

MUNI  
PHARM

# Electrochemistry II

Physical chemistry

# Electrochemistry

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graph TD; A[Electrochemistry] --> B["Electrode Processes (Redox reactions)"]; A --> C[Conductivity (measurement of electrical properties of solutions)]; B --> D["No current flows through the electrochemical cell"]; B --> E["Current flows through the electrochemical cell"]; D --> F[Potentiometry]; E --> G["Galvanic cells (batteries)"]; E --> H["Electrolytic cells (electrolysis)"];
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**Electrode Processes**  
(Redox reactions)

**Conductivity**  
(measurement of electrical properties of solutions)

No current flows through the electrochemical cell

Current flows through the electrochemical cell

**Potentiometry**

**Galvanic cells** (batteries)  
**Electrolytic cells** (electrolysis)

# Potentiometry

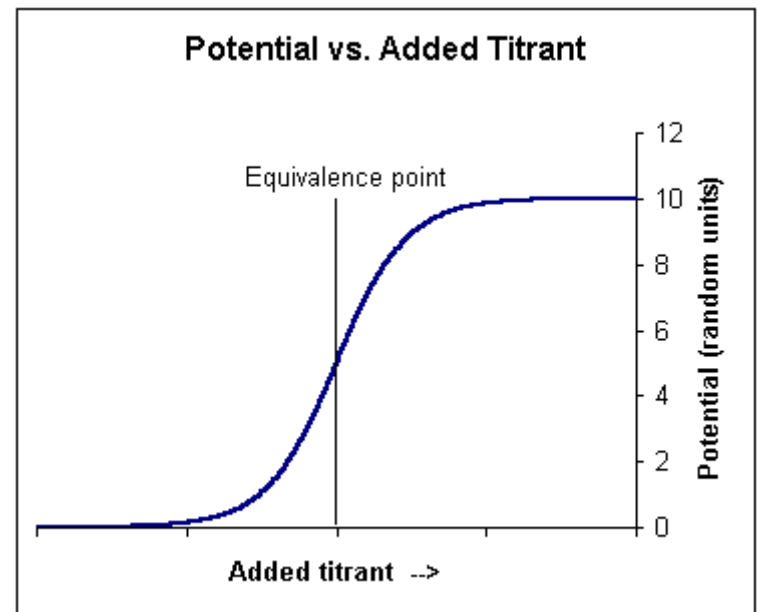
Potentiometry measured equilibrium voltage of galvanic cell consisting from **measurement** (indicator) and **reference** electrodes.

Indicator electrode potential is dependent on the **concentration of the ion**, reference electrode potential is constant.

**Potentiometry applications:** analytical chemistry, pharmacy, biochemistry, medicine, industry, etc.

**Direct potentiometry** – the concentration of the substance is determined from the measured potential (eg. **pH measurement**).

**Potentiometric titration** – measured potential versus volume of added titrant. The equivalence point is determined from the measured titration curve.



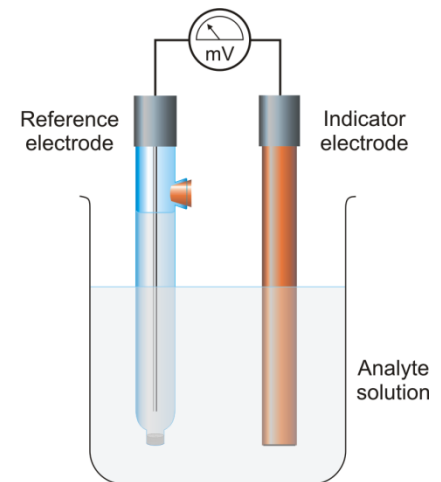
# Electrodes of the first kind

An **indicator** electrode in which a metal is in contact with a solution containing its ion is called an electrode of the first kind.

Metal electrodes: metal plate in a solution containing a metal cation (its activity determines the resultant potential - Nernst equation).

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

$$E = E^\circ + \frac{0.059}{n} \log [M^{n+}]$$



# Electrodes of the second kind

- are used as **reference** electrodes at potentiometry (their polarizability is small).

Electrodes of the second kind are metal electrodes assembly with the equilibrium potential being a function of the concentration of an anion in the solution.

## Argentochloride electrode

(Ag coated by AgCl in saturated KCl solution )

$$E_{\text{AgCl/Ag}} = E^{\circ}_{\text{AgCl/Ag}} - 0,059 \log [\text{Cl}^-]$$

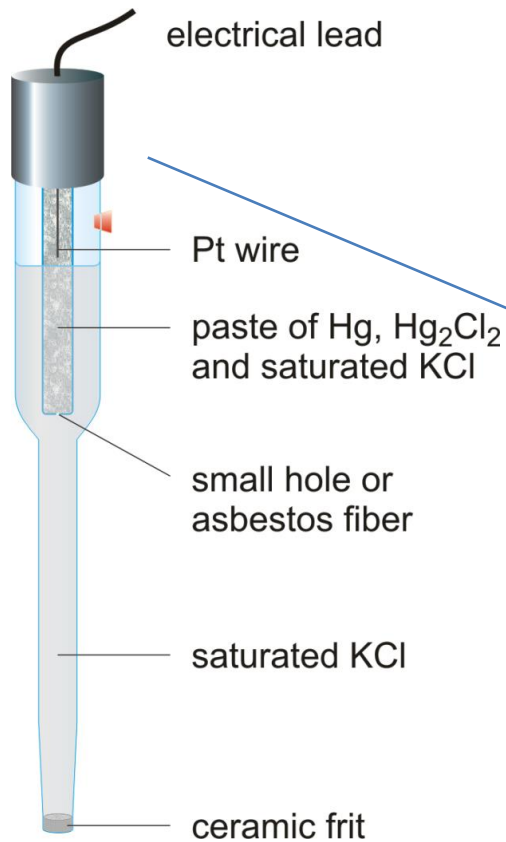
If we saturate the indicator electrode's half-cell with AgCl, the solubility reaction ( $\text{AgCl} \rightarrow \text{Ag}^+ + \text{Cl}^-$ ) determines the concentration of  $\text{Ag}^+$  ( $a_{\text{Ag}^+} = K_{s,\text{AgCl}} / a_{\text{Cl}^-}$ ).

$$E = E^{\circ}_{\text{Ag}^+} + 0,059 \log a_{\text{Ag}^+}$$

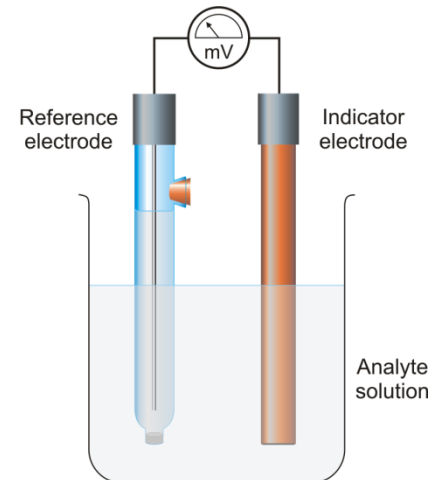
$$E = (E^{\circ}_{\text{Ag}^+} + 0,059 \log K_s) - 0,059 \log a_{\text{Cl}^-}$$

# Electrodes of the second kind

## Calomel electrode



$$E_{\text{Hg}_2\text{Cl}_2/\text{Ag}} = E^\circ_{\text{Hg}_2\text{Cl}_2/\text{Ag}} - 0,059 \log [\text{Cl}^-]$$



# Redox Electrodes

Redox electrodes (indicator) consist of **inert** metal (e.g. Pt) which is immersed in a solution containing two soluble forms of the same substance in **different oxidation states**. **Redox (inactive) electrode provides a surface for reaction**. It does not participate actively in the overall reaction. Inert electrodes are necessary, if none of the reactants can be used as an electrode.

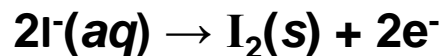
In the Nernst equation are only the activities of substances participating in the electrode reaction.

$$E_{\text{ox/red}} = E^{\circ}_{\text{ox/red}} - \frac{RT}{nF} \ln \frac{a_{\text{red}}}{a_{\text{ox}}}$$

# Redox Electrodes

**Standard reduction potentials** – if there are two redox systems, the stronger oxidizing agent that has a larger redox potential.

**Oxidation half-reaction**

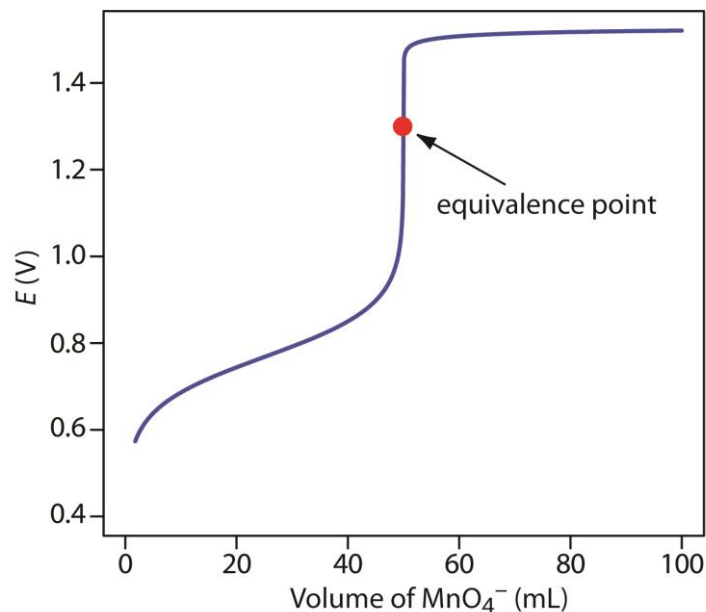
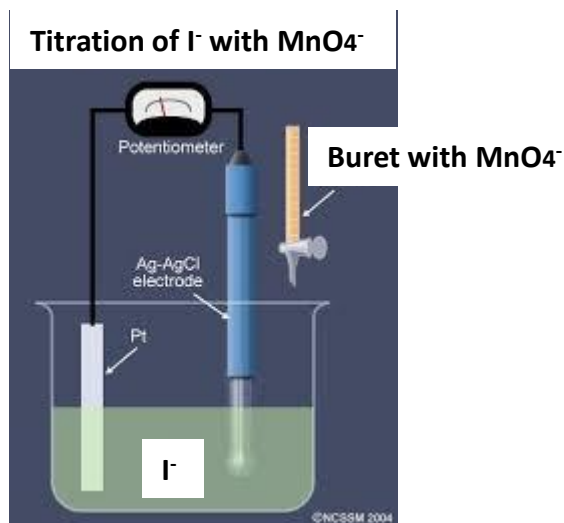


$$E^{\circ} = +0.54 \text{ V}$$

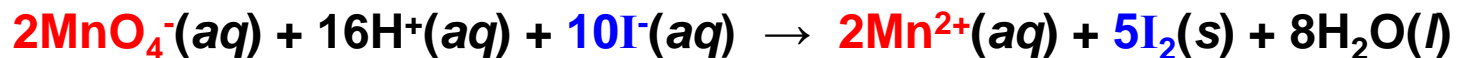
**Reduction half-reaction**



$$E^{\circ} = +1.51 \text{ V}$$



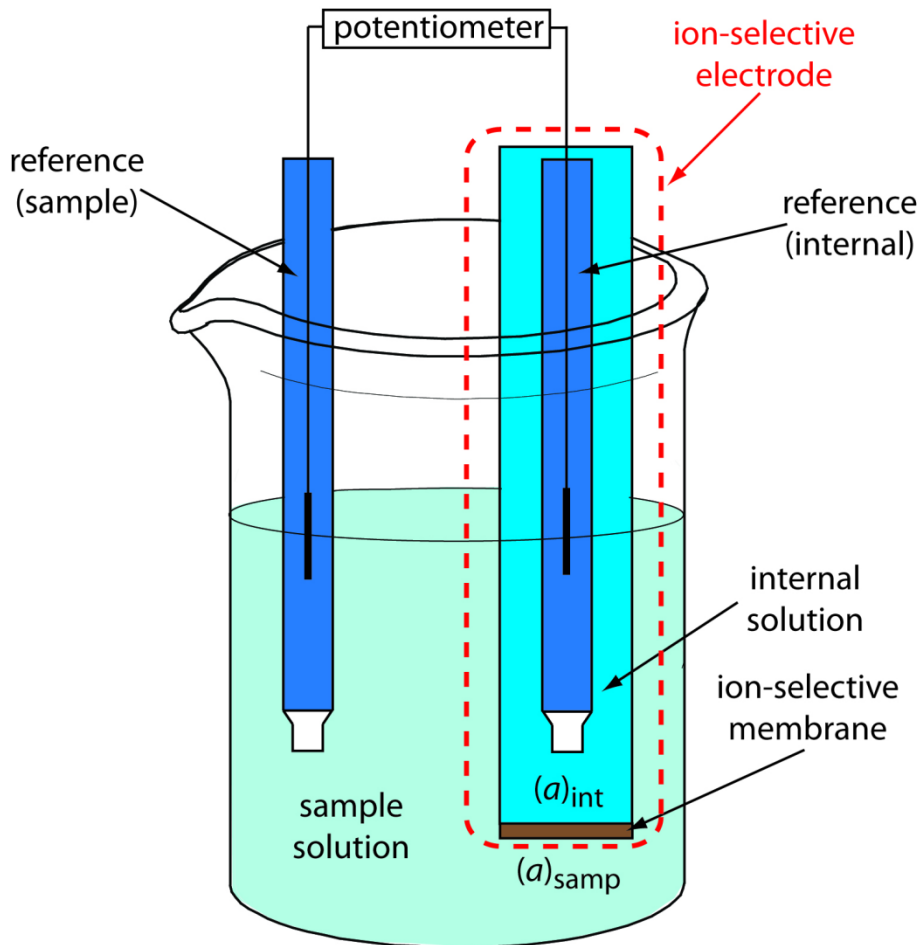
**Overall (cell) reaction**





# Membrane Electrodes (ion-selective electrodes)

The membrane is **semipermeable** (impermeable for some ions) = the concentration of diffusible ions and nondiffusible ions are different on different sides of the membrane and give rise to **membrane potential**.



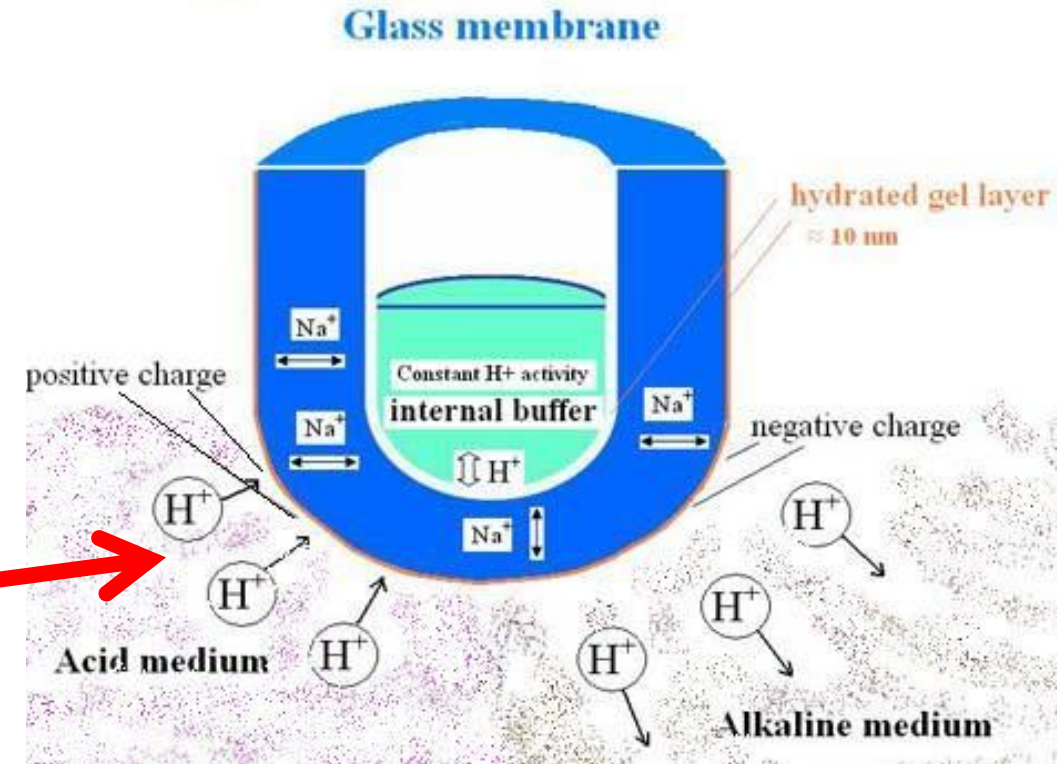
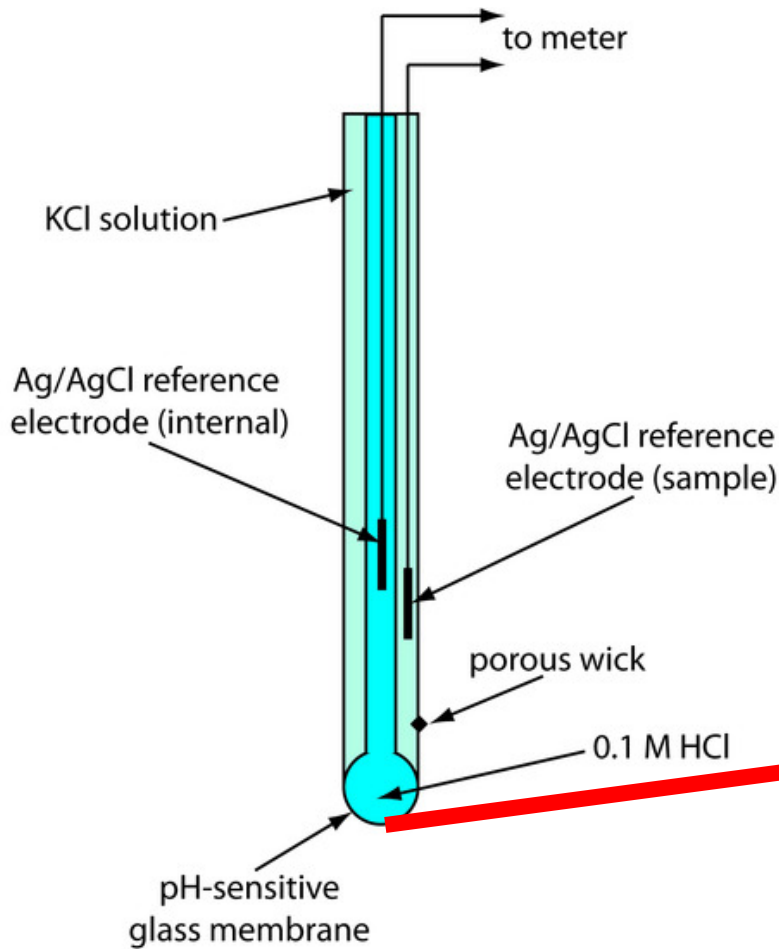
Membrane electrode separating the two solutions containing analyte—the sample solution and the ion-selective electrode's internal solution. In the internal solution is immersed the internal reference electrode. **Membrane potential depends on the ion concentration.**

$$E_{\text{cell}} = \underbrace{E_{\text{ref(int)}} - E_{\text{ref(samp)}}}_{\text{constant}} + E_{\text{membrane}}$$

# Membrane Electrodes

Measurement of pH - mostly glass electrode (pH increase by 1 means the potential decrease by 0.059 V).

$$E = E^\circ - 0,059 \log [H^+]$$

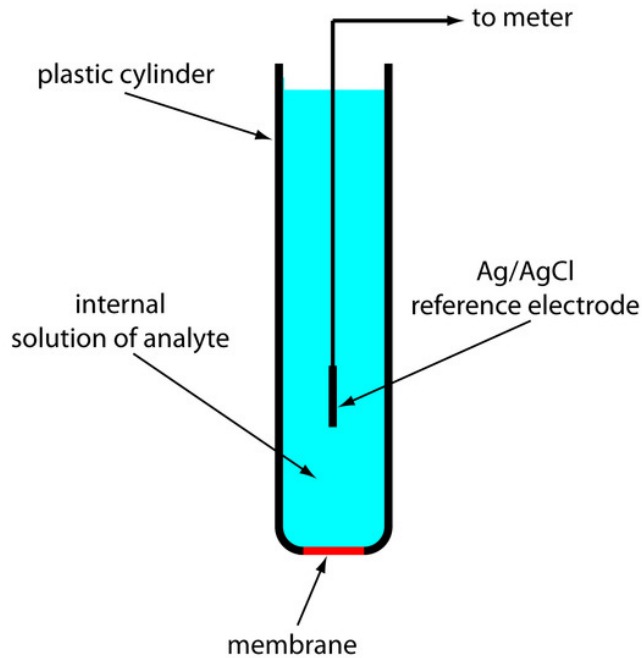


Membrane potential on the surface of the glass electrode is formed by ion exchange between the glass and the solution.

# Membrane Electrodes

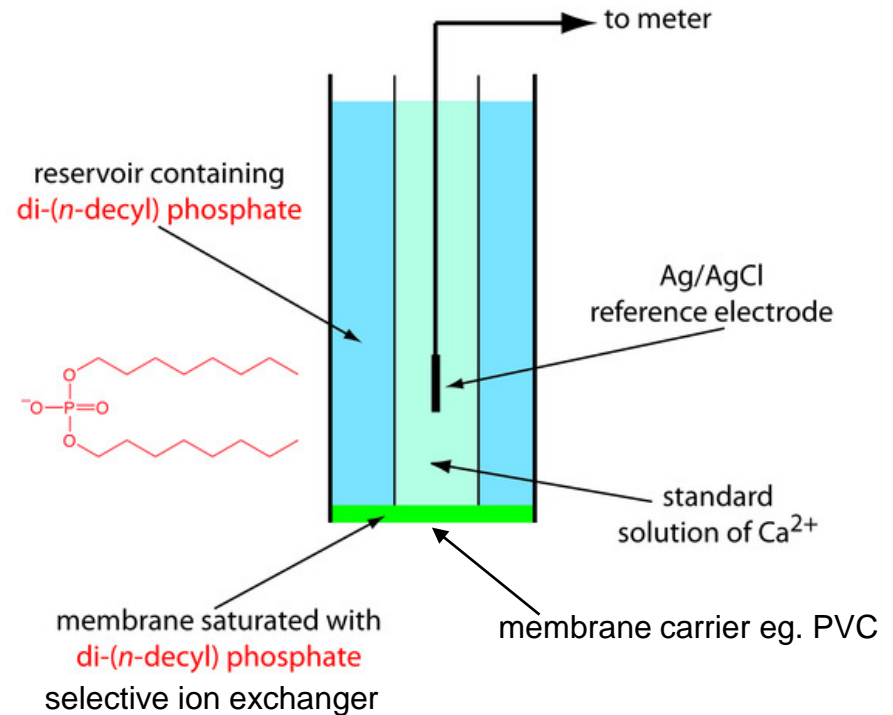
## Solid-state membranes

eg. Heavy metals determination,  $\text{Cl}^-$



## Liquid-based membranes

eg.  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$



## Other types of membrane electrodes:

**Gas-Sensing Electrodes** ( $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ )

**Potentiometric Biosensors:** measured molecule is formed by the reaction of the bioactive (e.g. enzyme) and analyzed molecules (eg. aminoacids, urea, penicillin, sugars).

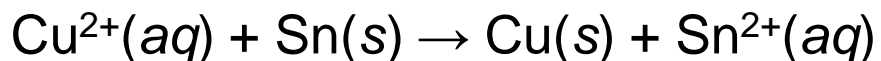
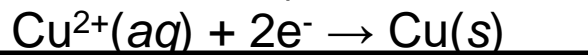
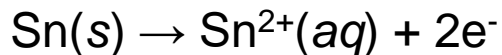
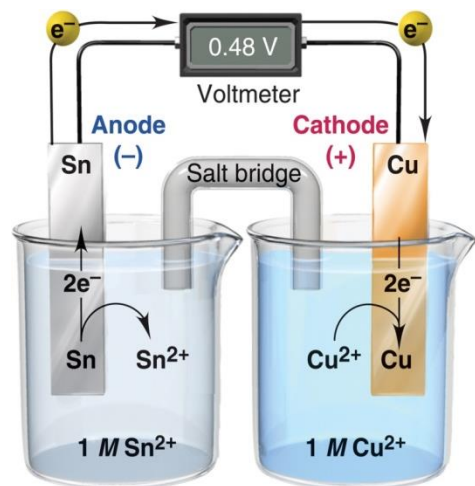
# Membrane Electrodes Applications

- Determination of acidity
- Medicine (**blood** - measurement of potassium, calcium, sodium, fluorides)
- Food industry (**meat** - nitrite and nitrate; **drinks** - determination of the concentration of chlorides, fluorides and carbonates)
- Medical products (determination of fluorides in **vitamines** and **tooth pastes**)
- Agriculture (**soil samples** - determination of calcium, nitrates, sodium, potassium, boron, ammonium and halogenides; **fertilizers** - determination of potassium, calcium, nitrogen and nitrates in fertilizers)
- Water systems (**drinking water** - fluorides and nitrates; **waste water** - concentration measurements of copper, silver, cyanides and ammonium)

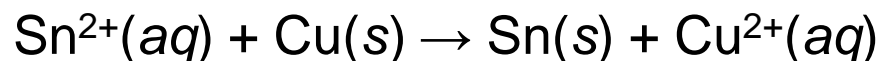
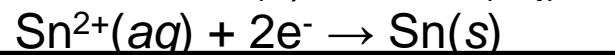
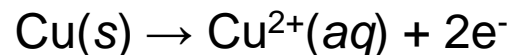
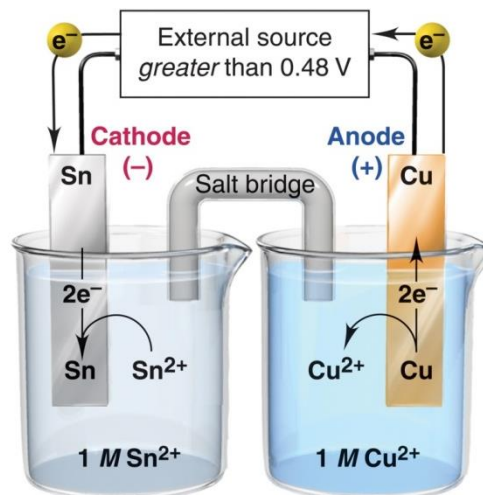
# The effects of electric current flows through the electrochemical cell

## Galvanic cell and Electrolytic cell

Electrolytic cell (**electrolysis**) - the cell on which electrodes is supplied current from an external source (non-spontaneous).



**galvanic cell**



**electrolytic cell**

# Electrolytic cell

To calculate the amount of electrodeposited substance on an electrode **Faraday's law** applies:

$$m = \frac{QM}{zF} = \frac{ItM}{zF}$$

m – weight (g)

Q – electric charge

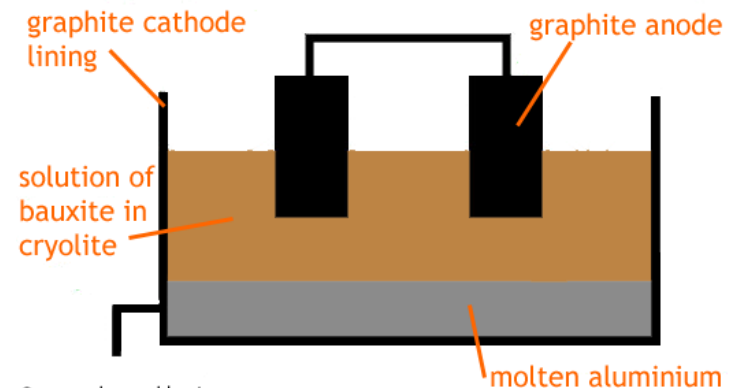
M – molecular weight of the substance (g mol<sup>-1</sup>)

z – the number of electrons been exchanged during the electrochemical process

F – Faraday constant (96500 C mol<sup>-1</sup>)

I – electric current (A)

t – time (s)



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**Industrial application: Extraction of Aluminium by Electrolysis**

## Differences between a Galvanic cell and an Electrolytic cell

Galvanic Cell	Electrolytic cell
A Galvanic cell converts chemical energy into electrical energy.	An electrolytic cell converts electrical energy into chemical energy.
Here, the redox reaction is spontaneous and is responsible for the production of electrical energy.	The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction.
Here the anode is negative and cathode is the positive electrode. The reaction at the anode is oxidation and that at the cathode is reduction.	Here, the anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction.
The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit.	The external battery supplies the electrons. They enter through the cathode and come out through the anode.

# Electrode polarisation

- side-effects influence the electrochemical process
- change in voltage of half-cell caused by the **passage of the current.**

## A. Concentration polarization

limiting action: the transport of ions (reactants or products of the electrode reaction)

## B. Electrochemical polarization

limiting action: the transfer of electrons between ions

## C. Chemical polarization

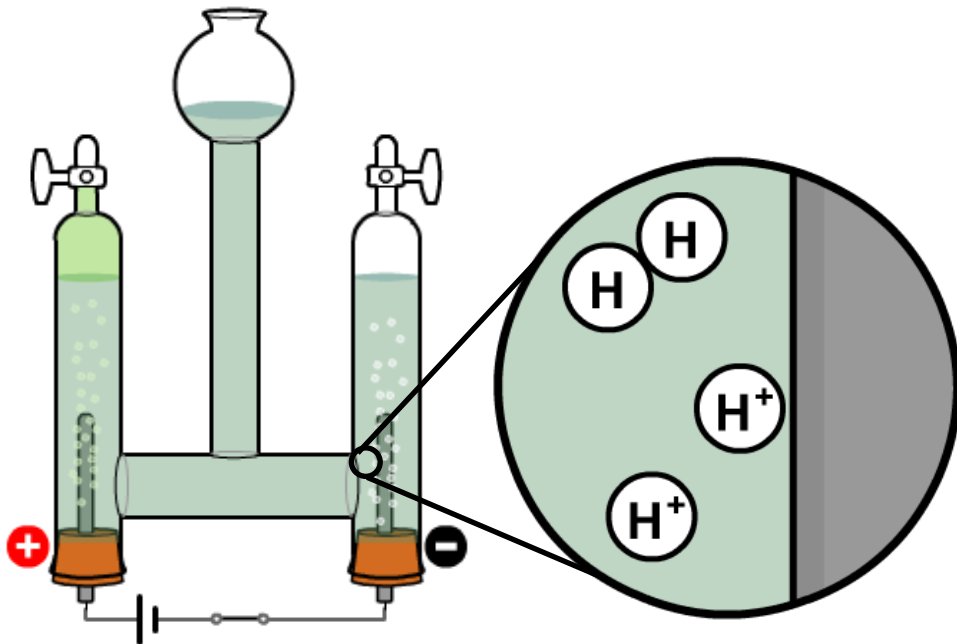
limiting action: the chemical change that occurs at the electrode (e.g. generation of gases during electrolysis and isolating the electrode from the electrolyte)

The **slowest process** which requires the greatest activation energy **determines the rate** of the electrode reactions, electrode potentials and the electric current.



# Overvoltage $\eta$

- indicates the degree of polarization
- difference between half-cell voltage at the load current ( $I \neq 0$ ) and voltage at zero current ( $I = 0 \Rightarrow$  EMF)
- the minimum voltage between anode and cathode of an electrolytic cell that is needed for electrolysis to occur - **decomposition voltage**

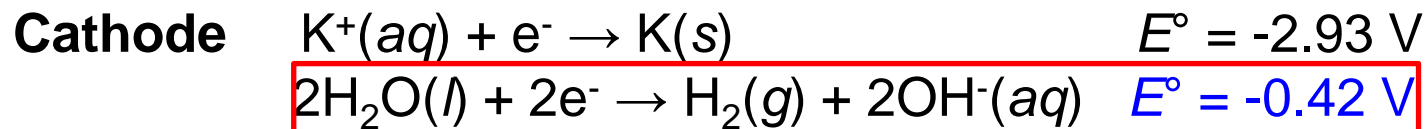


**Overvoltage needs to be taken into account when predicting the products of electrolysis for aqueous solutions.** Cations of less active metals (Au, Ag, Cu, Cr, Pt, Cd) are reduced to the metal. Cations of more active metals are not reduced.  $\text{H}_2\text{O}$  is reduced instead. **Overvoltage is ca. 0.4–0.6 V for  $\text{H}_2(g)$  or  $\text{O}_2(g)$ .**

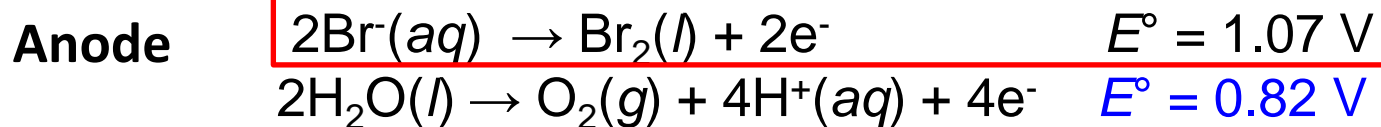
# Overvoltage $\eta$

The electrolysis of aqueous salt solutions:

What products will be produced during the electrolysis of aqueous KBr?



The overvoltage change  $E$  for the reduction of water ( $E \approx -0.8$  to  $-1.0 \text{ V}$ )  
 $\Rightarrow$  water is still easier to reduce than  $K^+$ . **At the cathode will be formed  $H_2(g)$ .**



The overvoltage change  $E$  for the oxidation of water ( $E \approx 1.2$  to  $1.4 \text{ V}$ ).  
Bromide solution is easier to oxidize than water. **At the anode will be formed  $Br_2(g)$ .**



# Depolarization

- process that eliminates causes of polarization

## Concentration polarization

Depolarization by – stirring of solution

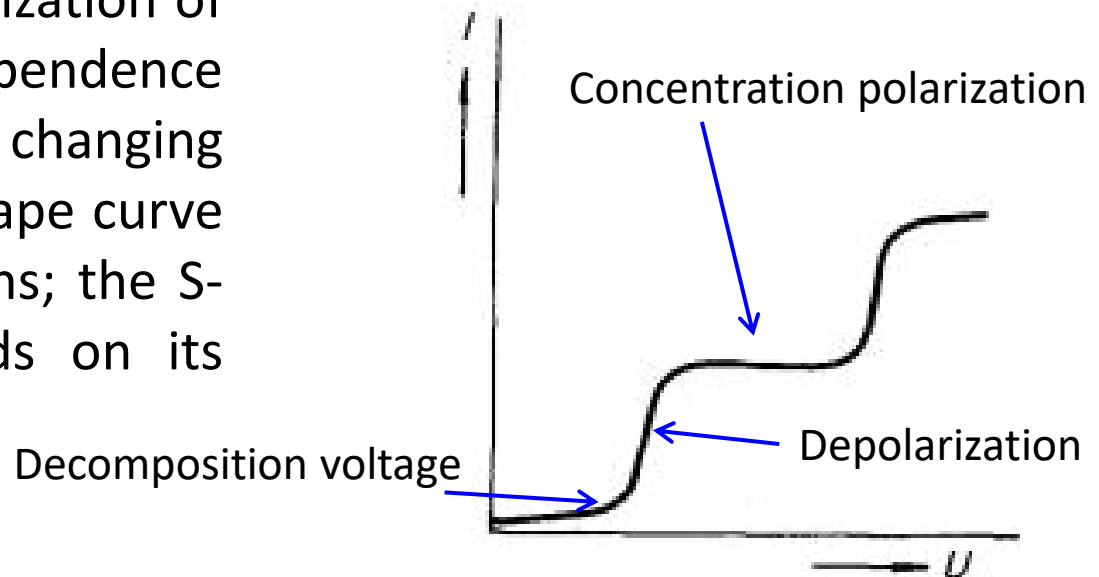
– using concentrated solutions

## Chemical polarization

Depolarization by removing of substances which cause polarization (e.g. removing of  $O_2$  or  $H_2$ ).

Polarization is not always undesirable:

**Polarography**: uses the polarization of electrodes; measure the dependence of the current passing on changing voltage. Location of the S-shape curve is related to the types of ions; the S-shape curve height depends on its concentration.



# Electrochemical cells



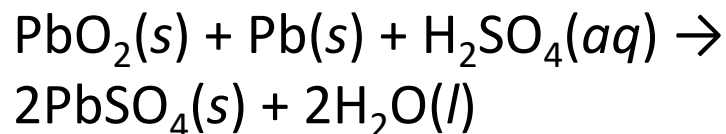
## A. Primary cells

The electrochemical **reaction** occurring in the cell **is not reversible**. A primary cell is a battery that is designed to be used once (can not be charged).

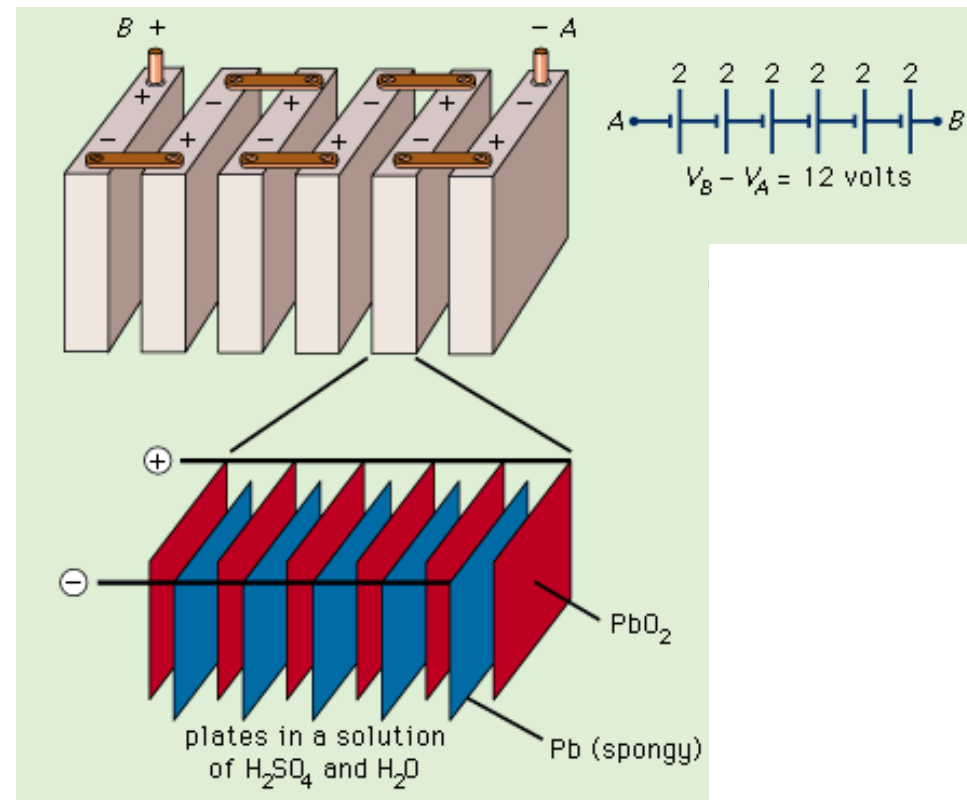
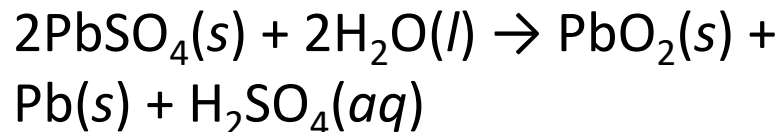
## B. Secondary cells (accumulator)

Electrochemical **reactions are reversible** – external electrical energy can transform the cell into the initial condition and the cycle can be repeated.

*The overall reaction (discharging):*



*The overall reaction (charging):*

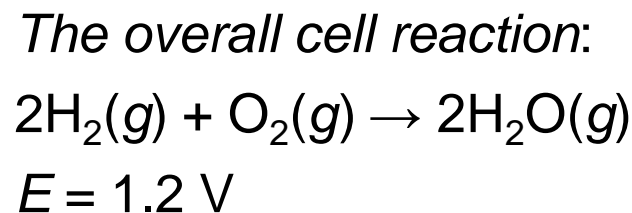
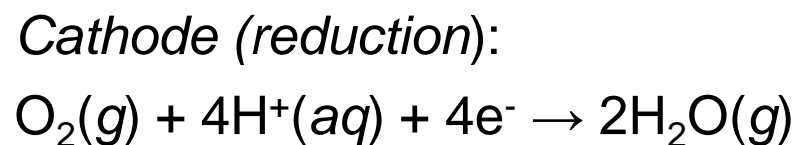
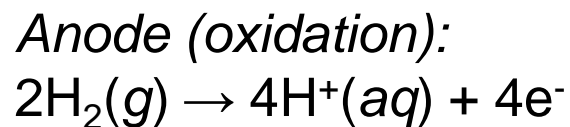
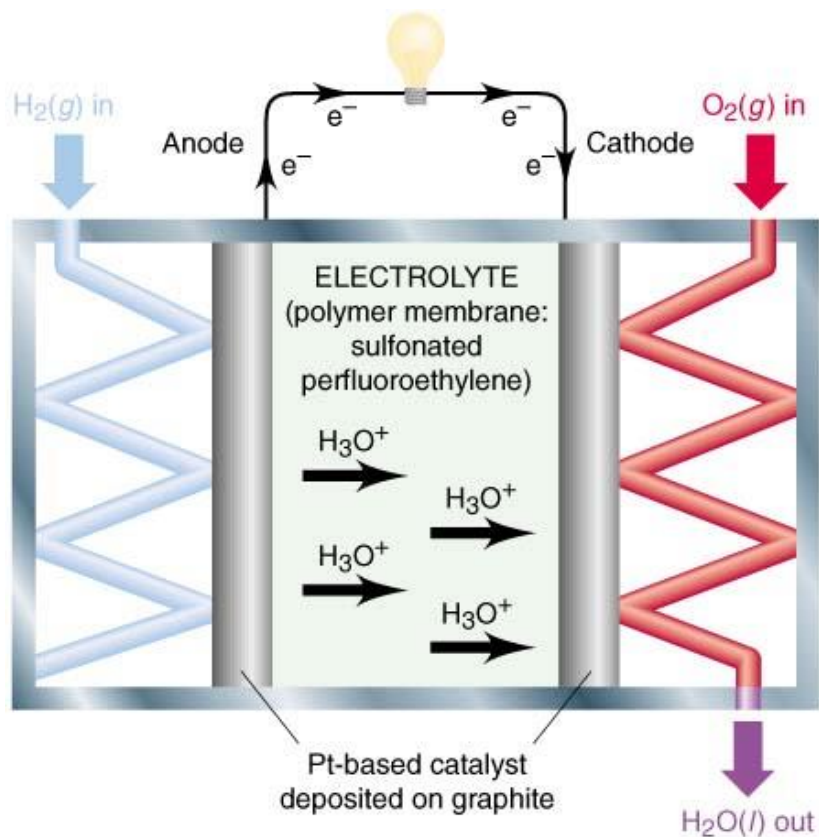


**Lead battery**

# Electrochemical cells

## C. Fuel cells

The active ingredients are continuously supplied from the outside - the electrochemical reaction takes place continuously and constantly.

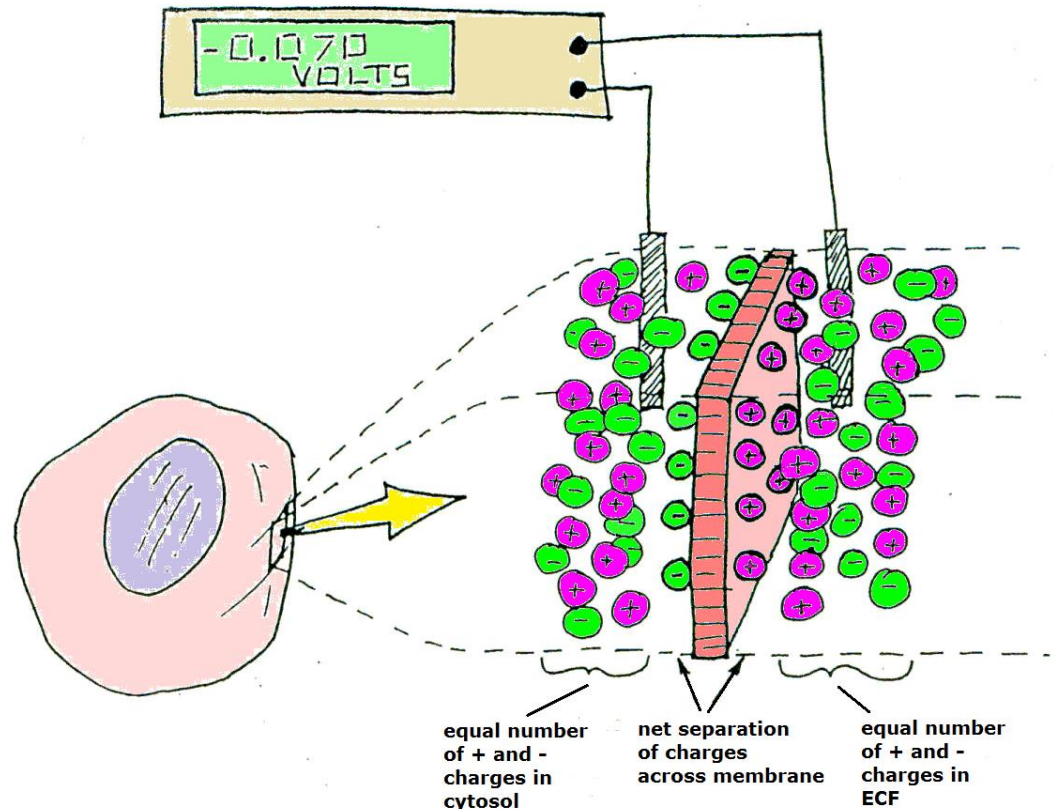


# Electrochemical potentials in living organisms

**Membrane potential** (resting or action) is determined by the uneven distribution of ions on both sides of the cell membrane.

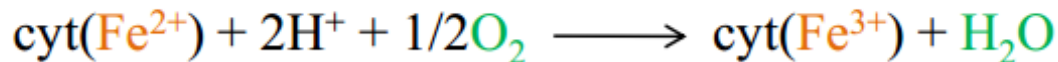
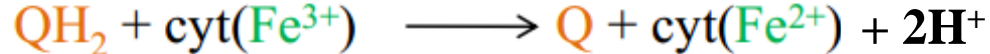
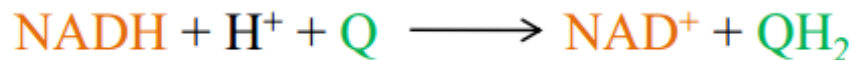
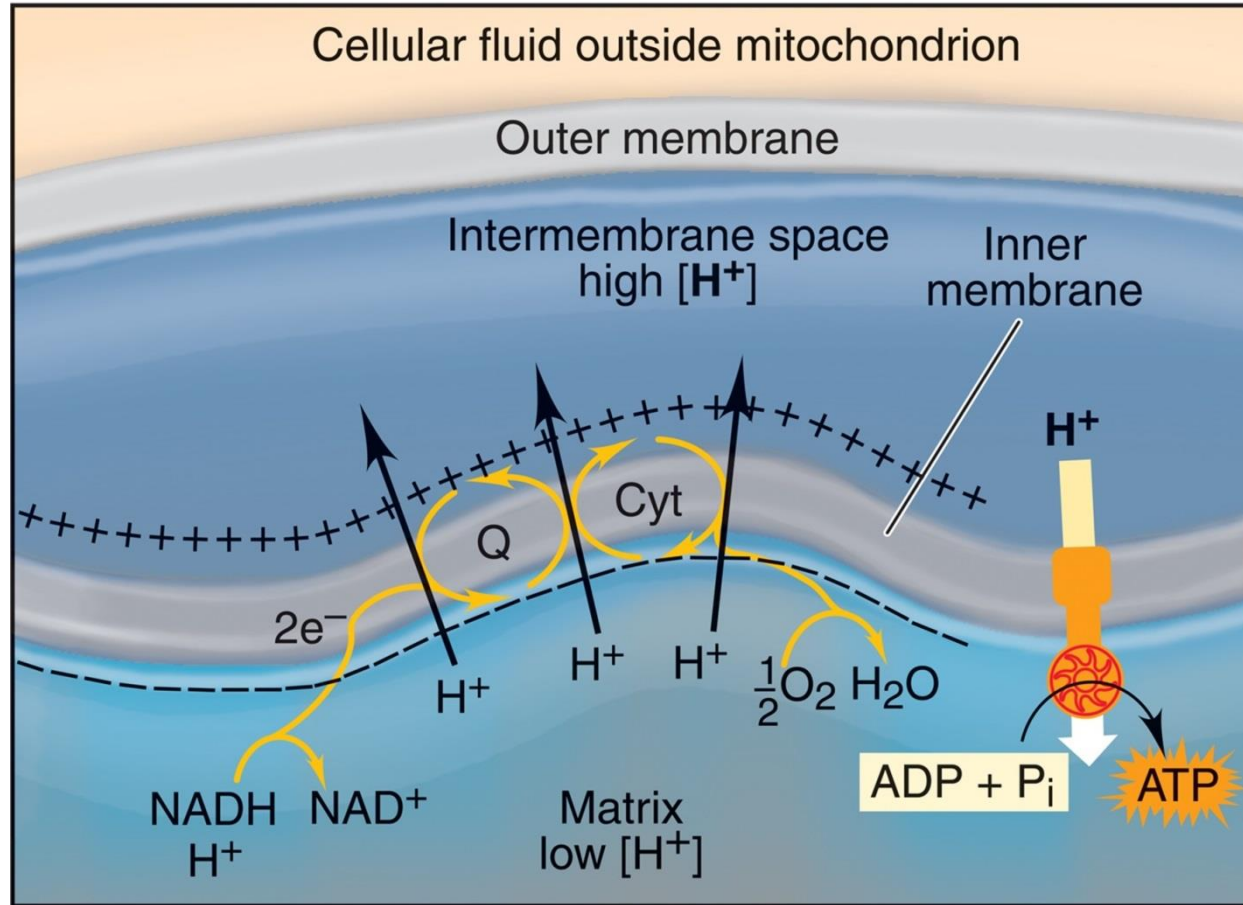
Electrical potentials have an important role in e.g. **excitation of muscle cells** or in **transfer of the information in nerve cells**.

$$E_K = \frac{RT}{nF} \ln \frac{[K^+]_{ex.}}{[K^+]_{in.}}$$



# Electrochemical potentials in living organisms

The electron transport chain (cellular respiration)



electrochemical gradient

=

proton gradient



energy for **ATP synthesis**