UNIVERSITÀ DEGLI STUDI DI TRIESTE

Dipartimento di Ingegneria e Architettura

BASICS OF ELECTROCHEMISTRY

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OUTLINE

1. Definitions and conventions
2. The Reference Potential
3. Chemical and Physical processes ruling EC devices

BIBLIOGRAPHY

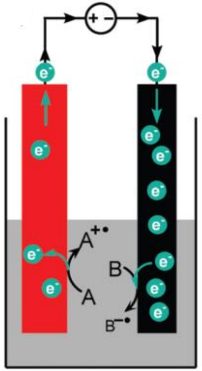
Reference	**Paragraph/Pages**
Fuel Cell Systems Explained - Andrew L. Dicks, David A. J. Rand - 2018, John Wiley & Sons Ltd.	§1.1, 3.3, 3.4
Fuel Cell Engines - Matthew M. Mench - 2008, John Wiley & Sons, Inc.	§2.1, 2.2
Electrochemistry Crash Course for Engineers - Slobodan Petrovic - 2021, Springer	Pg. 11-26; 49-64

1. DEFINITIONS AND CONVENTIONS

MIAN DEFINITIONS

Electrochemistry is the science dealing with the interconversion of electrical and chemical energies.

In particular, it deals with chemical reactions in which an electron transfer takes place in between two conductive electrodes, divided by an insulating and ionically conductive electrolyte.



Schotten C., Green Chem., 2020,22, 3358-3375

An electrochemical cell is a general device capable of converting chemical energy into electrical one. If current is generated during cell operation, the electrochemical cell is also known as Galvanic electrochemical cell.

In example, the electrochemical cell can be viewed as the fundamental brick constituting batteries.

REDOX (REDUCTION-OXIDATION) REACTIONS

Redox, is a term used to describe a couple of specular electrochemical reactions.

$$aA + bB \rightleftharpoons cC + dD$$

Composed by:

Reduction reaction

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

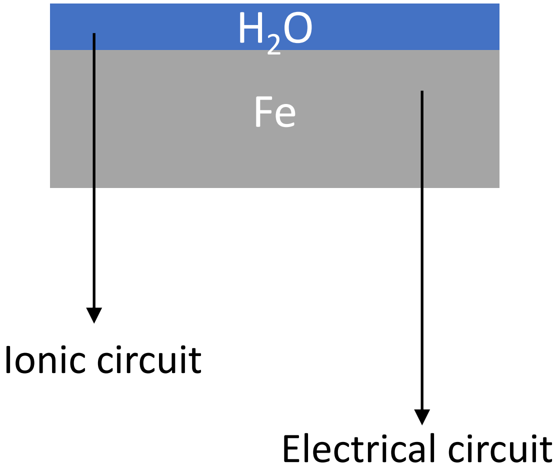
$$M^{n+} + ne^- \rightarrow M$$

Oxidation reaction

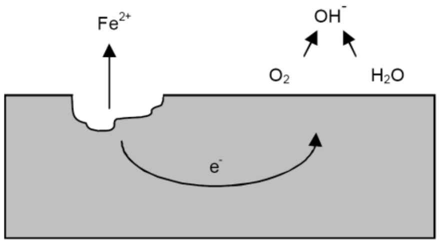
the oxidation number of a specimen is increasing (- e^-)

$$M \rightarrow M^{n+} + ne^-$$

AN EXAMPLE: IRON OXIDATION



1. In the anodic part of the circuit:
$$2Fe \rightarrow 2Fe^{2+} + 4e^-$$



https://it.wikipedia.org/wiki/Corrosione#cite_note-CEST-13

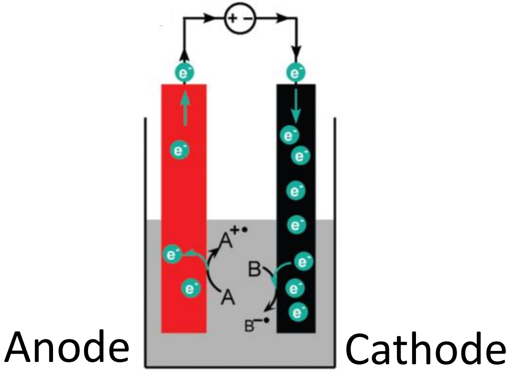
2. In the cathodic part of the circuit:
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

3. In the anodic part of the circuit:
$$2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2$$

4. Thus:
$$2Fe(OH)_2 + 1/2O_2 \rightarrow Fe_2O_3 \cdot nH_2O + H_2O$$

CONVENTIONS (1)

Anode Electrode	**Cathode Electrode**
Electrode at which **oxidation** takes place	Electrode at which **reduction** takes place



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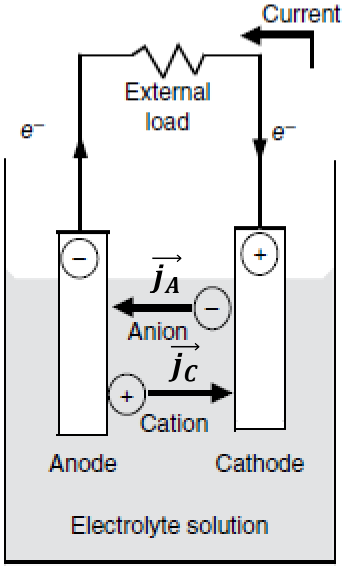
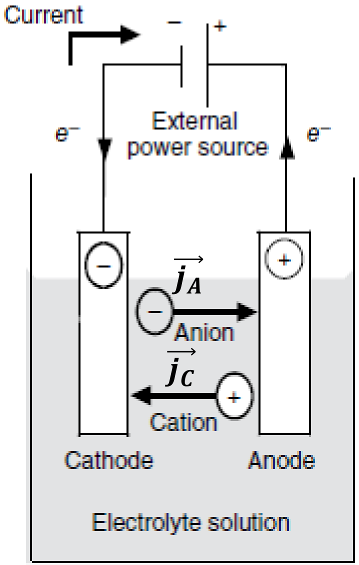
CONVENTIONS (2)

Galvanic cells
reactions are spontaneous (such as batteries)

Electrolytic cells
a current or potential is applied to drive a chemical reaction



- Cell potential is always positive
- Electrons spontaneously move (by the external circuit) from the negative electrode to the positive one.
- The anode is the negative electrode, while the cathode is the positive one.



- The voltage is always negative (a metal is plated out or a gas is evolved).
- Electrons are forced to move (via an external circuit) from the positive electrode to the negative one.
- The anode is the positive electrode, while the cathode is negative one.

CONVENTIONS (3)

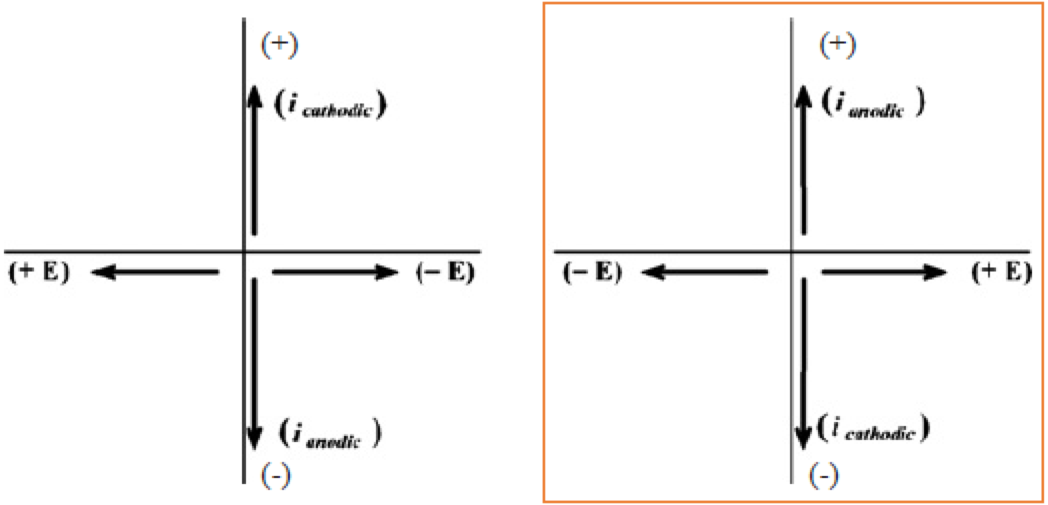
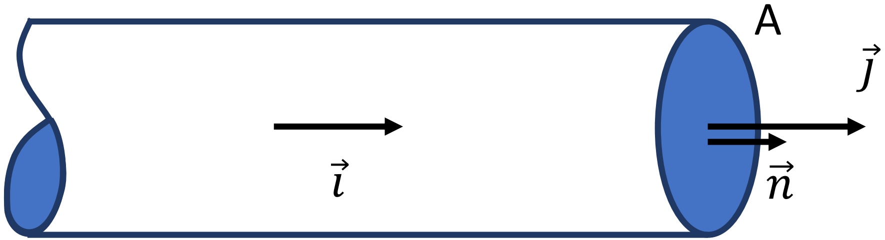


Figure 1.1 American (left) and IUPAC (right) voltammogram conventions.

CONVENTIONS (4)

The current density is the amount of charge per unit time that flows through a unit area of a chosen cross section



$$i = \int j dA$$

REDOX REACTIONS AND NERNST EQUATION

Let's consider the generic *redox* reaction composed by an oxidized and a reduced species:

$$O + ne^{-} \rightleftharpoons R$$

Where n (mol^{-1}) is the number of electrons involve in the reaction. The concentration of the oxidized and reduced species can be related to the Gibbs free energy by means of the Nernst equation:

$$\Delta G = \Delta G^{0} + RT \ln \frac{[R]}{[O]} \quad \left(\frac{J}{mol}\right)$$

Where R is the gas constant ($8.314\ J \cdot mol^{-1} \cdot K^{-1}$) and T is the temperature.

Where ΔG^0 ($J \cdot mol^{-1}$) is the standard Gibbs free energy change and E^0 (V) is known as standard electrode potential. The standard conditions are defined as room temperature (25°C) and pressure (1 bar).

LINKING TO THE GIBBS FREE ENERGY

The fundamental aspect of the Nernst equation is related to the fact that it can be related to the maximum potential which can develop among the electrodes as:

$$\Delta G = -nFE$$

Where E is also called Open Circuit Voltage (OCV, or open circuit potential), and is representative of the electromotive force. The OCV is the potential which establishes in an electrochemical circuit when no charge transport phenomena are taking place, that is there is no flow of electrical current.

Here, F is the Faraday constant (96485.3 C·mol^{-1}), representing the the electric charge per mole carried by the elementary charges.

LINKING TO THE GIBBS FREE ENERGY

Within the convection that E is positive towards the reduction reaction, bearing in mind that $\Delta G = \Delta G_0 + f(O)$, and within the assumption that reactant and product have unitary activity, the expression for the OCV can be rephrased as:

$$\Delta G^0 = -nFE^0$$

It worth to notice as the minus sign in the equation underlines the fact that (within the selected convention) a spontaneous reaction is characterized by:

- $\Delta G^0 < 0$
- $E^0 > 0$

GENERALIZATION OF THE NERNST EQUATION

By considering the generical redox reaction $aA + bB \rightleftharpoons cC + dD$

And its reaction quotient $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

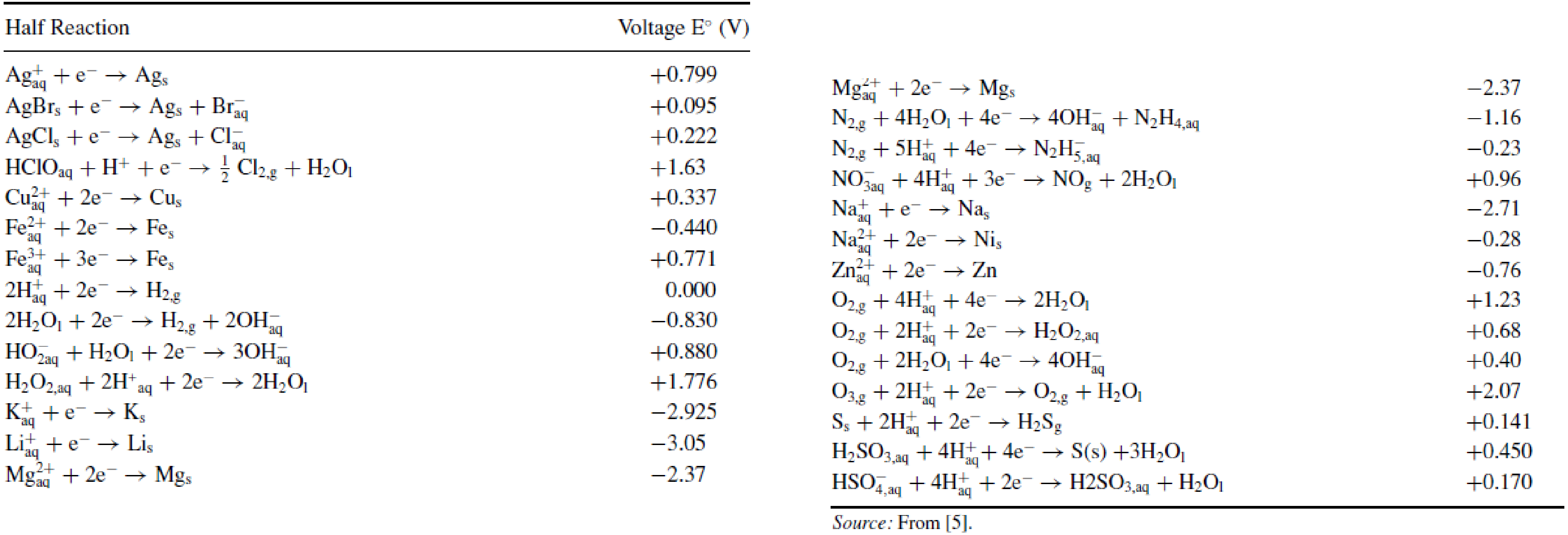
where lowercase letters indicate reaction activities of the specimens involved in the reaction (which in some cases can be approximated by their concentration). The Nernst equation connects the standard reduction potential to the reaction quotient:

$$E = E^0 + RT \ln \frac{[C]^c[D]^d}{[A]^a[B]^b} = E^0 + RT \ln \frac{[R]}{[O]}$$

Due to the fact that is here now possible to separately calculate the standard potential of an electrochemical cell via the sum of the standard potential of the anode and the cathode sides.

$$V_{cell}^0 = E_{cathode}^0 - E_{anode}^0$$

THE STANDARD POTENTIAL

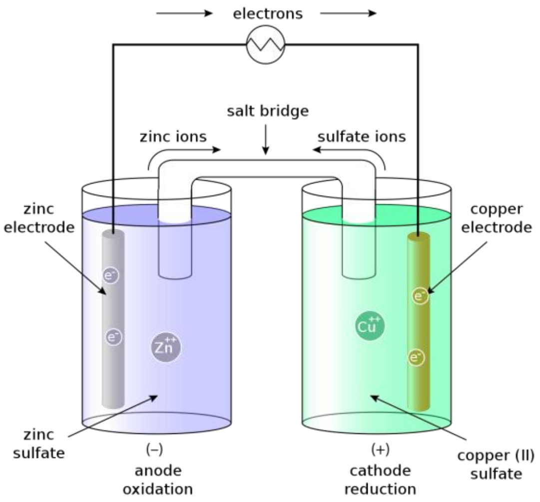


Half Reaction	Voltage E° (V)
$Ag^+_{aq} + e^- \rightarrow Ag_s$	+0.799
$AgBr_s + e^- \rightarrow Ag_s + Br^-_{aq}$	+0.095
$AgCl_s + e^- \rightarrow Ag_s + Cl^-_{aq}$	+0.222
$HClO_{aq} + H^+ + e^- \rightarrow \frac{1}{2}\, Cl_{2,g} + H_2O_l$	+1.63
$Cu^{2+}_{aq} + 2e^- \rightarrow Cu_s$	+0.337
$Fe^{2+}_{aq} + 2e^- \rightarrow Fe_s$	−0.440
$Fe^{3+}_{aq} + 3e^- \rightarrow Fe_s$	+0.771
$2H^+_{aq} + 2e^- \rightarrow H_{2,g}$	0.000
$2H_2O_l + 2e^- \rightarrow H_{2,g} + 2OH^-_{aq}$	−0.830
$HO^-_{2aq} + H_2O_l + 2e^- \rightarrow 3OH^-_{aq}$	+0.880
$H_2O_{2,aq} + 2H^+{}_{aq} + 2e^- \rightarrow 2H_2O_l$	+1.776
$K^+_{aq} + e^- \rightarrow K_s$	−2.925
$Li^+_{aq} + e^- \rightarrow Li_s$	−3.05
$Mg^{2+}_{aq} + 2e^- \rightarrow Mg_s$	−2.37
$Mg^{2+}_{aq} + 2e^- \rightarrow Mg_s$	−2.37
$N_{2,g} + 4H_2O_l + 4e^- \rightarrow 4OH^-_{aq} + N_2H_{4,aq}$	−1.16
$N_{2,g} + 5H^+_{aq} + 4e^- \rightarrow N_2H^-_{5,aq}$	−0.23
$NO^-_{3aq} + 4H^+_{aq} + 3e^- \rightarrow NO_g + 2H_2O_l$	+0.96
$Na^+_{aq} + e^- \rightarrow Na_s$	−2.71
$Na^{2+}_{aq} + 2e^- \rightarrow Ni_s$	−0.28
$Zn^{2+}_{aq} + 2e^- \rightarrow Zn$	−0.76
$O_{2,g} + 4H^+_{aq} + 4e^- \rightarrow 2H_2O_l$	+1.23
$O_{2,g} + 2H^+_{aq} + 2e^- \rightarrow H_2O_{2,aq}$	+0.68
$O_{2,g} + 2H_2O_l + 4e^- \rightarrow 4OH^-_{aq}$	+0.40
$O_{3,g} + 2H^+_{aq} + 2e^- \rightarrow O_{2,g} + H_2O_l$	+2.07
$S_s + 2H^+_{aq} + 2e^- \rightarrow H_2S_g$	+0.141
$H_2SO_{3,aq} + 4H^+_{aq} + 4e^- \rightarrow S(s) + 3H_2O_l$	+0.450
$HSO^-_{4,aq} + 4H^+_{aq} + 2e^- \rightarrow H2SO_{3,aq} + H_2O_l$	+0.170

Source: From [5].

AN EXAMPLE

Calculate the Gibbs free energy of the Zn-Cu Galvanic electrochemical cell



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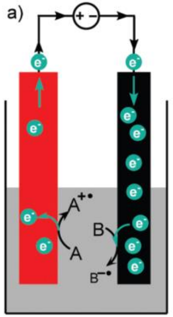

https://en.wikipedia.org/wiki/Galvanic_cell

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1. From the expression of the overall reaction:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + Cu_{(s)}$$

the half-cell reactions can be retrieved, together with the E^0:

Anode: $Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^0 = -0.76\ \mathrm{V} \rightarrow E_{anode}$

Cathode: $Cu^{2+} + 2e^- \rightleftharpoons Cu \quad E^0 = 0.34\ \mathrm{V} \rightarrow E_{cathode}$

2. Calculate cell potential and Gibbs free energy (of formation):

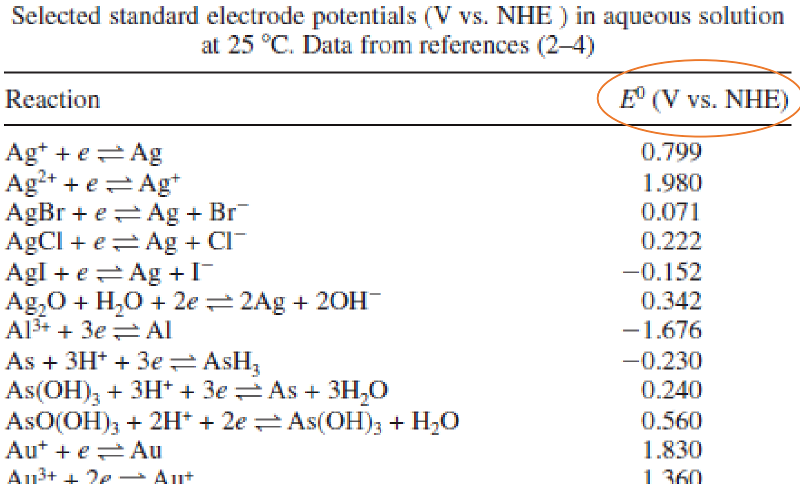
$$E^0_{cell} = E_{cathode} - E_{anode} = 0.34 - (-0.76) = 1.10\ \mathrm{V}$$

$$\Delta G^0 = -2F(1.10) = -212\ \mathrm{kJ/mol}$$

2. THE REFERENCE POTENTIAL

A REFERENCE FOR THE STANDARD POTENTIAL

Numerous tables exist referencing E^0 for the most typically encountered redox reactions. Initially these tables were derived from thermodynamic data, later confirmed experimentally.



Selected standard electrode potentials (V vs. NHE) in aqueous solution at 25 °C. Data from references (2–4)

Reaction	E^0 (V vs. NHE)
$Ag^+ + e \rightleftharpoons Ag$	0.799
$Ag^{2+} + e \rightleftharpoons Ag^+$	1.980
$AgBr + e \rightleftharpoons Ag + Br^-$	0.071
$AgCl + e \rightleftharpoons Ag + Cl^-$	0.222
$AgI + e \rightleftharpoons Ag + I^-$	−0.152
$Ag_2O + H_2O + 2e \rightleftharpoons 2Ag + 2OH^-$	0.342
$Al^{3+} + 3e \rightleftharpoons Al$	−1.676
$As + 3H^+ + 3e \rightleftharpoons AsH_3$	−0.230
$As(OH)_3 + 3H^+ + 3e \rightleftharpoons As + 3H_2O$	0.240
$AsO(OH)_3 + 2H^+ + 2e \rightleftharpoons As(OH)_3 + H_2O$	0.560
$Au^+ + e \rightleftharpoons Au$	1.830
$Au^{3+} + 2e \rightleftharpoons Au^+$	1.360

Normal Hydrogen Electrode (NHE)

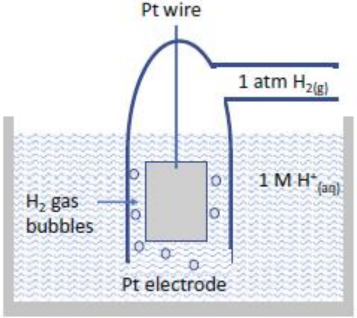
THE REFERENCE ELECTRODE

Consisting of body, top seal, junction, and by the active component which defines the reference potential of the device.

By definition, the NHE should be composed by a Pt electrode immersed in an acidic electrolyte in which hydrogen is bubbled. At standard conditions the concentration the pressure of the H_2 gas should be equal to 1 atm, and the concentration of the hydrogen ions in solution should be unitary

Being this condition experimentally difficult to attain, other concentrations and pressures are typically used, and the potential is corrected for these conditions.

Nowadays measurements are referred to the so-called **Standard Hydrogen Electrode (SHE)**, which is defined (by convention) as 0.0 V for any temperature.



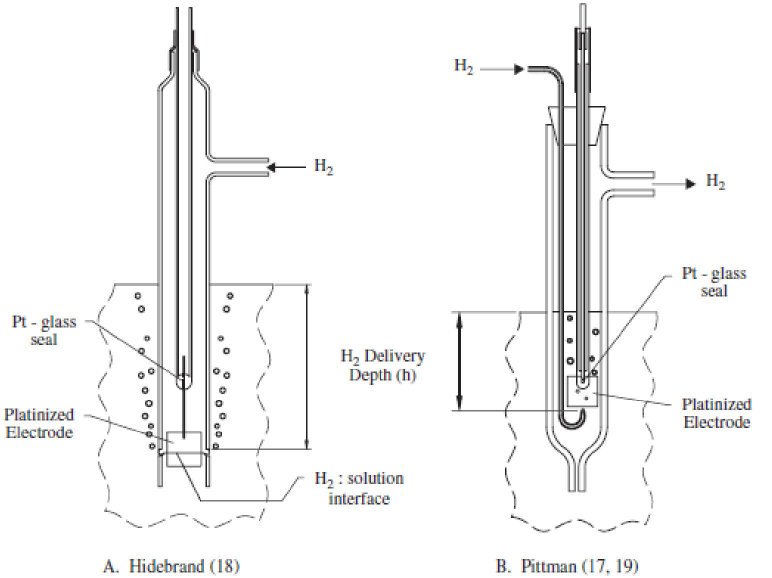


Figure 4.6 Normal Hydrogen Electrode and Reversible Hydrogen Electrode designs (17): (A) Hildebrand (18); (B) Pittman (17, 19).

THE REFERENCE ELECTRODE

The **Reversible Hydrogen Electrode (RHE)** is assembled directly in an electrochemical cell, with the electrolyte in the cell as the RE filling solution.

The most common RHE is the silver/silver chloride reference electrode (Ag|AgCl), which is composed by a AgCl coated Ag wire, immersed in a filling solution (saturated KCl or NaCl, or diluted HCl). This electrode is characterized by a standard potential equal to:

$$AgCl + e^- \rightleftharpoons Ag + Cl^-, \quad E^0_{Ag|AgCl} = 0.222\ V_{NHE}\ (25°C)$$

And is widely used due to its simplicity, inexpensive design, and nontoxic components, which make it suitable for being produced with microfabrication techniques as well as, to be incorporated into sensors.

And the potential is calculated as follows:

$$E_{Ag|AgCl} = E^0_{Ag|AgCl} - RT\ln a_{Cl^-}$$

A **Quasi-Reference Electrode (QRE)** is a general phrase for any poorly defined or unpoised RE. A QRE typically consists of an inert metal wire such as platinum or gold. A silver wire can also be used, so long as silver ions do not interfere with the measurements. The potential should ideally be steady, but the actual potential is not predictable if it is unpoised. A QRE is a low-impedance RE, but is also a polarizable electrode.

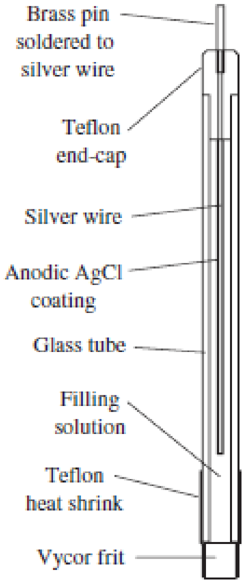
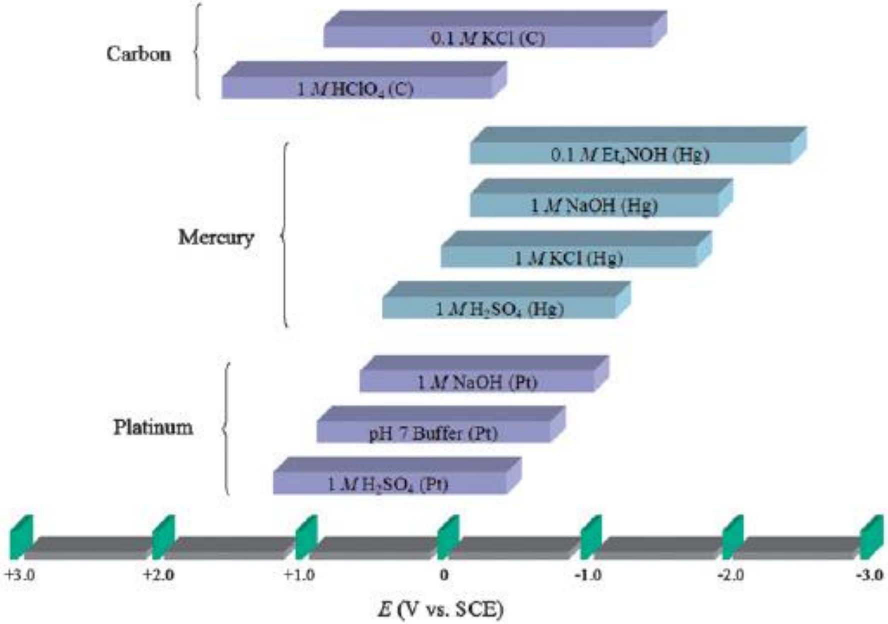


Figure 4.15 Ag|AgCl electrode.

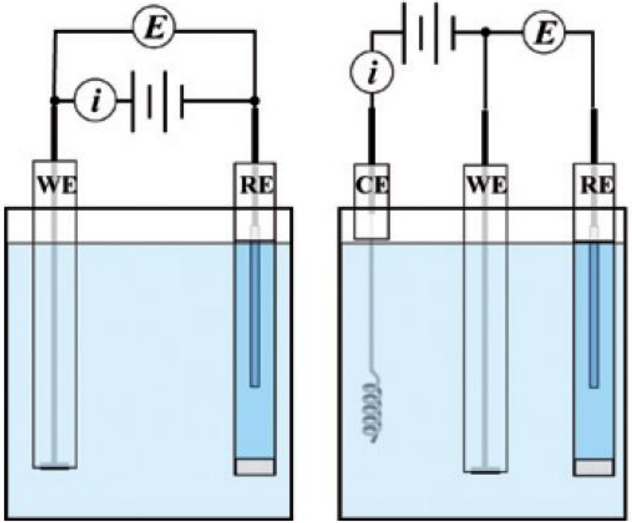
A REFERENCE FOR THE POTENTIAL

According to the RE used, the correction of the standard potential must be applied to convert to potentials to the NHE.



TWO ELECTRODES AND THREE ELECTRODES CONFIGURATIONS

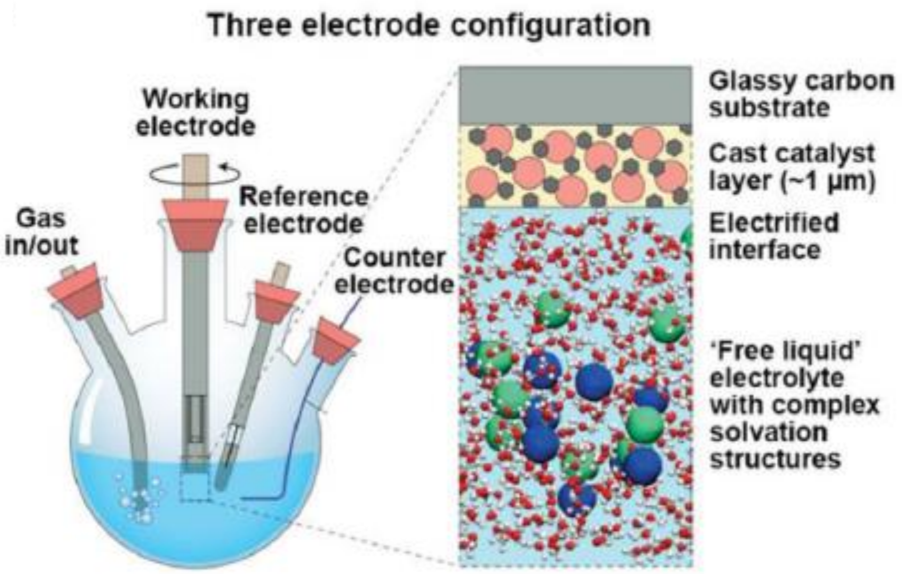
Since the potential of the working electrode is monitored relative to the reference electrode, the potential of the reference electrode must be maintained at a constant value. In other words, the reference electrode must behave as an ideal nonpolarized electrode with current passing between working and reference electrodes.

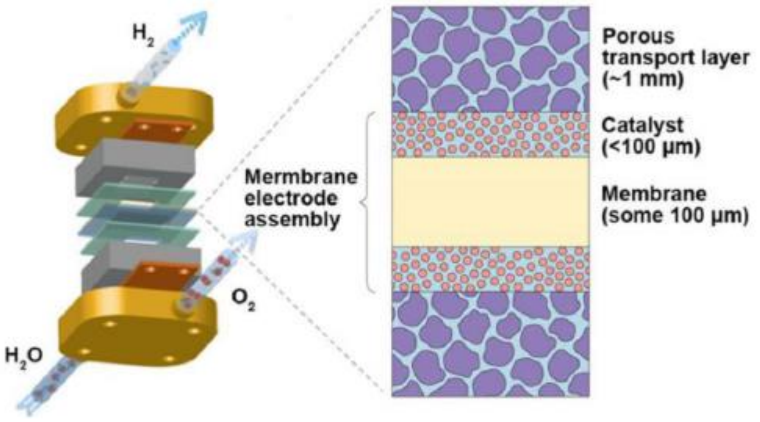


Three-electrode cells are the most commonly used setup in electrochemical studies. Here, the potential of the working electrode is monitored relative to the reference potential; however, the current passes between the working electrode and the counter electrode. Since no (or little) current passes to the reference electrode, this config approaches ideal non-polarizability and is hence a reliable reference for potential control.

TWO VS THREE ELECTRODES SETUP

The advantage of the 3-elelctrode setup relies in the fact that the electrode can be investigated in a controlled environment. But operative conditions and degradation phenomena can be quite different.

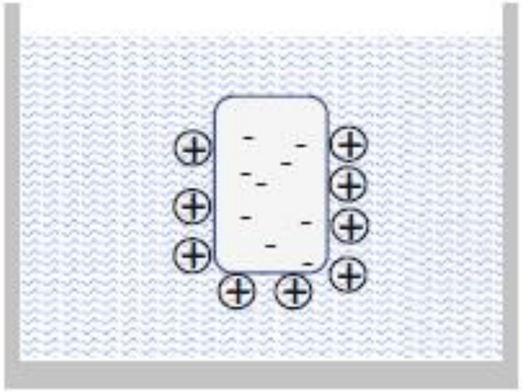




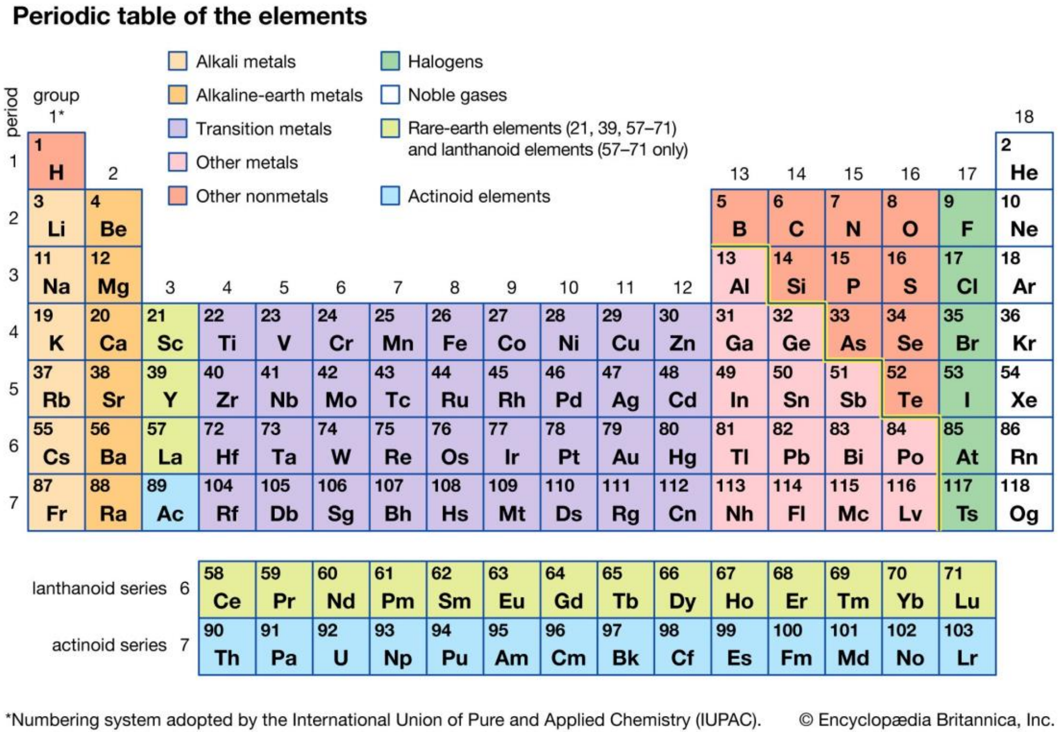
EnergyChem, 4, 5, (2022), 100087 doi.org/10.1016/j.enchem.2022.100087

3. CHEMICAL AND PHYSICAL PROCESSES RULING ELECTROCHEMICAL DEVICES

THE METAL/WATER INTERFACE



$$M_{(s)} + 2H_2O_{(l)} \rightarrow 2OH^-_{(aq)} + H_{2(g)}$$



Periodic table of the elements

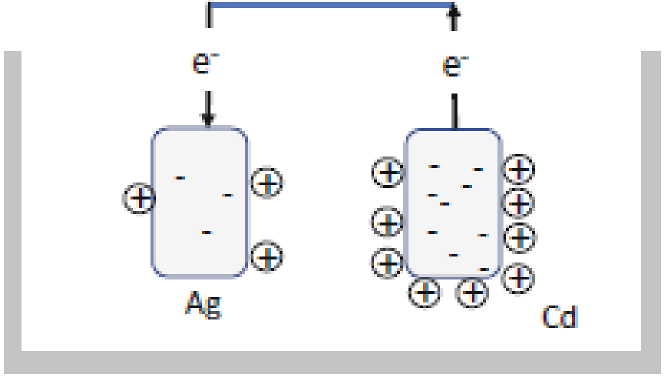
- 🟧 Alkali metals
- 🟧 Alkaline-earth metals
- 🟪 Transition metals
- 🟥 Other metals
- 🟥 Other nonmetals
- 🟩 Halogens
- ☐ Noble gases
- 🟨 Rare-earth elements (21, 39, 57–71) and lanthanoid elements (57–71 only)
- 🟦 Actinoid elements

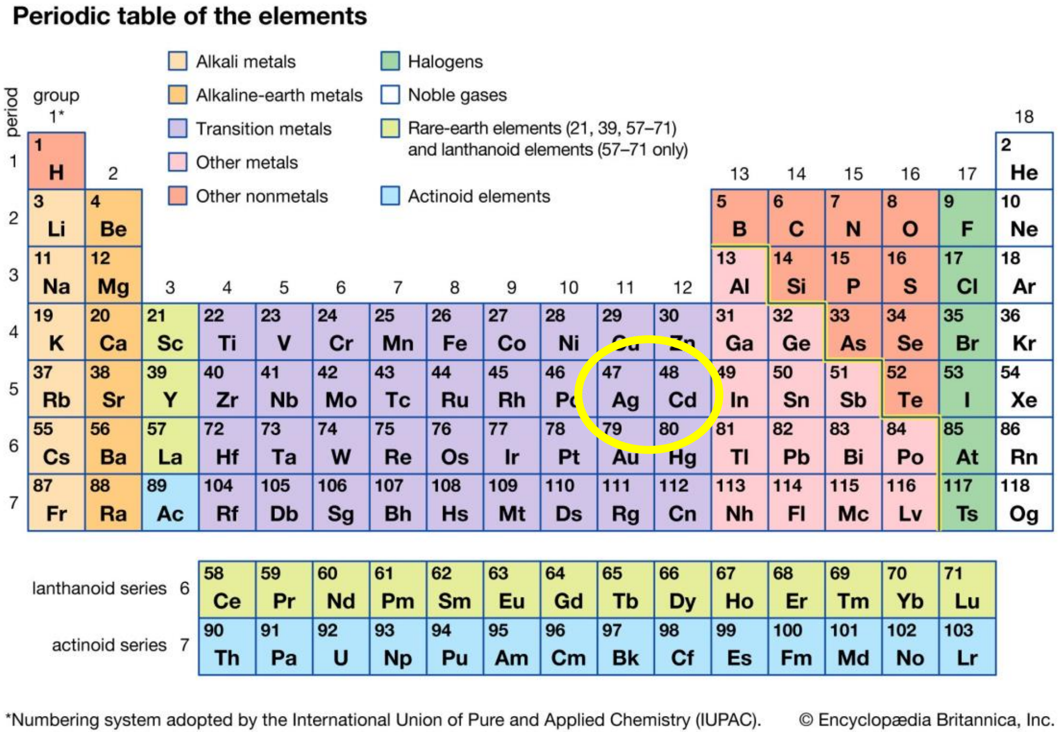
period \ group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

lanthanoid series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
actinoid series 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

THE METAL/WATER INTERFACE





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period \ group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

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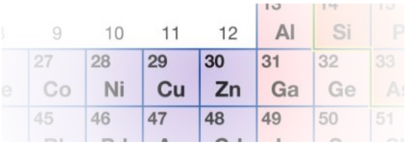
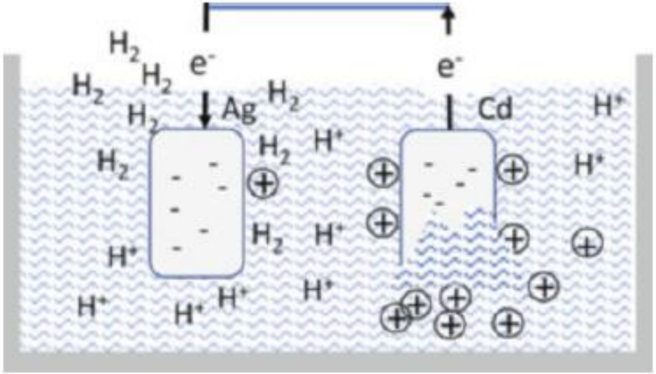
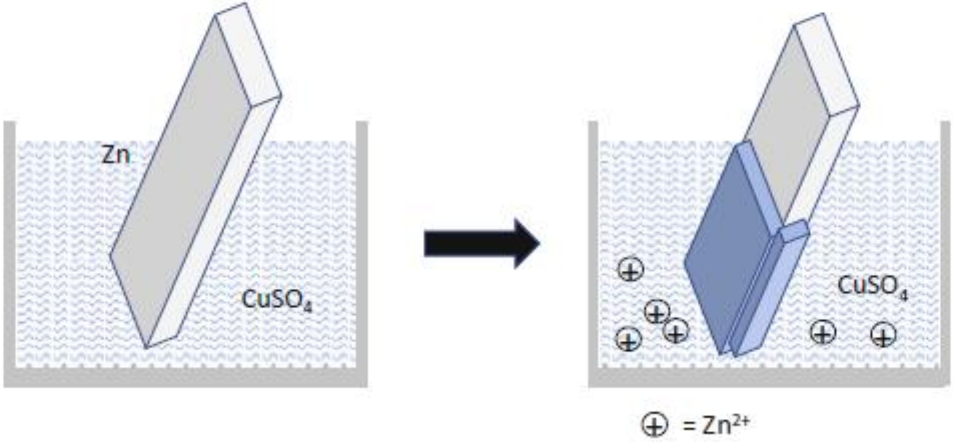




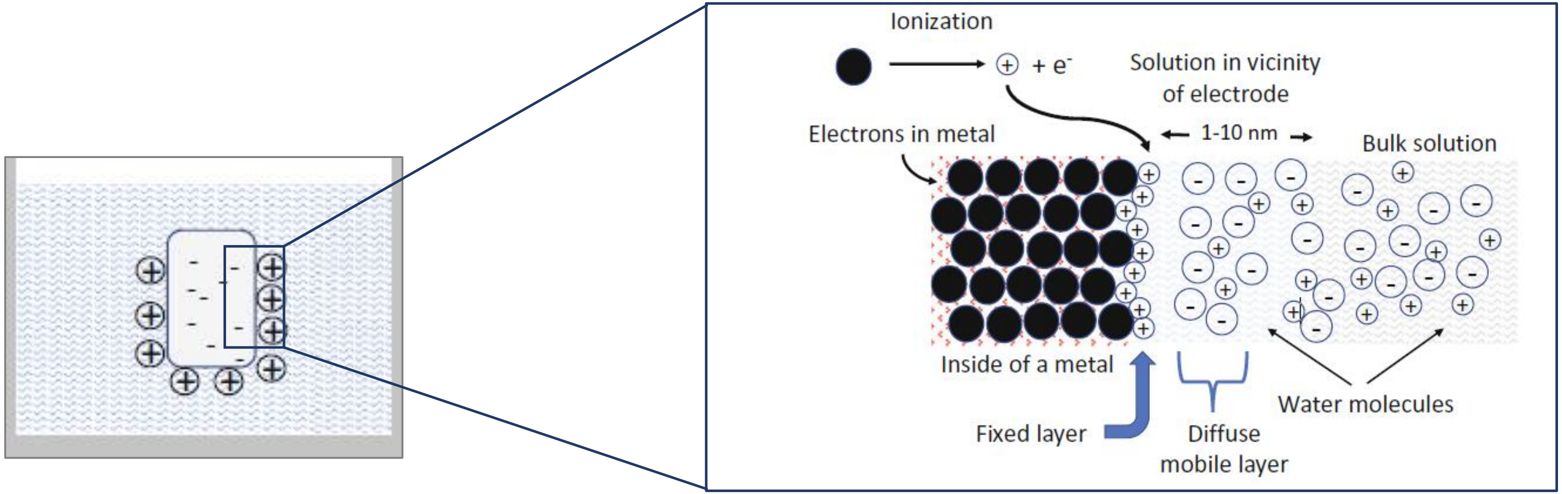


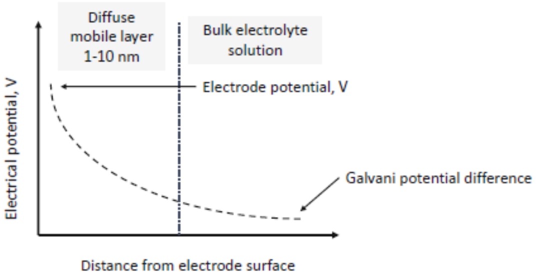
$$2H^+ + 2e^- \rightarrow H_2(g), \quad E^0_{red} = 0\,V$$

$$Cd^{2+} \rightarrow Cd^0 + 2e^- \quad E^0_{red} = -0.40\,V$$

$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$$

THE METAL/WATER INTERFACE



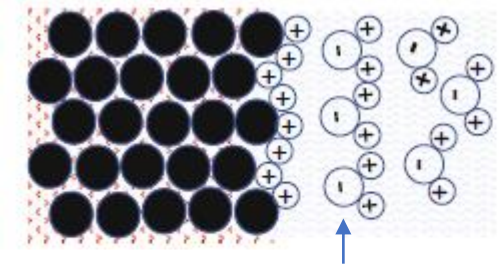


Fixed layer ↔ Inner Helzmolz layer
Diffuse mobile layer ↔ Outer Helzmolz layer

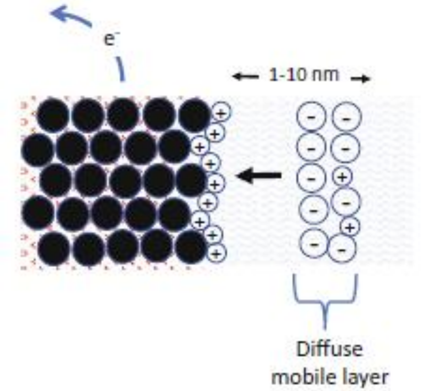
→ Double layer

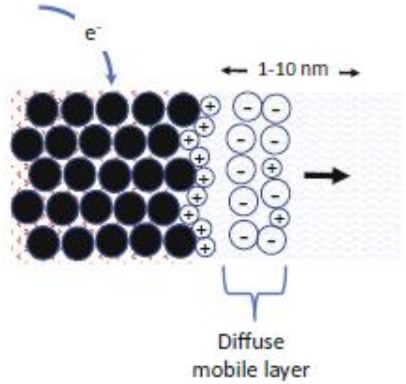
FEATURES AT THE SOLUTION-METAL INTERFACE: THE DOUBLE LAYER

metal | water



water dipoles oriented towards the surface





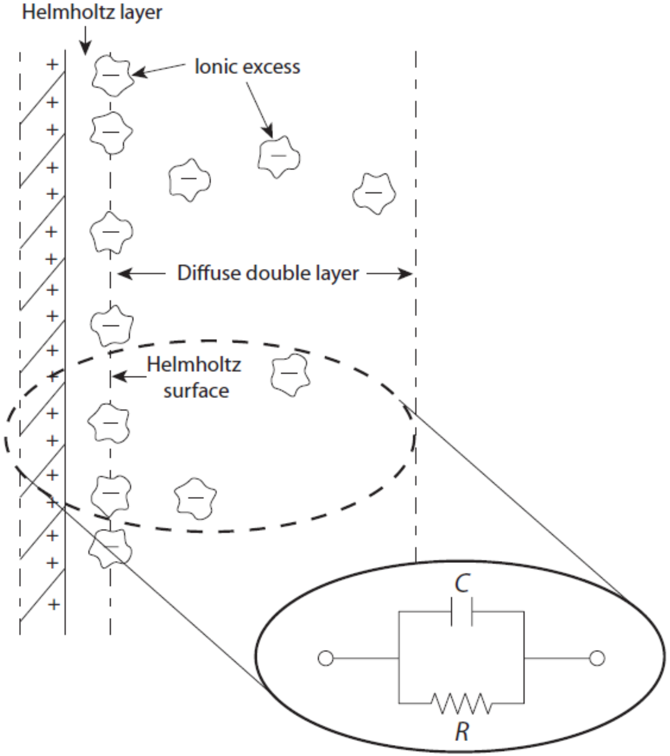
THE DOUBLE LAYER: MODELLING

The layer of charge on or near the electrode/electrolyte interface is a store of electrical energy, and as such behaves much like an electrical capacitor, and the double-layer can be thus represented by an electrical capacitor of capacitance:

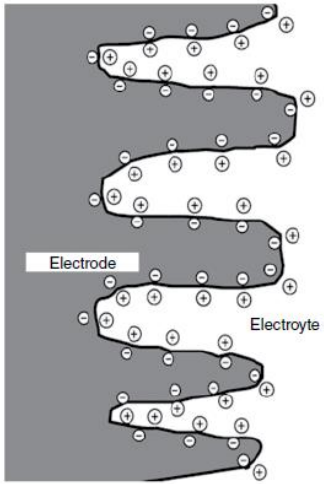
$$C = \varepsilon \frac{A}{d}$$

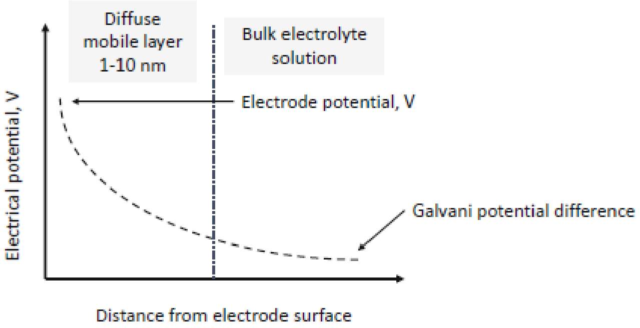
where ε is the electrical permittivity, A is the surface area and d is the separation of the plates. For a fuel cell, A is the real surface area of the electrode, which is several thousand times greater than its length × width. The separation, d, extends for few nanometres only.

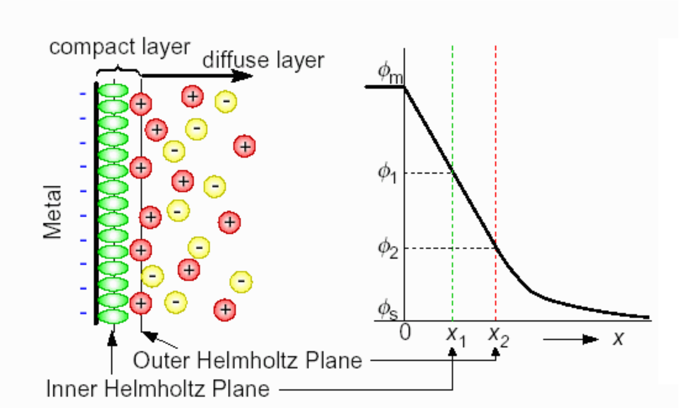
Typically the double layer capacitance is in the order of few Farads.



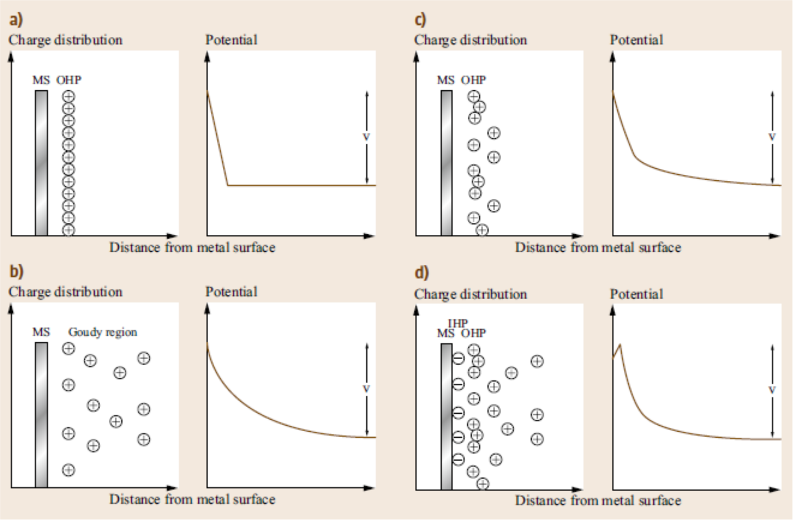
THE DOUBLE LAYER: MODELLING







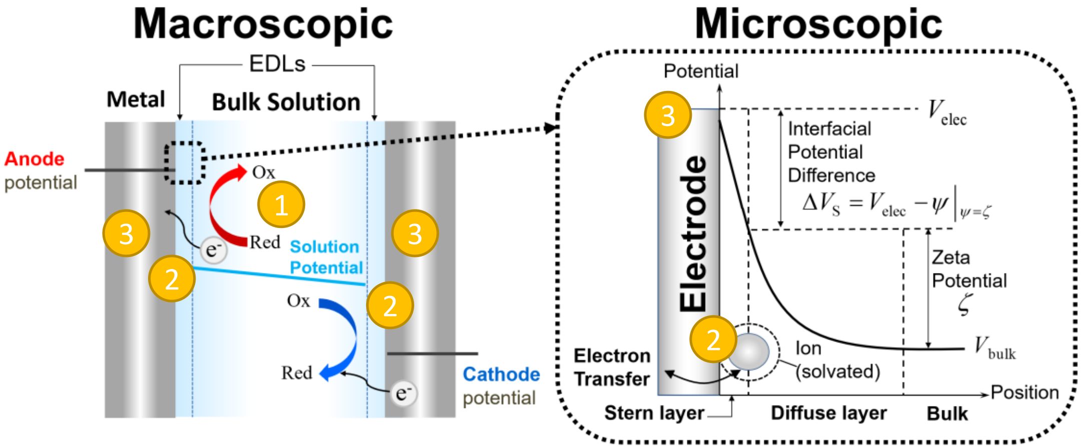
https://web.nmsu.edu/~snsm/classes/chem435/Lab14/double_layer.html



PROCESSES AT THE ELECTRODE SURFACE

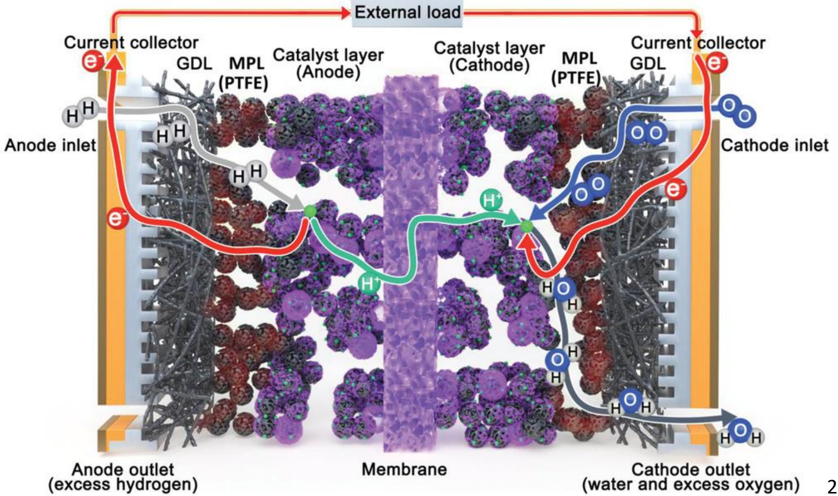
Processes involved in electrochemical reactions:

1. Transport by **diffusion** of the active species towards electrode surface
2. Ion adsorbance at the electrode surface and **charge transfer**.
3. **Charge transport** towards the external circuit.



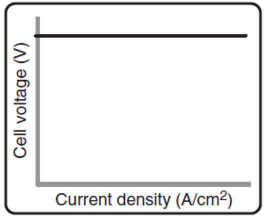
https://nanolab.engineering.ucsb.edu/research/electrochemistry-nanoscale

PROCESSES AT THE ELECTRODE SURFACE AND PERFORMANCE LOSSES



2021 Suter, Adv. Energy Mater., 11, 2101025

Theoretical behaviour



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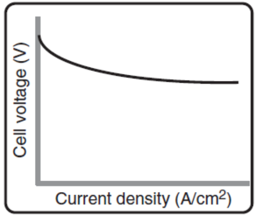
Reaction kinetics



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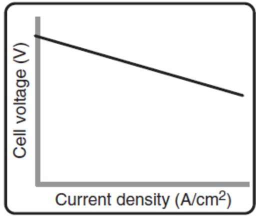
Charge transport



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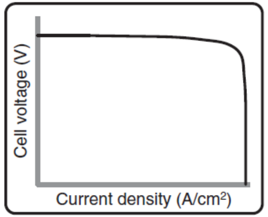
Diffusion



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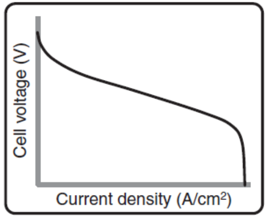


2016, Wiley, Fuel Cell Fundamentals

PROCESSES AT THE ELECTRODE SURFACE AND PERFORMANCE LOSSES

When introducing thermodynamic aspects of electrochemistry, the Gibbs free energy, ΔG, was defined as the available energy for the investigated redox reaction.

While thermodynamics allow to predict the direction of a reaction and the composition at equilibrium, they cannot provide information about the dynamics in which the reaction takes place. For this purpose, the investigation of reaction kinetics have been developed in order to define the rate at which redox reaction take place.

The rate of a chemical reaction is the change in concentration of reactants and products as a function of time. The rate of reaction can be expressed either as the rate of disappearance of reactant or the rate of appearance of product. For the generic reaction:

$$A + B \rightarrow C$$

$$reaction\, rate = -\frac{\Delta A}{\Delta t} = -\frac{\Delta B}{\Delta t} = \frac{\Delta C}{\Delta t}$$

FARADAY’S LAW

When investigating electrochemical devices, the rate among the amount of consumed reactants and produced current (or applied current and the amount of produced products of reaction) needs to be quantified.

In this extent, in 1932 Michael Faraday formulated the so-called two laws of electrolysis:

1. The mass of a substances formed at an electrode during electrolysis or consumed in a galvanic cell is directly proportional to the quantity of electricity involved in the reaction.
2. The mass of a substance altered, produced or consumed, at an electrode is directly proportional to its equivalent weight (equivalent weight: molar mass of a substance, divided by the number of electrons required to oxidize or reduce each unit of a substance).

Mathematically:

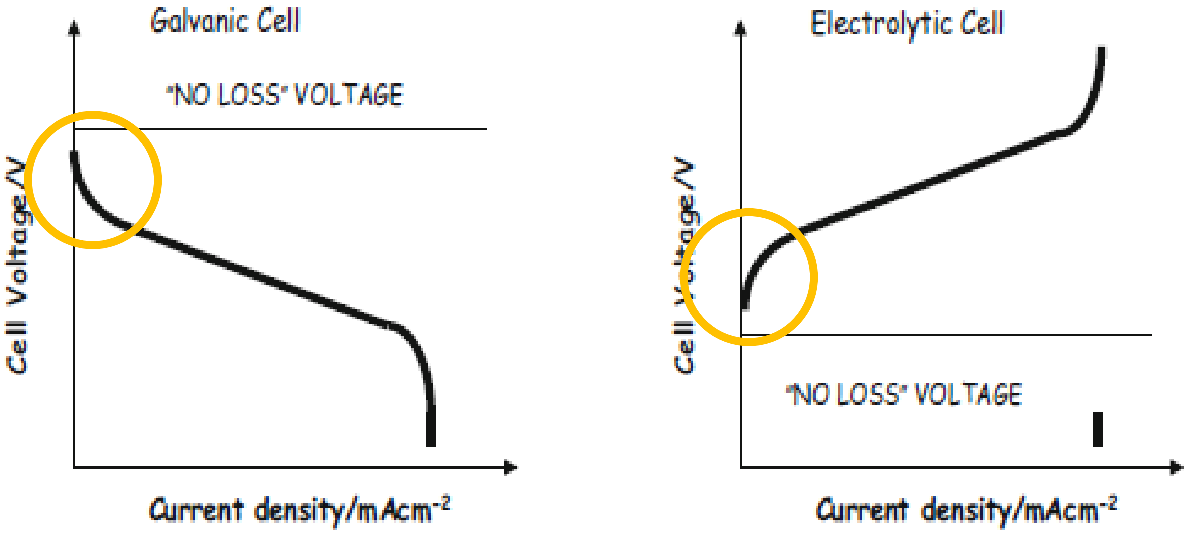
$$w = \frac{Q}{F} \cdot \frac{M}{n} \qquad m = \frac{w}{M} = \frac{Q}{nF} \qquad \dot{n_x} = \frac{dn_x}{dt} = \frac{I}{nF}$$

Where: w is the mass of the substance (m is its number of moles), Q ($\mathrm{I} \cdot t$) is the charge passed through the system, M is the molecular weight, n is the number of electrons involved in the reaction and F (96485 C) is the electric charge included in 1 mol of substance, known as Faraday constant, $\dot{n_x}$ is the rate of molar consumption (or production) of the substance.

REACTION KINETICS AND ACTIVATION LOSSES

Losses (also known as: irreversibilities, overpotentials, or potential drops) are expressed as a deviation from the ideal voltage:

$$\eta = E - E_{ideal}$$



Activation losses are related to reaction kinetics and charge transfer, more precisely to the voltage loss required to maintain the required rate of reaction on the electrodes. They result in a nonlinear potential drop from open circuit conditions, are predominant for low current density values, and diminish as the current density is increased.

REACTION KINETICS AND ACTIVATION LOSSES

Lets consider an individual electrode, initially at equilibrium. For example, considering the Hydrogen Oxidation Reaction:

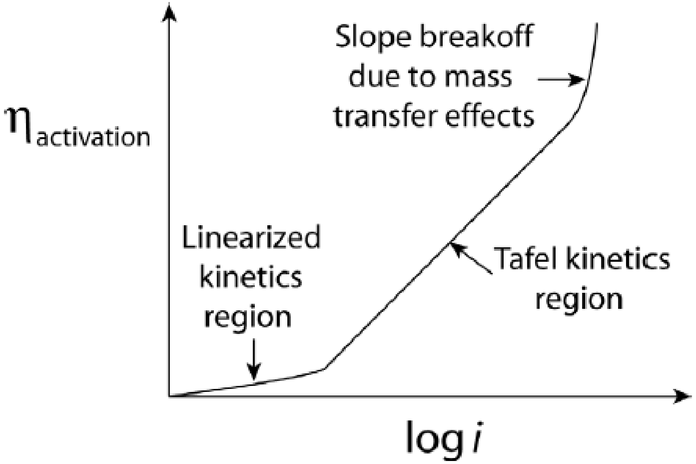
$$Reduced \xleftrightarrow{H_2 \leftrightarrow 2H^+ + 2e^-} Oxidized$$

At equilibrium (open circuit), this reaction actually proceeds in both directions across the anode double layer, with no net reaction in either direction. Some hydrogen is being oxidized, and an equivalent amount is being reduced. The amount of charge involved in such charge equilibrium process is called as **exchange current density**, i_0.

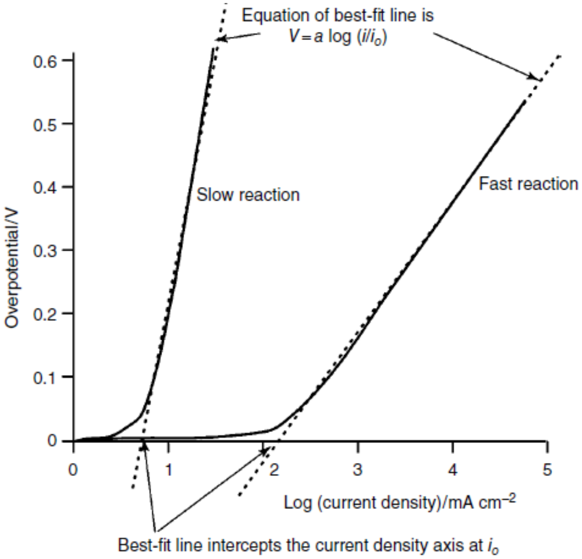
A net current is produced only when moving out from the equilibrium conditions: here is why the overpotential is required, to sustain the reaction towards one direction or the other.

REACTION KINETICS AND ACTIVATION LOSSES

The connection between the value of net current exchange and the required activation potential can be divided in three regions, which can be highlighted in the so-called Tafel plots:



REACTION KINETICS AND ACTIVATION LOSSES



While reaction kinetics can be in-depth modelled by means of the Butler-Volmer equations (later introduced), activation overpotential can be characterized by analyzing the Tafel plots with the Tafel equation:

$$\eta = a - b \ln\left(\frac{i}{i_0}\right)$$

REACTION KINETICS AND ACTIVATION LOSSES

Different activation losses occur at each electrode, and each electrode requires a specific level of current to sustain the redox reaction. Activation losses are influenced:

1. by **reaction mechanisms**: the more complex a reaction mechanism, the greater the overpotential required to break the chemical bonds and generate current.
2. by **catalyst type**: a poor choice of catalyst will require a greater polarization to enable the electrochemical reaction at that electrode to proceed.
3. by **catalyst layer morphology**: as later depicted, the microstructure of the catalyst has a strong effect on the overall effectiveness of the catalyst. In general, the maximization of the surface area available to host reaction sites, will reduce the activation polarization losses for a given current density.
4. by the **operating parameters**: electrochemical reactions are catalyzed by temperature and pressure increase.

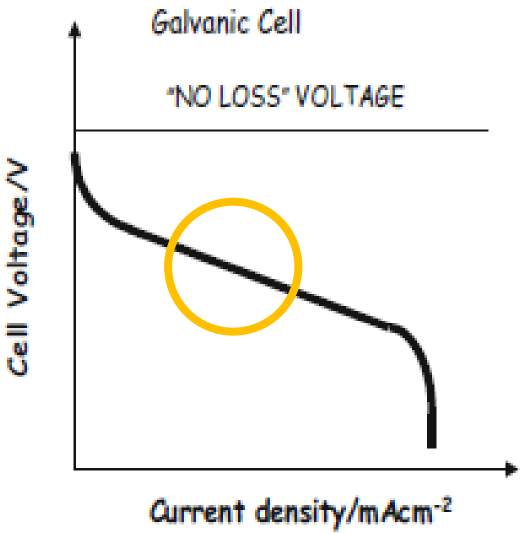
REACTION KINETICS AND ACTIVATION LOSSES

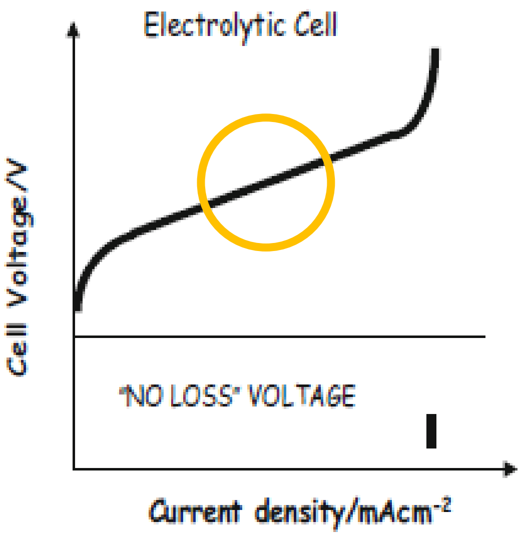
5. by the **presence of impurities and poisons**: the presence of any impurities or catalyst poisons in the reacting flow can have a highly deleterious effect on performance. n for low-temperature PEFCs but can be oxidized as a fuel in high-temperature MCFCs and SOFCs.
6. by the **species concentrations**: according to Nernst equation, voltage is a result of the equilibrium thermodynamic effect. During the highly nonequilibrium electrochemical reaction process, there is also a concentration effect on the activation polarization. As the reacting species become more sparse, the double-layer polarization required to attract sufficient reactants increases. In the extreme case, no reaction can take place across the double layer if there is no reactant available.
7. by the **catalyst age**: catalyst performance can change significantly over the operating lifetime, as a result of physical morphological or chemical changes in the catalyst.
8. according to the **service history** of the device, including environment, load cycling, and voltage history.

The positive side of all of these activation loss dependencies is that most of them can be engineered to some degree to reduce losses and increase efficiency.

CHARGE TRANSPORT AND OHMIC LOSSES

Ohmic losses prevail at intermediate current density values and are related to the charge transport of electrons (according to the Ohm's law) and ions.





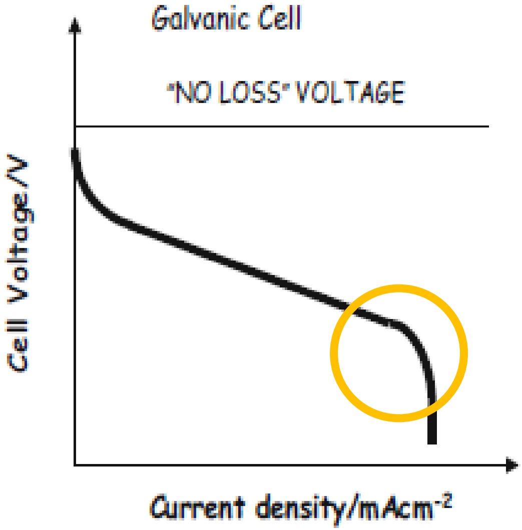
MASS TRANSPORT

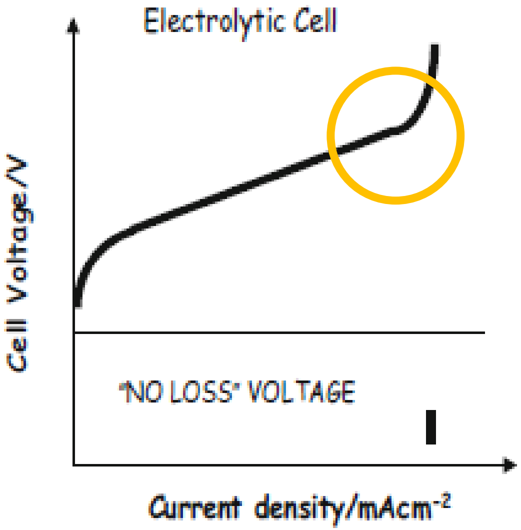
Mass transfer can be defined as the net movement of mass from one location to another one. Mass transport in a medium can take place among three different phenomena:

1. **Diffusion** is the movement of species as a result of the concentration gradient. In electrochemical devices diffusion takes place whenever a chemical change takes place at any electrode surface. Diffusion starts when the reaction consumes reactant at the electrode surface and lowers its concentration it initiates diffusion from the bulk that equalizes the concentration.
2. **Convection** is the movement of species as a result of the velocity gradient. It is a result of mechanical forces. Natural convection occurs because of small differences in solution density as a result of local temperature variations, while forced convection is induced by electrolyte or electrode movement.
3. **Migration** is the movement of charged species as a result of a potential gradient. It consists in the passage of ionic charge through the electrolyte and it is driven by electrostatic forces. In practice, migration does not make a significant contribution to mass transport.

MASS TRANSPORT AND CONCENTRATION LOSSES

Concentration losses prevail in the high current density regime and is related to diffusion phenomena.



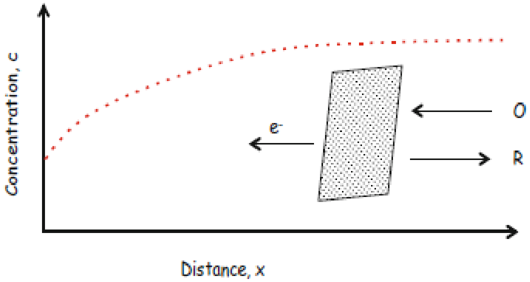


MASS TRANSPORT – FICK'S LAW OF DIFFUSION

Diffusion is described by means of Fick's first law (1855), which relates concentration gradient and diffusive flux (or flow rate), per unit area on a selected plane, stating as the diffusion flux (Φ) is proportional to the change of concentration over position or length ($\partial C/\partial x$).

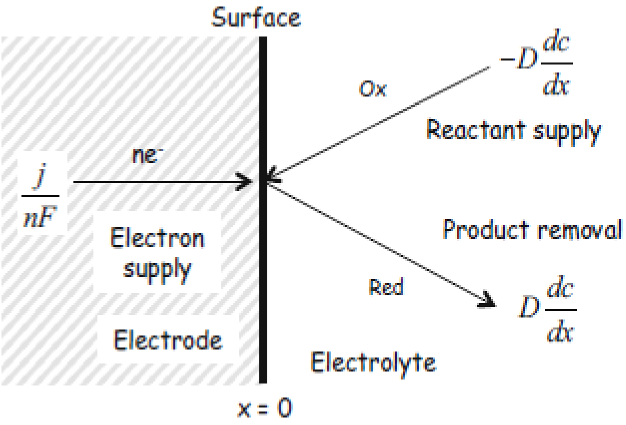
$$\Phi = -D\frac{\partial C}{\partial x}$$

D is called diffusion coefficient (or diffusivity, $m^2\ t^{-1}$)



MASS TRANSPORT – FROM FICK'S LAW OF DIFFUSION…

In an electrode immersed into a liquid, the mass balance among electrons involved in redox reaction, reactants and reaction products must be guaranteed. It is thus possible to relate Faraday's and Fick's laws and link the produced current in function of the reactant concentration at the surface of the electrode:



$$\dot{n}_x = \frac{I}{nF} \rightarrow I = \dot{n}_x nF$$

Being the flux defined as:

$$\Phi = \frac{\dot{n}_x}{A} \rightarrow \dot{n}_x = \Phi A$$

It turns out as:

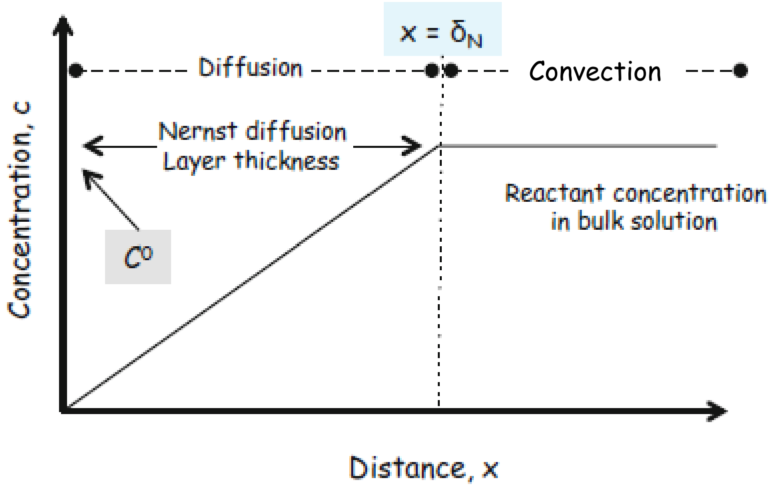
$$I = -nFAD_{OX}\frac{\partial c_{OX}}{\partial x} = nFAD_{RED}\frac{\partial c_{RED}}{\partial x}$$

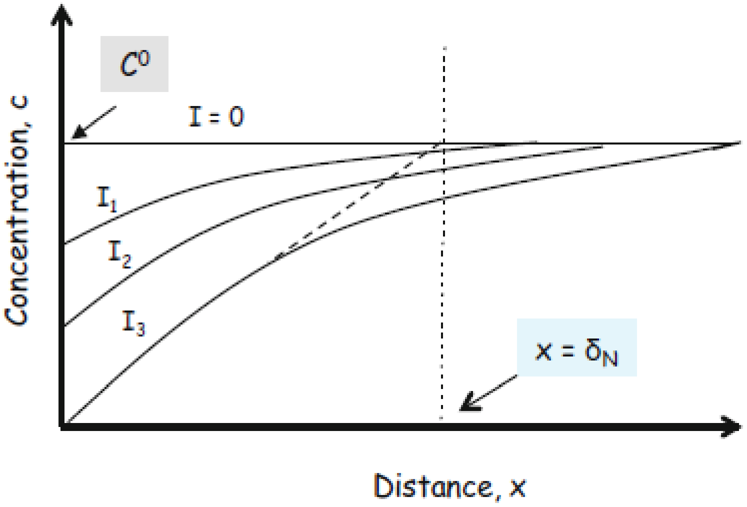
That is: in steady state conditions, the concentration profiles to and from the electrode surface are linear.

MASS TRANSPORT – … TO THE NERNST DIFFUSION MODEL

With the Nernst diffusion model, the presence of a stagnant layer in close contact with the surface is defined. Within this layer (of thickens δ_N), diffusion is the only phenomena ruling mass transport, while for larger distances, convection is assumed to be the leading phenomenon.

While in the ideal case the transition among the two regimes is strictly defined, in reality it is not as sharp to be determined, as the transition develops gradually.





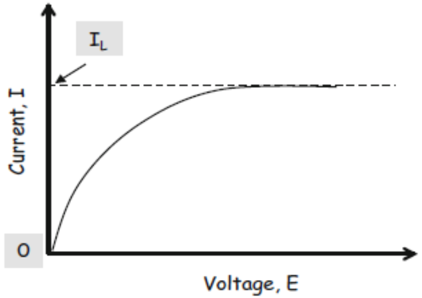
THE LIMITING CURRENT

As introduced, at large current density values, diffusion limits the efficiency of the electrochemical devices, as not enough reactants cannot be longer supplied to the electrode surface. This phenomenon leads to the definition of the so-called limiting current (I_L), that is the maximum possible current for the system under analysis.

For a particular reaction, controlled solely by mass transport, the current density increases as a function of potential until reaching a steady-state value, which defines the maximum possible current (under given conditions).

The limiting current density can be defined starting from the definition of current within the Nernst diffusion model

$$I = -nFAD\frac{\partial C}{\partial x} = -nFAD\frac{C_0 - (C_0)_{x=0}}{\delta_N}$$



Where C_0 is the reactant concentration in the electrolyte bulk. At limiting conditions, there is no reactant available at the surface of reaction, that is: $(C_0)_{x=0}$. Consequently:

$$I_L = -\frac{nFDC_0A}{\delta_N}$$

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