions and electrons inside the bar. The adsorbed layer of cations on the surface (i.e., positive ions) attracts nearby negative ions from the solution, which move towards the bar's surface and form a so-called diffuse mobile layer.

6.1. Equivalent electrical circuits

(A) Schematic representation of an electrode-electrolyte interface.
(B) Series of three capacitors (corresponding to the inner (IHP), outer (OHP) Helmholtz plane, and diffuse-layer) which models the charge distribution at the interface.
(C) Electrical circuit of an electrode-electrolyte interface. Re is the charge-transfer resistor and Ce is the double-layer capacitor.

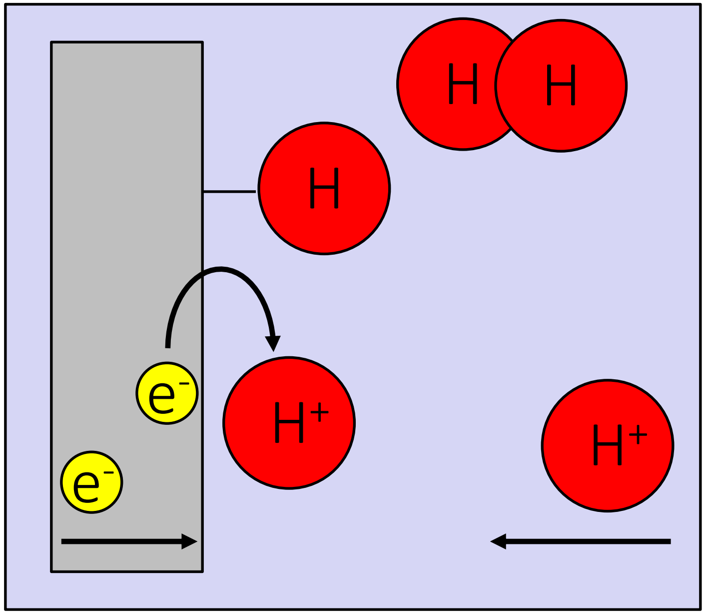


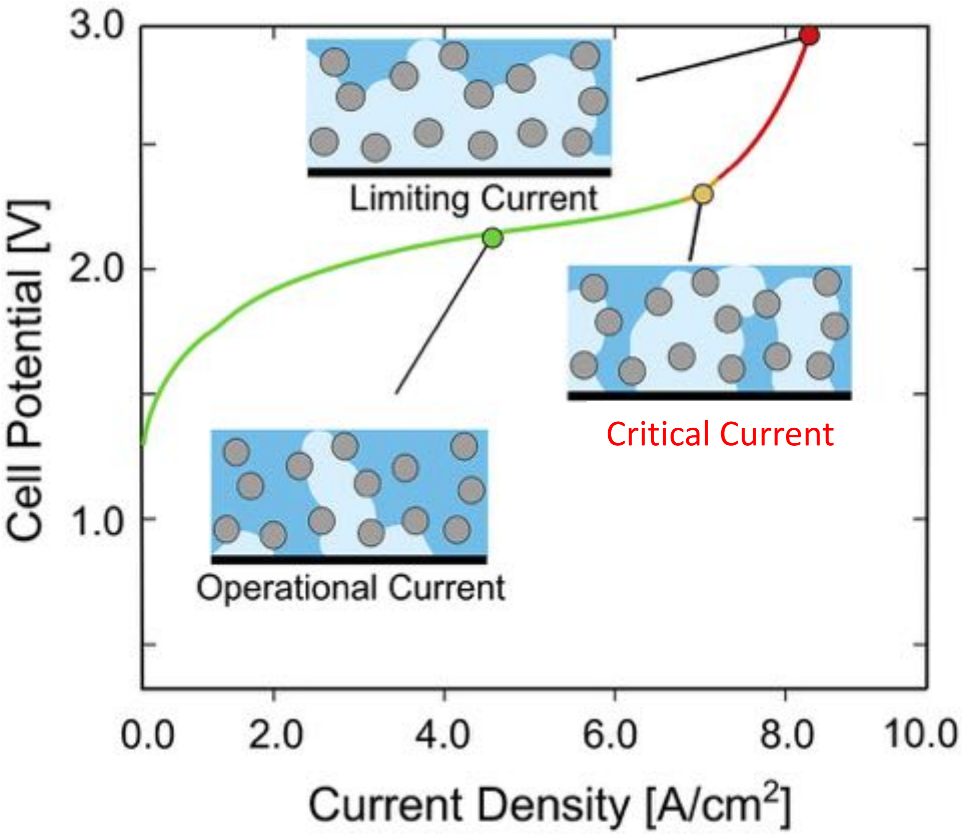
inner Helmholtz plane
outer Helmholtz plane

Ref.: Bockris, J. O. M., and Reddy, A. K. N. (1977). Modern Electrochemistry. New York, NY: Plenum-Rosetta.

7. Current density and limits

Operating at higher current densities is vital for electrochemical energy conversion devices. Specifically, the critical current density has been identified as a performance indicator for gas-evolving electrochemical devices.

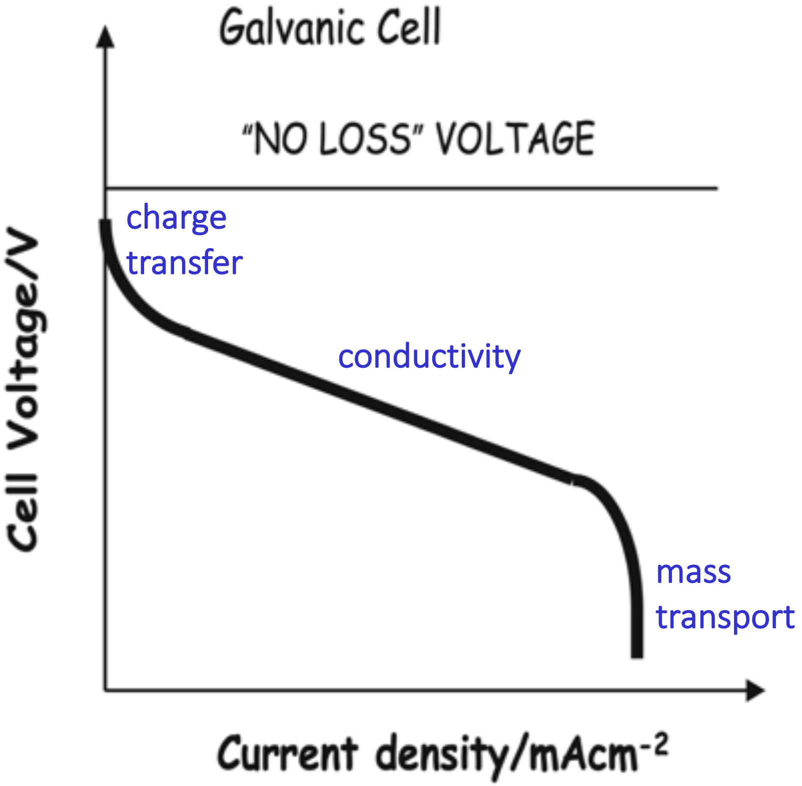


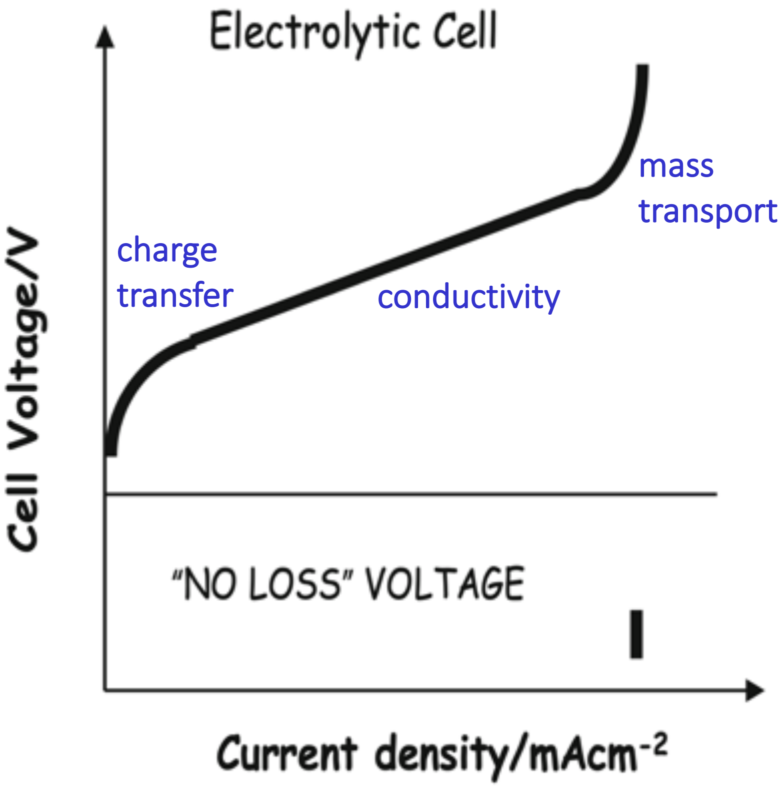


Ref.: Jason K. Lee, ChungHyuk Lee, Kieran F. Fahy, Benzhong Zhao, Jacob M. LaManna, Elias Baltic, David L. Jacobson, Daniel S. Hussey, Aimy Bazylak, “Critical Current Density as a Performance Indicator for Gas-Evolving Electrochemical Devices”, Cell Reports Physical Science, Volume 2, Issue 5, 19 May 2021, Pages 100440

8. Overpotential $\eta = \Delta E - \Delta E_{eq}$

There are several commonly used names for overpotential (or overvoltage): polarization, irreversibility, voltage drop, or losses.





charge transfer
$\eta_{\text{Tafel}} = A \cdot \ln(i/i_0)$
Tafel equation

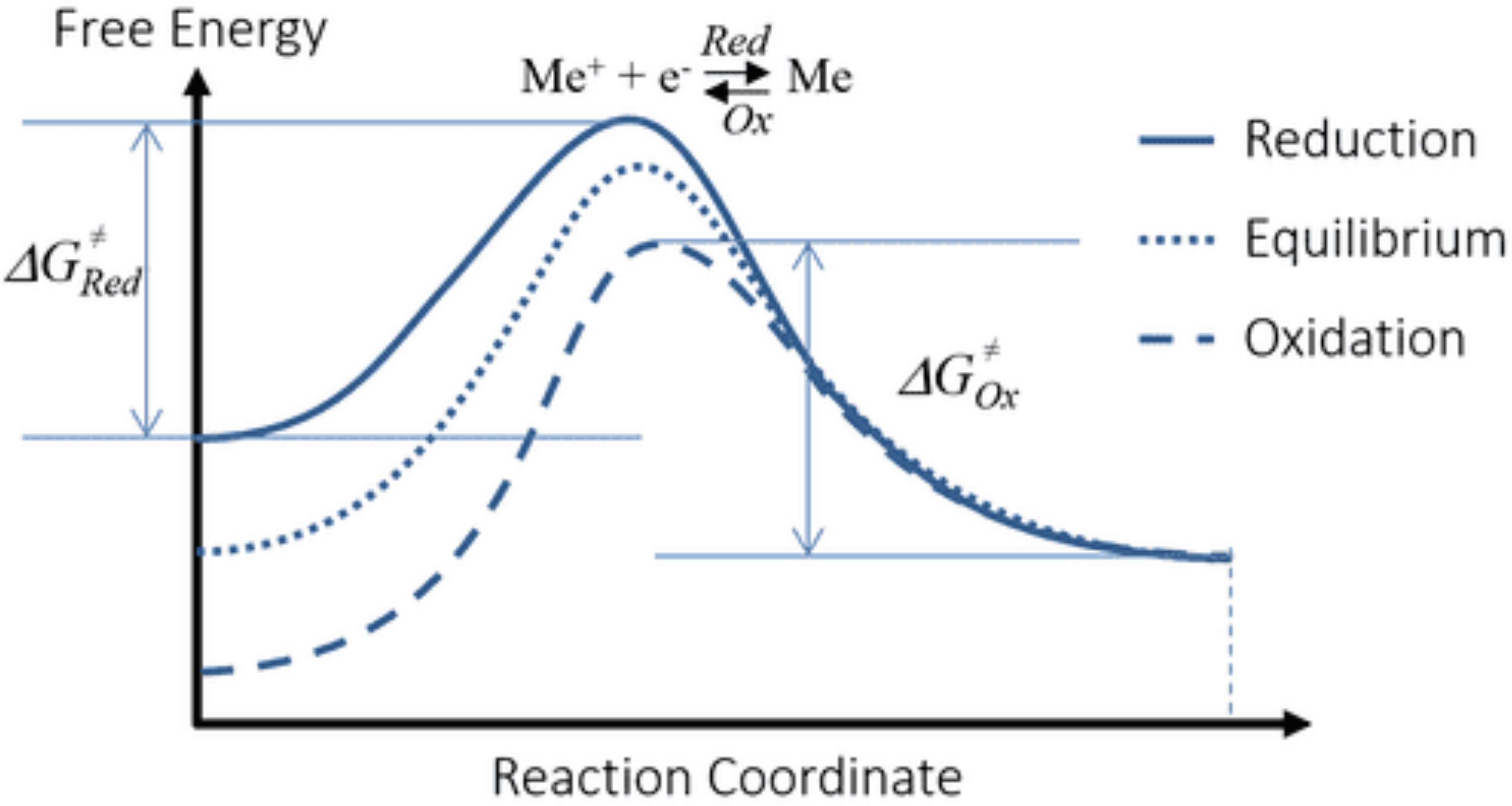
conductivity
$\eta_{\Omega} = i \cdot R$
Ohms law

mass transport
$\eta_{\text{diff}} = -B \cdot (1 - i/i_{lim})$
Diffusion

The overpotential of the electrode is the sum of the three contributions $\eta = \eta_{\text{Tafel}} + \eta_{W} + \eta_{\text{diff}}$.

9. Charge transfer kinetics

The potential difference between the electrode surface and the outer Helmholtz plane can be varied to get a net reduction or oxidation.



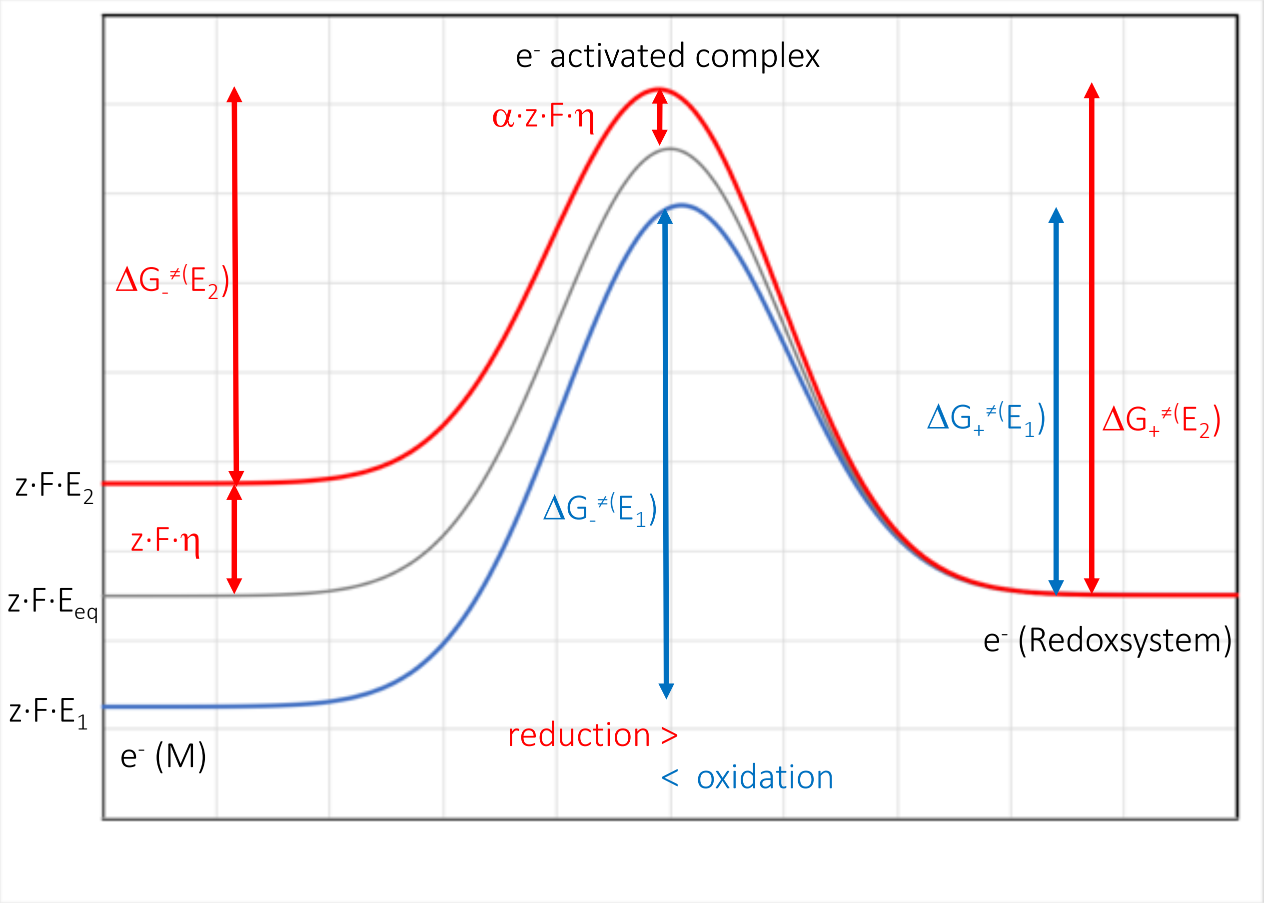
Ref.: https://www.physicsforums.com/threads/electrokinetics-charge-transfer-coefficient.921195/#google_vignette

9.1. Activated charge transfer

Arrhenius equation: $k = k_0 \cdot exp\left[-\frac{E^A}{R \cdot T}\right]$

E^A: activation energy
R: gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$
T: Temperature
k_0: preexponential factor
k: rate constant in $dc/dt = k \cdot c^n$

The activation overpotential is $\eta = E - E_{eq}$



Ref.: Edmund J.F. Dickinson ⁎, Andrew J. Wain, "The Butler-Volmer equation in electrochemical theory: Origins, value, and practical application", Journal of Electroanalytical Chemistry 872 (2020) 114145

9.2. Exchange current density

Close to the equilibrium potential E_{eq} the absolute current density of the reduction (j^+) and oxidation (j^-) reaction become equal to the exchange current density j_0. α is the transfer coefficient in reductive direction, electroanalytical Butler-Volmer equation.

$$j_0 = j^+(E_{eq}) = \left|j^-(E_{eq})\right|$$

$$j^+(\eta) = j_0 \cdot \left\{exp\left[\alpha \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta\right]\right\}$$

$$j^-(\eta) = -j_0 \cdot \left\{exp\left[-(1-\alpha) \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta\right]\right\}$$

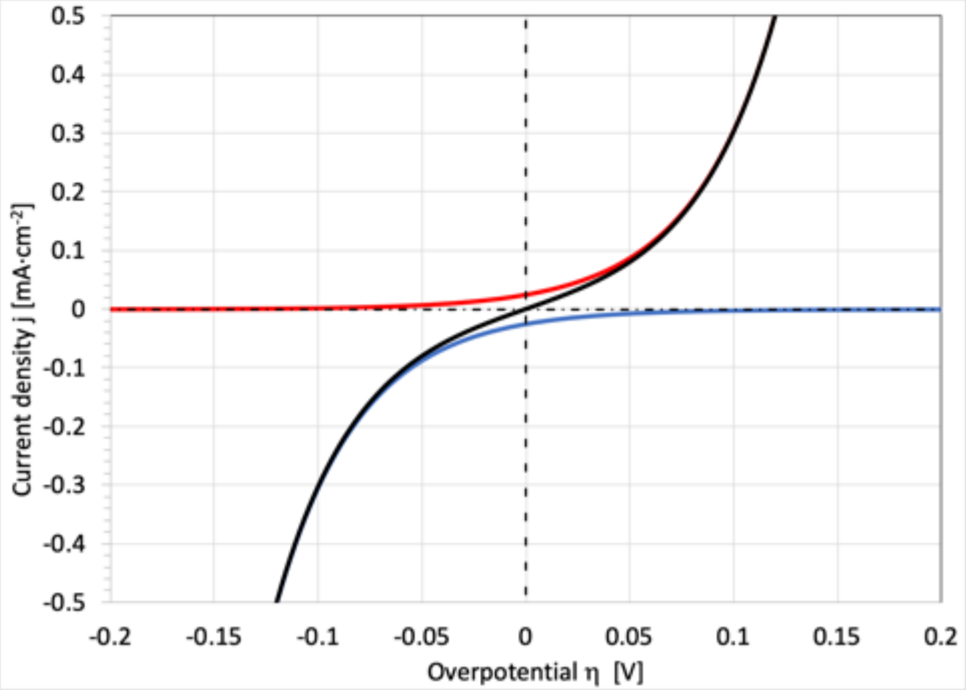
α is the transfer coefficient in reductive direction
η is the overpotential = $E - E_{eq}$
R is the gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$)
T is the temperature (standard temperature 298 K)

Ref.: https://www.physicsforums.com/threads/electrokinetics-charge-transfer-coefficient.921195/#google_vignette

9.3. Butler-Volmer equation

The current density $j = j^{+}(\eta) + j^{-}(\eta)$

$$j = j_0 \cdot \left\{ exp\left[\alpha \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta\right] - exp\left[-(1-\alpha) \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta\right] \right\}$$



John Alfred Valentine Butler (1899–1977)

Max Volmer (1885–1965)

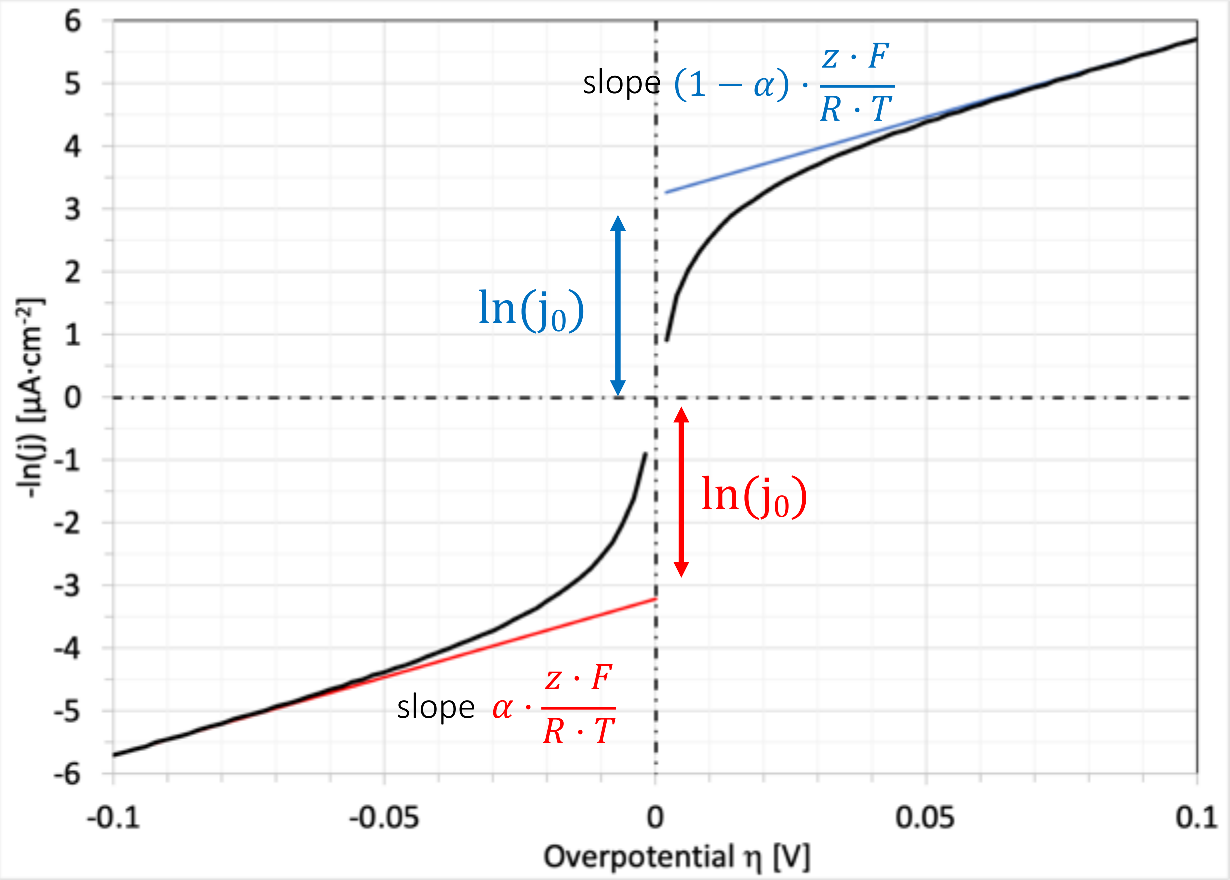
The **Butler–Volmer equation** describes how the electrical current through an electrode depends on the voltage difference between the electrode and the bulk electrolyte for a simple, unimolecular redox reaction, considering that both a cathodic and an anodic reaction occur on the same electrode.

Ref.: https://www.physicsforums.com/threads/electrokinetics-charge-transfer-coefficient.921195/#google_vignette

9.4. Logarithmic current density

$$ln(j) = ln(j_0) + \alpha \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta$$

$$ln(j) = ln(j_0) + (1-\alpha) \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta$$



Ref.: https://www.physicsforums.com/threads/electrokinetics-charge-transfer-coefficient.921195/#google_vignette

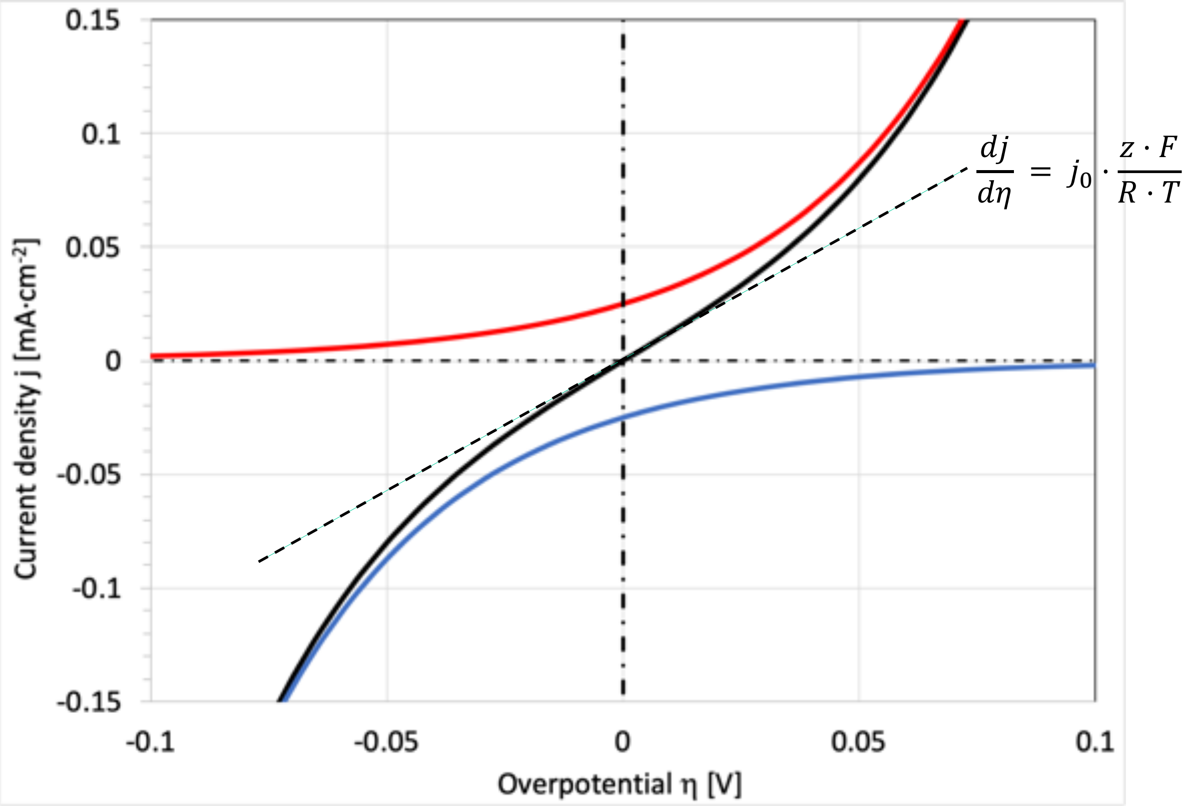
9.5. Exchange current density close to equilibrium

With $e^x \approx 1 + x$ for $x \ll 1$ and $\alpha = 0.5$, the Butler-Volmer equation simplifies to

$$j = j_0 \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta$$

$$\frac{dj}{d\eta} = j_0 \cdot \frac{z \cdot F}{R \cdot T}$$

$$\mathbf{R_T} = \frac{R \cdot T}{z \cdot F} \cdot \frac{1}{j_0} = \frac{d\eta}{dj}$$

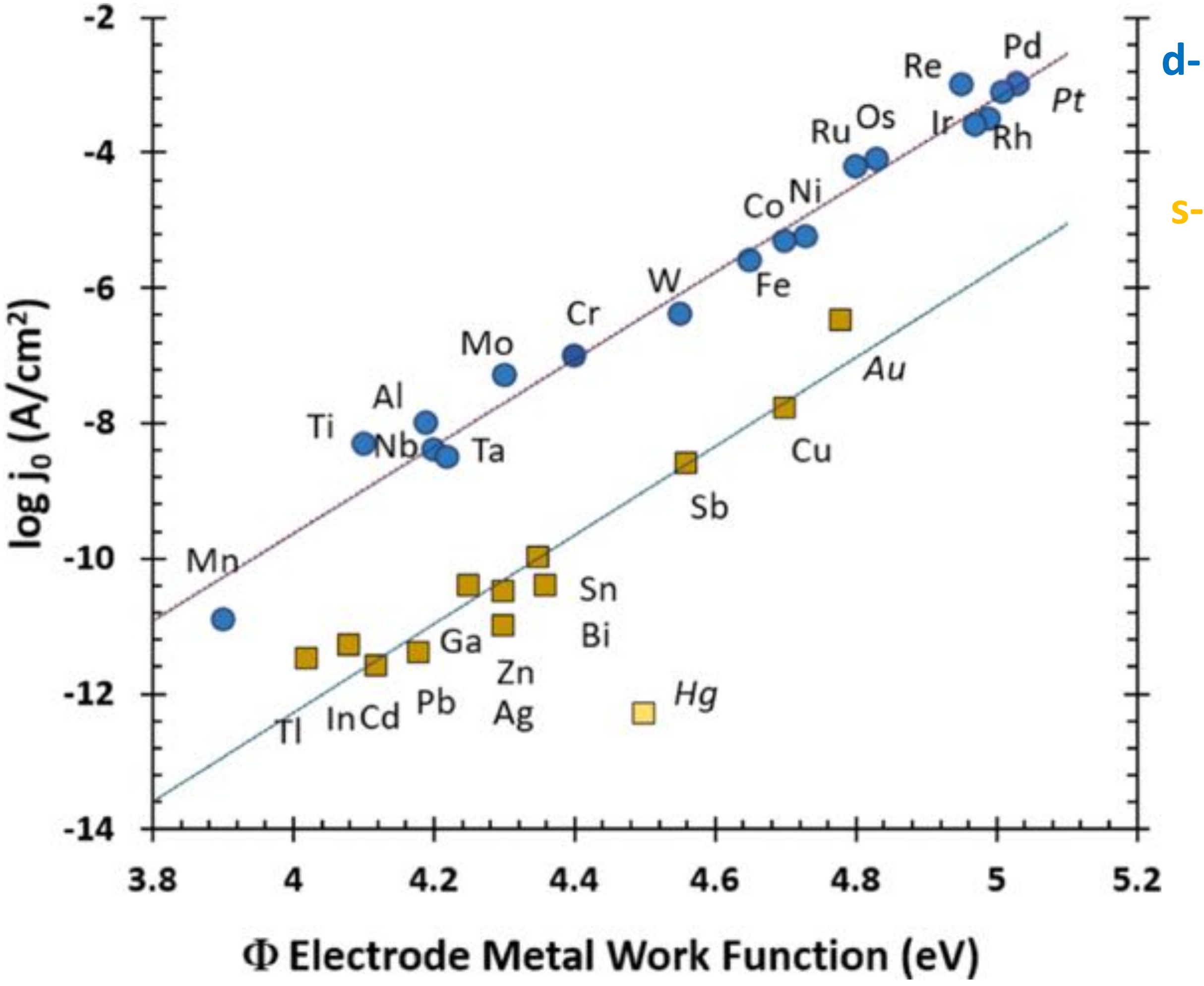


In the range n ≤ 10 mV, the current-voltage curve therefore becomes a straight line whose slope depends only on j_0, but not on a. To determine j_0, it is sufficient to know the leakage current-voltage curve for small overvoltage.

Since j_0 has the unit of a current density, the unit of the resistance must assume a surface area and is therefore referred to as the activation resistance R.

9.6. Exchange current density and work function

Plot of log10 j_0 against metal work function for the hydrogen evolution reaction (HER) on a range of metal electrodes.



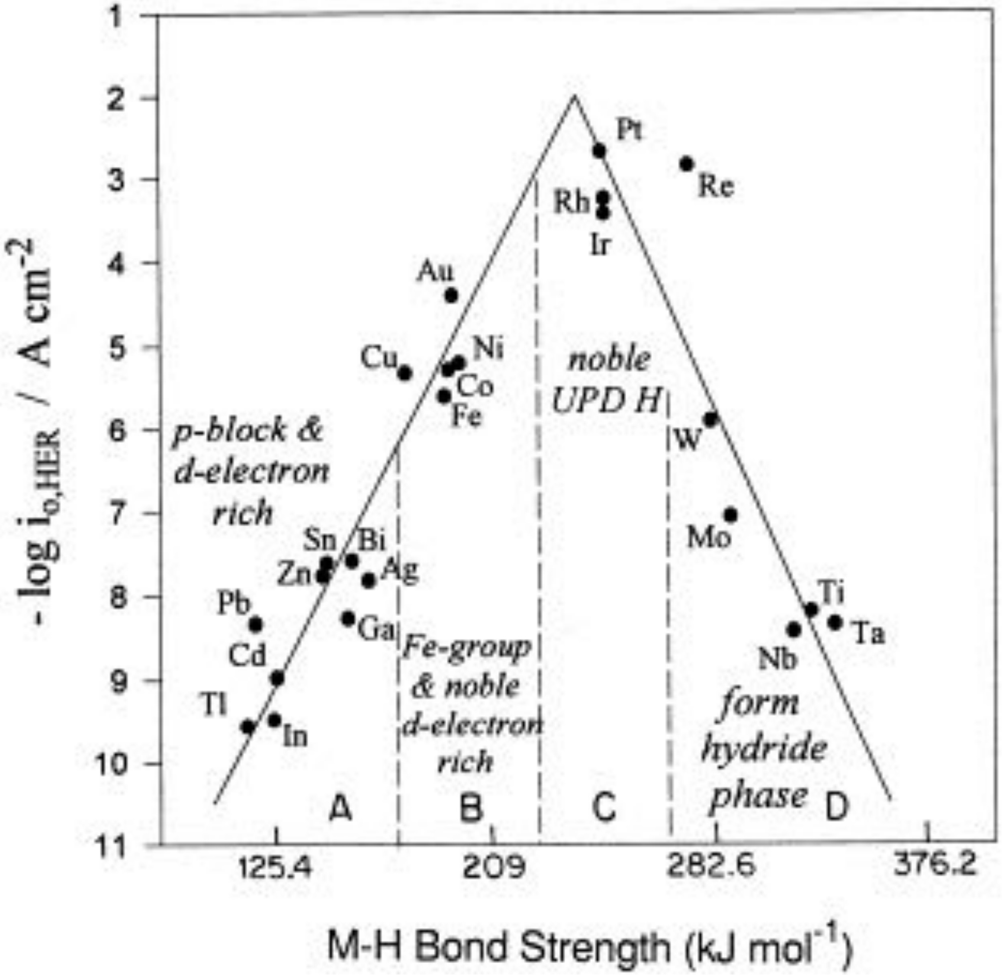
d-metals 6.44 eV^{-1}

s-metals 6.56 eV^{-1}

Ref.. D. Noel Buckley and Johna Leddy, "The Butler-Volmer Equation Revisited: Effect of Metal Work Function on Electron Transfer Kinetics", J. Electrochem. Soc. 171 (2024), 116503

9.7. Exchange current density and M-H bond energy

Relationships between log i_0 and metal properties, including the M-H bond energy, exhibit a 'volcano'-shaped curve of the kind already recognized in works on heterogeneous catalysis.

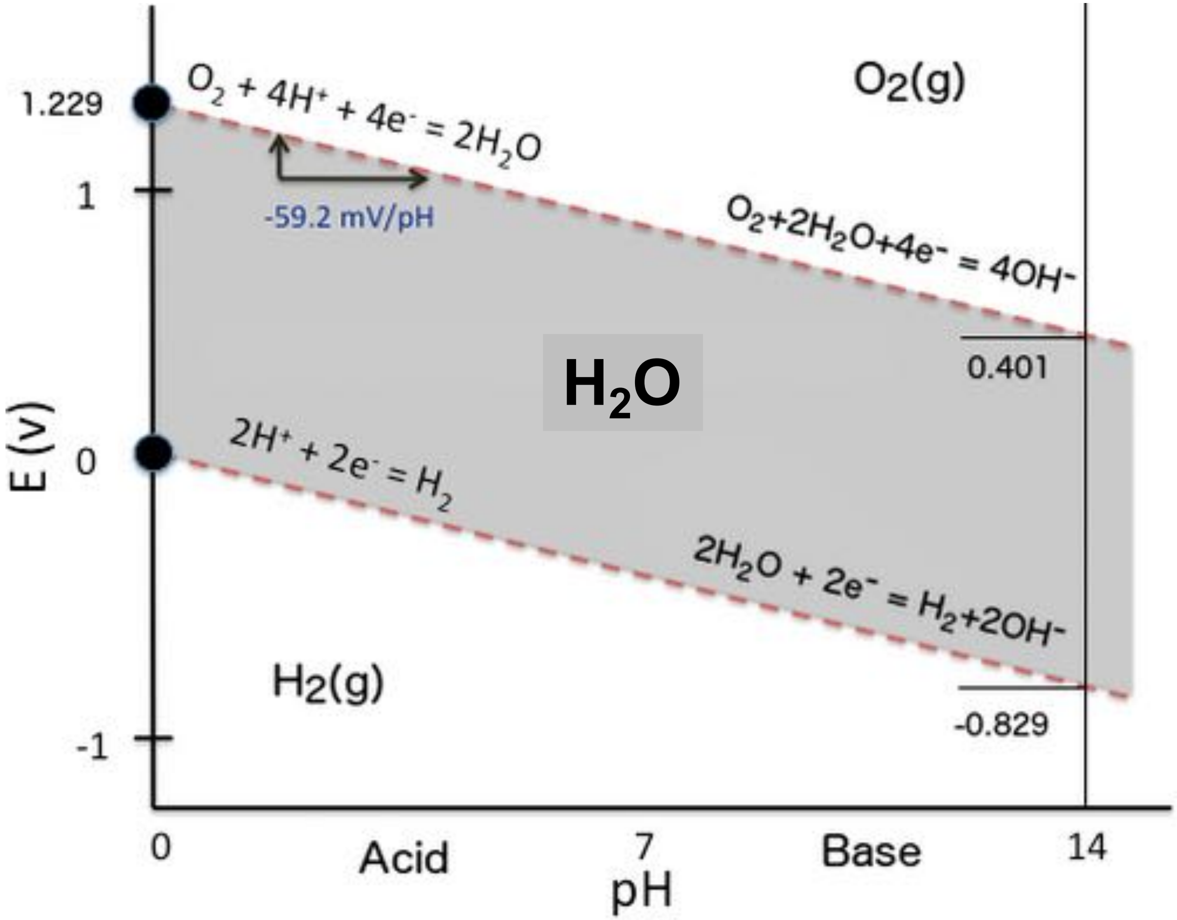


Ref.. B.E. Conway, G. Jerkiewicz, "Relation of energies and coverages of underpotential and overpotential deposited H at Pt and other metals to the 'volcano curve' for cathodic H_2 evolution kinetics", Electrochimica Acta Volume 45, Issues 25–26, 31 August 2000, Pages 4075-4083

10. Stability of water (Pourbaix diagram)

Pourbaix diagram for water, including stability regions for water, oxygen and hydrogen at standard temperature and pressure (STP).

T = 298 K
p = 100 kPa

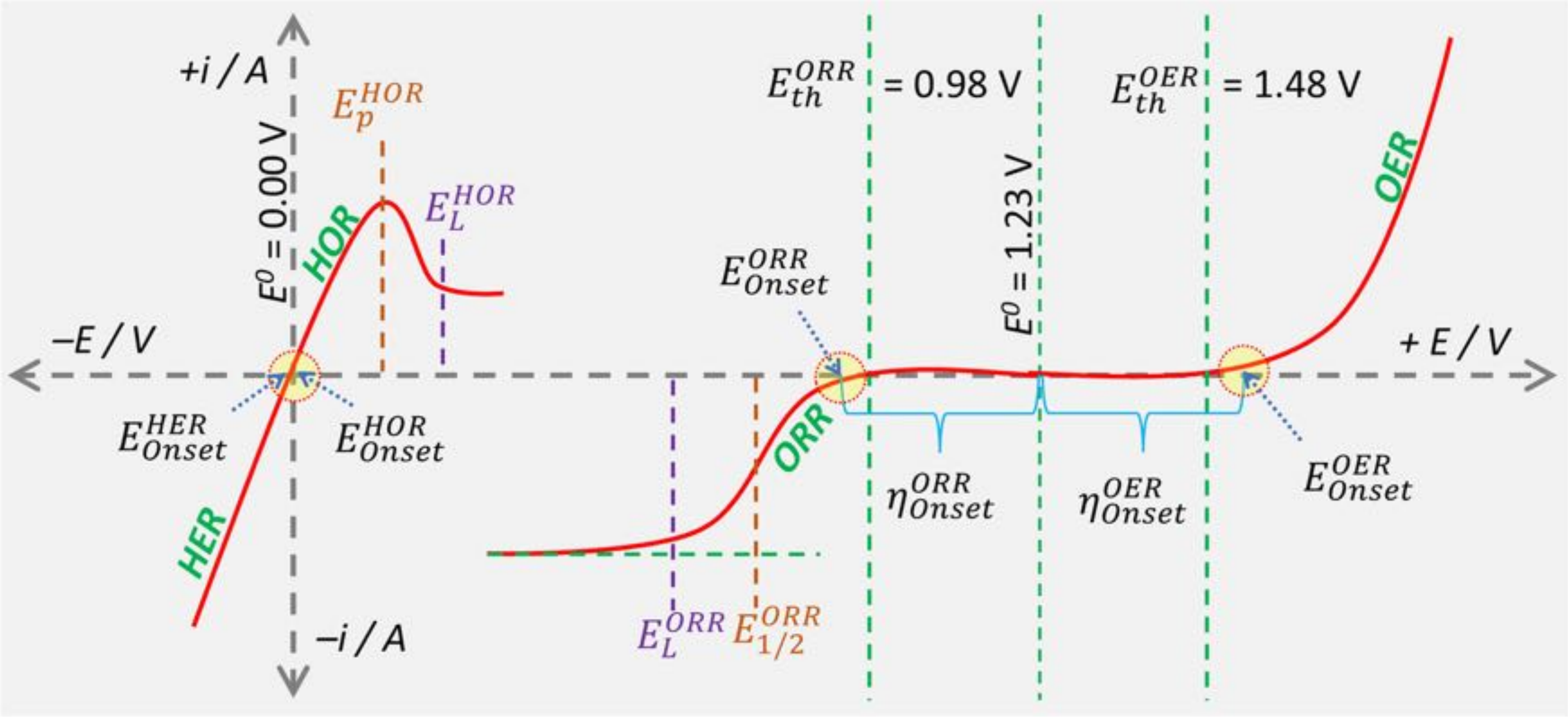


Marcel Pourbaix
(1904–1998)

The vertical scale (ordinate) is the electrode potential (of a hydrogen or non-interacting electrode) relative to a standard hydrogen electrode (SHE), the horizontal scale (abscissa) is the pH of the electrolyte (otherwise non-interacting).

10.1. Hydrogen and oxygen evolution reaction (HER and OER)

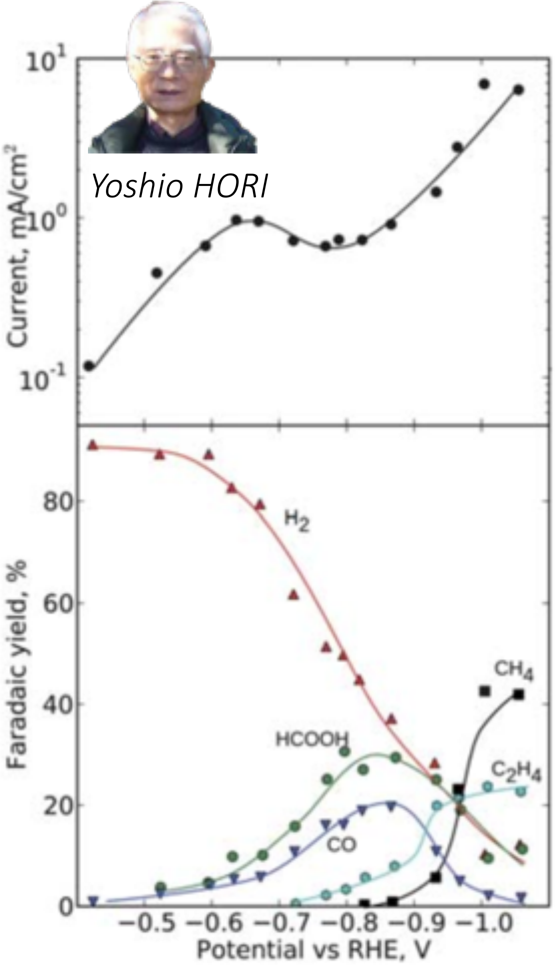
Depiction of the OER, ORR, HER, and HOR polarization curves detailing different types of potentials (electrode/solution) used in electrochemical energy conversion reactions. Note that the HOR is shown to form a peak-shaped voltammogram by assuming that the HER is conducted with a stationary electrode in an unstirred electrolyte whereas the ORR is conducted with a rotating disc electrode (RDE) that eliminates diffusion limitation and results in a sigmoidal polarization curve.



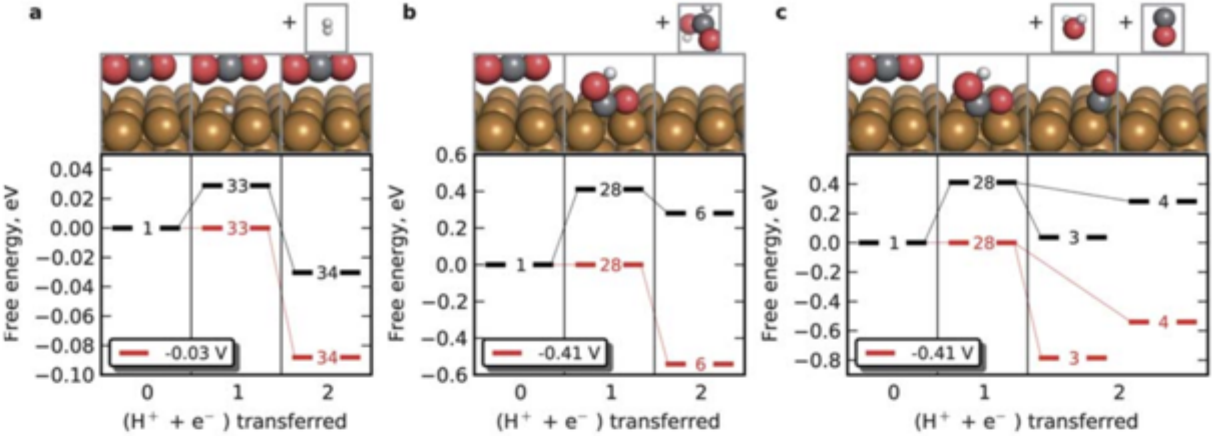
Ref.: Anantharaj Sengeni, “How reliable are the overpotentials reported in energy conversion electrocatalysis?”, Catalysis Science & Technology 14 (2024), pp. 2025-2039

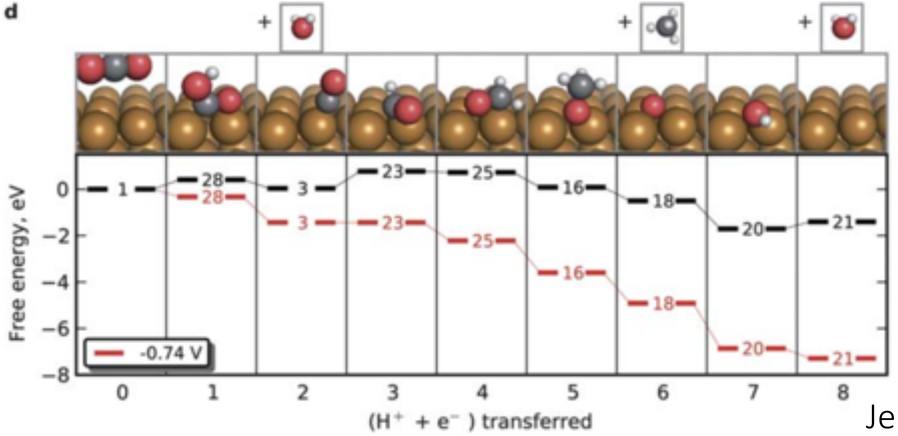
11. Electrochemical CO_2 reduction on Cu

Free energy diagrams for the lowest energy pathways to (a) H_2, (b) HCOOH, (c) CO, and (d) CH_4. The black (higher) pathway represents the free energy at 0 V vs. RHE and the red (lower) pathway the free energy at the indicated potential.



Yoshio HORI

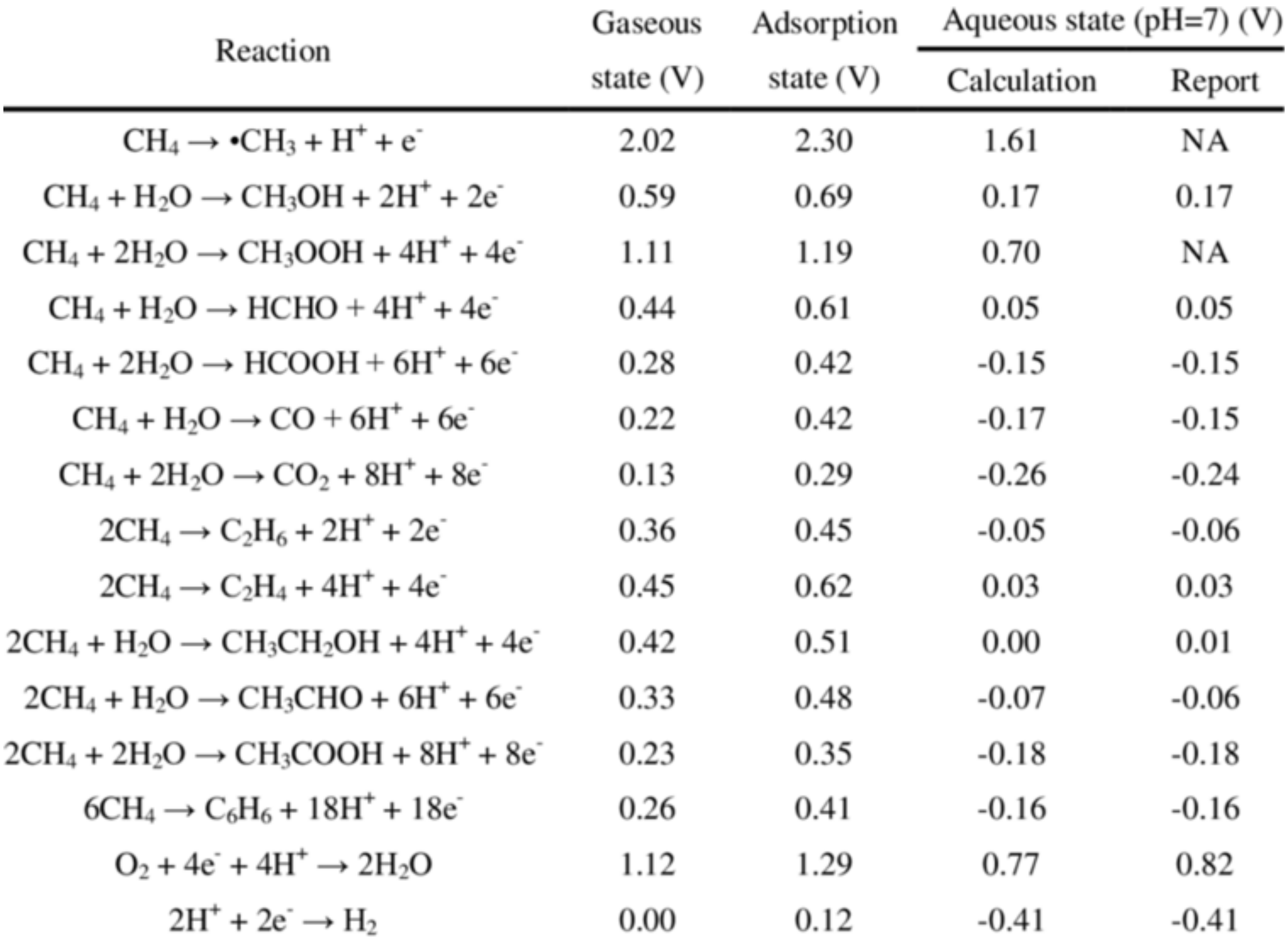




Jens NORSKOV

Ref.: Andrew A. Peterson, Frank Abild-Pedersen, Felix Studt, Jan Rossmeisl and Jens K. Nørskov, “How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon”, Energy Environ. Sci. 3 (2010), pp. 1311–1315. DOI: 10.1039/c0ee00071j

11.1. Standard electrode potentials E^0 of the CH_4 oxidation



Reaction	Gaseous state (V)	Adsorption state (V)	Aqueous state (pH=7) (V) Calculation	Aqueous state (pH=7) (V) Report
$CH_4 \rightarrow \bullet CH_3 + H^+ + e^-$	2.02	2.30	1.61	NA
$CH_4 + H_2O \rightarrow CH_3OH + 2H^+ + 2e^-$	0.59	0.69	0.17	0.17
$CH_4 + 2H_2O \rightarrow CH_3OOH + 4H^+ + 4e^-$	1.11	1.19	0.70	NA
$CH_4 + H_2O \rightarrow HCHO + 4H^+ + 4e^-$	0.44	0.61	0.05	0.05
$CH_4 + 2H_2O \rightarrow HCOOH + 6H^+ + 6e^-$	0.28	0.42	-0.15	-0.15
$CH_4 + H_2O \rightarrow CO + 6H^+ + 6e^-$	0.22	0.42	-0.17	-0.15
$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^-$	0.13	0.29	-0.26	-0.24
$2CH_4 \rightarrow C_2H_6 + 2H^+ + 2e^-$	0.36	0.45	-0.05	-0.06
$2CH_4 \rightarrow C_2H_4 + 4H^+ + 4e^-$	0.45	0.62	0.03	0.03
$2CH_4 + H_2O \rightarrow CH_3CH_2OH + 4H^+ + 4e^-$	0.42	0.51	0.00	0.01
$2CH_4 + H_2O \rightarrow CH_3CHO + 6H^+ + 6e^-$	0.33	0.48	-0.07	-0.06
$2CH_4 + 2H_2O \rightarrow CH_3COOH + 8H^+ + 8e^-$	0.23	0.35	-0.18	-0.18
$6CH_4 \rightarrow C_6H_6 + 18H^+ + 18e^-$	0.26	0.41	-0.16	-0.16
$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$	1.12	1.29	0.77	0.82
$2H^+ + 2e^- \rightarrow H_2$	0.00	0.12	-0.41	-0.41

Ref.: Fang S, Hu YH, “Temperature, pressure, and adsorption-dependent redox potentials: Ⅱ. Processes of CH_4 oxidation to value-added compounds.”, Energy Sci Eng. 2023;11: pp. 762-782. doi:10.1002/ese3.1361

11.2. Standard electrode potentials E^0 of the CO_2 reduction

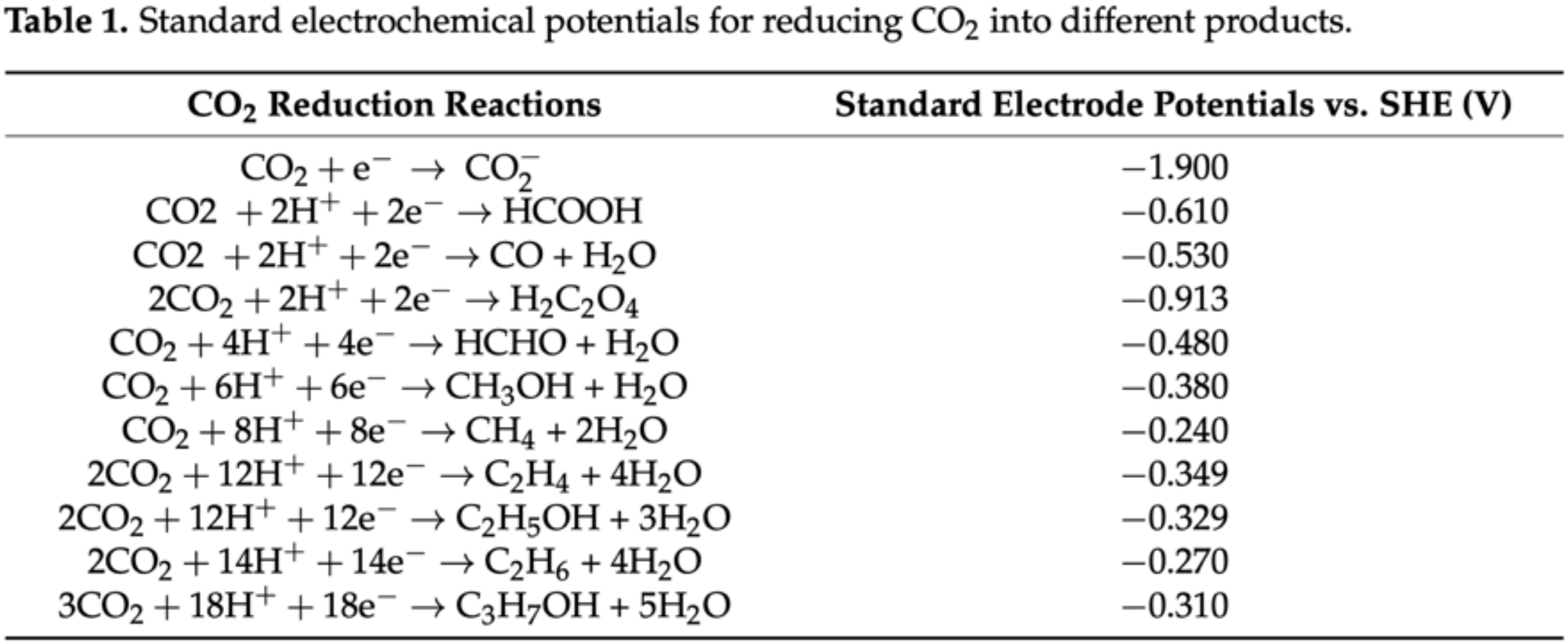


Table 1. Standard electrochemical potentials for reducing CO_2 into different products.

CO_2 Reduction Reactions	Standard Electrode Potentials vs. SHE (V)
$CO_2 + e^- \rightarrow CO_2^-$	−1.900
$CO2 + 2H^+ + 2e^- \rightarrow HCOOH$	−0.610
$CO2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.530
$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$	−0.913
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	−0.480
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	−0.380
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	−0.240
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	−0.349
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	−0.329
$2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_6 + 4H_2O$	−0.270
$3CO_2 + 18H^+ + 18e^- \rightarrow C_3H_7OH + 5H_2O$	−0.310

Ref.: Lu, Song & Lou, Fengliu & Yu, Zhixin. (2022). Recent Progress in Two-Dimensional Materials for Electrocatalytic CO_2 Reduction. Catalysts. 12. 228. 10.3390/catal12020228.

12. Exercises

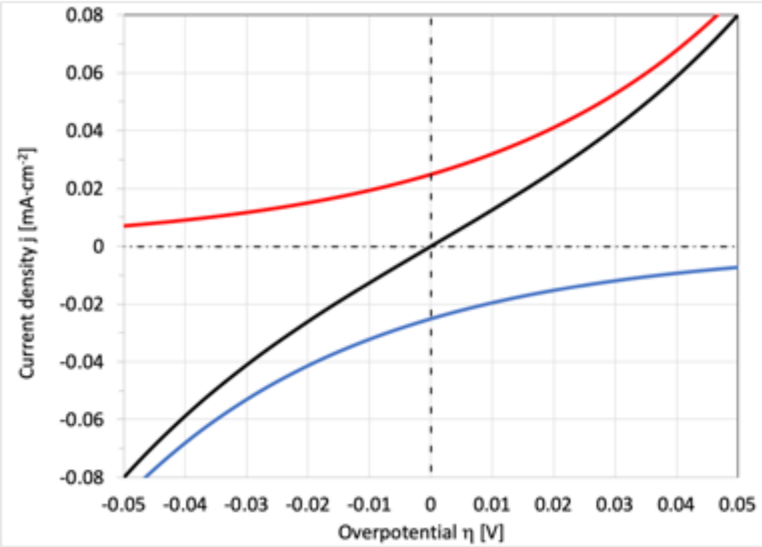
12.1. Butler-Volmer equation for small overpotential

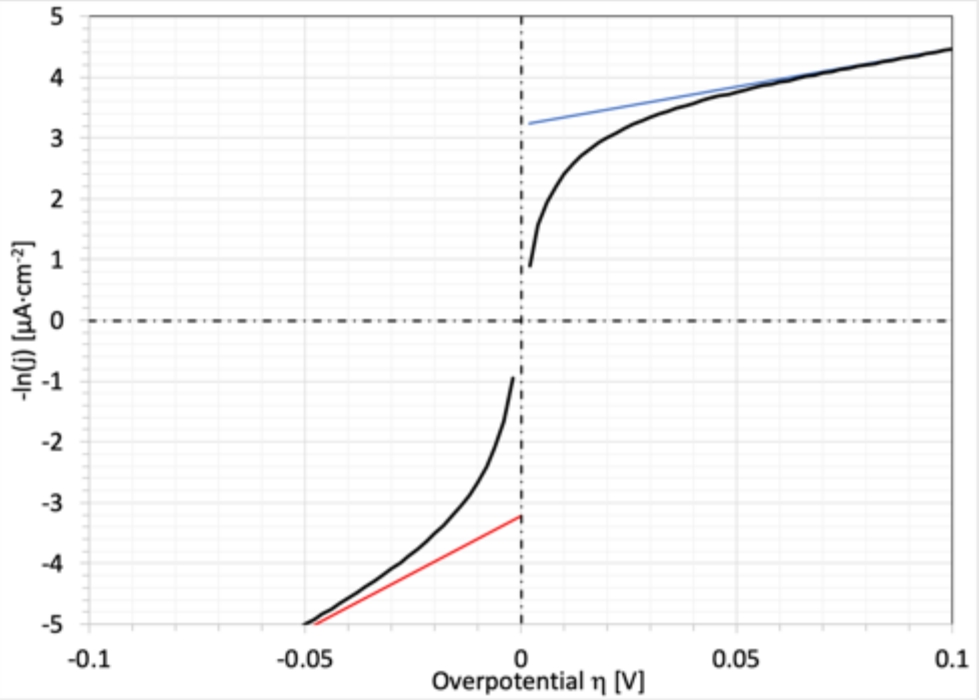
Determine the Butler-Volmer equation at small overpotential using the $\mathrm{e}^{\mathrm{x}} \approx 1 + \mathrm{x}$ for x $\ll$ 0.1 approximation and α = 0.5.

$$j = j_0 \cdot \left\{exp\left[\alpha \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta\right] - exp\left[-(1-\alpha) \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta\right]\right\}$$

12.2. Transfer current density

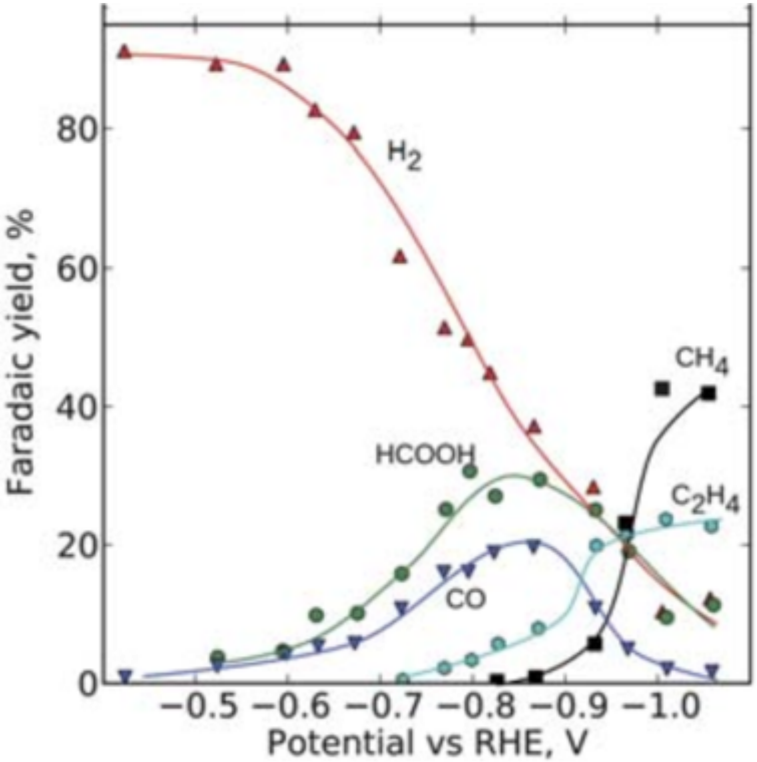
Determine the exchange current density [µA·cm^{-2}] and the transfer coefficient for the reduction and oxidation reaction.





12.3. CO_2 reduction to methane

a) Describe to two half reactions and the complete electrochemical reaction of the CO_2 reduction to methane.
b) Calculate the standard potential for the electrochemical CO_2 reduction to methane and compare with the potential observed by Hori.
c) What is the estimated Faradaic and energy efficiency?



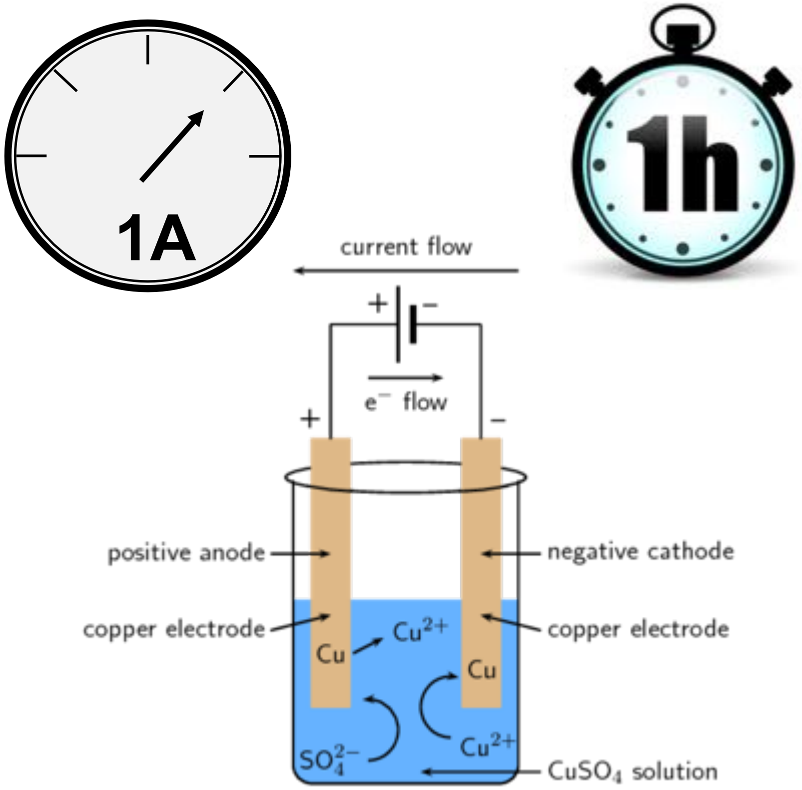
Electrochemistry

12.4. Charge and mass

a) Calculate the mass of Cu deposited in an electrolytic cell on a Cu electrode immersed in a 1M $CuSO_4$ solution passing a current of 1A between two Cu electrodes for 1h.

b) Describe the half reactions on the cathode and the anode.

c) What is the min. potential?



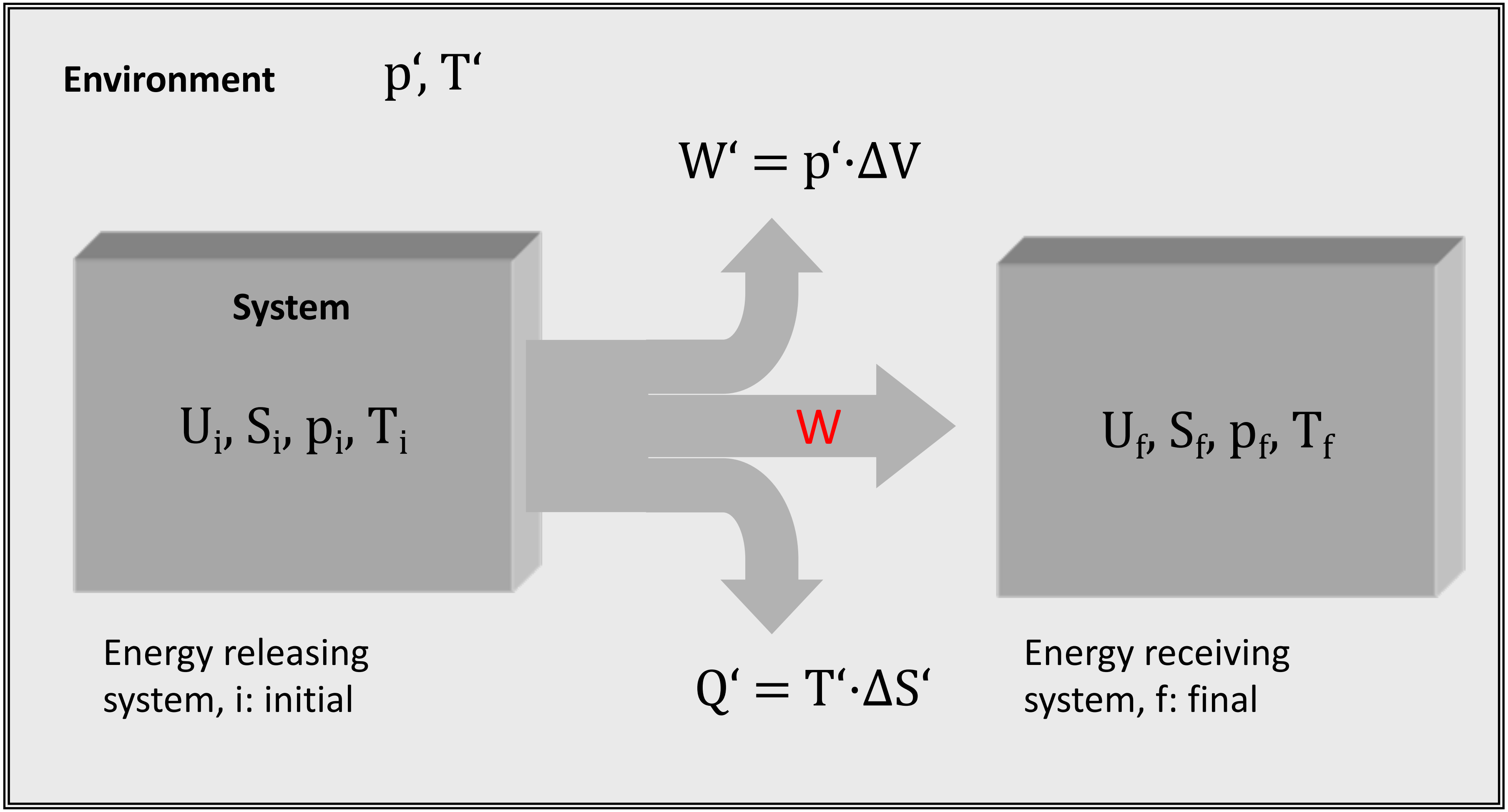
A1.1 Thermodynamics of energy conversion

$\Delta U = \Delta Q + \Delta W$ ($\Delta U = 0$ in Universe, 1st law of TD, $\Delta U = \Delta Q$ for V = const.)

$\Delta H = \Delta U + p \cdot \Delta V$ (Enthalpy, $\Delta H = \Delta Q$ when p = const.)

$\Delta S_{\mathrm{Univ.}} \geq 0$ (2nd law of TD)

U : inner energy
S : entropy
Q : heat
W : work
p : pressure
T : temperature



A1.2. Gibbs free enthalpy

$S_f - S_i = \Delta S$ and $\Delta S' = Q'/T'$

$\Delta S_{Univ.} = \Delta S + \Delta S' = S_f - S_i + Q'/T'$ ... $Q' = T' \cdot (\Delta S_{Univ.} - \Delta S)$

$U_f - U_i = \Delta U = -W - W' - Q'$ ... $W = -\Delta U - W' - Q'$

$W + T' \cdot \Delta S_{Univ.} = -\Delta U - W' + T' \cdot \Delta S$

$= -(U_f - U_i) - p' \cdot (V_f - V_i) + T'(S_f - S_i)$

for $\Delta S_{Univ.} = 0$ ... $W = -\Delta U - p' \cdot \Delta V - T'\Delta S = -\Delta H + T'\Delta S$

for $\Delta S_{Univ.} > 0$ ... spontaneous reaction

$\Delta S_{Univ.} = \Delta S + Q'/T'$ for p = const. ... $\Delta S_{Univ.} = \Delta S^0 - \Delta H^0/T'$

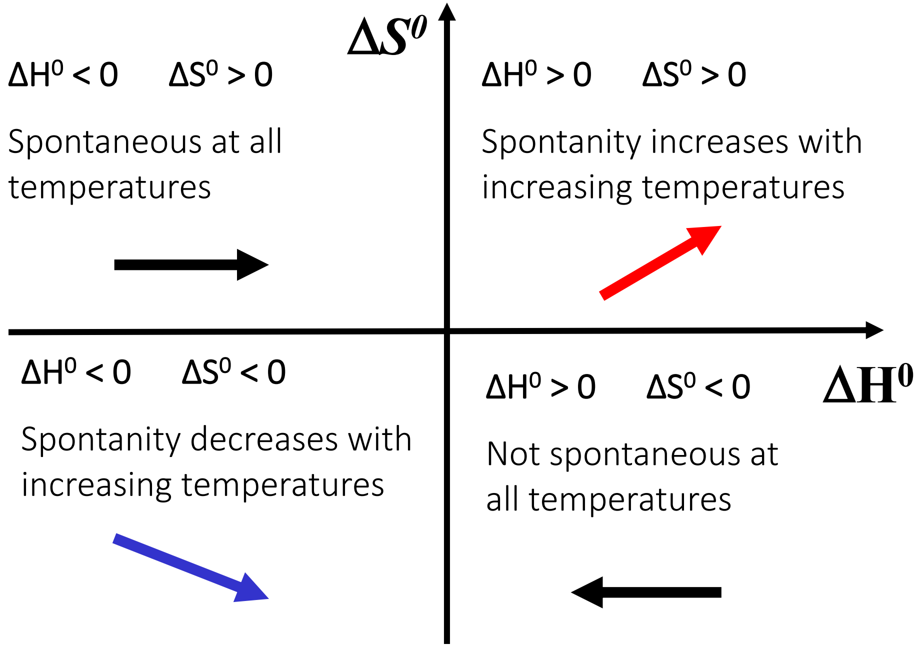
$\Delta G^0 = -T' \cdot \Delta S_{Univ.} = \Delta H^0 - T \cdot \Delta S^0$ Standard Gibbs free energy

$\Delta G = \Delta G^0 + R \cdot T \cdot \ln(Q)$

A1.3. Spontaneous reaction

$$\Delta_r G^0 = \Delta_r H^0 - T \cdot \Delta_r S^0$$

Hypothesis: $\Delta_r H^0$, $\Delta_r S^0$ don’t vary with temperature



$\Delta H^0 < 0$ $\Delta S^0 > 0$

Spontaneous at all temperatures

$\Delta H^0 > 0$ $\Delta S^0 > 0$

Spontanity increases with increasing temperatures

$\Delta H^0 < 0$ $\Delta S^0 < 0$

Spontanity decreases with increasing temperatures

$\Delta H^0 > 0$ $\Delta S^0 < 0$

Not spontaneous at all temperatures

Energy efficiency:

$$\eta_W = \frac{W}{Q} = \frac{-\Delta G}{\Delta H}$$

Fradaic efficiency:

$$\eta_F = \frac{Q_{Product}}{Q_{tot}} = yield$$

The maximum amount of work that can be produced by an electrochemical cell (W) is equal to the product of the cell potential (E_{cell}) and the total charge transferred during the reaction (n·F):

$$W = -n \cdot F \cdot \Delta E_{cell} \quad \ldots \quad \Delta G = -n \cdot F \cdot \Delta E_{cell} \quad \text{and} \quad \Delta G^0 = -n \cdot F \cdot \Delta E^0_{cell}$$

Work is expressed as a negative number because work is being done by a system (an electrochemical cell with a positive potential) on its surroundings.

12. Exercise solutions

12.1. Butler-Volmer equation for small overpotential

Determine the Butler-Volmer equation at small overpotential using the $e^x \approx 1 + x$ for $x \ll 0.1$ approximation and $\alpha = 0.5$.

$$j = j_0 \cdot \left\{exp\left[\alpha \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta\right] - exp\left[-(1-\alpha) \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta\right]\right\}$$

$$j = j_0 \cdot \left\{1 + \left[\alpha \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta\right] - 1 - \left[-\frac{z \cdot F}{R \cdot T} \cdot \eta + \alpha \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta\right]\right\}$$

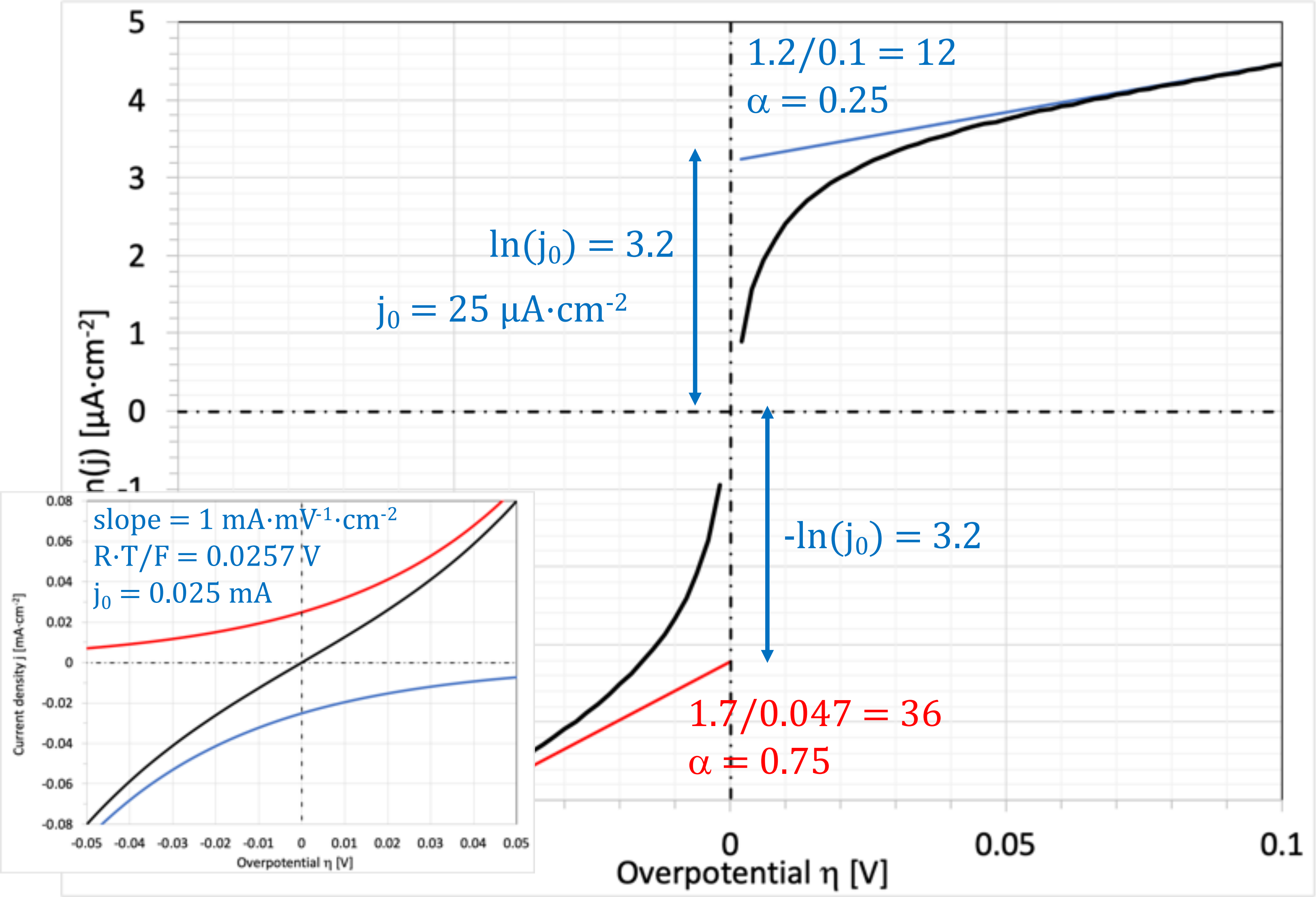
$$j = j_0 \cdot \left\{\left[\alpha \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta\right] + \left[\frac{z \cdot F}{R \cdot T} \cdot \eta - \alpha \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta\right]\right\}$$

$$j = j_0 \cdot \left\{\left[\frac{z \cdot F}{R \cdot T} \cdot \eta\right]\right\}$$

$$j = j_0 \cdot \frac{z \cdot F}{R \cdot T} \cdot \eta$$

12.2. Transfer current density

Determine the exchange current density [$\mu A \cdot cm^{-2}$] and the transfer coefficient for the reduction and oxidation reaction.



$1.2/0.1 = 12$

$\alpha = 0.25$

$\ln(j_0) = 3.2$

$j_0 = 25\ \mu A \cdot cm^{-2}$

$-\ln(j_0) = 3.2$

$1.7/0.047 = 36$

$\alpha = 0.75$

slope $= 1\ mA \cdot mV^{-1} \cdot cm^{-2}$

$R \cdot T/F = 0.0257\ V$

$j_0 = 0.025\ mA$

12.3. CO_2 reduction to methane

a) Describe to two half reactions and the complete electrochemical reaction of the CO_2 reduction to methane.

b) Calculate the standard potential for the electrochemical CO_2 reduction to methane and compare with the potential observed by Hori.

c) What is the estimated Faradaic and energy efficiency?

a) $CO_2 + 8H^+ + 8e^- \rightleftarrows CH_4 + 2H_2O$	Cathode (Reduction)	$E^0 = -0.24V$
$4H_2O \rightleftarrows 2O_2 + 8H^+ + 8e^-$	Anode (Oxidation)	$E^0 = +1.23V$
$CO_2 + 4H_2O \rightleftarrows CH_4 + 2H_2O$		

$E^0_{cell} = E^0_{cathode} - E^0_{anode} = -0.24V - 1.23V = -1.47V$

b) Hori observed CH_4 at -0.8V and max CH_4 at -1.0V vs. RHE. The standard potential is $E^0 = -0.24V$.

c) At -0.8V vs. RHE the Faradaic efficiency is <10% and the energy efficiency is <10%*30% = 3%. At -1.0V vs. RHE the Faradaic efficiency is 40% and the energy efficiency is 40%·25% = 10%.

12.4. Charge and mass

a) Calculate the mass of Cu deposited in an electrolytic cell on a Cu electrode immersed in a 1M $CuSO_4$ solution passing a current of 1A between two Cu electrodes for 1h.

b) Describe the half reactions on the cathode and the anode.

c) What is the min. potential?

$$n = \frac{I \cdot t}{z \cdot F}$$

$$n = \frac{I \cdot t}{z \cdot F} = \frac{1A \cdot 3600s}{2 \cdot 96485\ A \cdot s/m\,ol} = 0.0187\ mol$$