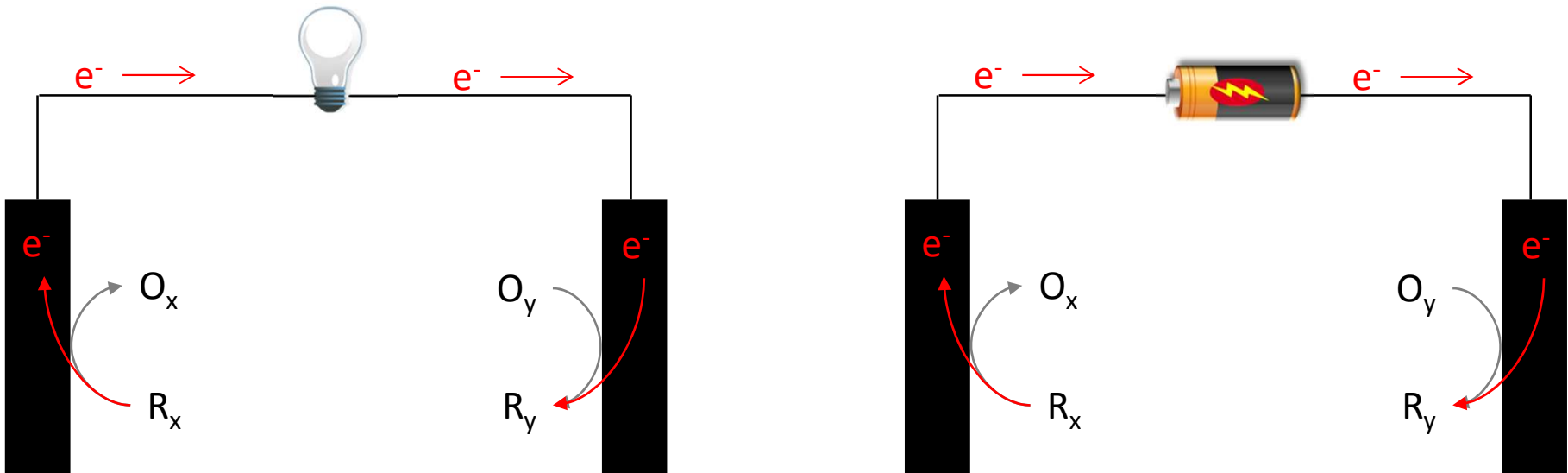


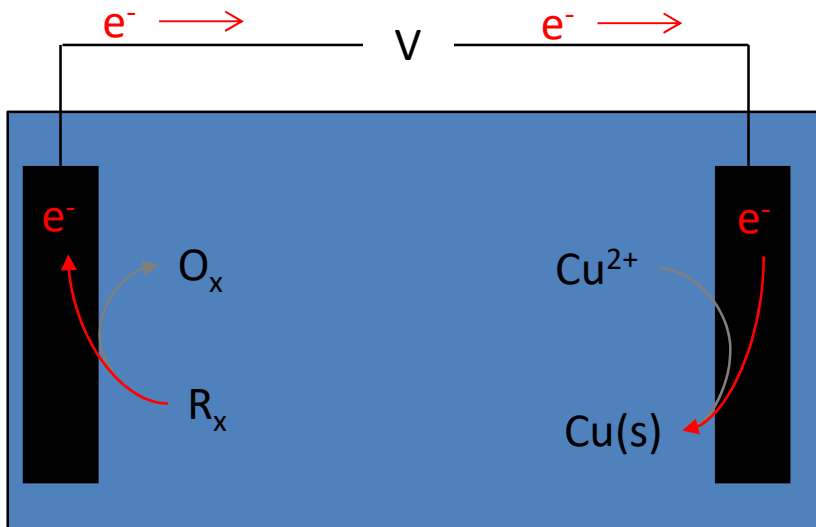
Microbial electrochemical technologies – fundamental aspects and methods of analysis

Before we start...

- **Galvanic cells**
 - Reactions occur spontaneously at the electrodes when they are connected
 - Chemical energy can be converted into electrical energy
 - E.g. fuel cells, batteries
- **Electrolytic cells**
 - An external voltage must be applied to drive reactions at the electrodes
 - Electrical energy can be converted into chemical energy

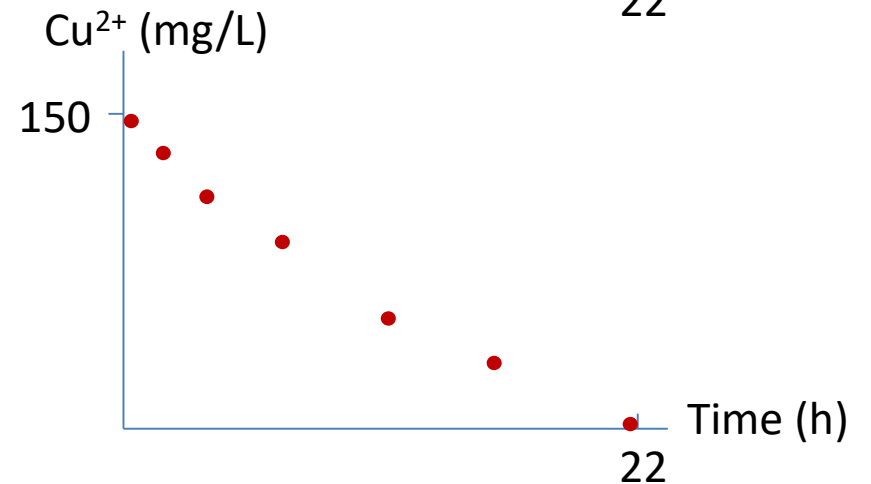
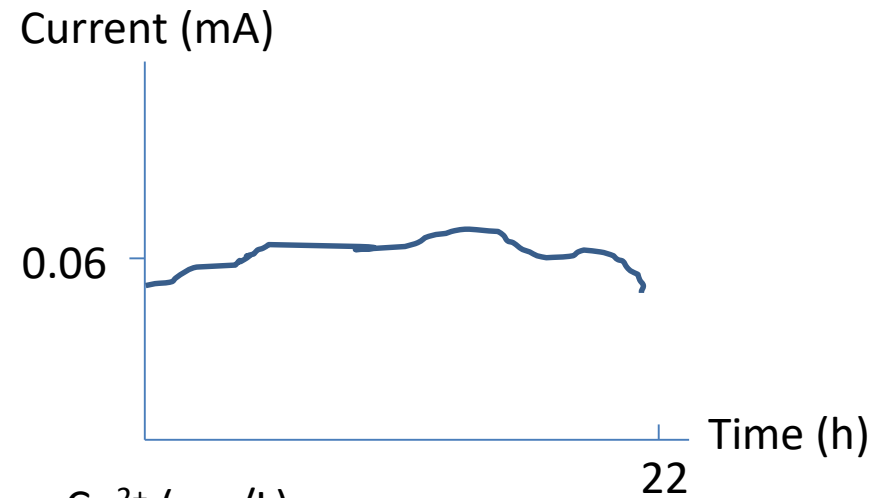


An important lesson from last week's exercises



Liquid volume = 0.3 L

DO THE RESULTS MAKE SENSE?
(DO THE CALCULATIONS!)



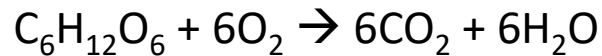
Week 2 – Thermodynamics

- Gibb's free energy
- Half-reactions
- *emf* and reduction potentials
- Nernst equation
- Reference electrodes
- Potential losses in electrochemical reactors
 - Terminology
 - Internal resistance

Gibb's free energy 1

- Some chemical reactions are spontaneous because they give off heat (enthalpy decrease, $\Delta H < 0$), some because they increase the disorder of a system (entropy increase, $\Delta S > 0$)
- Gibb's free energy accounts for both enthalpy and entropy and is a measure of the available energy associated with a chemical reaction
 $G = H - T \times S$
- A chemical reaction can proceed spontaneously if the change in Gibb's free energy is less than zero ($\Delta G < 0$)
- If $\Delta G > 0$, energy must be provided to drive the reaction
- $\Delta G^0 = \sum \Delta G^0_{f, \text{products}} - \sum \Delta G^0_{f, \text{reactants}}$

Gibb's free energy 2



$$\Delta G^\circ_{\text{reaction}} = (6 \times \Delta G^\circ_{\text{f,CO}_2} + 6 \times \Delta G^\circ_{\text{f,H}_2\text{O}}) - (\Delta G^\circ_{\text{f,C}_6\text{H}_{12}\text{O}_6} + 6 \times \Delta G^\circ_{\text{f,O}_2})$$

"Gibb's free energy of formation" for various compounds are tabulated in chemistry or biochemistry textbooks.

Thauer et al. Bacteriological Reviews, vol 41(1), 100-180, 1977, lists many compounds of biological interest.

Values are usually given for standard conditions: temp = 298 K, pressure = 1 atm, {act}=1 M

$$\Delta G^\circ_{\text{f,C}_6\text{H}_{12}\text{O}_6} = -917.22 \text{ kJ/mol}$$

$$\Delta G^\circ_{\text{f,O}_2} = 0 \text{ kJ/mol}$$

$$\Delta G^\circ_{\text{f,CO}_2} = -386.02 \text{ kJ/mol}$$

$$\Delta G^\circ_{\text{f,H}_2\text{O}} = -237.178 \text{ kJ/mol}$$

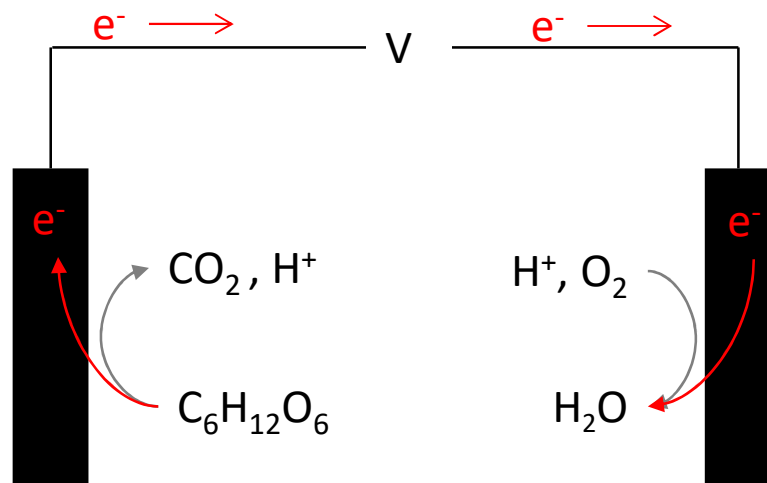
$$\Delta G^\circ_{\text{reaction}} = (-6 \times 386.02 - 6 \times 237.178) - (-917.22 + 6 \times 0) = \mathbf{-2822 \text{ kJ/mol glucose}}$$

Half-reactions

Let's say we want to use the reaction, $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$, in a galvanic cell

Oxidation: $C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24e^- + 24H^+$ (anode reaction)

Reduction: $6O_2 + 24e^- + 24H^+ \rightarrow 12H_2O$ (cathode reaction)



Electromotive force (*emf*)

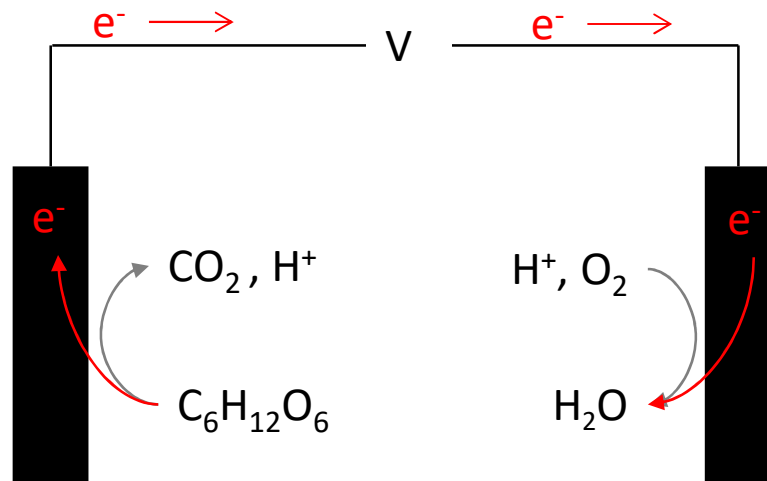


$$emf = -\Delta G / (z \cdot F)$$

z = mol electrons involved

F = Faraday's constant, 96485.3 J/(V·mol e⁻)

$$emf = 2822 \cdot 1000 / (24 \cdot 96485.3) = 1.22 \text{ V}$$



Reduction potentials

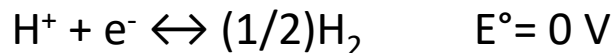
By convention, the half-reactions are written as reduction

(Anode reaction): $(1/4)\text{CO}_2 + \text{H}^+ + \text{e}^- \leftrightarrow (1/24)\text{C}_6\text{H}_{12}\text{O}_6 + (1/4)\text{H}_2\text{O}$ $\Delta G^\circ = -1.0 \text{ kJ/mol}$
Reduction potential, $E^\circ = -(-1.0) * 1000 / 96485.3 = 0.01 \text{ V}$

(Cathode reaction): $(1/4)\text{O}_2 + \text{H}^+ + \text{e}^- \leftrightarrow (1/2)\text{H}_2\text{O}$ $\Delta G^\circ = -118.6 \text{ kJ/mol}$
Reduction potential, $E^\circ = 1.23 \text{ V}$

$$\text{emf} = E_{\text{cathode}} - E_{\text{anode}} = 1.23 - 0.01 = 1.22 \text{ V}$$

Potentials are always in reference to something, what are the reduction potentials in reference to?



The Nernst Equation

- What if we don't have standard conditions (T=25°C, P = 1 atm)?
- $E = E^\circ - \frac{R \times T}{z \times F} \times \ln Q$
- R = 8.314 J K⁻¹ mol⁻¹
- T = temperature (K)
- z = mol electrons transferred
- F = 96485.3 C/mol e⁻
- Q = reaction quotient

If, $aA + bB \rightarrow cC + dD$

$$\text{then, } Q = \frac{\{C\}^c \times \{D\}^d}{\{A\}^a \times \{B\}^b}$$

Applying the Nernst equation

Assume:

$$[CO_2]_{(aq)} = 0.005 \text{ M}$$

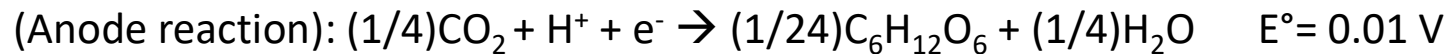
$$[C_6H_{12}O_6] = 0.002 \text{ M}$$

$$pO_2 = 0.2 \text{ atm}$$

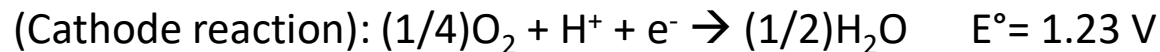
$$pH = 7$$

$$T = 25^\circ\text{C}$$

$$[\text{concentration}] = \{\text{activity}\}$$



$$E = 0.01 - (8.314 \cdot 298 / 96485.3) \cdot \ln[(0.002^{1/24} \times 1^{1/4}) / (0.005^{1/4} \times 10^{-7})] = -0.43 \text{ V}$$

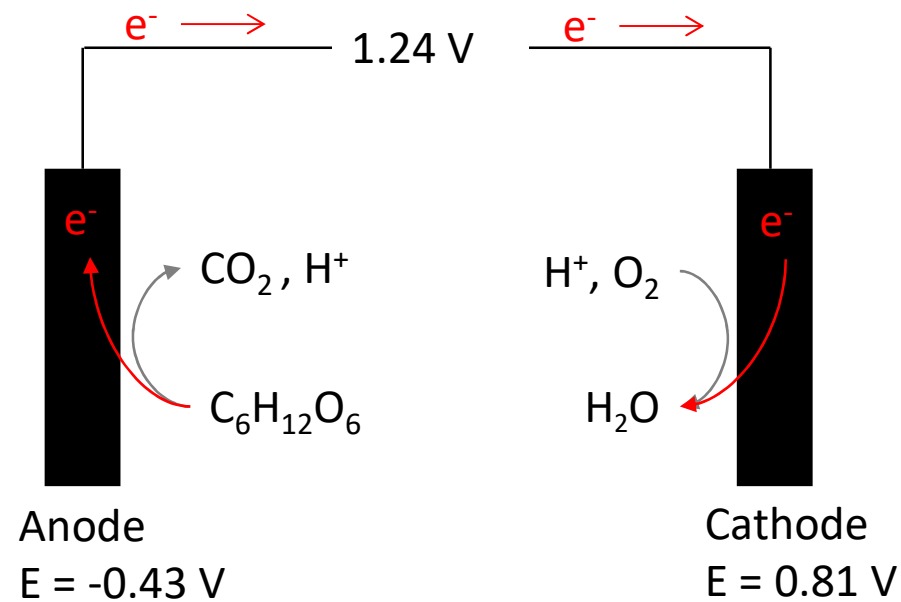


$$E = 1.23 - (8.314 \cdot 298 / 96485.3) \cdot \ln[(1^{1/2}) / (0.2^{1/4} \times 10^{-7})] = 0.81 \text{ V}$$

$$\text{emf} = 0.81 - (-0.43) = 1.24 \text{ V}$$

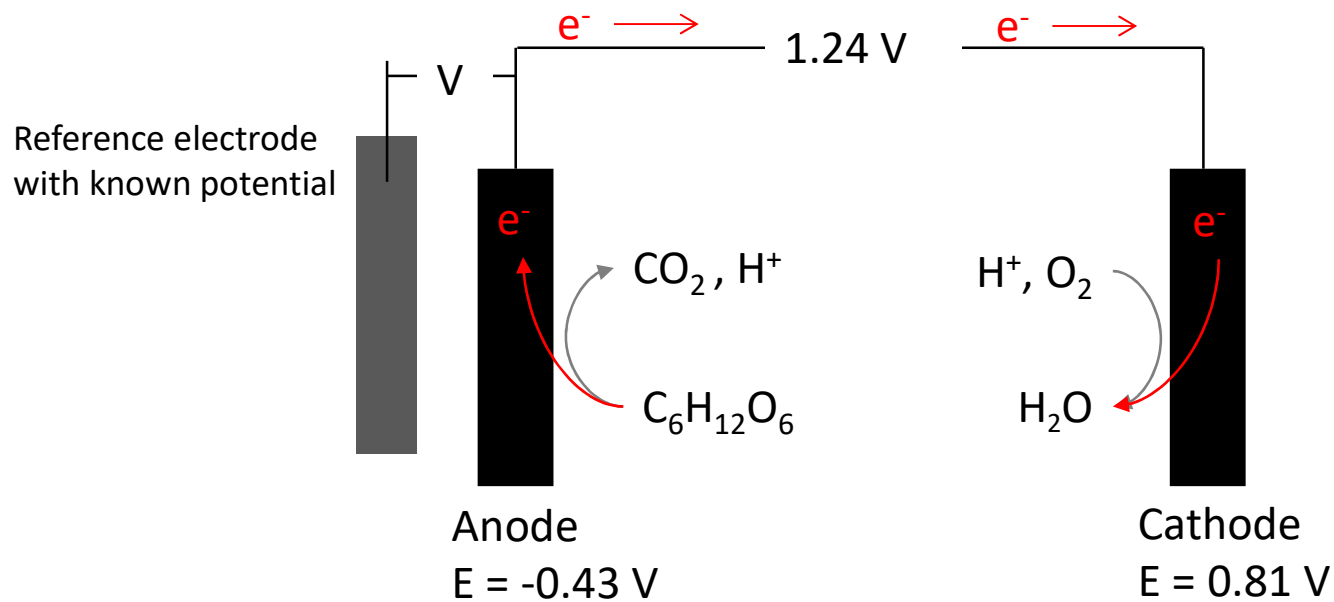
Our example system

In theory, our example system could generate a maximum output voltage of 1.24 V
The anode potential would be -0.43 V
The cathode potential would be 0.81 V

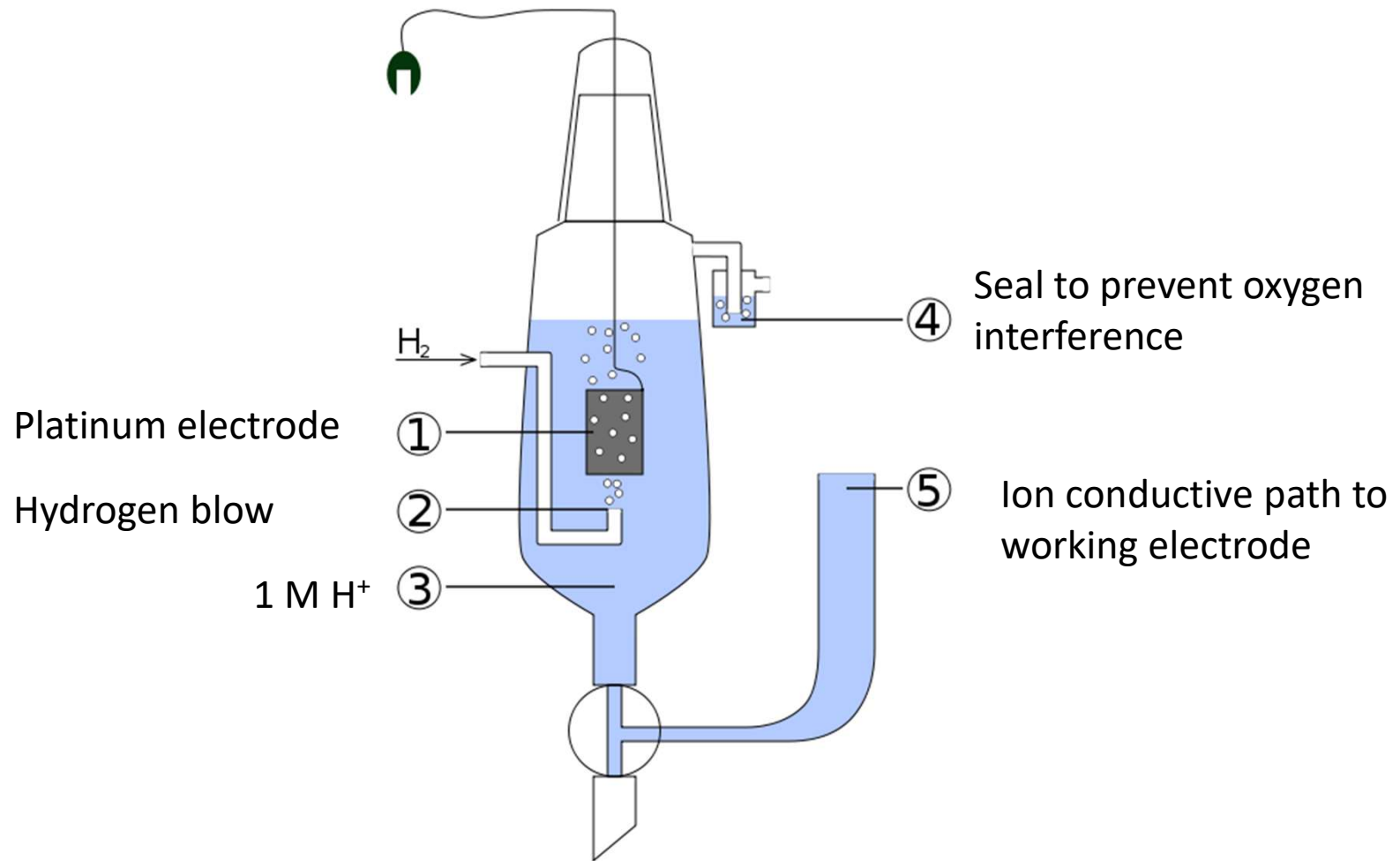


Reference electrodes

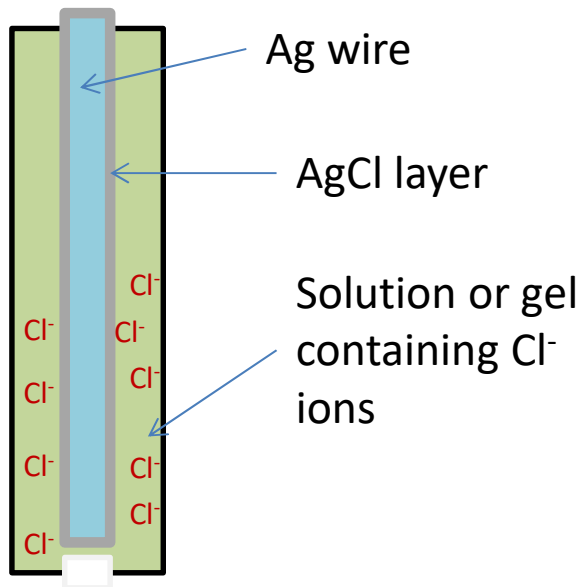
- How do we measure potential of individual electrodes?



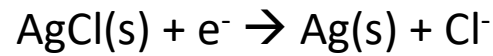
Standard hydrogen electrode, $E = 0 \text{ V}$



Silver/Silver chloride reference electrode



Reaction:



$$E^\circ = 0.222 \text{ V}$$

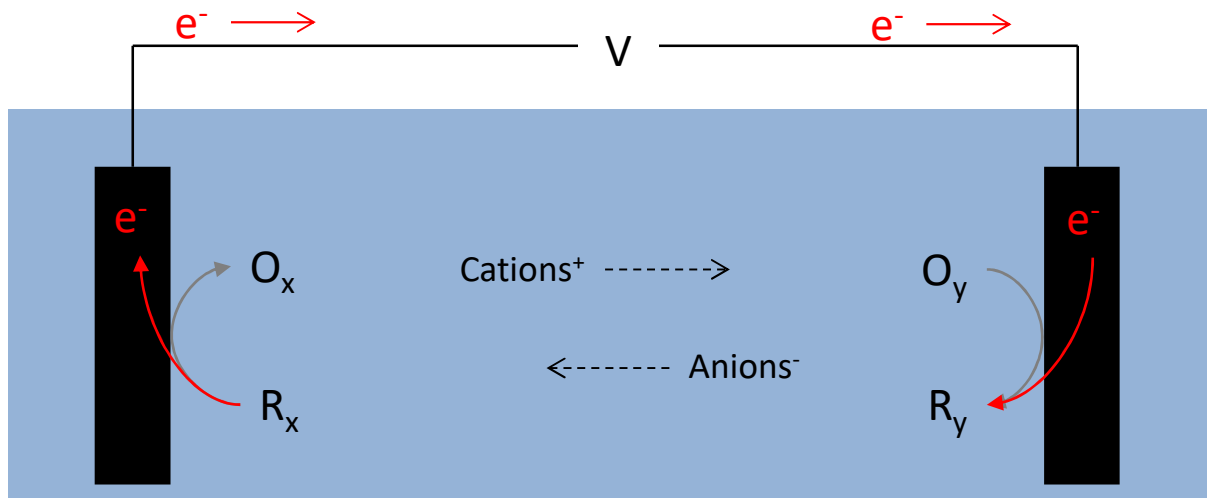
$$\text{If } [\text{Cl}^-] = 3 \text{ M, } E = 0.194 \text{ V}$$

We can assume this electrode has a constant potential.

Potential problems:

- If Cl⁻ leaches out, E will rise:
- e.g. [Cl⁻]=0.01 M → E = 0.35 V
- Ionic contact with cell electrolyte may clog.
- AgCl layer could deteriorate

Potential losses in electrochemical systems



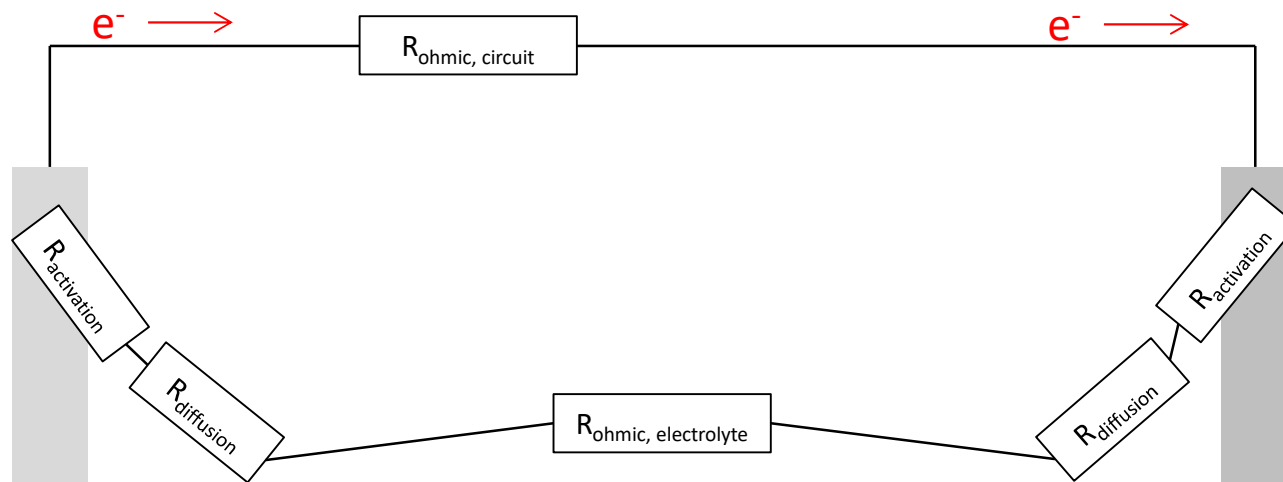
Activation losses: Transfer of electrons from molecule to electrode surface or vice versa.

Diffusion losses: Consumption of reactants near electrode surface

Ohmic losses: Migration of ions in electrolyte and flow of electrons in circuit

These losses are called **overpotentials**

Internal resistance



Actual voltage output from a galvanic cell:

$$V = \text{emf}_{\text{theoretical}} - I * (R_{\text{ohmic}} + R_{\text{activation}} + R_{\text{diffusion}})$$



Internal resistance