UNIVERSITÀ
DEGLI STUDI
DI TRIESTE

Inorganic Electrochemistry and electrocatalysis

Dr. Federico Franco

[035CM] - CFU: 4 (36 h)

LM in Chemistry - Academic Year 2024-2025

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Class Schedule

Frontal lessons (24 h): Tuesday afternoon – hrs. 1 -2 pm

Wednesday afternoon – hrs. 9 -11 am

Starting date of lectures: 4th March 2025

Practical laboratory (12 h): at the end of the course (schedule to be defined)

Exam

Oral examination consisting in at least 4-5 questions on both the theoretical and the laboratory part

Final mark given in n/30 (minimal mark for passing the exam: 18/30)

The students should submit a **brief report** on the laboratory part **at least 7 days** before the exam date

Next dates for exams:
(on Esse3 platform)

18th June 2025, 9 am
2nd July 2025, 9 am
22nd July 2025, 9 am
16th September 2025, 9 am

Textbooks and bibliography

A. J. Bard, L. R. Faulkner, "Electrochemical Methods. Fundamentals and Applications", Wiley, 2001

P. Zanello, C. Nervi, F. Fabrizi de Biani, "Inorganic Electrochemistry. Theory, Practice and Application", RSC, 2011

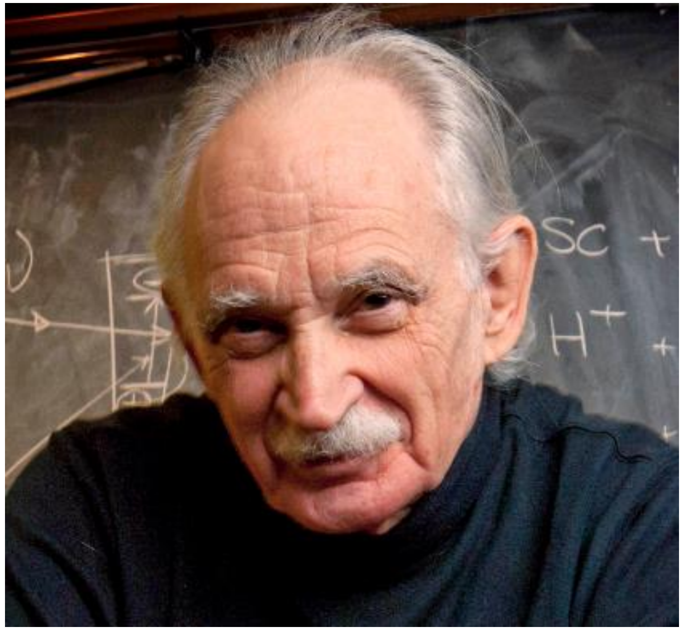
R. G. Compton, C. E. Banks, “Understanding Voltammetry” (3rd Ed.), World Scientific Pub., 2018

J.-M. Savéant, “Elements of Molecular and Biomolecular Electrochemistry: An Electrochemical Approach to Electron Transfer Chemistry”, Wiley, 2006

J. O'M. Bockris, A. K. N. Reddy, “Modern Electrochemistry” volumes 1-2B

Slides showed during the lectures available on Teams/Moodle

Scientific articles will be also available on Teams/Moodle



A. J. Bard (Dec. 1933 – Feb. 2024)

Electrochemistry – the scope of the course

Electrochemistry: field of chemistry based on the investigation of the interrelation between **electrical energy** and **chemical energy**

Electrified interfaces

Electrode: **electronic** conductor
(e.g. metals, carbon-based materials, …)

Electrolyte : **ionic** conductor
(e.g. aqueous or non-aqueous electrolyte solutions,…)

- Study of the fundamental properties of the electrode/electrolyte interface
- description/interpretation of the phenomena and events occurring at it (including the **catalytic** processes)

Electrochemistry - applications

First prototype of
battery in history
(Cu/Zn, 1800)

Luigi Galvani (1737-1798)

Alessandro Volta (1745-1827)

Batteries

(rechargeable vs. non-rechargeable)

for transportation, consumer electronics & devices, grid energy and industry, portable energy storage systems, etc.

Electrochemistry - applications

Fuel cells

e.g. H_2-O_2 fuel cells for transportation

$$2H_2 + O_2 \rightarrow 2H_2O$$

Fuel cell Electric Vehicles

Hyundai Nexo

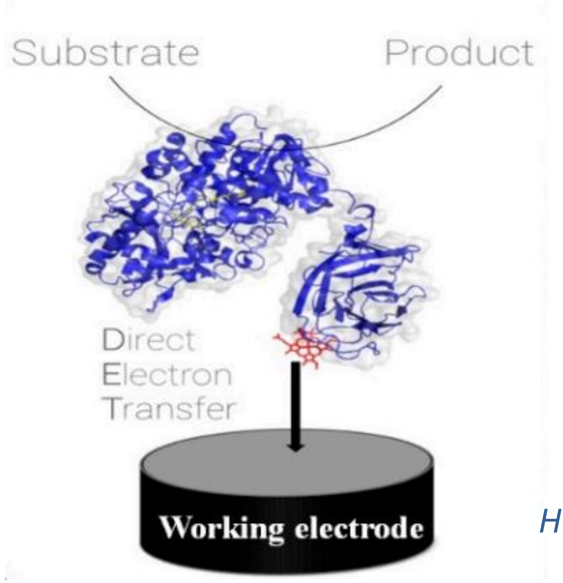
Photovoltaics

Solar cells

Electrochemistry - applications

Electroanalysis and (bio)sensing applications

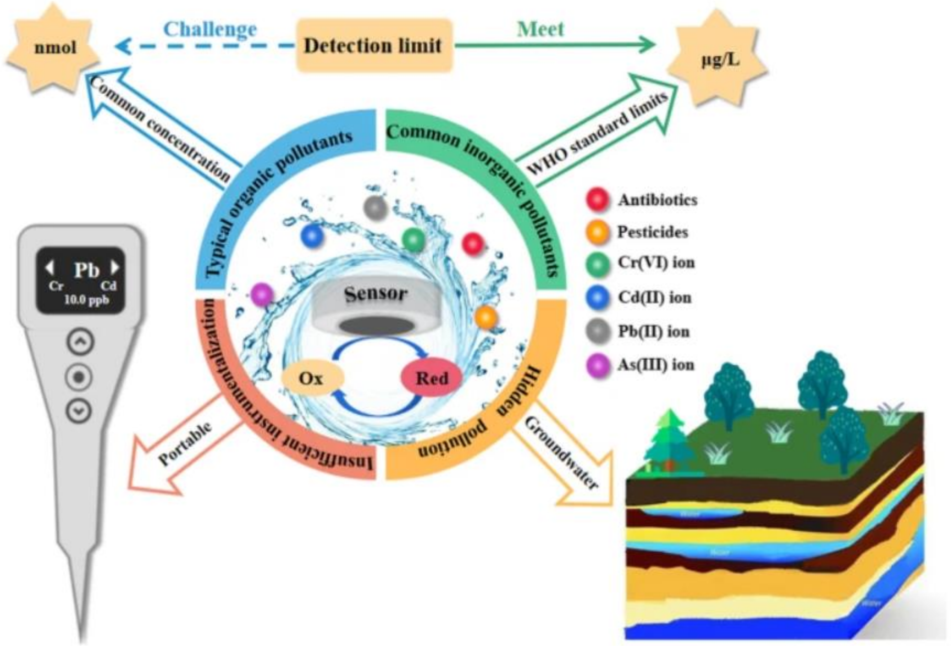
Healthcare & Biomedical applications



*Hassan, Sensors **2022**, 22, 7539*

Glucose sensors

Environmental monitoring of air/water quality



*Liu et al., Analytical Sciences **2022,** 38, 55–70*

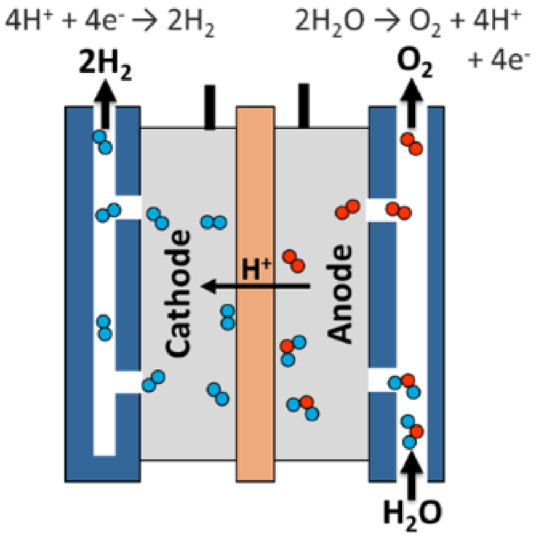
Electrochemistry - applications

Electrosynthesis and electrocatalysis

Development of materials to implement efficient electrolyzers for decarbonization/electrification of chemical industry

Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
Cathode: $4H^+ + 4e^- \rightarrow 2H_2$

Electrolyzers for green H_2 production from H_2O electrolysis



From Department of Energy (DOE) U.S. website

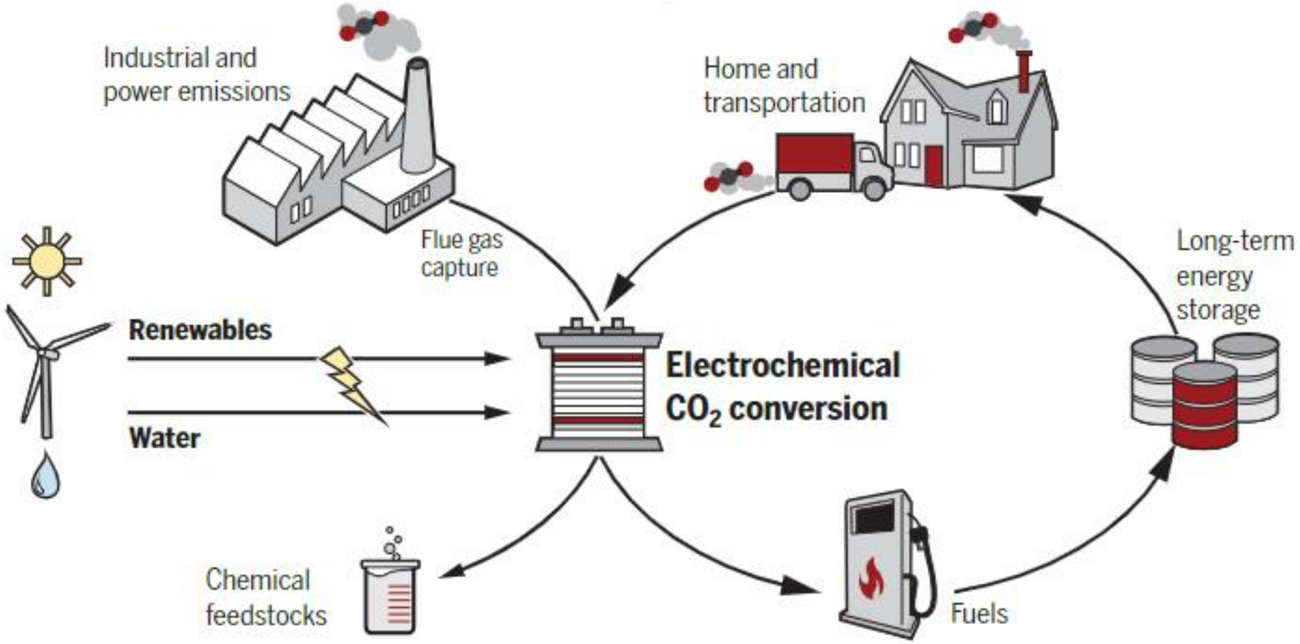
Electrochemistry - applications

Energy optimization

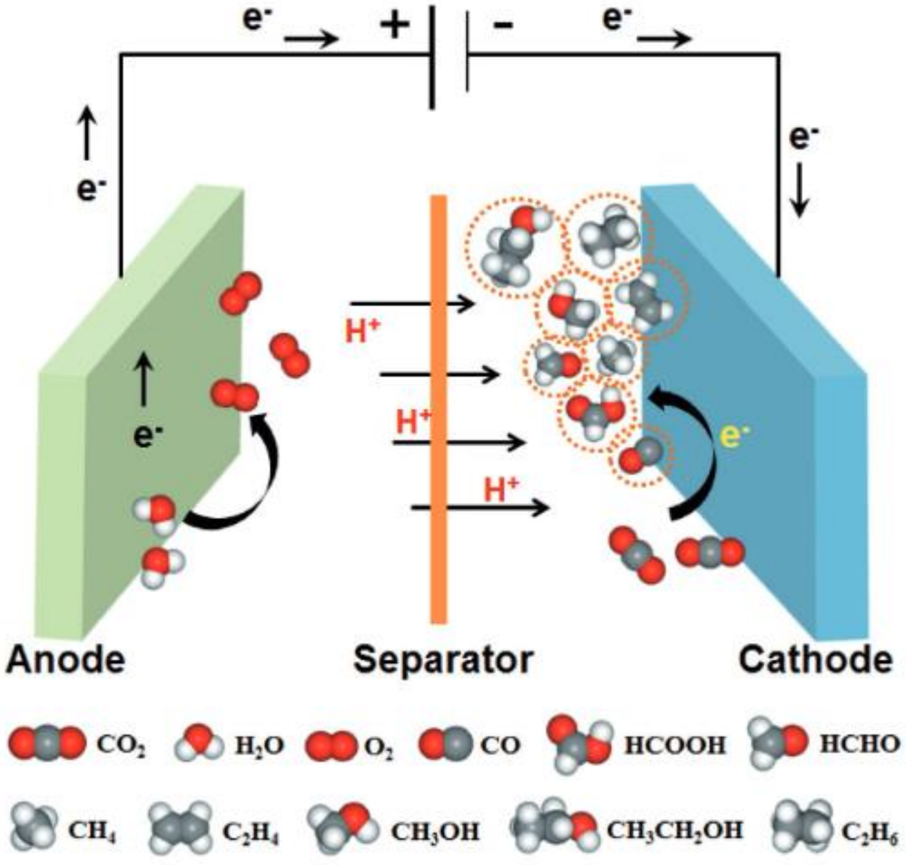
High catalytic activity

Product Selectivity

CO_2 as a feedstocks for e-fuels production
(C_1-C_{2+} hydrocarbons)



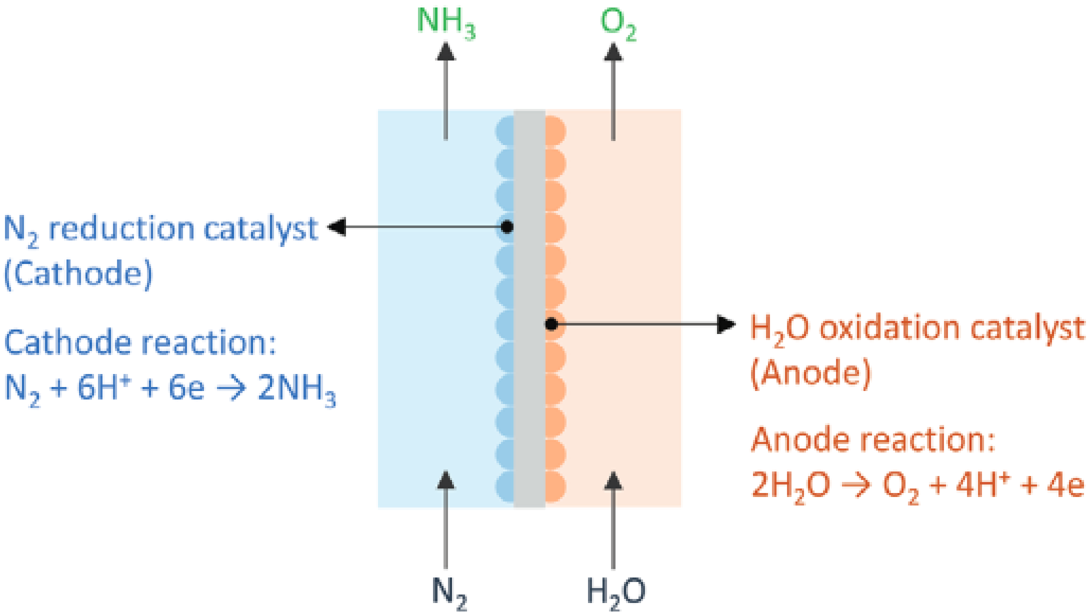
*De Luna et al., Science **2019**, 364, 350*



*Z. Jin et al., Adv. Sci. **2018**, 5, 1700275*

Electrochemistry - applications

Electrochemical Haber-Bosch process for N_2-to-NH_3 production



N_2 reduction catalyst
(Cathode)

Cathode reaction:
$N_2 + 6H^+ + 6e \rightarrow 2NH_3$

H_2O oxidation catalyst
(Anode)

Anode reaction:
$2H_2O \rightarrow O_2 + 4H^+ + 4e$

F. Jiao et al., Adv. Mater. ***2019****, 31, 1805173*

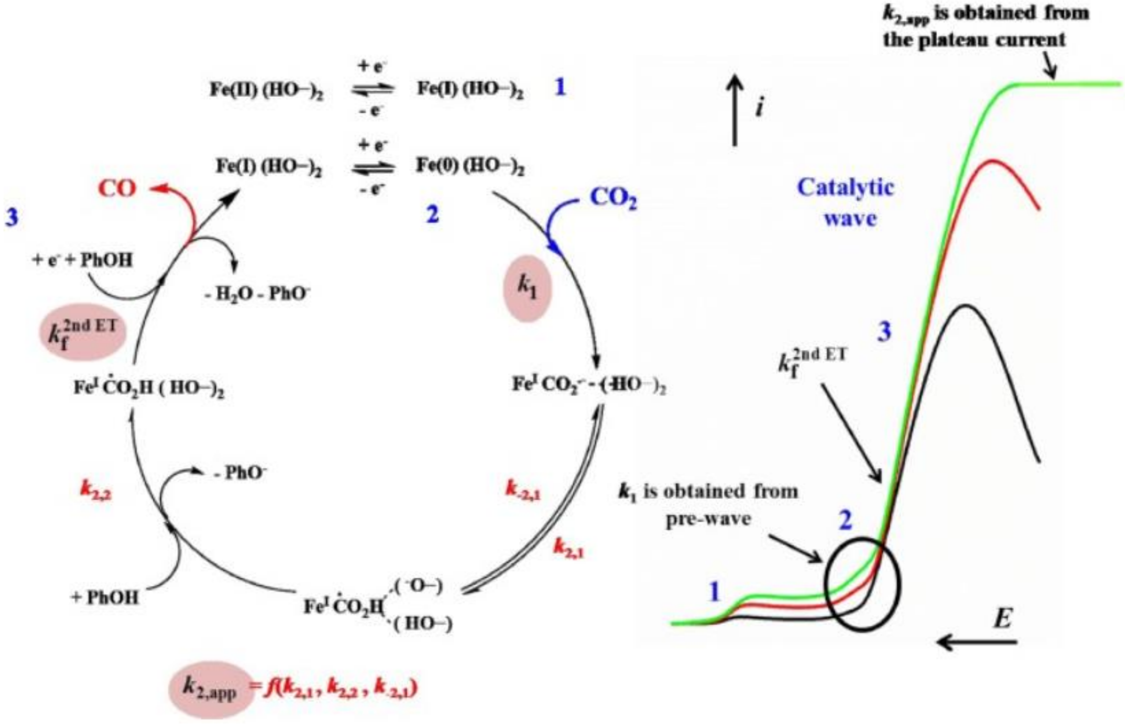
Organic electrosynthesis

IKA™ ElectraSyn 2.0

Electrochemistry as a tool for mechanistic investigation

Molecular electrochemistry

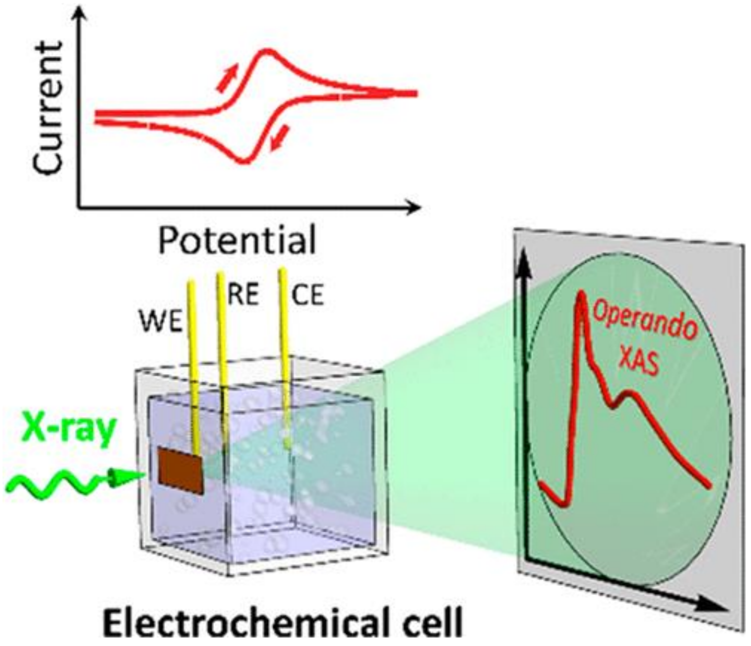
Elucidation of reaction pathways for electrochemical reactions (catalysis)



C. Costentin et al., Curr. Op. Electrochem. **2017**, 2, 26-31

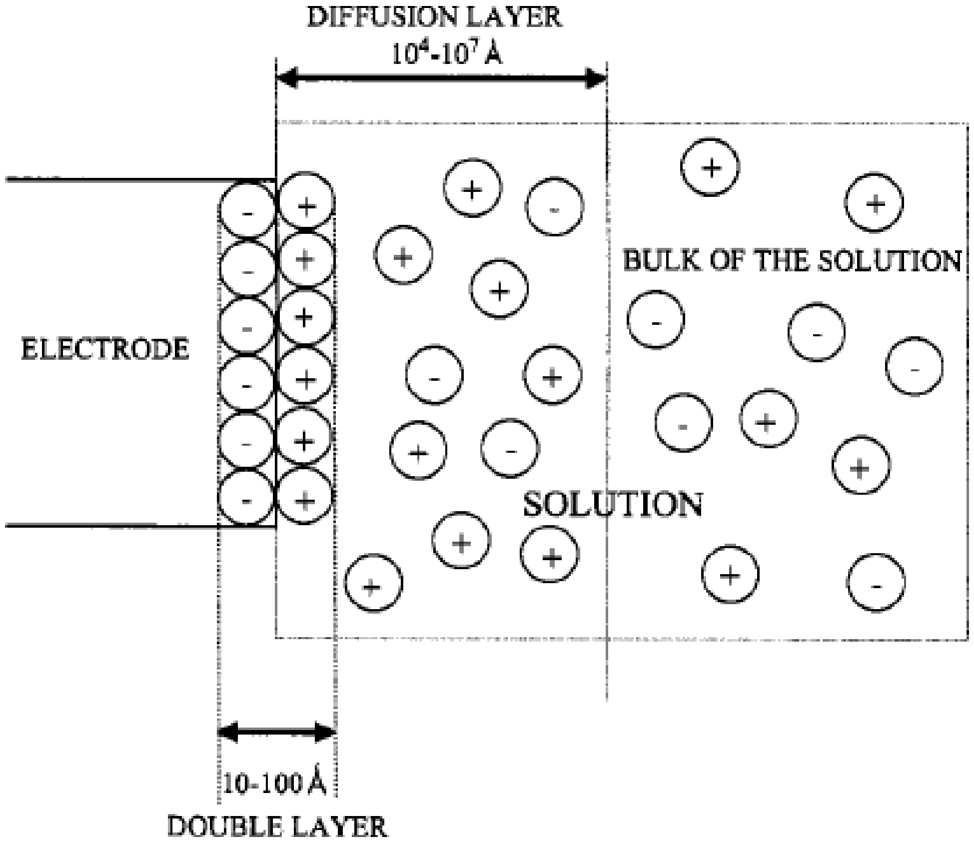
In situ/operando techniques

In combination with spectroscopic or microscopic techniques to investigate the dynamic changes in morphology/chemical state of a material during an EC reaction



J. Timoshenko et al., Chem. Rev. **2021**, 121, 882–961

The electrode-electrolyte interface: a simplified view



From Zanello, Nervi, Fabrizi de Biani, Inorganic Electrochemistry. Theory, Practice and Application", RSC, 2011

Electrode/solution interface is the result of different regions (in terms of distribution of electrical charge) in proximity of the electrode surface, due to an excess of charge at the electrode surface (e.g. negative)

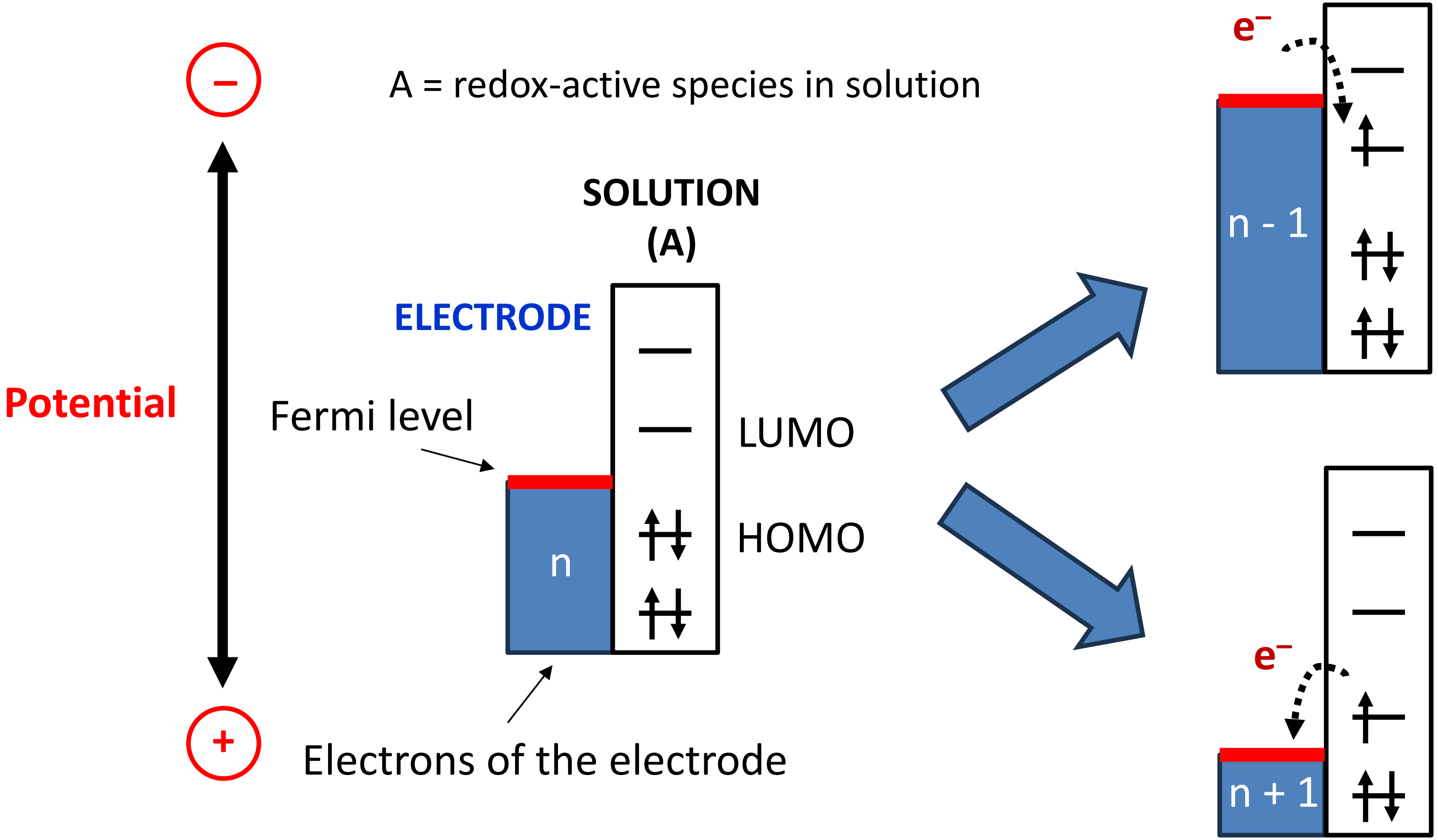
Electrical double layer: generated by an excess of charge of the opposite sign as the electrode surface (e.g. positive) in close contact

Diffusion layer: region where the concentrations are different from their value in the *bulk solution (IUPAC)*

The electrode potential

Potential, *E (V)* → *controls the **energy** of electrons within the electrode*

A = redox-active species in solution



Reduction

$\mathbf{A + e^- \rightarrow A^-}$

Oxidation

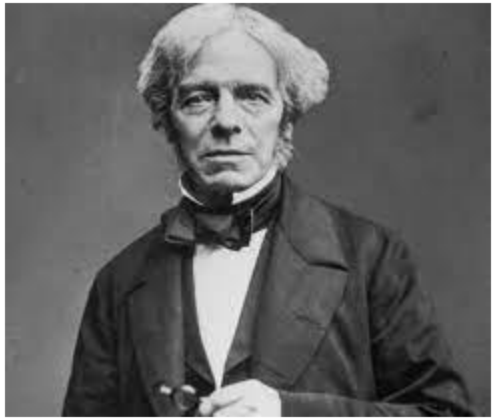
$\mathbf{A - e^- \rightarrow A^+}$

E^0 (A/A^-) and **E^0 (A^+/A)** ≈ the threshold values at which these processes take place

Current of an electrode reaction

Current, *i (A)* → *proportional to the* ***rate*** *of an electrodic reaction (heterogeneous)*

Faraday's law



M. Faraday (1791-1867)

$$Q = n \cdot F \cdot N$$

Charge [C]

e⁻ *consumed*

Faraday's constant

F = 96485 [C mol^{-1}]

mol electrolyzed

$$\frac{dQ}{dt} = i = n \cdot F \cdot \frac{dN}{dt}$$

Faradaic current

[A = C · s^{-1}]

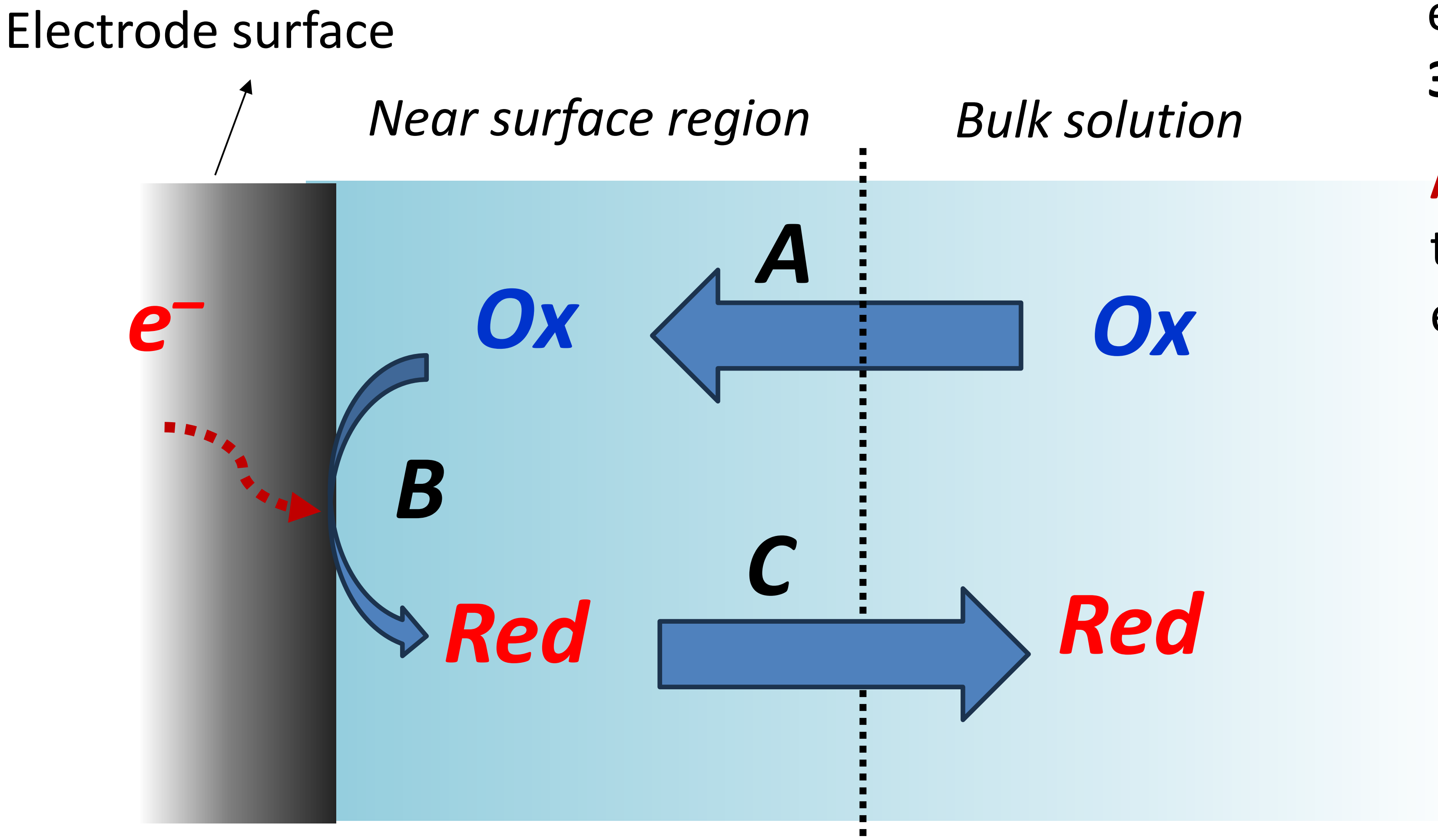
$$\boxed{\text{Rate (mol s}^{-1}\text{ cm}^{-2}\text{)} = \frac{1}{A} \cdot \frac{dN}{dt} = \frac{j}{n \cdot F}}$$

Current density *[A · cm^{-2}]*

A = electrode surface area *[cm^2]*

The electrochemical experiment

$Ox + e^{-} \rightarrow Red$



The **current** (or rate of electron transfer) depends on **3 elementary steps**:

A) Mass transport of Ox from the bulk solution to the electrode surface

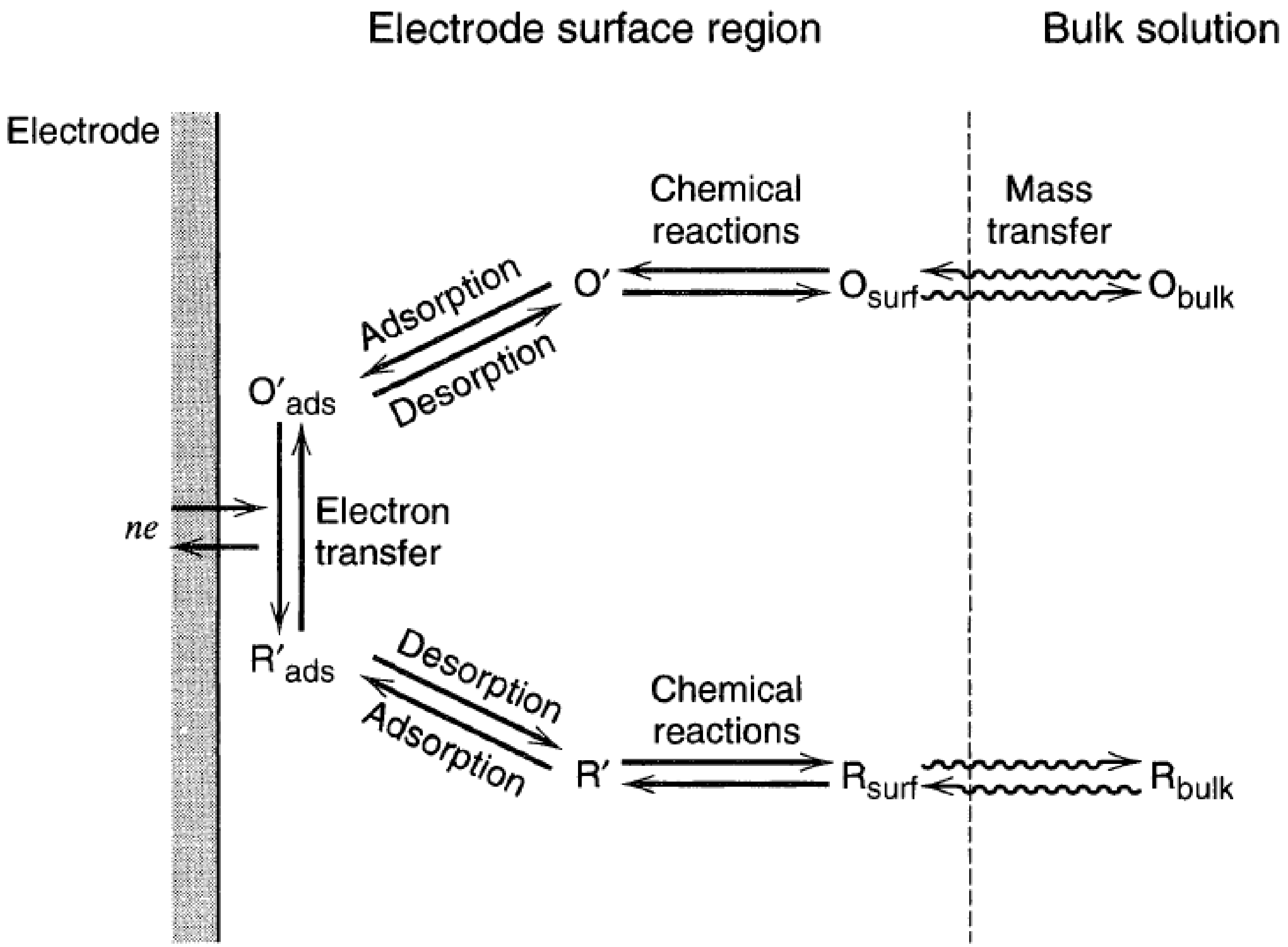
B) Heterogeneous electron transfer from the electrode to Ox → Red

C) Mass transport of Red from the electrode surface to the bulk solution

The electrochemical experiment

- **Mass transfer** is determined by **3 main contributions:**
  - **Diffusion** (concentration gradient)
  - **Migration** (electrical potential gradient)
  - **Convection** (stirring or hydrodynamic transport) – it can be *natural* or *forced*
- Usually, the contribution of both migration and convection are considered negligible by using **inert supporting electrolyte** in high concentration and by avoiding stirring, respectively

Factors complicating the electrochemical response



From Bard, Faulkner, "Electrochemical Methods. Fundamentals and Applications", Wiley, 2001

- **Coupled chemical reactions** to electron transfer (e.g. following, preceding, catalytic,…)
- **Adsorption/desorption** (e.g. electrode poisoning,…); the electrode may form stable reaction intermediates (heterogeneous), altering the reaction pathway
- **Formation of phases** (e.g. electrodeposition, crystallization,…)

i – E curves informative about the reactions at the interface

Variables in an electrochemical experiment

- **Electrical variables** (*E, i, Q*…)
- **External variables** related to the operating conditions (T, p, time, gas atmosphere during the experiment…)
- **Working Electrode material** (chemical composition, structural/morphological features, surface area, geometry, …)
- **Mass transfer** (diffusion, convection, immobilization of electroactive species, adsorption phenomena…)
- **Solution** (pH, composition, electrolyte, concentration of electrolyte and electroactive species,…)

Electrochemical cells

Devices for the interconversion of electrical and chemical energy; in a simplified view, they are typically defined by two electrodes separated by (at least) one electrolyte phase

Electrochemical Cells

GALVANIC CELLS

Spontaneous redox processes

Chemical energy ⇨ **Electricity**

Anode (–)
Cathode (+)

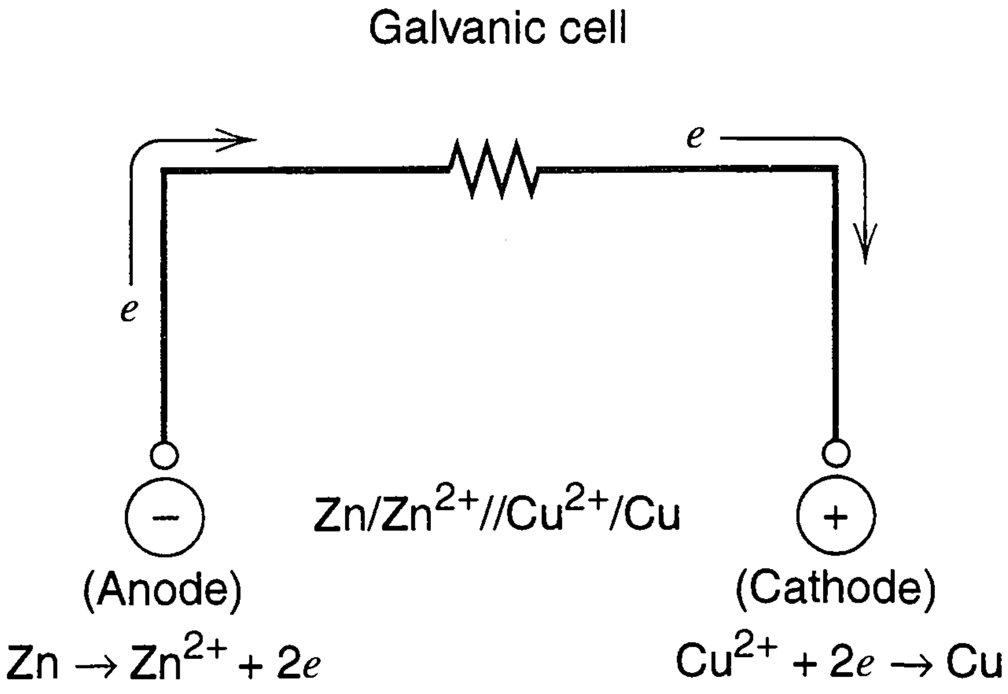
ELECTROLYTIC CELLS

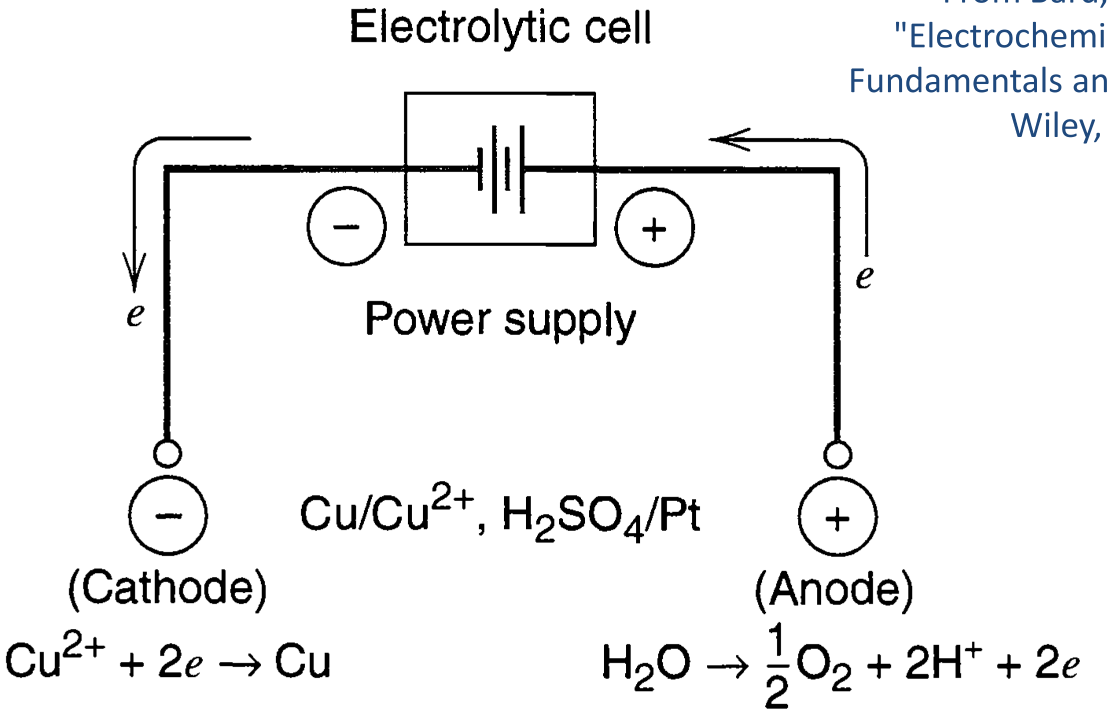
Non-spontaneous redox processes

Electricity ⇨ **Chemical energy**

Anode (+)
Cathode (–)

Electrochemical cells





From Bard, Faulkner,
"Electrochemical Methods.
Fundamentals and Applications",
Wiley, 2001

Anode (–): oxidation
Cathode (+): reduction

Anode (+): oxidation
Cathode (–): reduction

The terms “anodic” and “cathodic” refers to **flow of electrons** (or current),
not to the potential!!

Measuring potentials in electrochemical cells

- Accurate control of E(V) is one of the most important features of electrochemical measurements
- Rigorous determination of the absolute potentials of an electrode is not possible
- Experimentally, the **potential difference (cell voltage, V)** between a **working electrode** (WE, at which the process of interest takes place) and a **counter electrode** (CE, to maintain electroneutrality) is measured

Disadvantages of two-electrode setup

1) *Unpredictable changes in the potential of the CE,* caused by variations of V between the two electrodes

Highly Stable and non-polarizable CE, in order to maintain a *constant potential* even upon the flow of (small) currents

Es. Saturated Calomel Electrode (SCE) (Hg/Hg_2Cl_2 in saturated KCl), which is better defined as **reference electrode (RE)**

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2\,Hg(l) + 2Cl^-$$

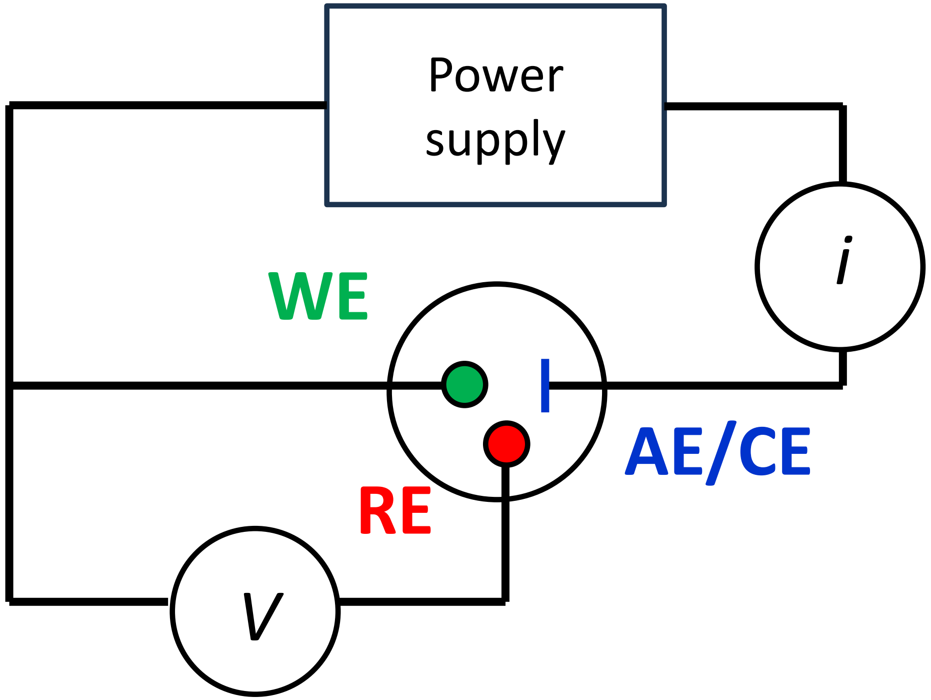
High concentration of the components

Disadvantages of two-electrode setup

2) The solution in which the electrodes are immersed features an *intrinsic resistance* R_S (property of the electrolyte solution, not of the electrode reaction) which introduces an additional contribution due to the **ohmic drop, $\mathbf{i \cdot R_S}$,** in the experimentally measured potential (only for $i \cdot R_S = 0$, $V = \Delta E$)

The current flowing between the WE and RE/CE can induce instantaneous variations in the RE potential and $i \cdot R_S$ drop, especially for high-current experiments (e.g. bulk electrolysis, high scan rate voltammetry, etc…) in non-aqueous solvents

Three-electrode configuration



- An **auxiliary or counter electrode (AE/CE)** is added together with WE and RE
- Majority of the **current** is conveyed between **WE and CE**
- **Potential** is measured between **WE and RE**
- Negligible *i* passes through RE in this configuration (constant E_{RE}(V))
- To study only electrode process at WE, the AE/CE material is not so important as long as its electrochemical reactivity does not affect the response at the WE (products of oxidation/reduction counter reaction)

- Sometimes, AE/CE is placed into a separate compartment (sintered frit-glass tubes) to prevent any interferences

Ohmic drop correction

- Even in this, configuration, the iR drop cannot not completely eliminated, since a residual fraction of **uncompensated solution resistance, R_u,** leads to an uncompensated ohmic drop $i \cdot R_u$:

$$V_{cell} = (E_{WE} - E_{RE}) + i \cdot R_u = \Delta E + i \cdot R_u$$

- Modern potentiostats generally possess several tools for estimation and compensation of the $i \cdot R_u$ ohmic drop (e.g. Positive-feedback circuit, …)
- $i \cdot R_u$ also depends on *geometric factors*: it can be also optimized by proper cell design and can be minimized by reducing the distance between WE and RE (e.g. Luggin capillary)

Basic equipment for electrochemical experiments

Potentiostat

- In a simplified view, it controls and modulates *V* between WE-RE and records *i* flowing between WE-CE
- The potentiostat circuitry prevents significant *i* flowing between WE-RE
- Electronic iR compensation
- Other features, such as voltage compliance, max current, etc.

Electrochemical cell

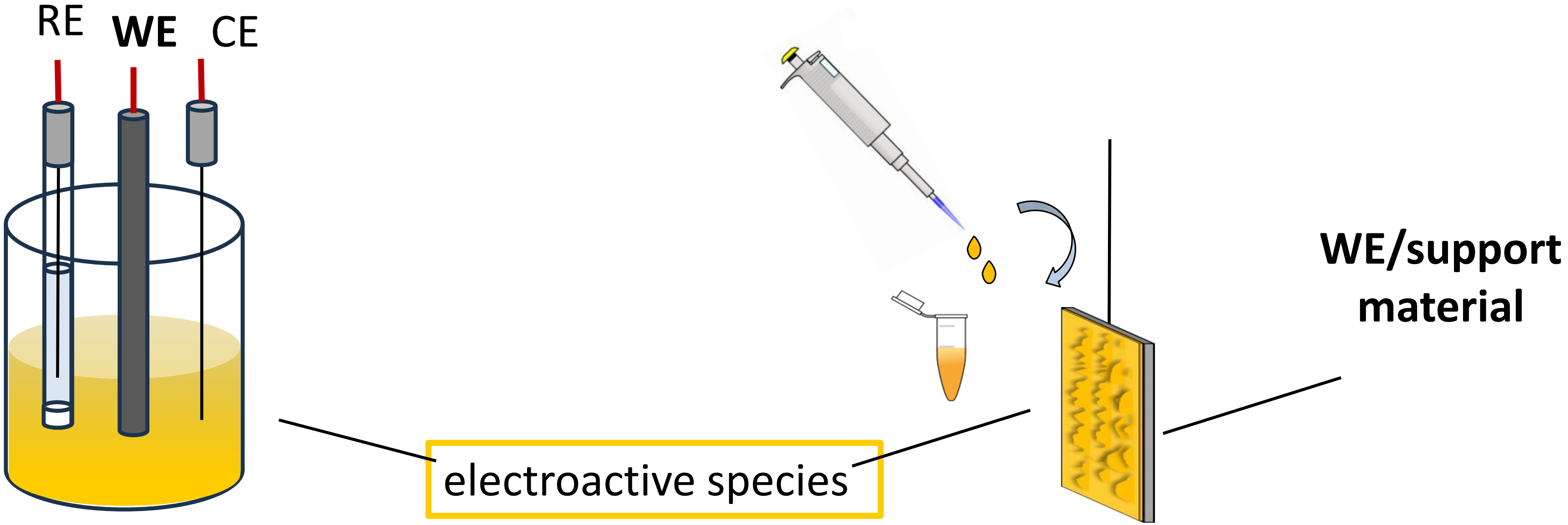
- Reactor design
- Working electrode
- Reference electrode
- Counter/Auxiliary electrode

Solution

- Solvent
- Supporting electrolyte
- Sample (if electroactive species is dissolved in solution)

Working electrodes

- **Highly conductive materials**, which should be **redox-inert** in the potential range of interest
- WE could act simply as a current collector (homogeneous processes), or also as a support for immobilized electroactive species
- A variety of geometrical and physicochemical features (spherical, planar, porosity, …)



Working electrodes

- **Highly conductive materials**, which should be **redox-inert** in the potential range of interest
- WE could act simply as a current collector (homogeneous processes), or also as a support for immobilized electroactive species
- A variety of geometrical and physicochemical features (spherical, planar, porosity, …)

Carbon electrodes (Glassy carbon, MWCNTs, Vulcan…)

Dropping Mercury electrode (DME)

Metal electrodes (Pt, Au, Ag, Cu…)

Auxiliary (Counter) electrodes

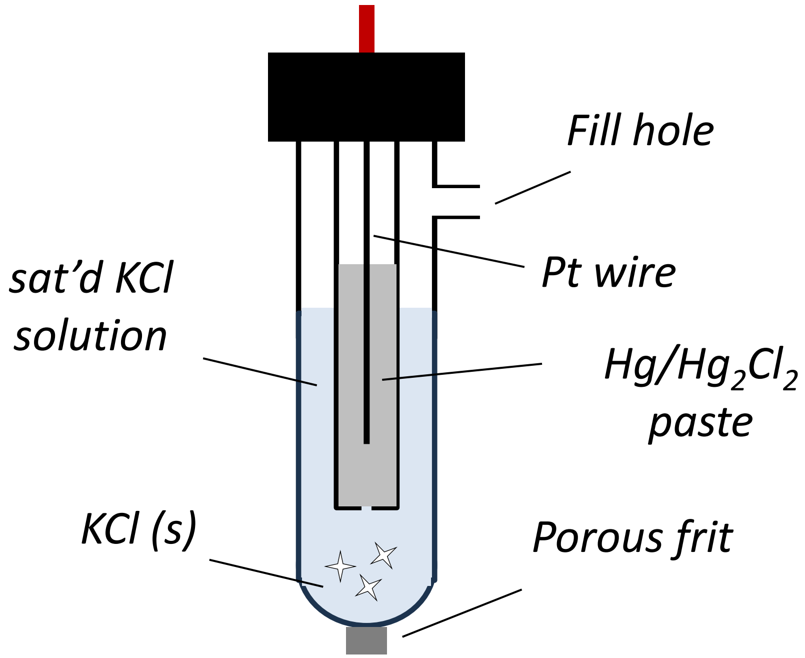
- Complete the electrical circuit
- Material chosen in a way that the side-products of the counter electrode process do not affect the response at WE
- CE may be separated from the main solution by a separator (membrane, glass frit…) to avoid cross-contamination (especially for bulk electrolysis)
- Higher surface area compared to WE (at least 3 times larger)

Platinum

Graphite/C rod

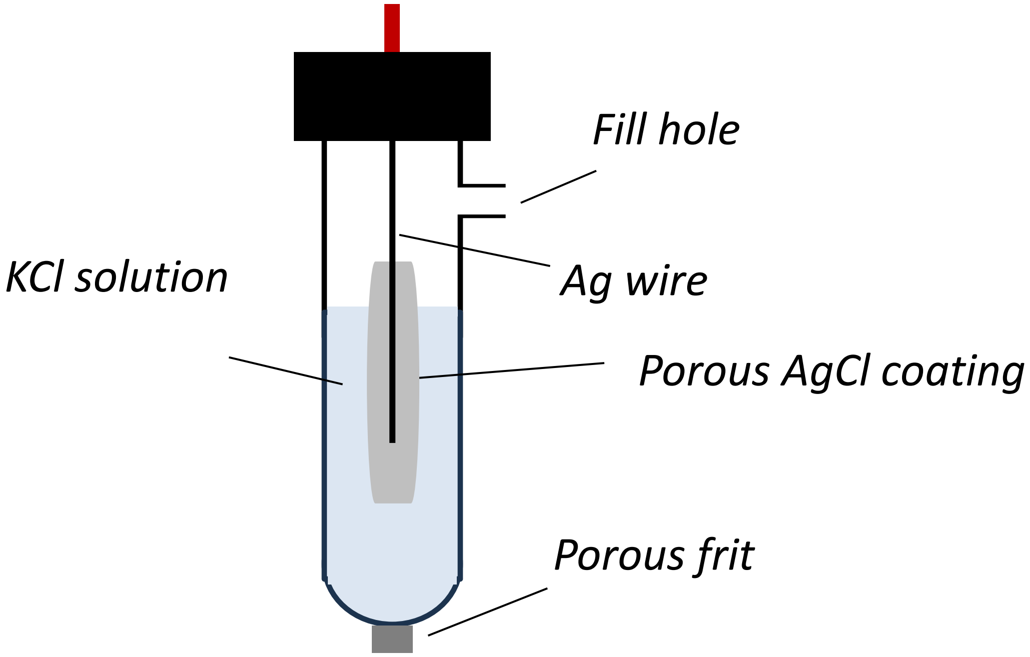
Aqueous reference electrodes

Saturated Calomel Electrode (SCE)



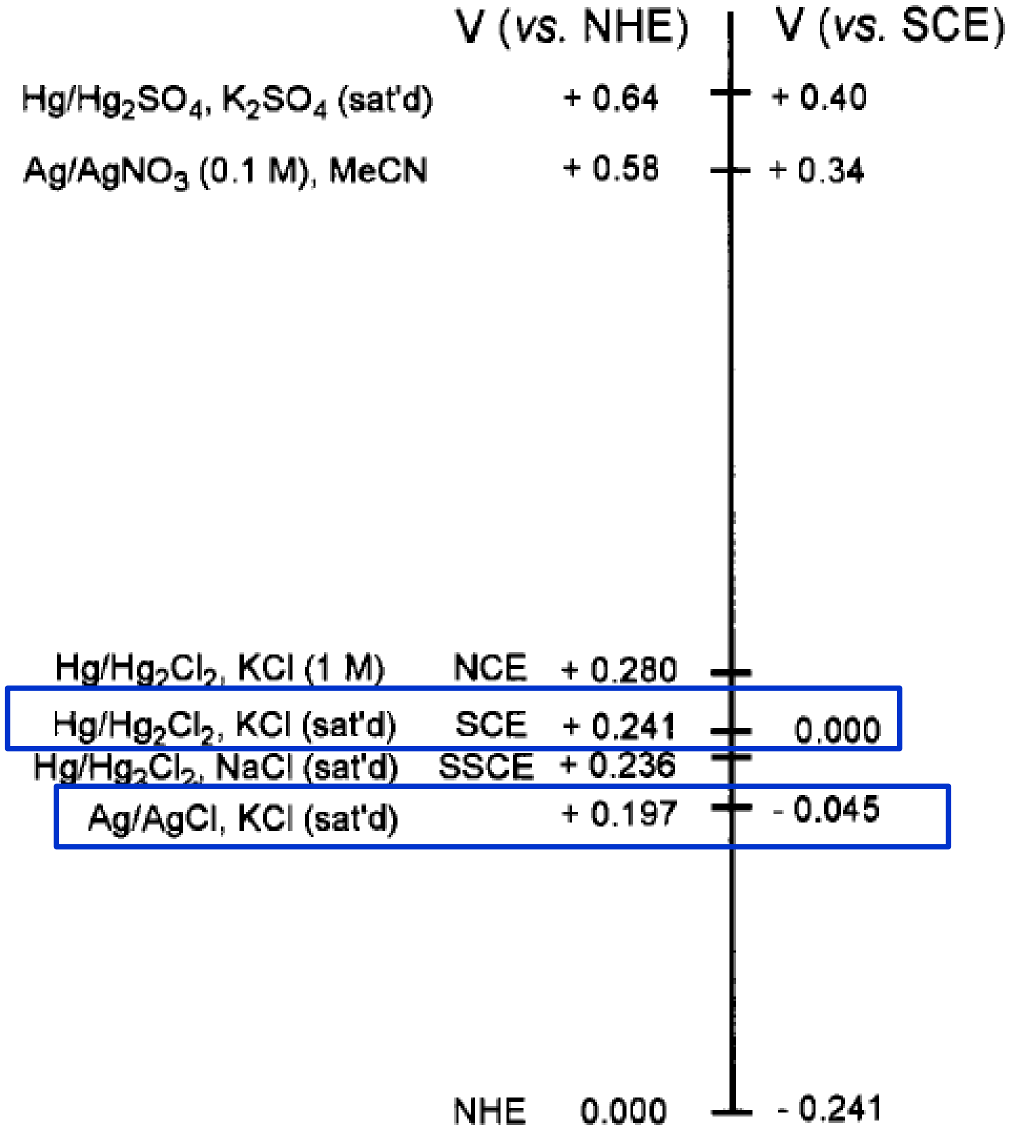
$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2\,Hg(l) + 2Cl^-$$

Silver/Silver chloride Electrode (Ag/AgCl)



$$AgCl(s) + 1e^- \rightleftharpoons Ag(s) + Cl^-$$

Potentials of reference electrodes



		V (*vs.* NHE)	V (*vs.* SCE)
Hg/Hg_2SO_4, K_2SO_4 (sat'd)		+ 0.64	+ 0.40
$Ag/AgNO_3$ (0.1 M), MeCN		+ 0.58	+ 0.34
Hg/Hg_2Cl_2, KCl (1 M)	NCE	+ 0.280	
Hg/Hg_2Cl_2, KCl (sat'd)	SCE	+ 0.241	0.000
Hg/Hg_2Cl_2, NaCl (sat'd)	SSCE	+ 0.236	
Ag/AgCl, KCl (sat'd)		+ 0.197	- 0.045
	NHE	0.000	- 0.241

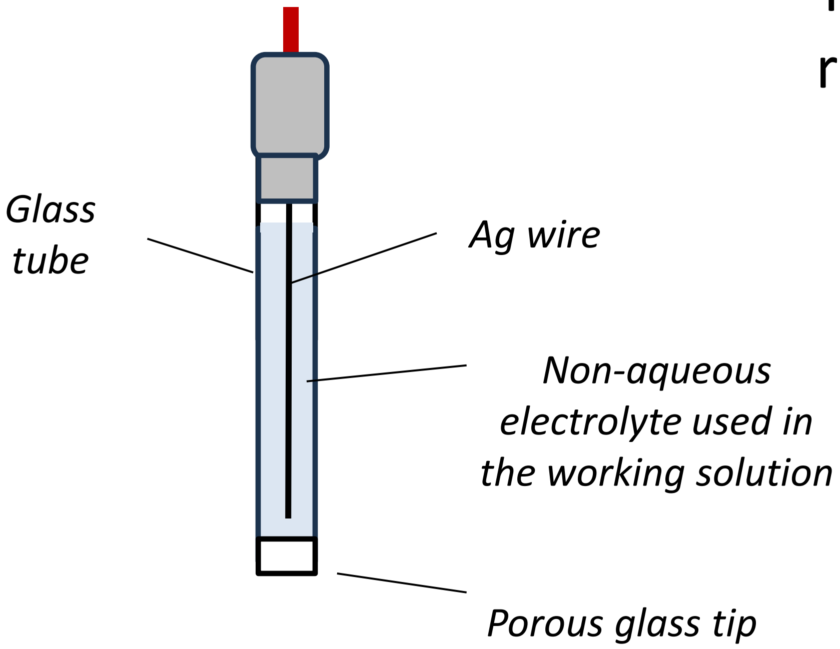
From Zanello, Nervi, Fabrizi de Biani, Inorganic Electrochemistry. Theory, Practice and Application", RSC, 2011

Always beware of the reference scale used for a reported potential value!!!

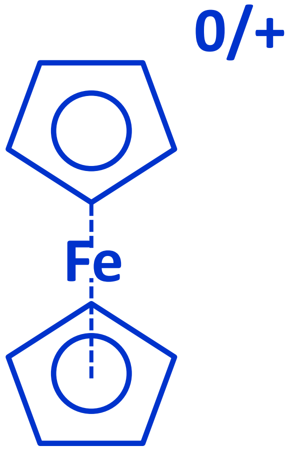
Non aqueous reference electrodes

The main drawbacks of using aqueous REs in non-aqueous electrolytes are **water and Cl^- contamination** into the working solution. To avoid these issues, **non-aqueous REs** are used:

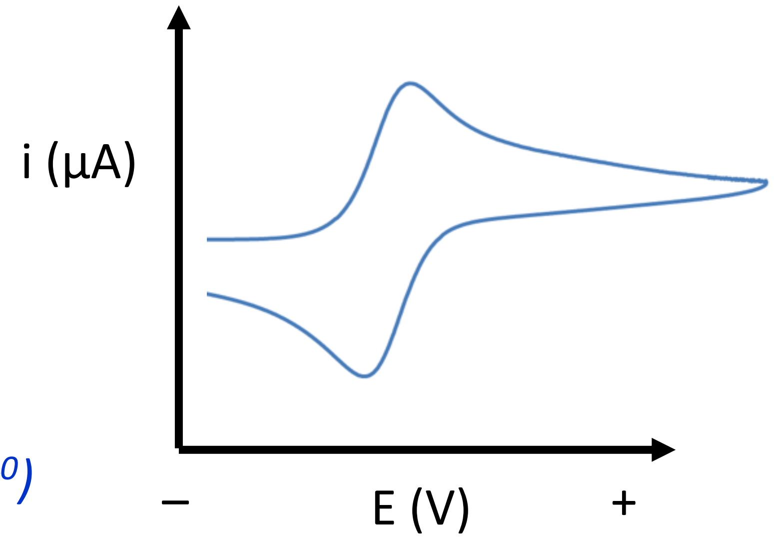
- **Ag/Ag^+ (0.01 – 0.1 M) →** Leaking of Ag^+ into the rest of the analyte
- **Pseudoreference electrode →** metal wire (Ag) immersed into the same non-aqueous electrolyte used in the working solution (ill-defined Ag_2O/Ag couple).



The actual potential of the pseudoRE vs. a true RE rigorously requires a **calibration** with an **internal standard**.



Ferrocene/ferrocinium (Fc^+/Fc^0) redox couple

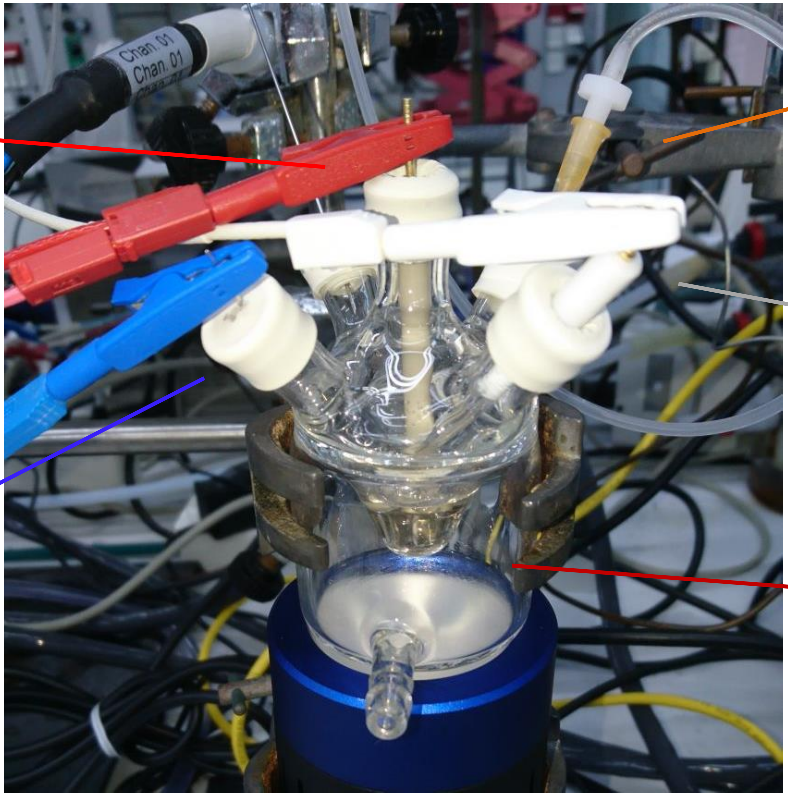


Cell configuration

- The choice primarily depends on the **type of experiment** to perform (voltammetry, bulk electrolysis, rotating-disk electrode, etc.)
- It also depends on the **type of electroactive system** to be studied, e.g. whether it is immobilized on the electrode (material) or is dissolved in solution (homogeneous solution)
- Electrochemical cells are typically home-made and customized!!!

Multi-necked low-volume cell

- Ideal for non-aqueous solvents (V = 2-3 mL)
- minimize ohmic drop
- thermostated (control T)



Working electrode

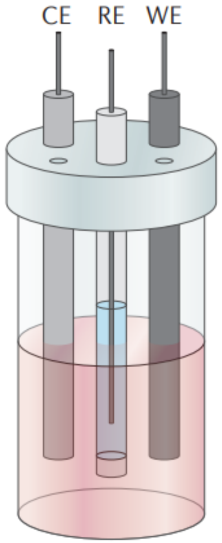
Inlet/outlet for continuous gas flowing ***(inert atmosphere)***

Reference electrode

Counter electrode

Double-wall jacket

Cell configuration

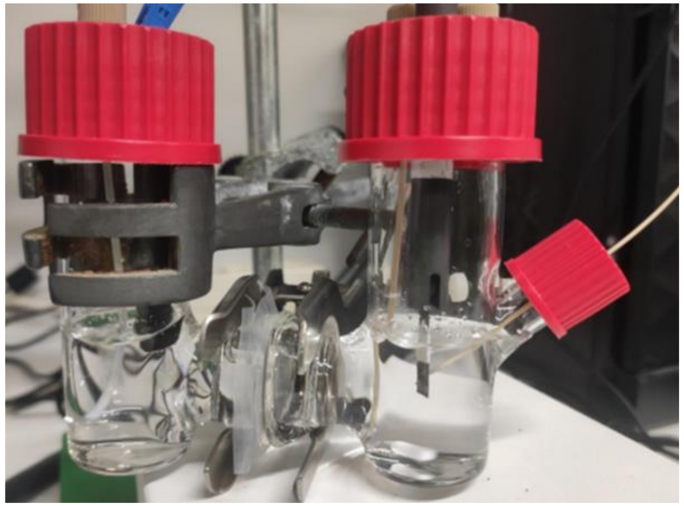


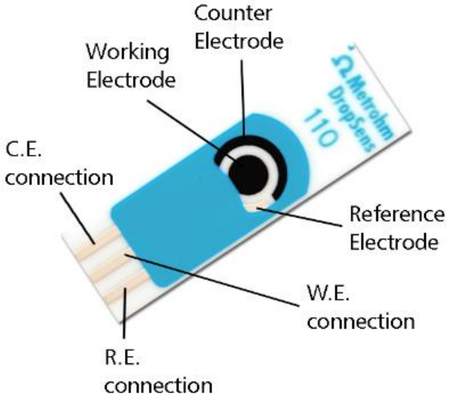
Simple becher-type cell

J. Dempsey et al., *Nat. Rev. Chem.* **2017**, 1, 0039

H-type EC cell

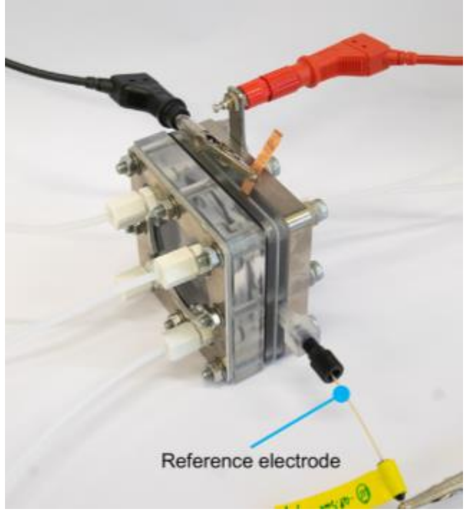
- Two separate anode-cathode chambers
- Fitted with a membrane separator





Disposable EC cell

Screen-printed electrodes



Flow-cell reactor

T. Burdiny et al. , *ACS Energy Lett.* ***2023***, *8, 4156–4161*

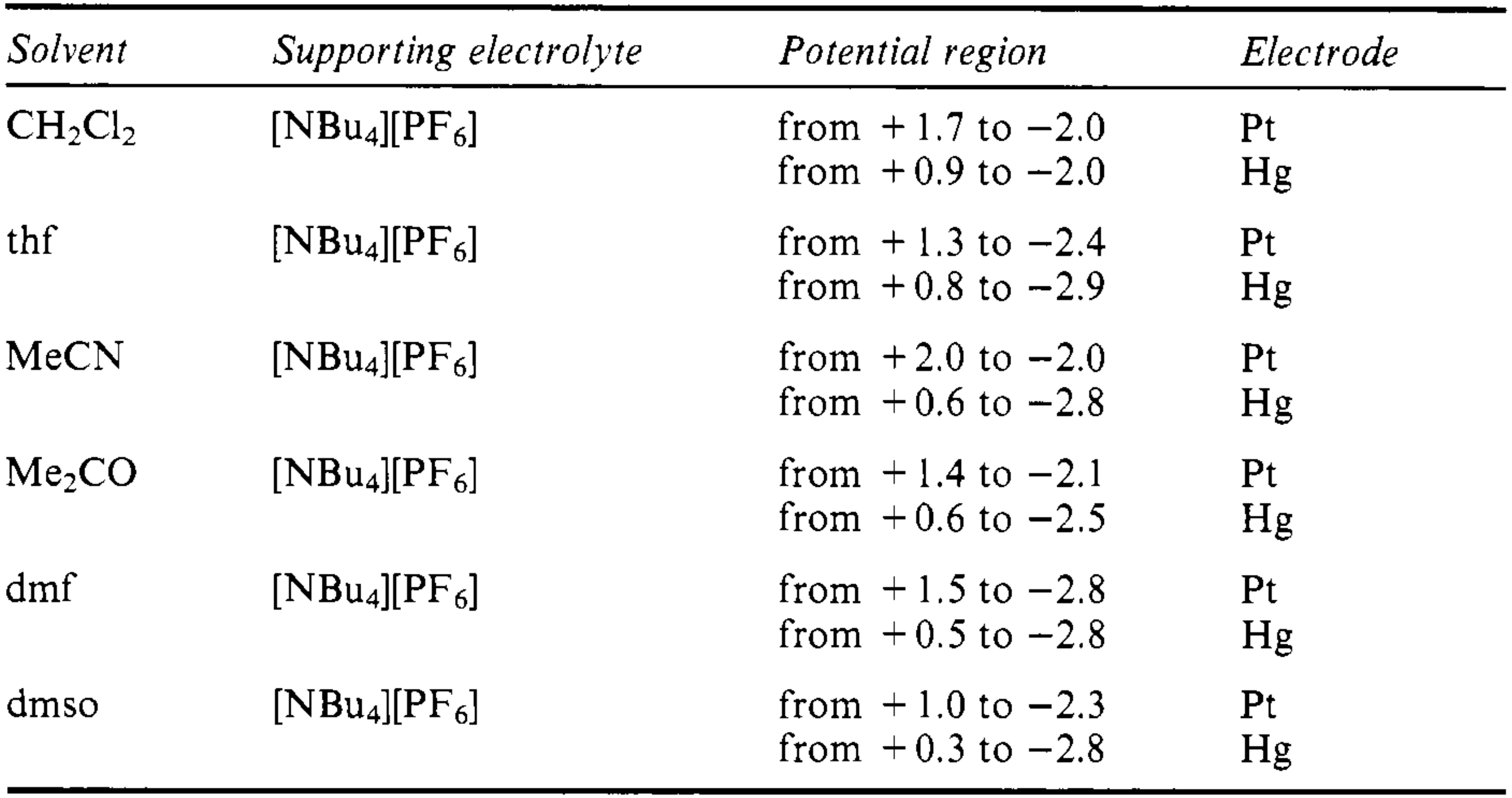
The supporting electrolyte

- Dissolved in **high concentration**
- The effect of the supporting electrolyte in an electrochemical experiment mainly consists in:
  - ➢ *increase the conductivity of the solution*
  - ➢ *reduce the Ohmic drop effect*
  - ➢ *suppress the migration of electroactive species*
  - ➢ *keep constant ionic strength of the solution*
- Basic requirements for the choice of a suitable supporting electrolyte:
  - ➢ **Redox-Inert** in the potential window
  - ➢ **Chemically inert** for the studied reaction (including the reactivity of the counterion)
- **Tetraalkylammonium salts** (e.g. $NBu_4N^+ X^-$) are common supporting electrolytes in non-aqueous solvents

The choice of solvent for electrochemical measurements

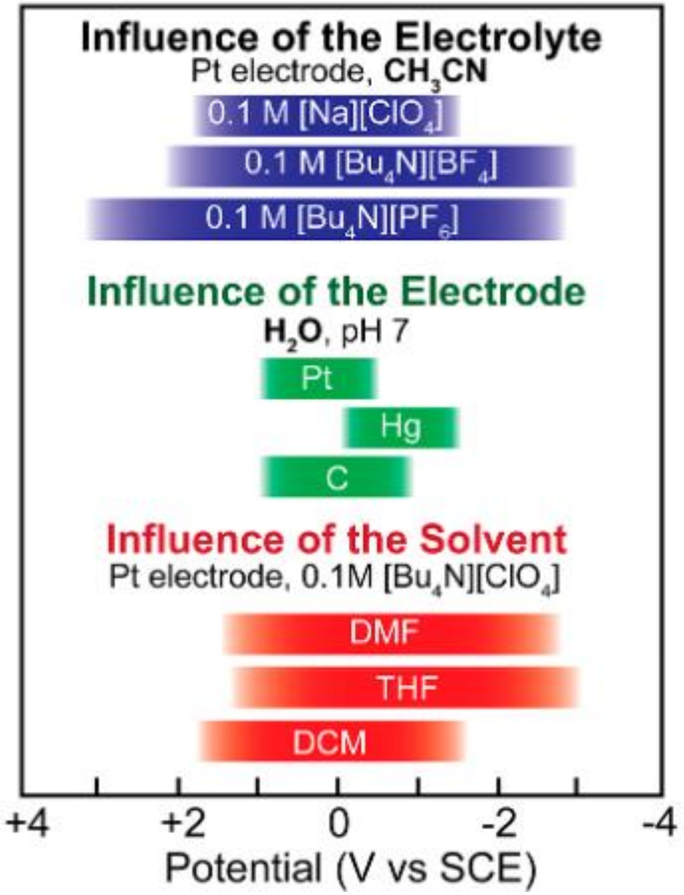
- Obvious requirements related to **solubility** of the electroactive species of interest (in the case of homogeneous molecular systems) and the supporting electrolyte
- **Low viscosity** solvents are preferable (low resistance of the solution)
- Uncompensated Ohmic drop correction is often critical for non-aqueous solvents
- **Chemical inertness** towards the species involved in the process under study (e.g. solvent coordinative ability of the solvent)
- The proper solvent should be selected depending on the **width of the potential window**
- *The nature of WE material and solvent are usually critical to determine the background limits for an electrochemical experiment*

The background limits of common electrolytes



Solvent	*Supporting electrolyte*	*Potential region*	*Electrode*
CH_2Cl_2	$[NBu_4][PF_6]$	from +1.7 to −2.0	Pt
		from +0.9 to −2.0	Hg
thf	$[NBu_4][PF_6]$	from +1.3 to −2.4	Pt
		from +0.8 to −2.9	Hg
MeCN	$[NBu_4][PF_6]$	from +2.0 to −2.0	Pt
		from +0.6 to −2.8	Hg
Me_2CO	$[NBu_4][PF_6]$	from +1.4 to −2.1	Pt
		from +0.6 to −2.5	Hg
dmf	$[NBu_4][PF_6]$	from +1.5 to −2.8	Pt
		from +0.5 to −2.8	Hg
dmso	$[NBu_4][PF_6]$	from +1.0 to −2.3	Pt
		from +0.3 to −2.8	Hg

From Zanello, Nervi, Fabrizi de Biani, Inorganic Electrochemistry. Theory, Practice and Application", RSC, 2011



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