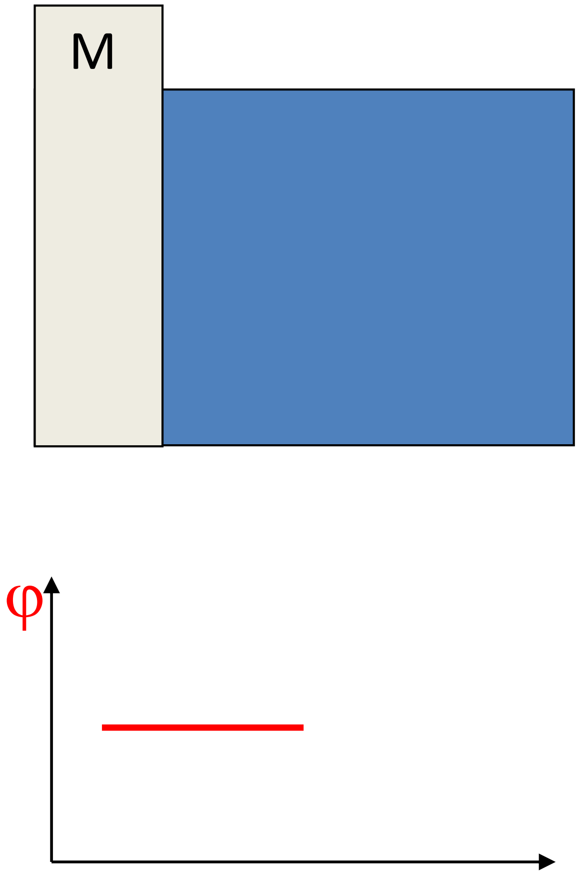
Electrochemistry for materials technology

Chapter 3

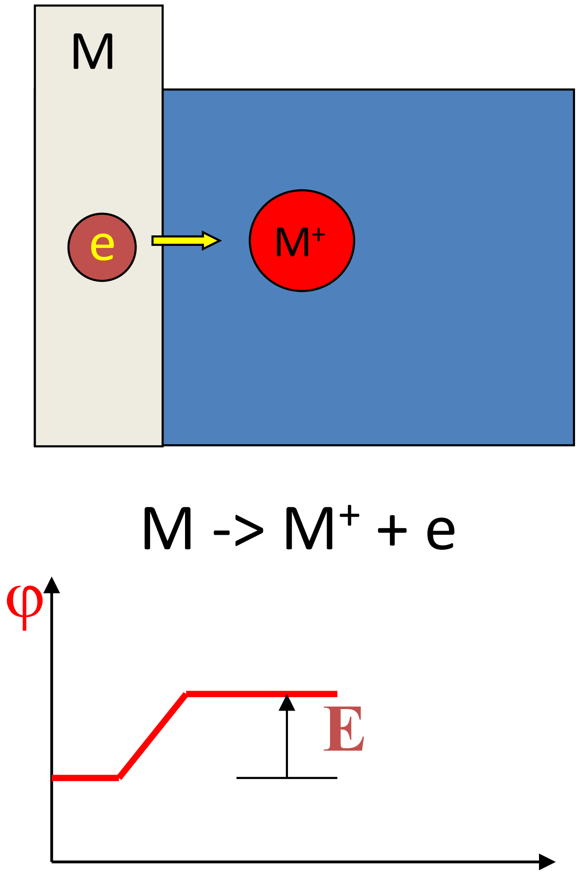
Electrode potential

Origin of the electrode potential E

(difference in electric potential φ between electrode and electrolyte)

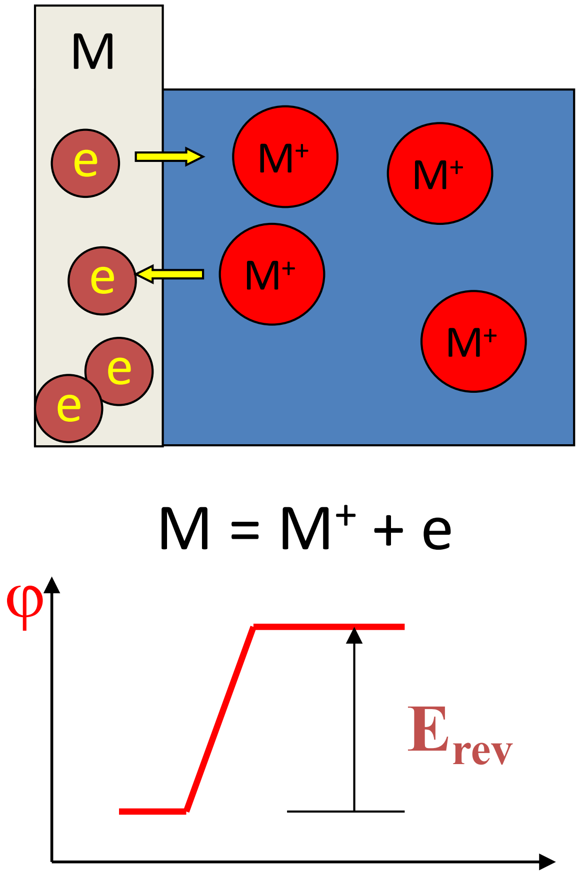


Initial situation



$M -> M^+ + e$

Dissolution

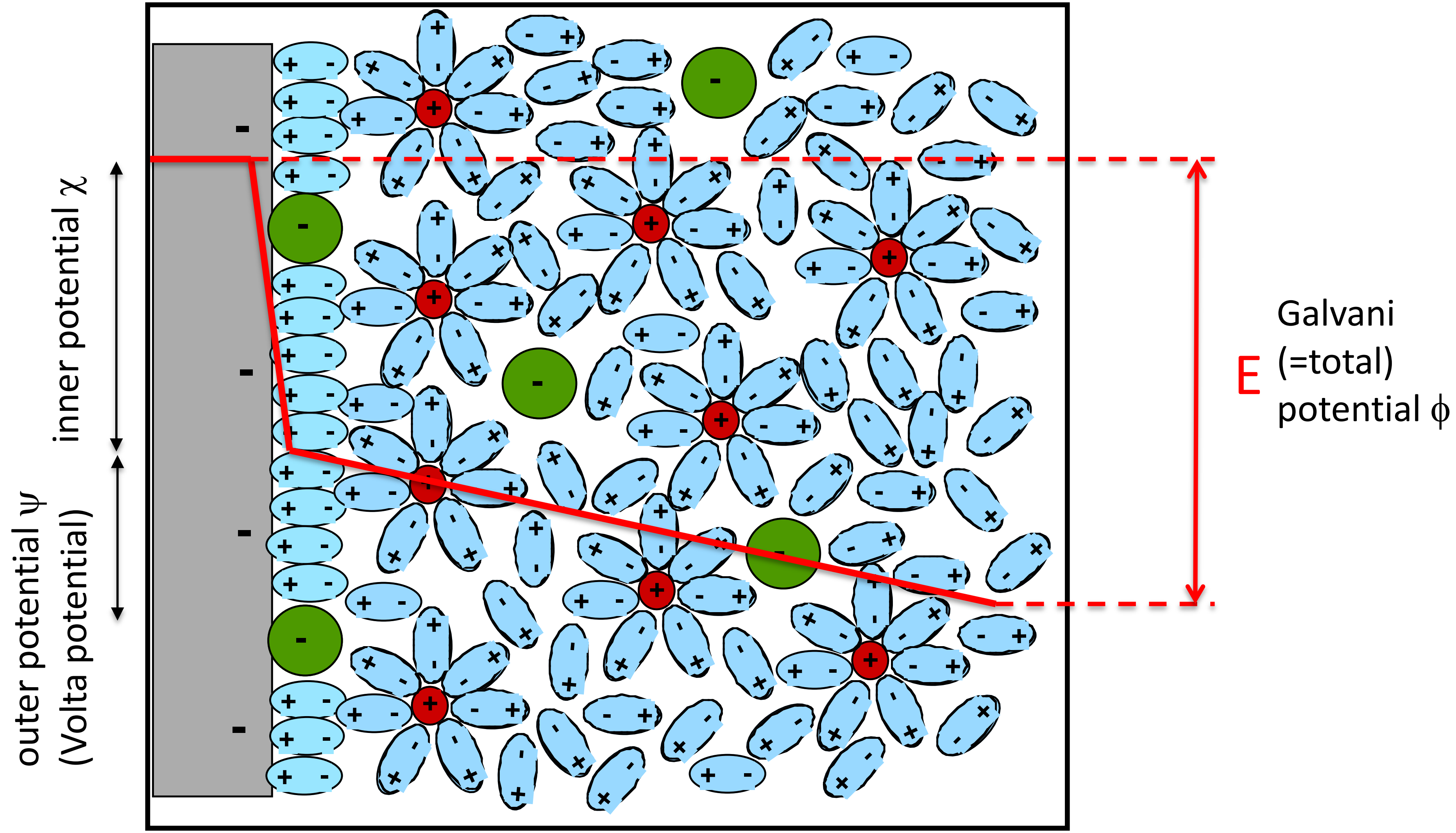


$M = M^+ + e$

Equilibrium

$(E_{rev} = - \Delta G \; / \; n \; F)$

Electrical double layer (capacitance) at metal-electrolyte interface



Total = Galvani potential (ϕ) : potential difference between the bulks of 2 (different) phases, which can be 2 solids or a solid and liquid.
Cannot be measured with a voltmeter since always a second reaction is needed !
Inner potential = χ Outer potential (or Volta potential) = ψ
The double layer represents an electrical capacitance.

Principle of hydrogen/oxygen fuel cell

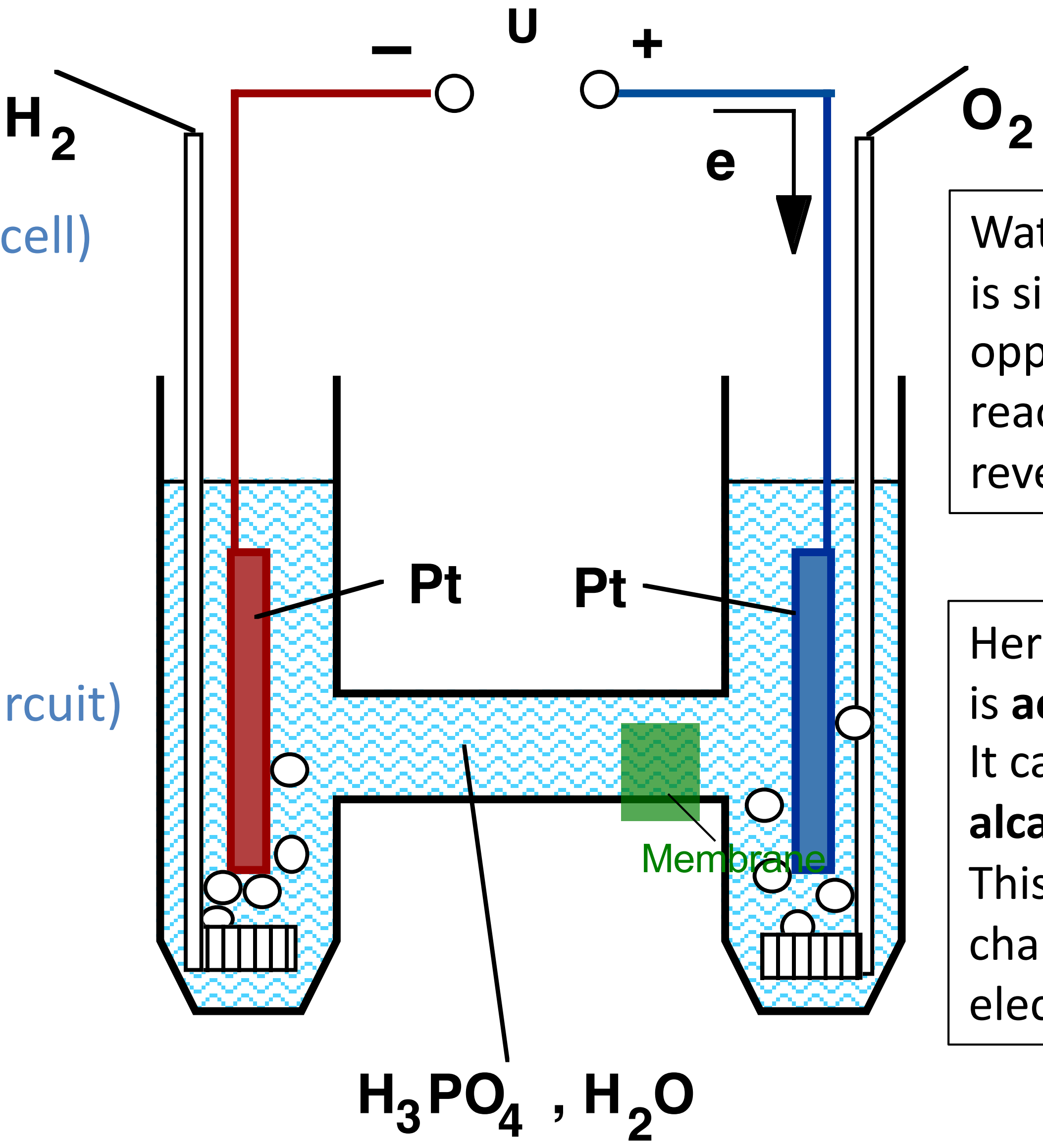
Electrode reactions (half cell)

$2\ H_2 = 4H^+ + 4e$

$O_2 + 4H^+ + 4\ e = 2\ H_2O$

Global reaction (closed circuit)

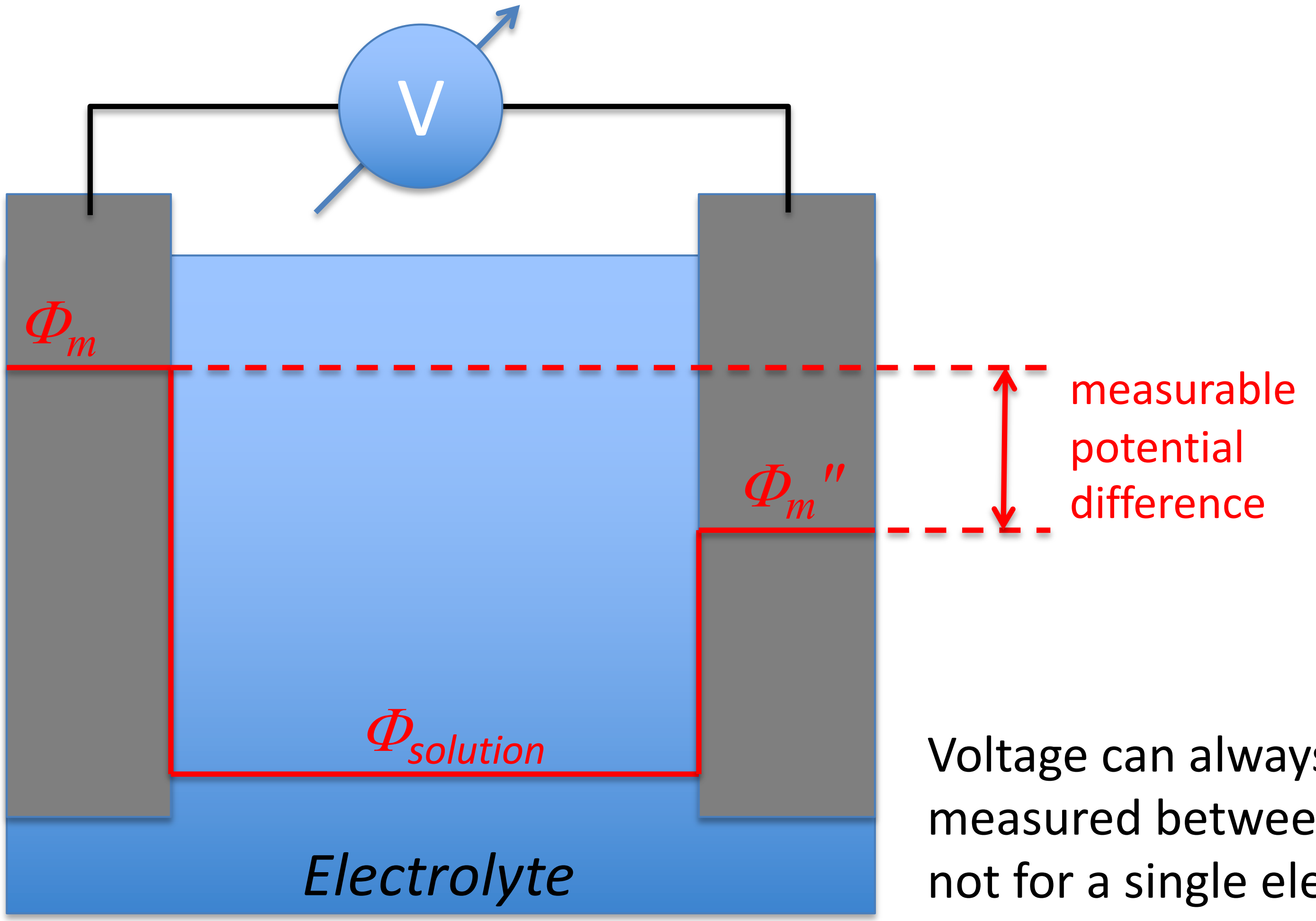
$2\ H_2 + O_2 = 2\ H_2O$



Water **electrolysis** is simply the exact opposite, with the reactions reversed.

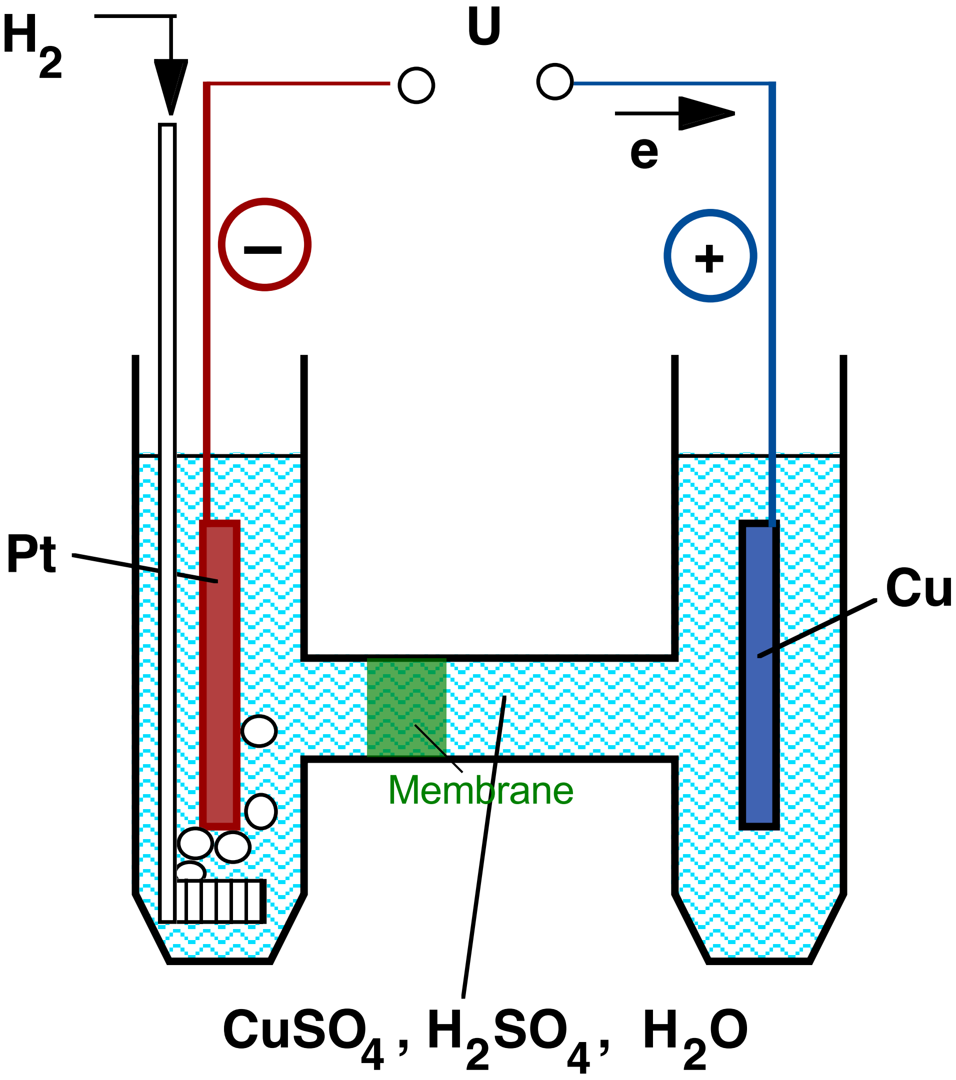
Here the medium is **acidic** (low pH). It can also be **alcaline** (high pH). This radically changes the electrochemistry!

Potential levels in electrochemical cells



Voltage can always only be measured between 2 electrodes, not for a single electrode.

Copper/hydrogen cell



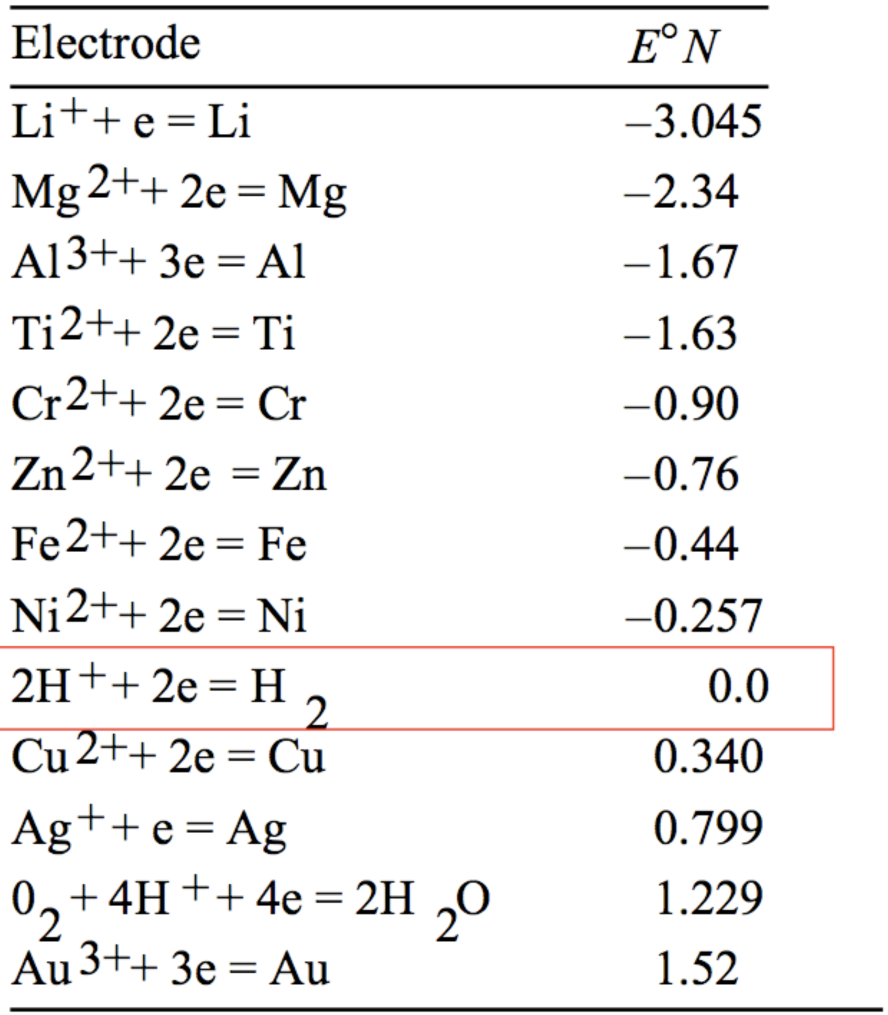
Electrode reactions

$2H^+ + 2e = H_2$

$Cu^{2+} + 2e = Cu$

Standard electrode potentials E_0 of electrode reactions

Standard conditions
25°C
activities=1



Electrode	$E^{\circ} N$
$Li^+ + e = Li$	–3.045
$Mg^{2+} + 2e = Mg$	–2.34
$Al^{3+} + 3e = Al$	–1.67
$Ti^{2+} + 2e = Ti$	–1.63
$Cr^{2+} + 2e = Cr$	–0.90
$Zn^{2+} + 2e = Zn$	–0.76
$Fe^{2+} + 2e = Fe$	–0.44
$Ni^{2+} + 2e = Ni$	–0.257
$2H^+ + 2e = H_2$	0.0
$Cu^{2+} + 2e = Cu$	0.340
$Ag^+ + e = Ag$	0.799
$0_2 + 4H^+ + 4e = 2H_2O$	1.229
$Au^{3+} + 3e = Au$	1.52

determines the relative scale

water electrolysis
1.23V (25°C, 1 atm)

Nernst equation for the reversible potential E_{rev} of electrode reactions

$$\sum \nu_{ox,i}\, B_{ox,i} + ne = \sum \nu_{red,i}\, B_{red,i}$$

B_{ox} : species at « oxidized » state (left side of reduction reaction)
B_{red} : species at « reduced » state (right side of reduction reaction)
ν : stoichiometry coefficient a: activity f(concentration)

$$\boxed{E_{rev} = E^0 + (RT/\,n\,F)\ln \prod \frac{a_{ox,\,i}^{\;\nu_{ox,i}}}{a_{red,\,i}^{\;\nu_{red,i}}}}$$

Follows directly from $\Delta G = \Delta G^0 + RT ln K$ and $\Delta G = -nFE$

Link between (equilibrium cell) voltage E^0 and thermodynamics (Gibbs free enthalpy)

- in a fuel cell or battery at equilibrium (start-up, no net current), e.g. fed with H_2/O_2 (air), one observes the **creation of a voltage**, characteristic for the reaction H_2/O_2 : **1.229 V** (at 298K and 1 atm)
- likewise, in an electrolyser, no reaction occurs before exceeding this voltage
- the theoretical **work** (here: **electricity**) retrieved from (fuel cell or battery) or invested in (electrolysis or reverse battery reaction) the reaction is given by the **Gibbs free enthalpy** of the corresponding chemical reaction $\Delta G_r = \Delta H_r - T\,\Delta S_r$:

  for $H_2 + 0.5\ O_2 \;\text{->}\; H_2O$

  ΔG^0_r(298K, 1 atm) = **-237'150 J/mole**

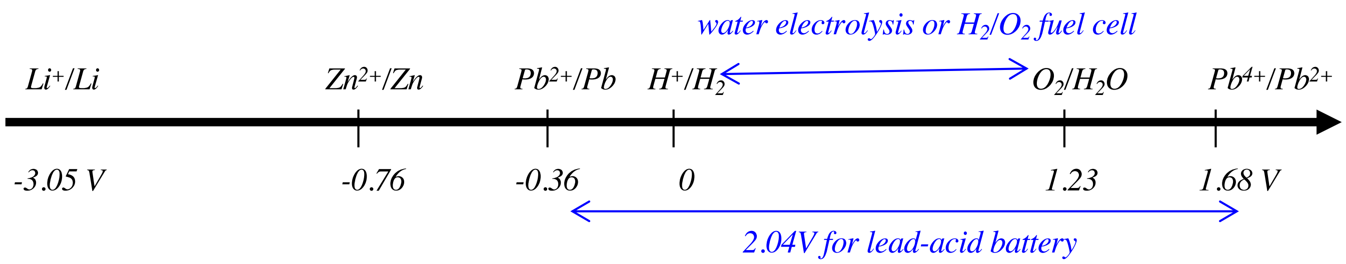
- the link between ΔG_r (J/mole) and the created (applied) voltage, E (or V, or U) is given by the amount of charge (C) that can be exchanged across this voltage :

  $\Delta G_r = -\ nF.E$

  (with n = 2 exchanged electrons for H_2, F = Faraday const = 96484 C / mole e^-)

  whence the value E^0= **1.229 V** (for H_2/O_2 at 1 atm, 298 K)

Electrochemical potential series



water electrolysis or H_2/O_2 fuel cell

Li^+/Li | Zn^{2+}/Zn | Pb^{2+}/Pb | H^+/H_2 | O_2/H_2O | Pb^{4+}/Pb^{2+}

-3.05 V | -0.76 | -0.36 | 0 | 1.23 | 1.68 V

2.04V for lead-acid battery

- Only a voltage ***difference*** between any 2 electrodes can be experimentally measured, not a single potential
- The scale value of ‘0’ is attributed to one electrode (H_2/H^+) which then defines all the others
- A value negative to H^+/H_2 means the material is oxidized by H^+ (=corroded (dissolved) by acid); a value positive to H^+/H_2 means the material oxidizes (combusts) H_2
- Historically, this attribution of H^+/H_2 as ‘0’ value comes from the observation that it separates noble metals (positive) from non-noble metals (negative, and thus corroded by acid)

How to compute the Gibbs free reaction enthalpy for any reaction / battery

$$\Delta H_r(T) = \Delta G_r(T) + T.\Delta S_r(T)$$

ΔG_r = fraction of ΔH_r (total heat) that can theoretically be converted to work.
Entropy S : unavoidable heat fraction (T. ΔS_r)

ν = stoechiometric factors of the reaction

$$\Delta H_r(T) = \sum_{prod} \nu_{prod} \Delta H_f(T) - \sum_{reac} \nu_{reac} \Delta H_f(T) \qquad \Delta S_r(T) = \sum_{prod} \nu_{prod} S_f(T) - \sum_{reac} \nu_{reac} S_f(T)$$

Products of the reaction (H_2O, CO_2,…) of formation Educts of the reaction (H_2, CO, CH_4, O_2,…)

$$\Delta H_f(T) = \Delta H_f^0(298K) + \int_{298}^{T} C_p(T)\,dT \qquad S_f(T) = S_f^0(298K) + \int_{298}^{T} \frac{C_p(T)}{T}\,dT$$

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tables

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tables

$$C_p(T) = a + b.T + c/T^2$$

→Message: the Nernst voltage $E^0(T)$ can be computed for any reaction,
from the thermodynamic data tables of the reactants and product species of the reaction

Nernst equation for electrode reactions

Example 1: reaction $Cu^{2+} + 2e = Cu$

$$E_{rev,Cu} = E^0_{Cu} + RT/\ 2F \ln (a_{Cu2+} / a_{Cu})$$

In case of pure metal, and at T=25°C, the expression can be further simplified as:

$$E_{rev,Cu} = 0.34\ V + (0.059 / 2)\ \log_{10} (a_{Cu2+})$$

Example 2: reaction $2H^+ + 2\,e = H_2$

$$E_{rev,H2} = E^0_{H2} + (RT/\ 2F) \ln (a_{H+}{}^2 / a_{H2})$$

$$= (RT/F) \ln a_{H+} - (RT/2F) \ln p_{H2}\ (a_{H2} = p_{H2})$$

At T=25°C, the expression can be further simplified as:

$$= 0.059 \log a_{H+} - 0.0295 \log p_{H2}$$

$$= -0.059\ pH - 0.0295 \log p_{H2} \quad (pH = -\log_{10} a_{H+})$$

Nernst equation for the oxygen half cell (oxygen as dissolved species in water)

$$O_2 + 4H^+ + 4e = 2\ H_2O$$

$$E_{rev,O2} \quad = \ E^0_{O2} + (RT/\ 4F)\ \ln\ (\ a_{H+}^4\ \ a_{O2}\ /\ \ a_{H2O}^2)$$

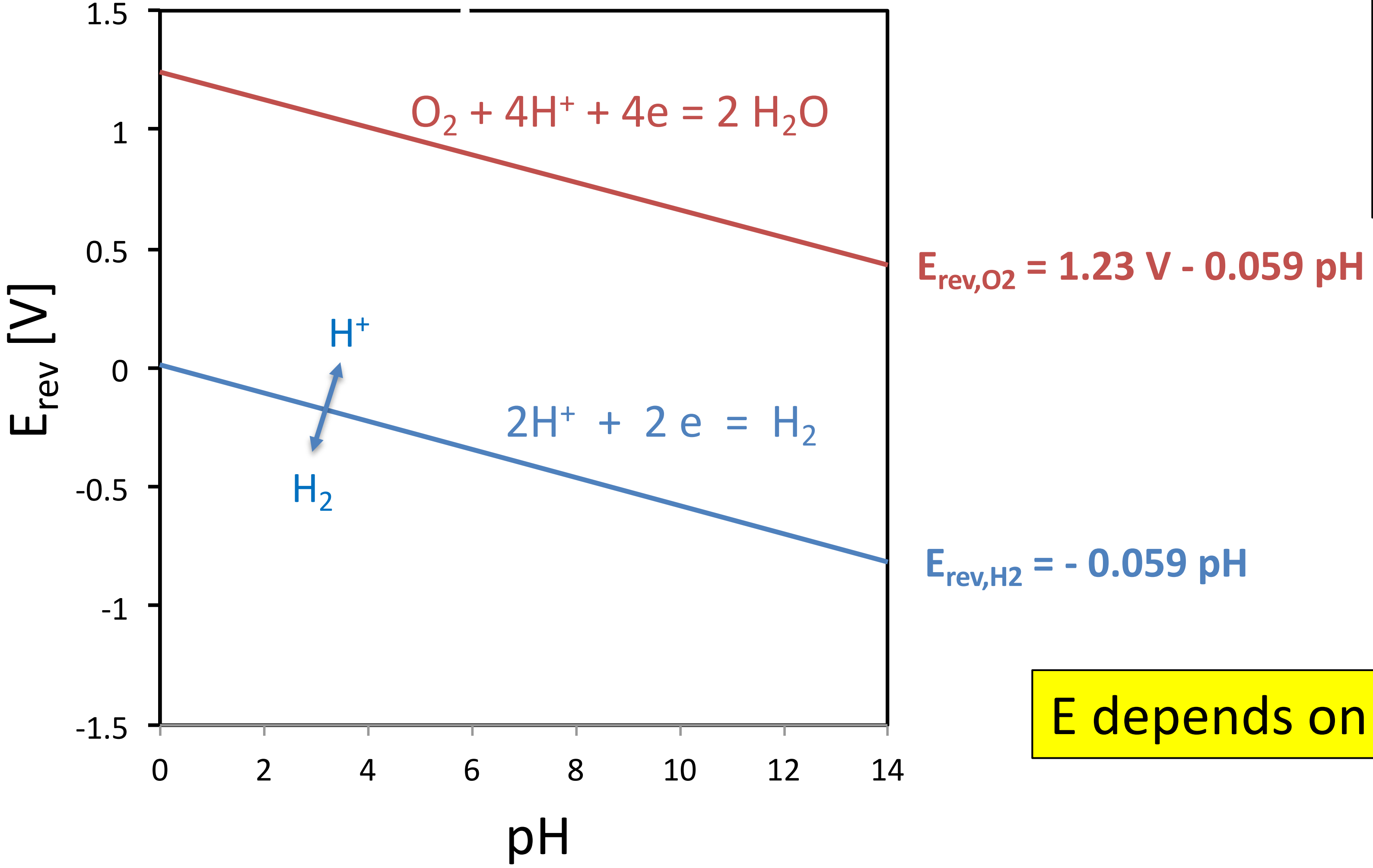
$E^0_{O2} = 1.23\ V$ $\qquad a_{O2} = p_{O2}$ $\qquad a_{H2O} = 1$

$$E_{rev,O2} = 1.23\ V + (RT/F)\ \ln a_{H+} + (RT/\ 4F)\ \ln p_{O2}$$

$E_{rev,O2} \quad = 1.23\ V + 0.059\ \log_{10} a_{\ H+} + 0.01475\ \log_{10} p_{O2}$ *(T = 25°C)*

$\mathbf{E_{rev,O2} \quad = 1.23\ V - 0.059\ pH + 0.01475\ \log_{10} p_{O2}}$ $(pH = -\log_{10} a_{H+})$

Pourbaix diagram (E_{rev} *vs pH* plot) for hydrogen and oxygen half cells



$E_{rev,O2}$ = 1.23 V - 0.059 pH

$E_{rev,H2}$ = - 0.059 pH

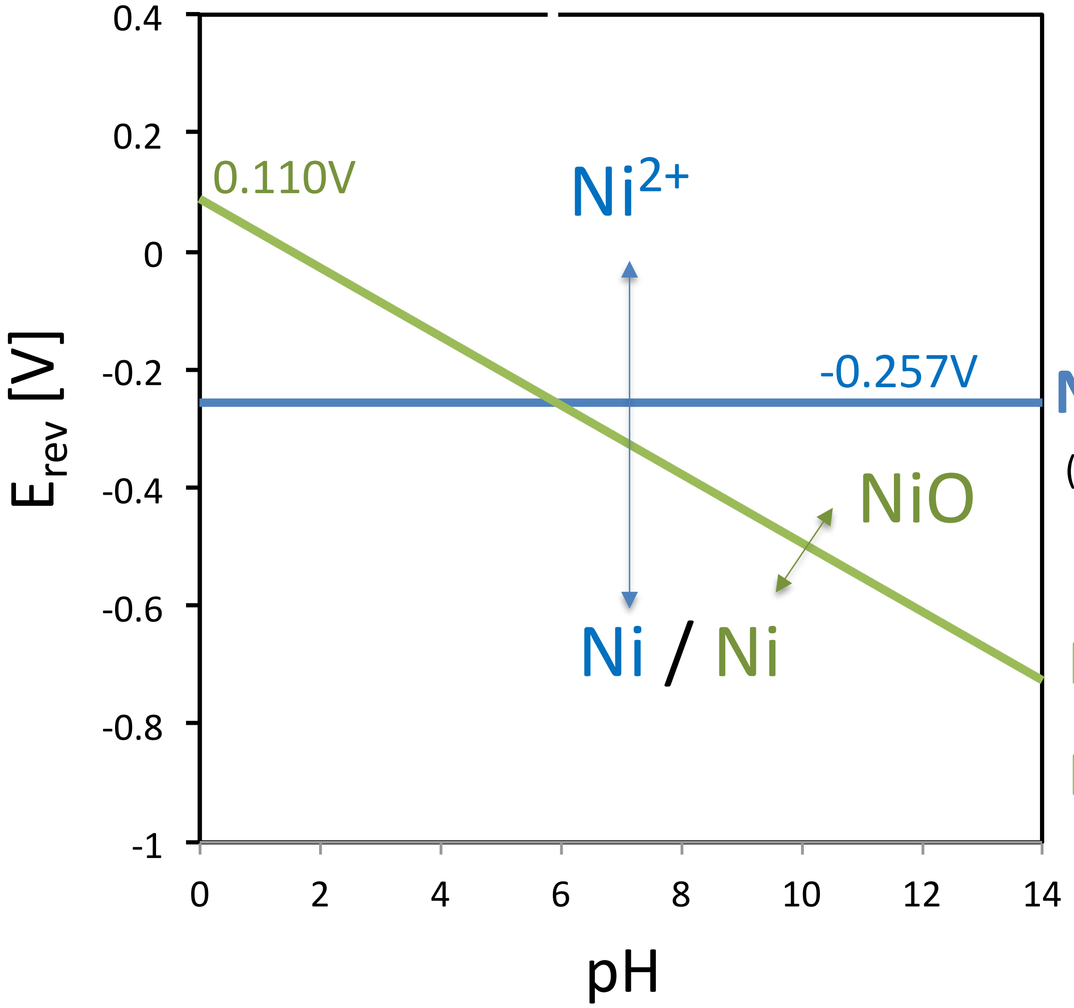
T = 25°C

$a_{O2} = 1$

$a_{H2} = 1$

E depends on the pH

Pourbaix diagram for Nickel



T = 25°C

$a_{Ni^{2+}} = 1$

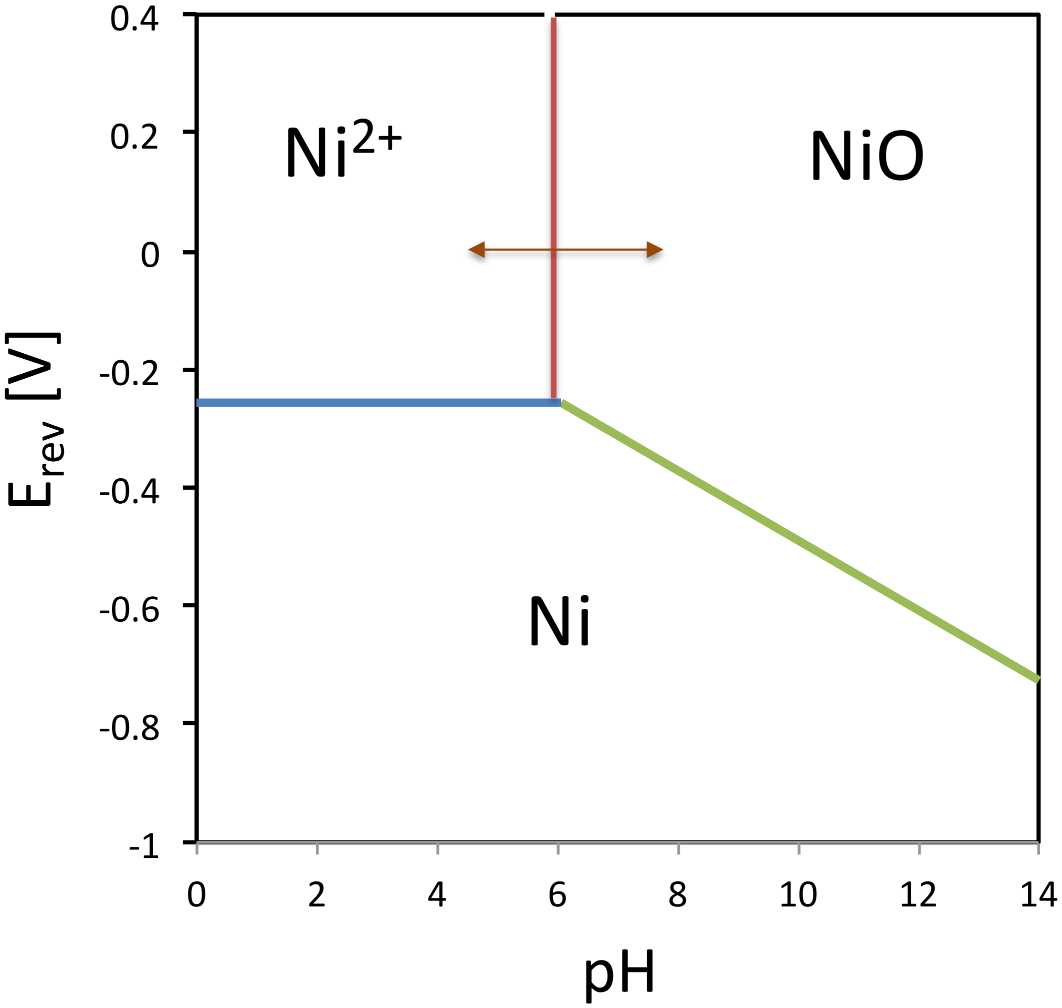
Ni^{2+} + 2 e = Ni

(no pH dependence, since no H+ in the reaction)

$NiO + 2H^+ + 2 e = Ni + H_2O$

E_{rev}= 0.110 V – 0.059 pH

Pourbaix diagram for Nickel



T = 25°C

$a_{Ni^{2+}} = 1$

pH = 6

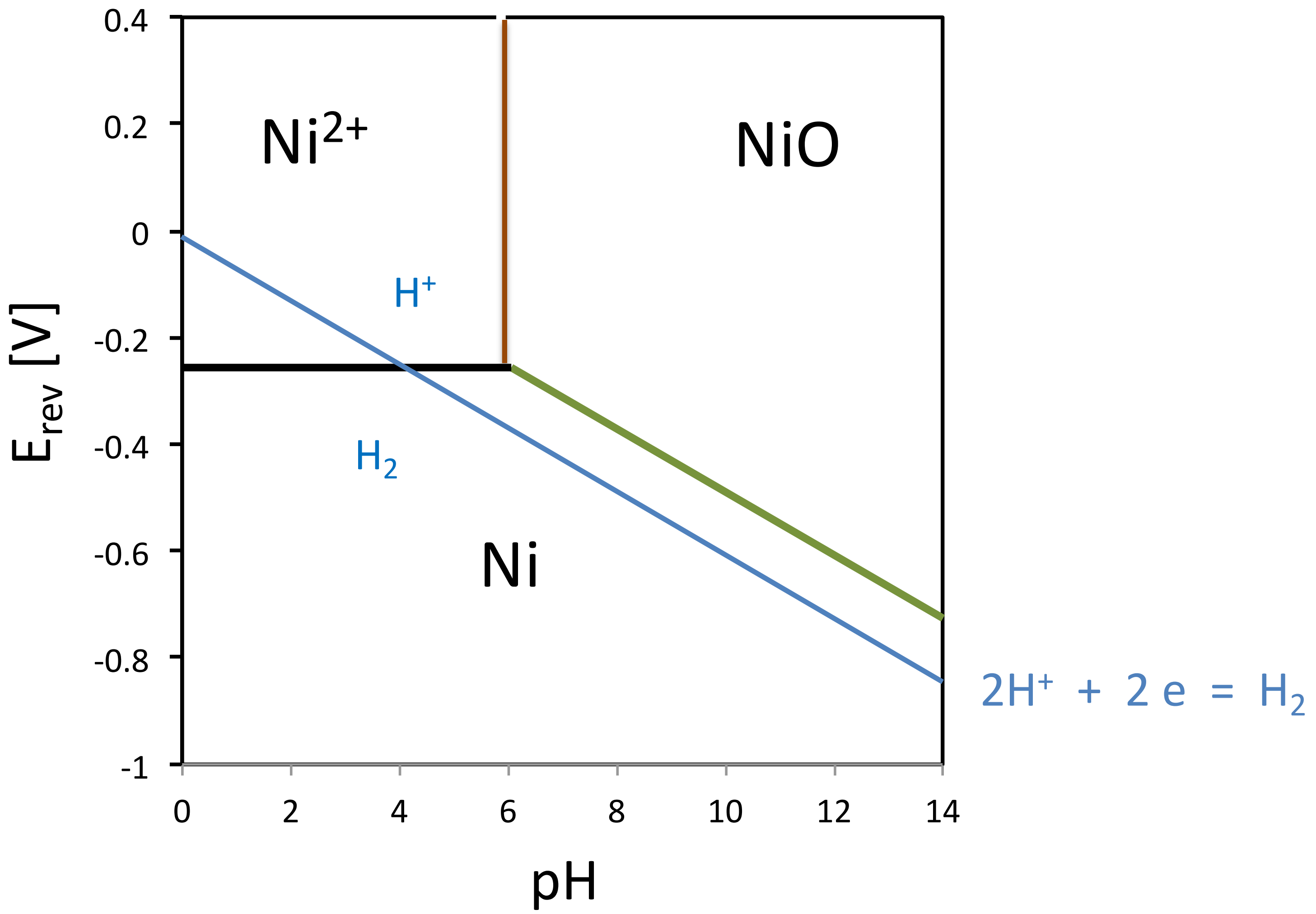
$NiO + 2H^+ = Ni^{2+} + H_2O$

$K = a_{Ni^{2+}} / (a_{H^+})^2 = 10^{12}$

$pH_{eq} = -\log_{10} (a_{Ni^{2+}} / K)^{0.5}$

For a_Ni^{2+} = 1, pH = 6
For a_Ni^{2+} = 0.01, pH = 7
For lower Ni^{2+}, eq. is shifted from left to right, hence H$^+$ is consumed, therefore to less H+ and thus higher pH.

Pourbaix diagram for Nickel

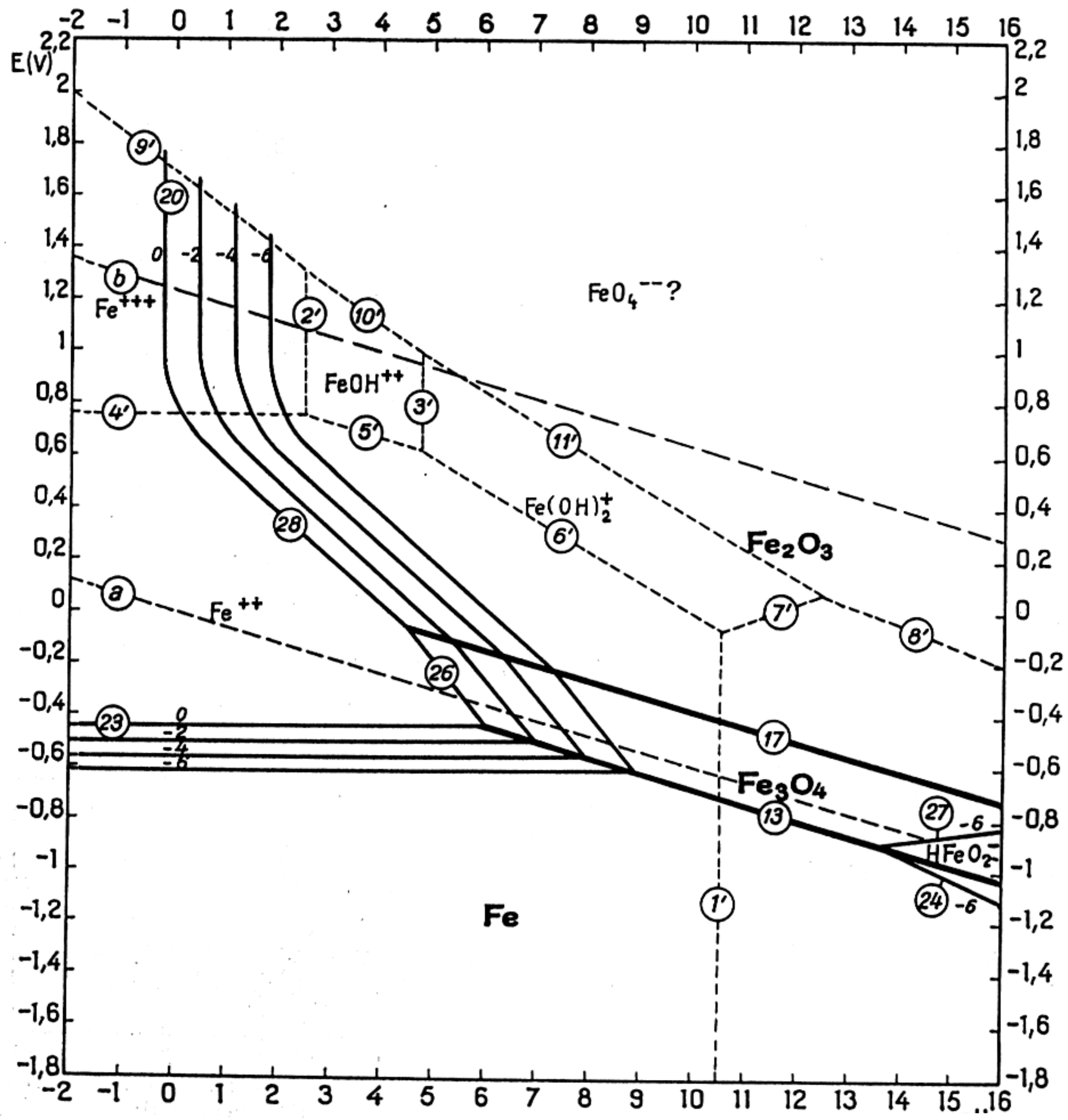


T = 25°C

$a_{Ni^{2+}} = 1$

Adding the H_2 reaction from slide 14.
Acidic solution below pH4 will dissolve (corrode) the Ni electrode into Ni^{2+}, generating H_2 from H^+
However, Ni is stable in alkaline solution down to -0.8 V, allowing its use as electrode catalyst in alkaline electrolysis.

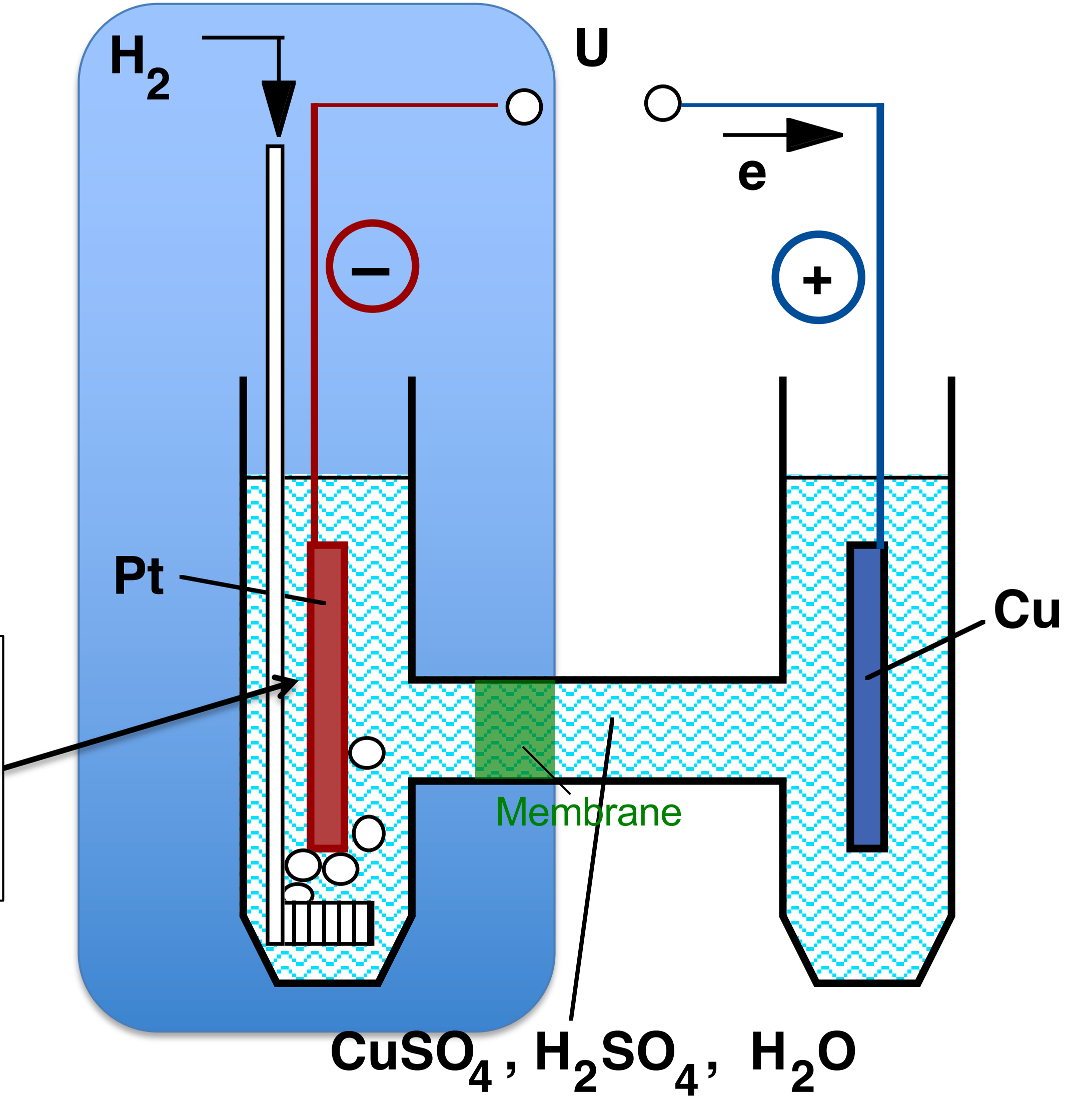
Pourbaix diagram of Iron



E_{rev} [V]

pH

Reference electrodes:
the standard hydrogen electrode



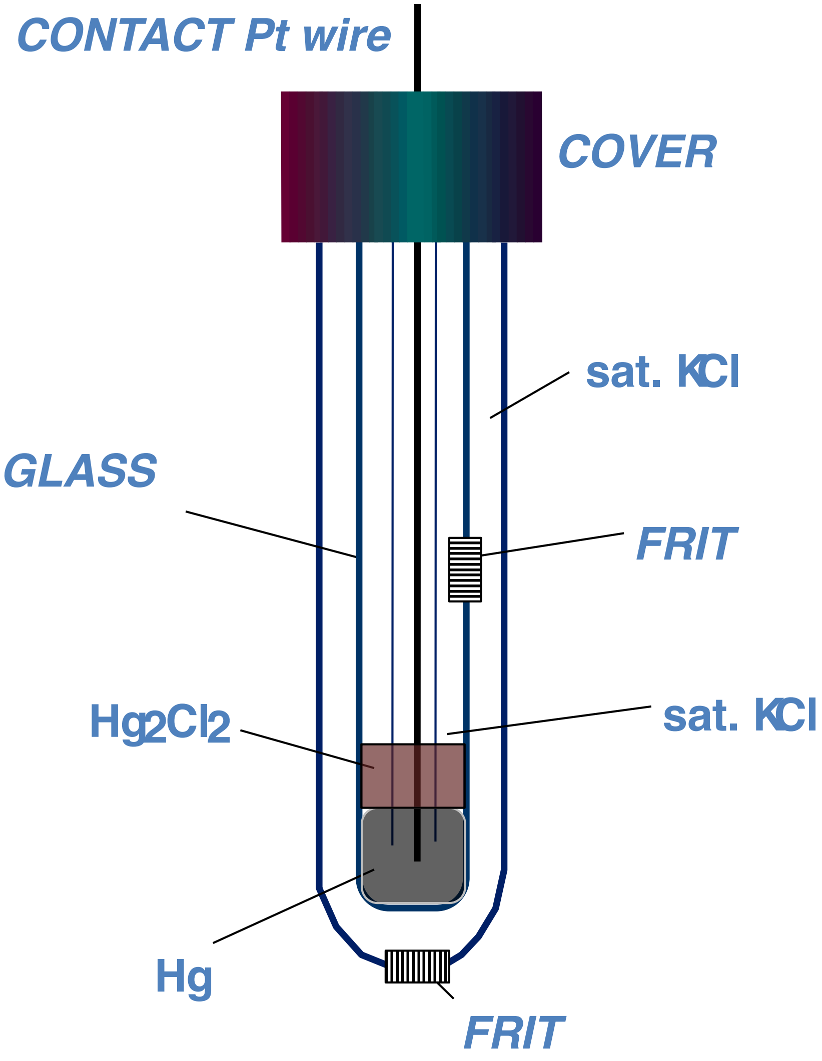
all activities = 1
p_{H2} = 1 atm
a_{H^+} = 1 mol/kg

Reference electrodes: the standard **calomel** electrode

$Hg_2Cl_2 + 2e = 2\ Hg + 2\ Cl^-$

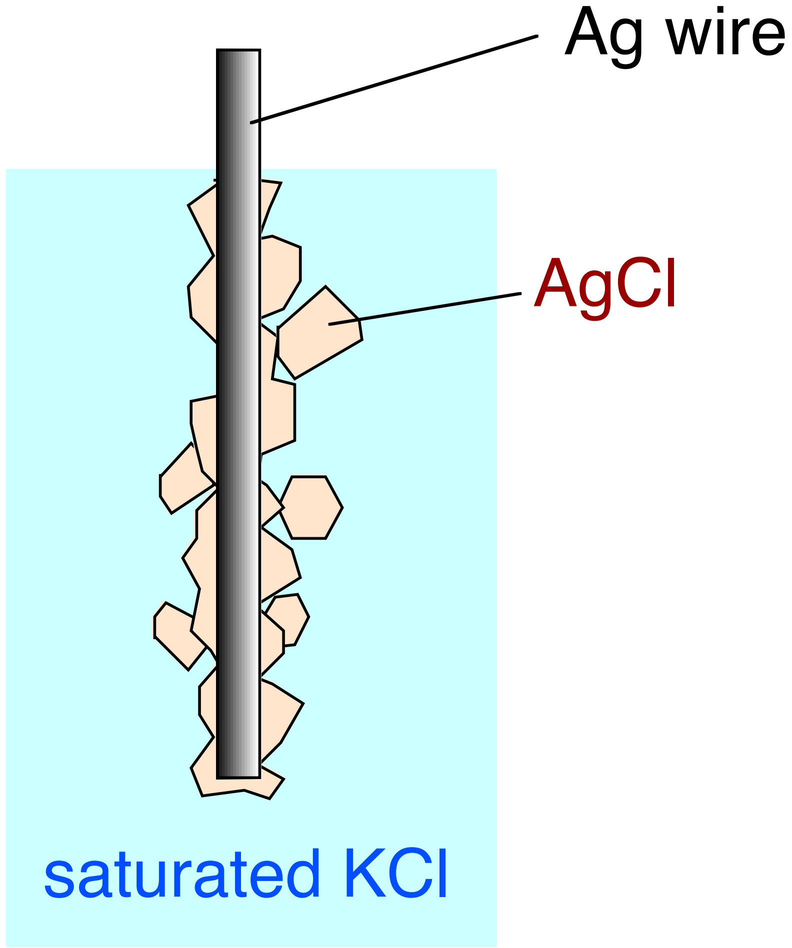
$E^0 = 0.268$ V

$E_{rev}(25°) = 0.268\ V - 0.059 \log a_{Cl-}$



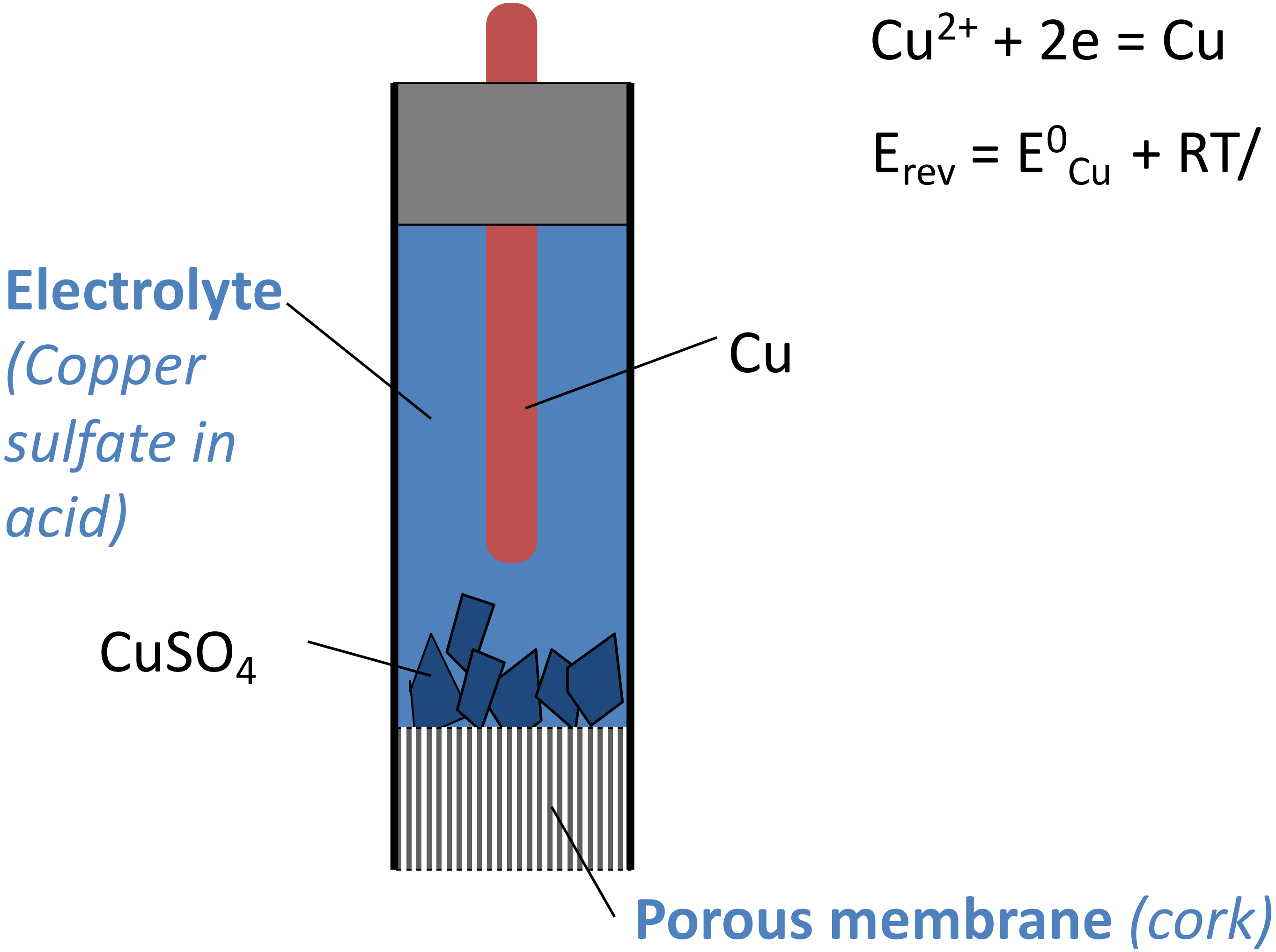
Reference electrodes:
the **silver chloride** electrode

$AgCl + e = Ag + Cl^-$ $E^o = 0.222$ V



$E_{rev} = E^0 - (RT/F) \ln a_{Cl-}$

Reference electrodes: the **copper sulphate** electrode



$Cu^{2+} + 2e = Cu$

$E_{rev} = E^0_{Cu} + RT/\, 2\, F \ln (a_{Cu2+})$

Commercial reference electrode for measuring corrosion potential of concrete steel

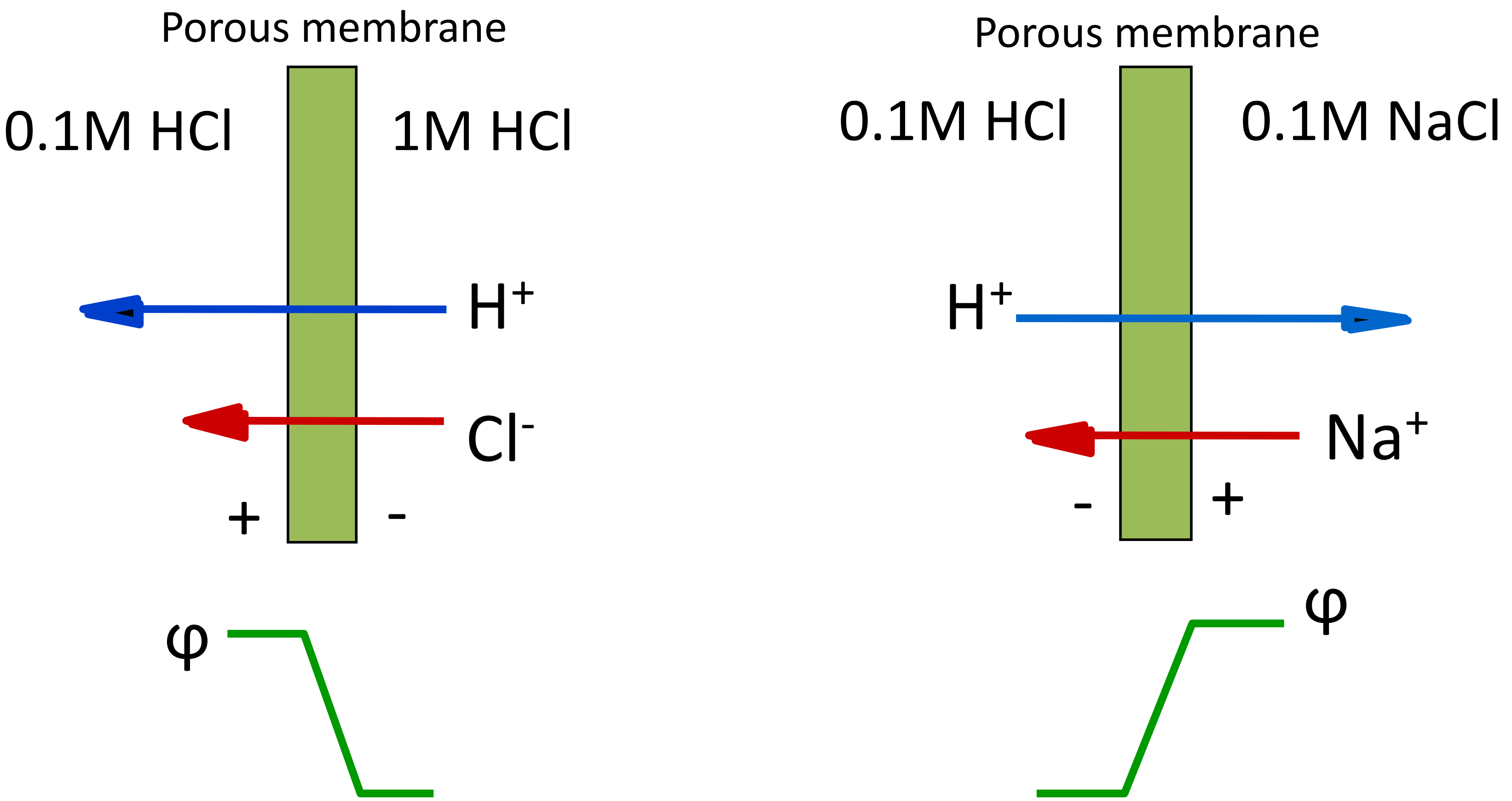
= at what potential will the steel dissolve (release electrons) e.g. in contact with seawater or pH7 water (e.g, O_2 + 4e + $4H^+$ => H_2O) as e- uptake (sink).

Reference electrodes:
the silver chloride electrode

Electrode ***Electrode***	**Electrolyte** ***Electrolyte***	**Potential [V]** ***Potentiel [V]***
calomel *calomel*	saturated KCl 1M KCl 0.1M KCl	0.241 0.280 0.333
à sulfate mercureux *mercury sulfate*	saturated K_2SO_4	0.658
à oxyde mercurique *mercury oxide*	1 M NaOH	0.098
à chlorure d'argent *silver chloride*	saturated KCl	0.195
à sulfate de cuivre *copper sulfate*	saturated $CuSO_4$	0.316

The junction potential

(electric potential difference φ established across membranes due to different ion mobility)



Porous membrane

0.1M HCl

1M HCl

H^+

Cl^-

+

-

φ

Porous membrane

0.1M HCl

0.1M NaCl

H^+

Na^+

-

+

φ