Electrochemistry for materials technology

1. Introduction

gem.epfl.ch

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Content purpose of the course

- Part 1: Fundamental aspects and theory of electrochemistry (3-4 weeks)
  - Electrode potential (thermodynamics)
  - Electrode reactions (kinetics)
- Part 2 : Application - Energy conversion (4-5 weeks)
  - Batteries
  - Fuel cells
  - Electrolysers. Electrochemical synthesis / separation processes.
- Part 3 : Application - Electrodeposition and materials surface-modifications by electrochemistry (3-4 weeks)
  - Galvanic coatings, patterning
  - Corrosion
  - Mems. Sensors. Nanowires…
- Optional : topical excursions (depending on remaining time)

Support and bibliography

- Copies of the slides on http://moodle.epfl.ch/ (MSE-441)
- Exercises + solutions
- Textbooks :
  - Electrochemical Engineering (2012); Christos Comninelllis, Gyorgo Foti
  - Electrochemical Methods: Fundamentals and Applications (2001); Allen J. Bard, Larry R. Faulkner
  - An Introduction to Electrochemical Engineering; Carlos M. Marschoff and Pablo D. Giunta
  - Christine LEFROU, Pierre FABRY and Jean-Claude POIGNET, Electrochemistry - The Basics, with Examples, EDP Sciences (2009), available as e-book at EPFL library.
  - Dieter LANDOLT, Corrosion and Surface Chemistry of Metals, EPFL Press (2007) (Chapters 1 - 5)
  - many more

Changes in 2024

- This class in 2024 merges students from **MSE-441** (Electrochemistry for Materials – MX section) and **CHE-407** (Electrochemical Engineering – Prof A. Boghossian)
- Monday, 14h-16h: Lectures. **16-17h: Exercise**
- **3 credits**
- Previously, the exam format was a poster presentation during semester.
- Now, the **exam is written** (3h) during the Jan/Feb exam session. **Open book.**
- Guest teachers:
  - Dr Cédric Frantz (same Lab as MER J Van herle STI-IGM) : Electrodeposition (Part 3)
  - Dr Priscilla Caliandro (Univ. Appl. Sciences, Biel/Bienne) : batteries (**OCT 7 + OCT 14**)

- For semester/master projects on electrochemistry : pls check our website https://www.epfl.ch/labs/gem/student-projects/
  - see examples given later during this Introduction

Tentative schedule (subject to changes)

Date	Lecture	Topic	Teacher	Exercise
2024-Sep-09	Intro	Electrochemistry general / examples	J Van herle	Y
2024-Sep-16	holiday			
2024-Sep-23	1	Electrode Potential / Thermodynamics	J Van herle	Y
2024-Sep-30	2	Electrode Kinetics	J Van herle	Y
2024-Oct-07	3	Batteries	Dr Priscilla Caliandro (BFH)	Y
2024-Oct-14	4	Batteries	Dr Priscilla Caliandro (BFH)	Y
2024-Oct-21	free			
2024-Oct-28	5	Fuel Cells	J Van herle	Q & A
2024-Nov-04	6	Electrolysis	J Van herle	Y
2024-Nov-11	7	Electrolysis / Electricity storage	J Van herle	Y
2024-Nov-18	8	Electrodeposition 1	Cédric Frantz	Y
2024-Nov-25	9	Electrodeposition 2	Cédric Frantz	Y
2024-Dec-02	10	Electrodeposition 3	Cédric Frantz	Y
2024-Dec-09	11	Electrochemical methods (instrumentation)	C. Frantz / J. Van herle	Y
2024-Dec-16	12	(reserve)	J Van herle	Q & A

Electrochemical reactions

Chemical reactions which take place at the interface between an electrode, usually a solid metal or a semiconductor, and an ionic conductor, the electrolyte.

These reactions involve electric charges moving between the electrodes and the electrolyte.

At those interfaces, transfer of charge and mass takes place. These translate to voltage loss (overvoltage).

Electrochemistry deals with the interaction between electrical energy and chemical change.

History of Electrochemistry (< 1800)

Joseph Priestley

1767: Experiments on charged spheres to study electric force.

attraction of electricity has similar laws than gravitation

Charles Augustin de Coulomb

1785: Coulomb's law

repulsive action of 2 electrified spheres of the same nature follows square rule of distance inversed

Luigi Galvani

1791: Observed "animal electricity", which activated nerves and muscles spanned by metal probes.

Alessandro Volta created a battery, to disprove theory on "animal electricity".

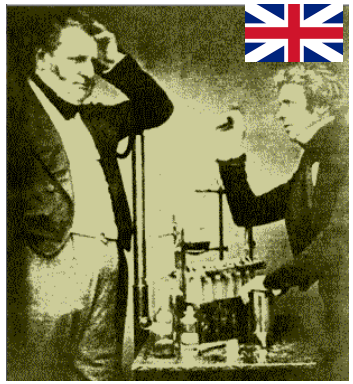
Volta coined the term "galvanism" for a direct current of electricity produced by chemical action.

History of Electrochemistry (< 1900)

William Nicholson

1800: First demonstration of electrolysis by decomposing water into hydrogen and oxygen and discovery of electroplating.

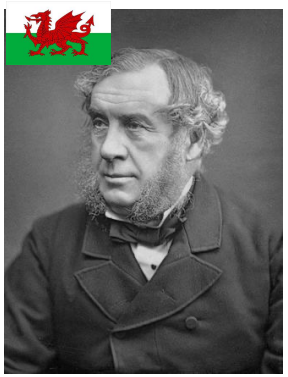
Johann W. Ritter



John Daniell **Michael Faraday**

1832: Faraday's laws of electro-chemistry.

1836: Daniell invents primary cell (Zn/Cu).



William Grove

1839: First fuel cell.

Georges Leclanché

1868: Patented the world's first widely used battery, the zinc carbon cell.

History of Electrochemistry (≈1900)

Svante Arrhenius
1884: concluded that electrolytes, when dissolved in water, become to varying degrees split or dissociated into electrically opposite positive and negative ions.

Walter Nernst
1888: showed how the characteristics of the current produced could be used to calculate the free energy change in the chemical reaction producing the current.
Nernst equation

In 1902, The **Electrochemical Society** (ECS) was founded.

Julius Tafel (CH)
1905: **Tafel equation**

Historical recap

- **1791**: L. **Galvani** linked electricity to chemical reactions (bioelectricity).
- **1800**: A. **Volta** discovered the first battery.
- **1800**: Discovery of water electrolysis as method to produce hydrogen and oxygen.
- **1805**: Electroplating as manufacturing technique
- **1832**: **Faraday**'s law formulated.
- **1839**: First fuel cell by W. **Grove**.
- **1868**: First patent related to the zinc-carbon cell, i.e. the first widely used battery.
- **1886**: Héroult-Hall electrolysis of molten alumina for aluminium production.
- **1889**: **Nernst** equation for the Gibbs free energy change (thermodynamics) in electrochemical reactions.
- **1902**: Foundation of the Electrochemical Society in the USA.
- **1905**: **Tafel** equation describing electrochemical kinetics

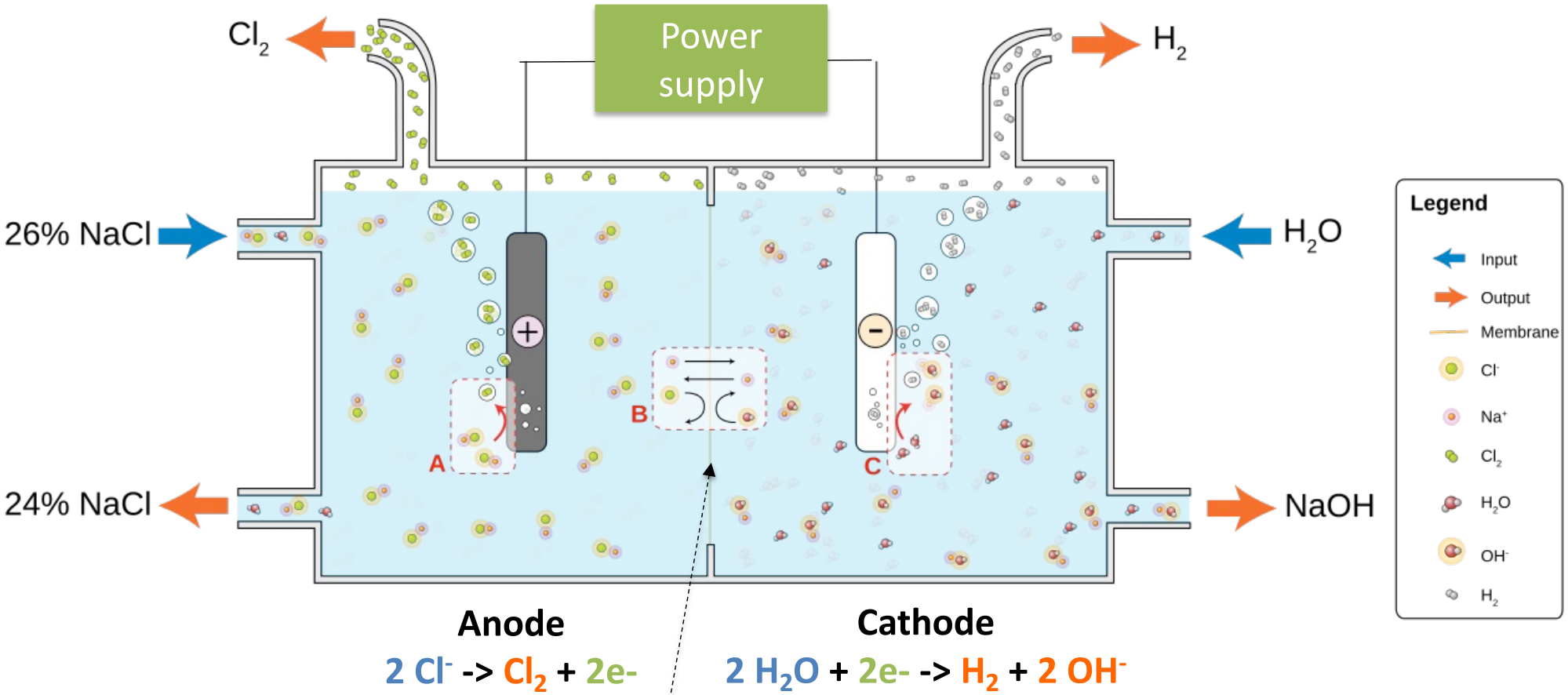
Engineering use of electrochemistry

- Electrosynthesis (electricity used as separation process)
  - Large scale production of Al, Cl_2, H_2, NaOH, organics, metals,…
- Energy conversion / storage
  - Batteries, fuel cells, water electrolysis
- Surface treatments
  - Coatings, anodic films, polishing, electroforming, …
- Corrosion
  - Mechanisms, protection
- Analysis and measurement
  - Sensors for pH, glucose, pollutants
- …

Electrosynthesis of Cl_2, H_2 and NaOH by electrolysis of NaCl solutions and water

=> Exercise 1 today

650 large plants worldwide (consuming ≈ 0.5 % of world electricity)



Adapted from Wikimedia Commons

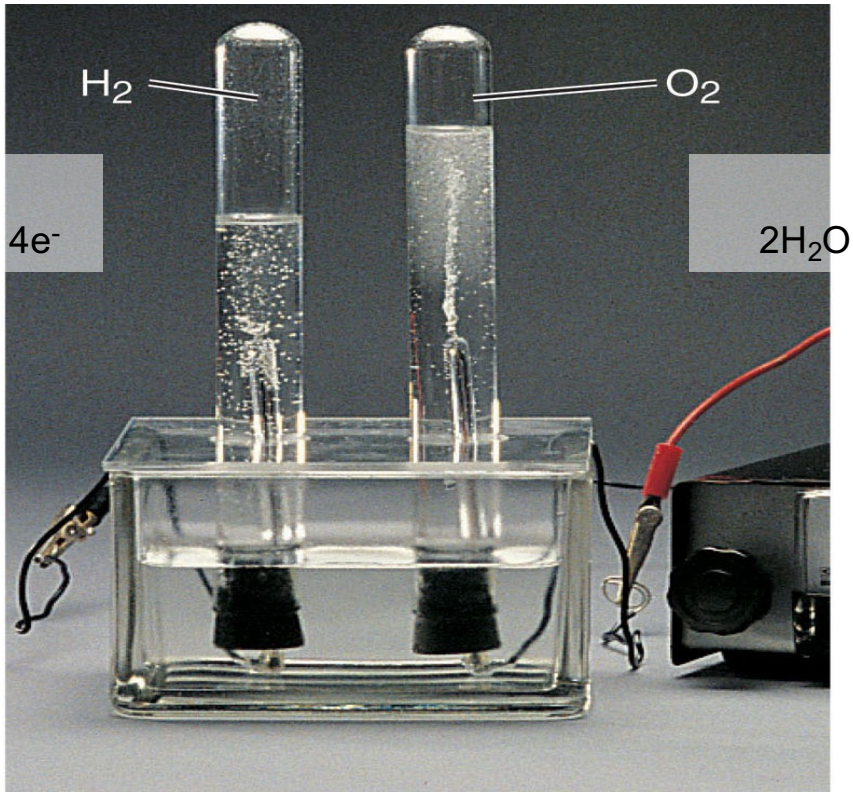
Lab-scale water electrolysis

Overall (cell) reaction

$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

Oxidation half-reaction

$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

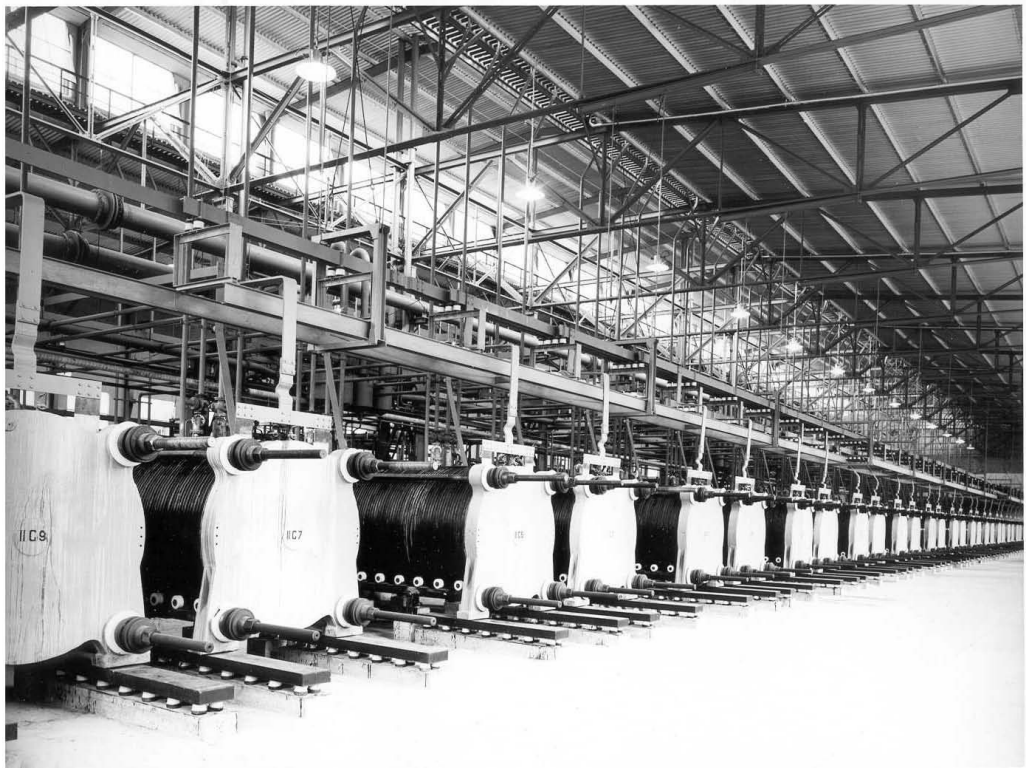


Reduction half-reaction

$2H_2O(l) + 4e^- \rightarrow 2H_2(g) + 2OH^-(aq)$

Industrial scale water electrolysis => H_2

150 MW: it has been done before !



Norsk Hydro's 30,000 Nm^3/h (~150 MW) Electrolyzer Plant (1948 - 1990)

Knut Harg, Hydro Oil & Energy, Hydrogen Technologies
NAS – Hydrogen Resource Committee, April 19, 2007

Connected to a hydroelectric plant, generating 70 t H_2/day

Questions:

1) Verify correspondence between 30'000 m^3 H_2/h and 70 t H_2/ day.

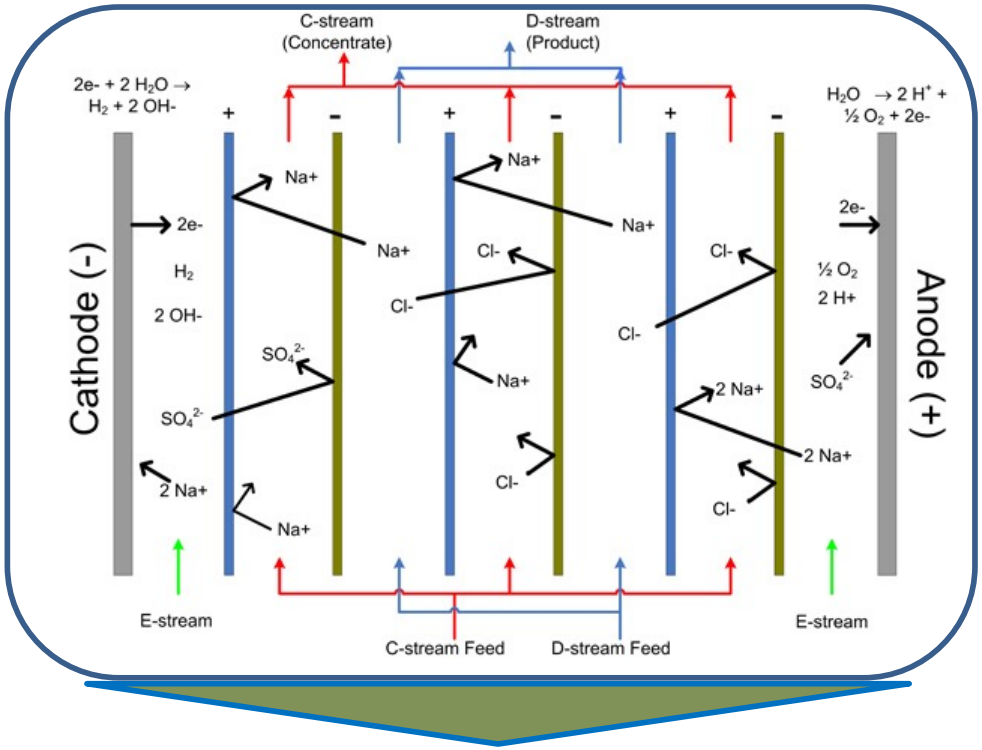
2) Estimate the efficiency of this plant.

Examples of separation process:

use electricity to separate or extract desired products.

Electrodialysis

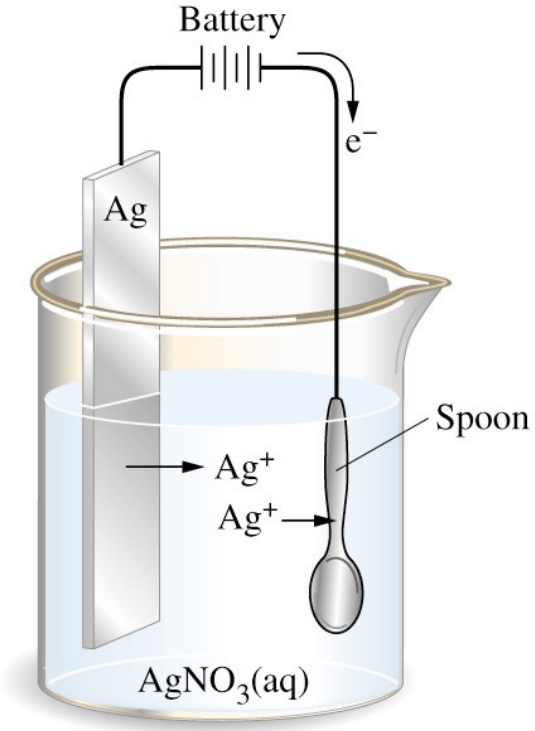
(transport of salt ions across membrane)



Alternating **anionic** and **cationic** exchange membranes

Electroplating

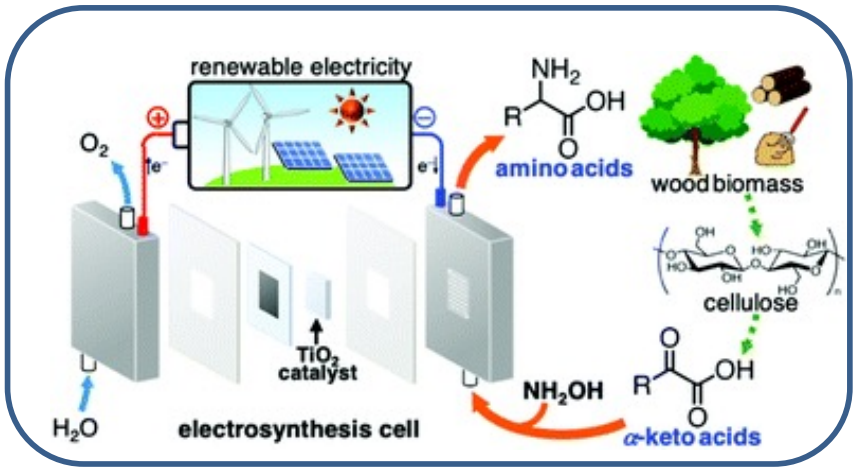
(coating surface with another metal)



Electrosynthesis

use electricity to produce valuable chemicals

e.g. amino-acid synthesis



Fukushima, T. and Yamauchi, M. *Chem. Comm.* (2019)

=> general principle: use electricity (the electron as the ultimate reducing agent) to force non-spontaneous reactions.

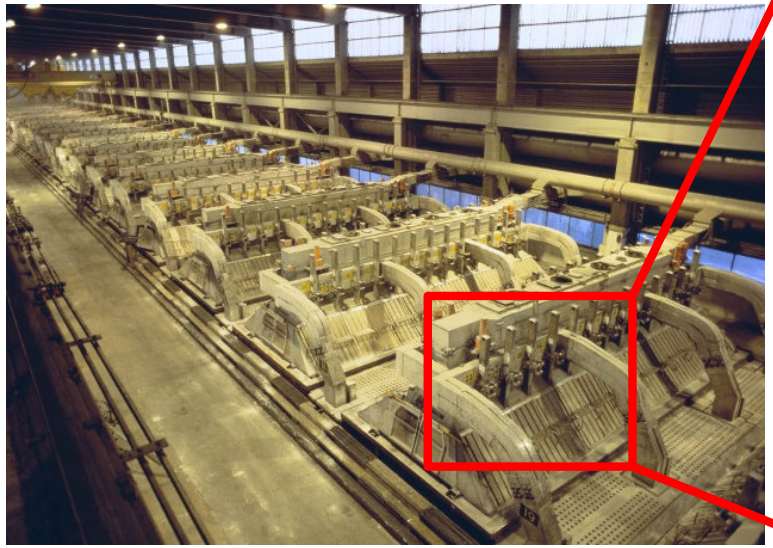
=> accurate regulation of voltage and current allow for precise **control** of the desired reactions/products (other than thermal processes can do)

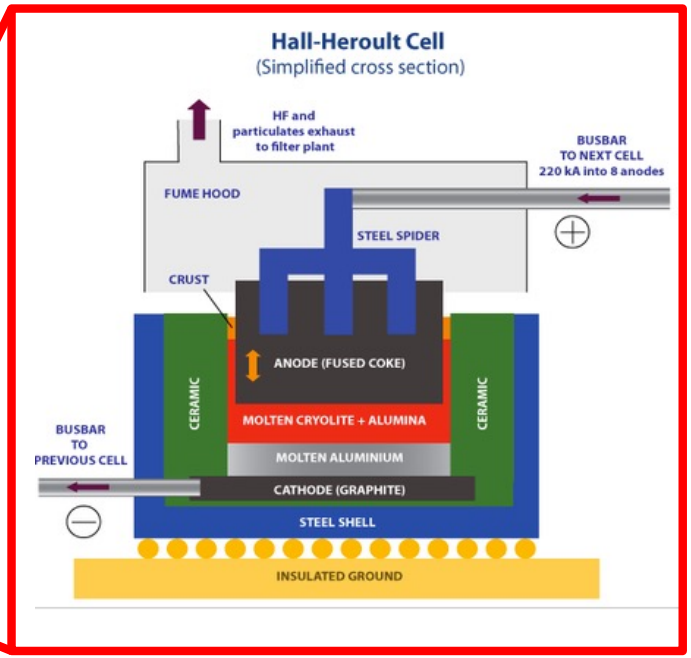
Example of separation process:

Electrowinning/electroextraction

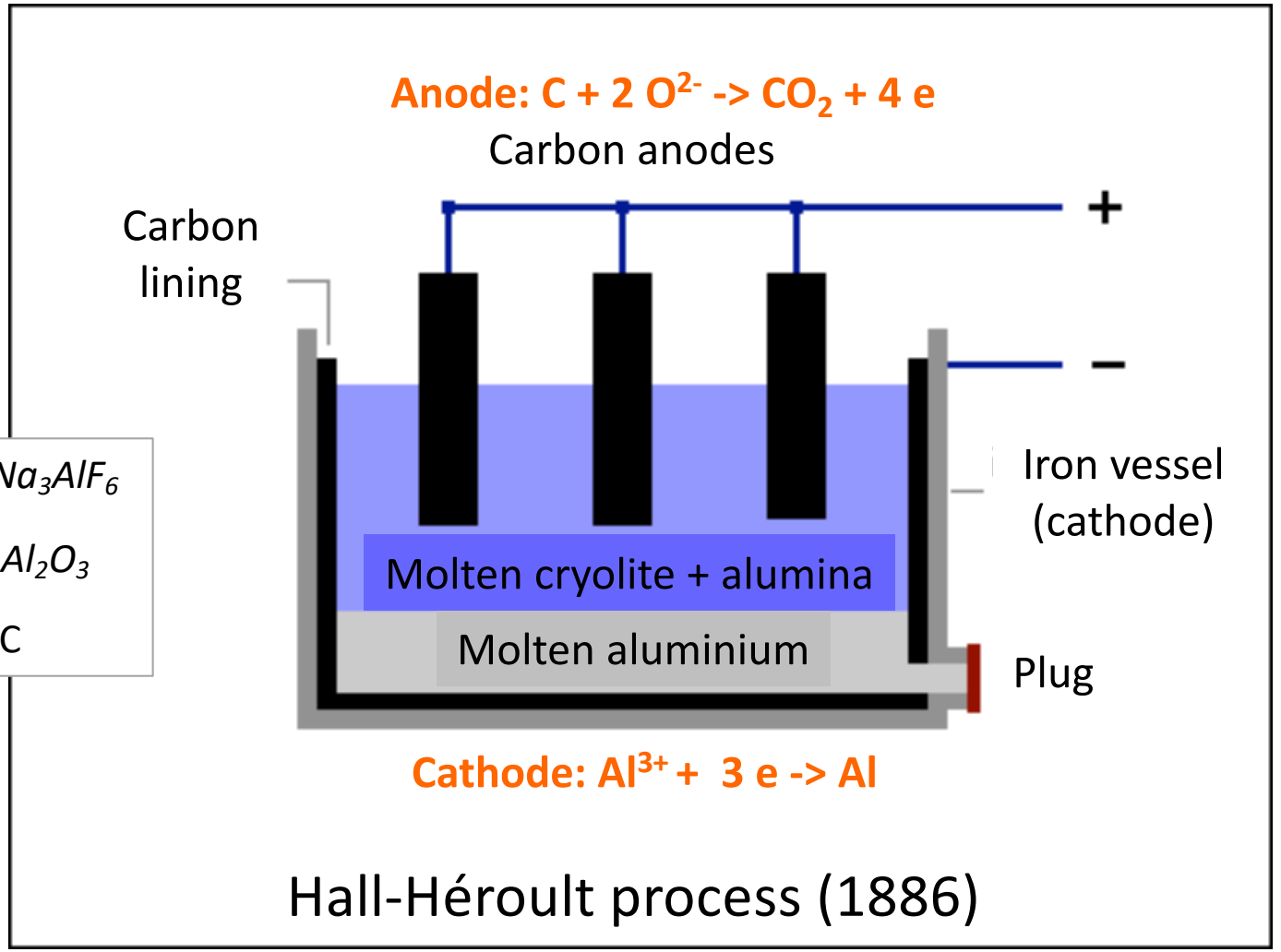
e.g. Al metal from Al_2O_3 oxide (bauxite)

(electrodeposition of metals from their liquefied ores)





Aluminium production through the electrolysis of aluminium molten salt



Cryolite: Na_3AlF_6

Alumina: Al_2O_3

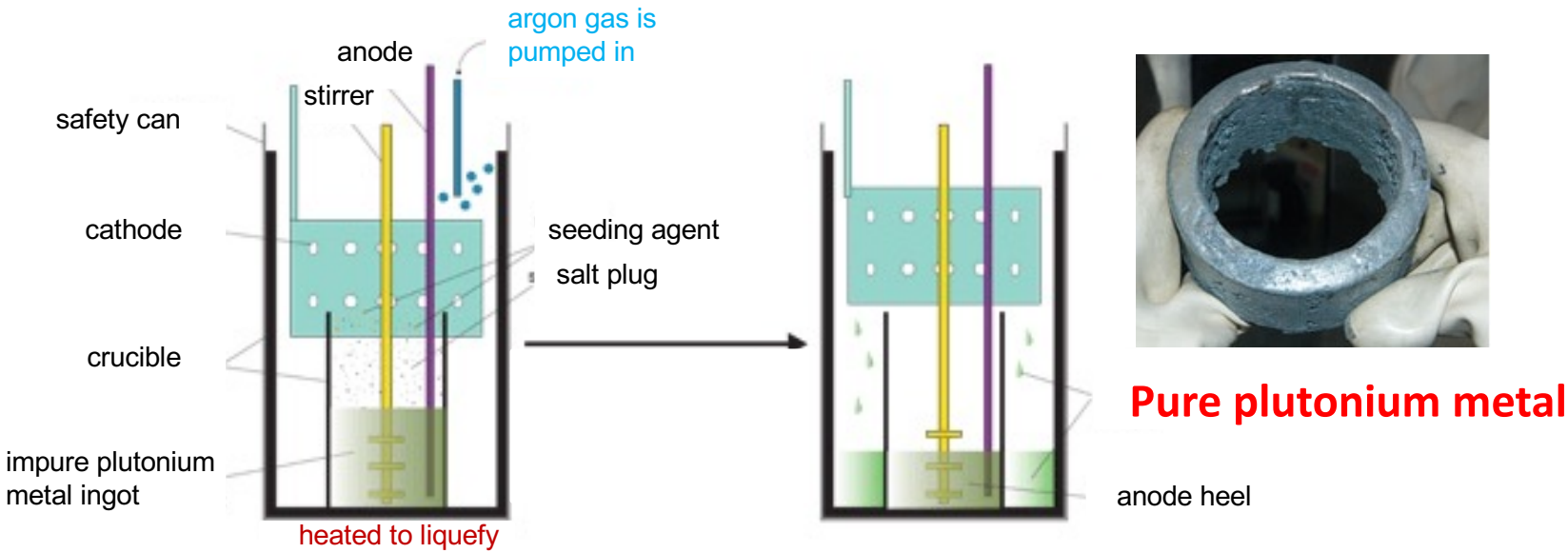
T ≈ 1000°C

≈ 4 % of the world's electricity goes into aluminium extraction !

Example of separation process:

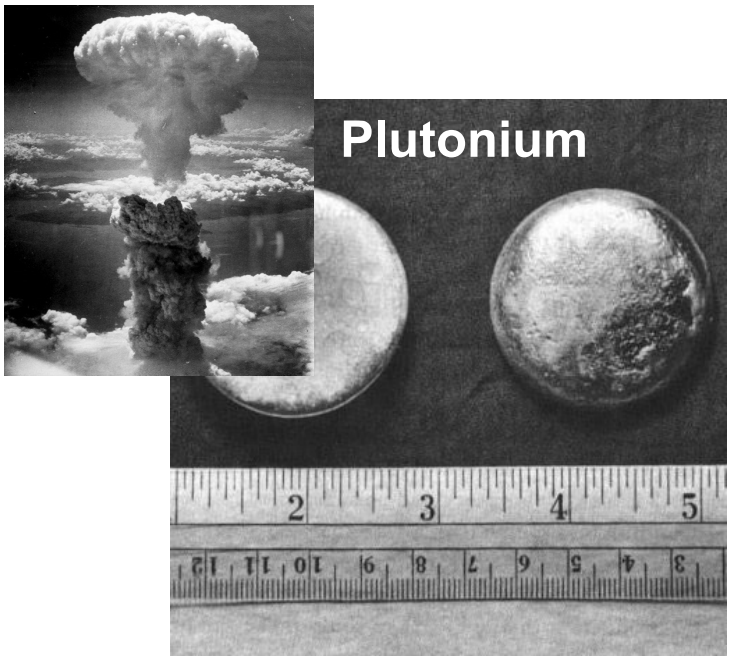
Electrorefining

(impure metal selectively corrodes into solution and deposits onto an electrode)

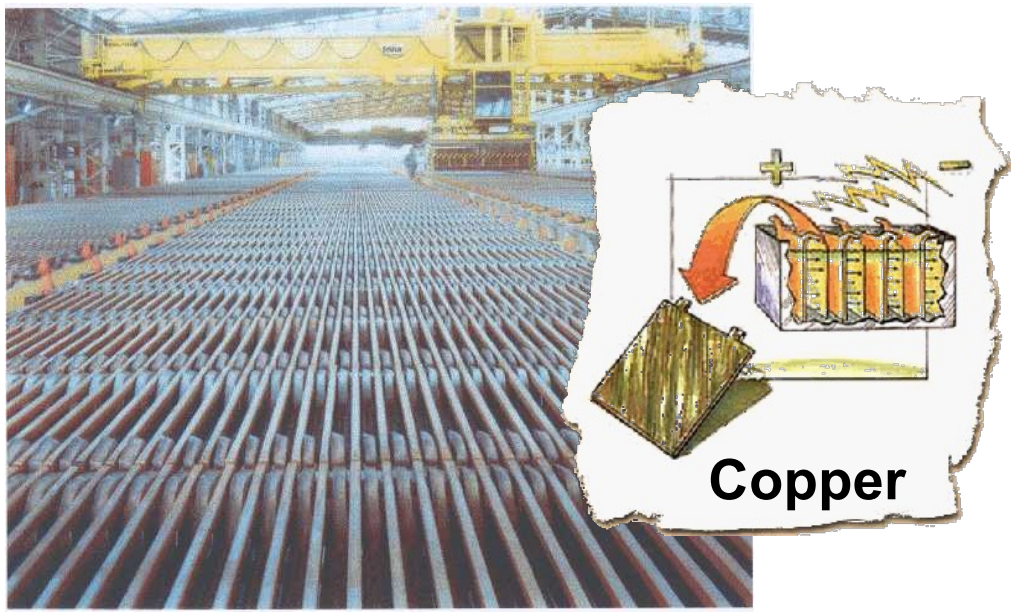


Electrorefining

Small amounts…



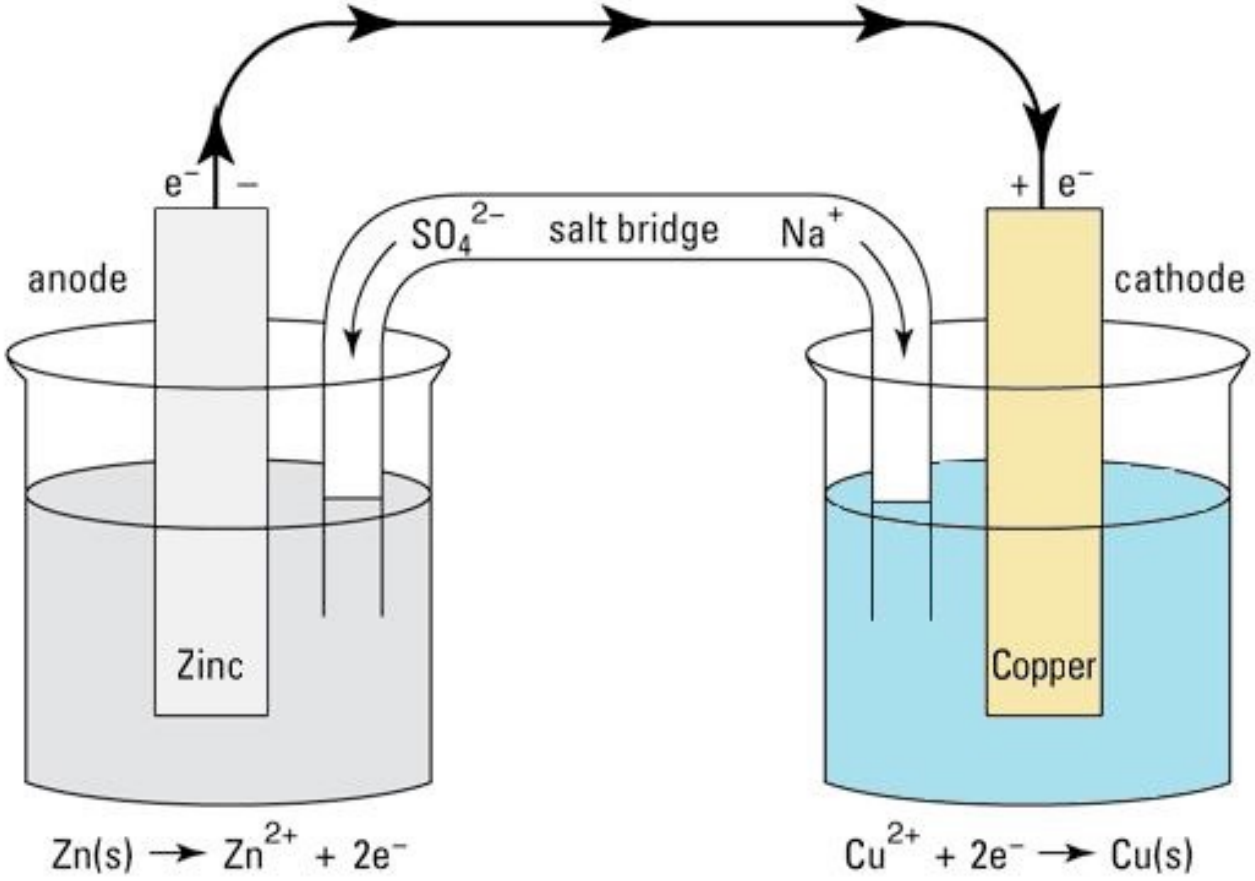
..to large amounts



Engineering use of electrochemistry

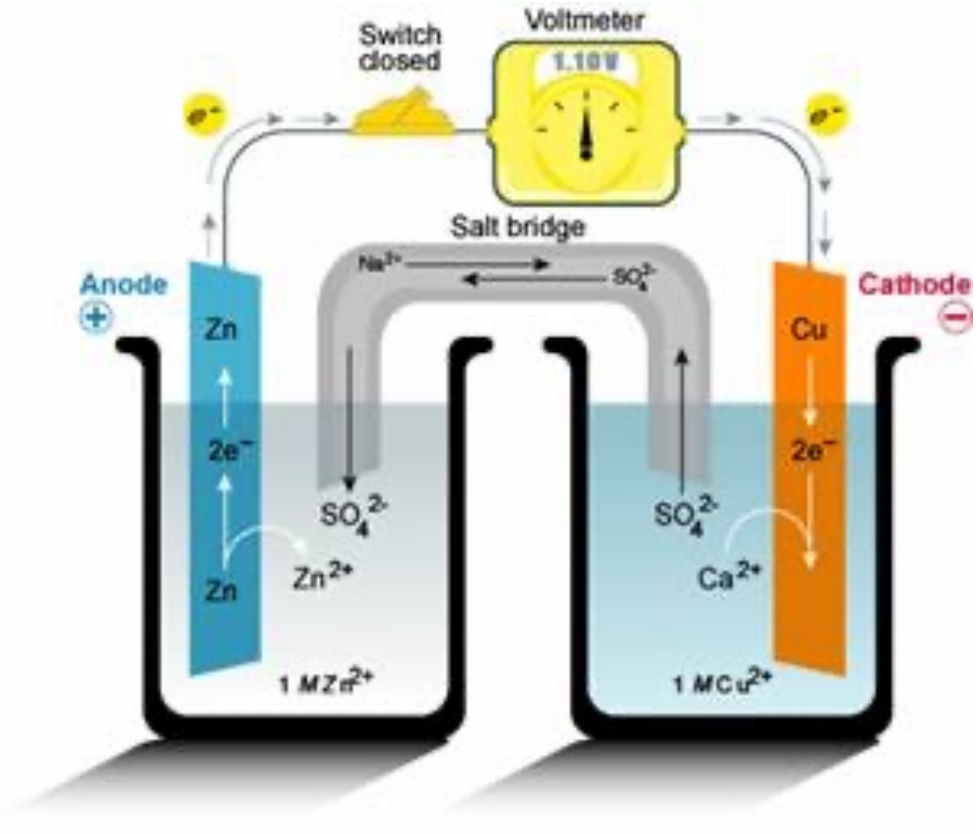
- Electrosynthesis (electricity used as separation process)
  - Production of Al, Cl_2, H_2, NaOH, …
- Energy conversion / storage
  - Batteries, fuel cells, water electrolysis
- Surface treatments
  - Coatings, anodic films, polishing, electroforming, …
- Corrosion
  - Mechanisms, protection
- Analysis and measurement
  - Sensors for pH, glucose, pollutants
- …

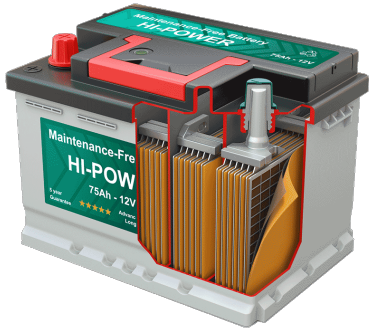
Chemical to electrical energy conversion: the Daniell cell



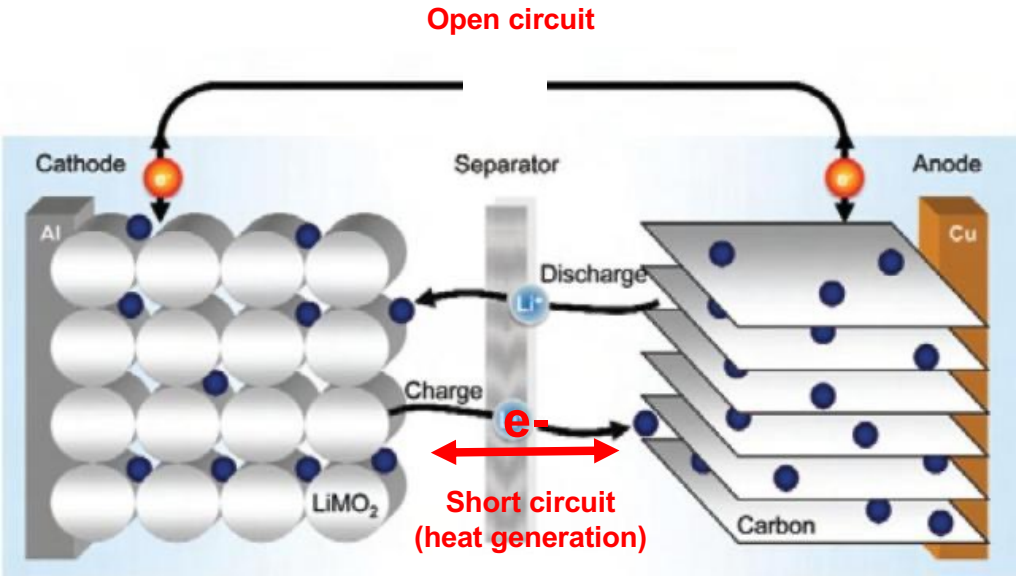
Batteries

Storing electricity in the form of chemical energy



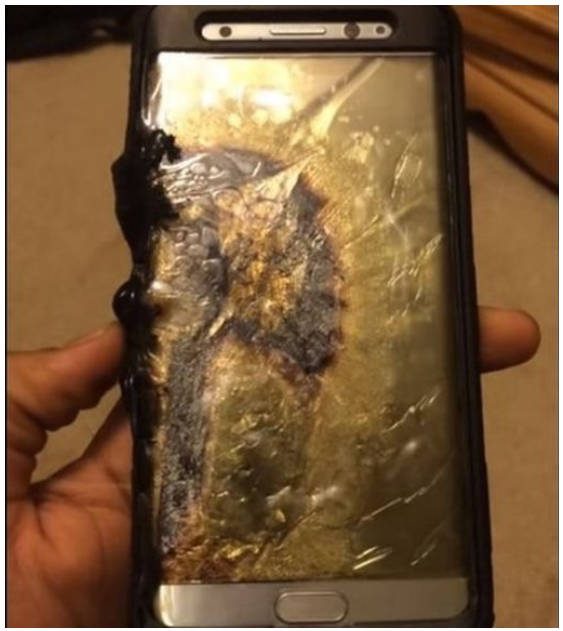


Batteries



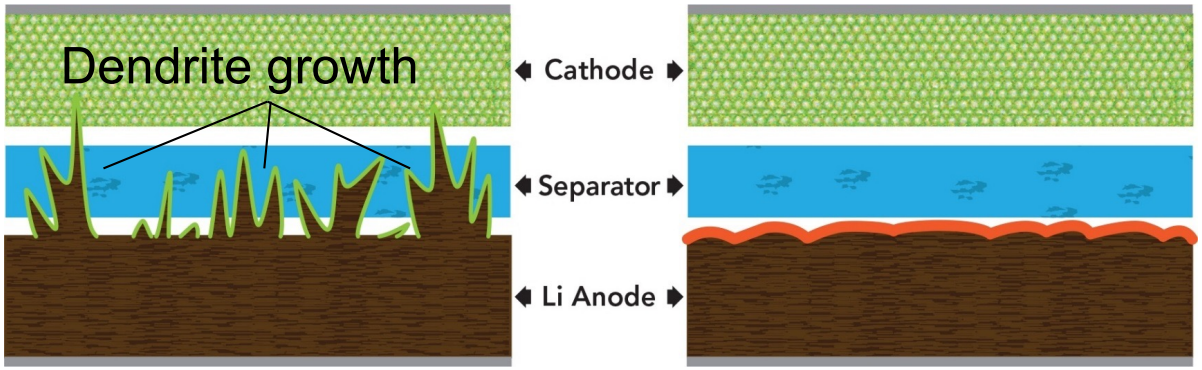
Li ion solution dissolved in organic solvent (flammable!)

Failure:



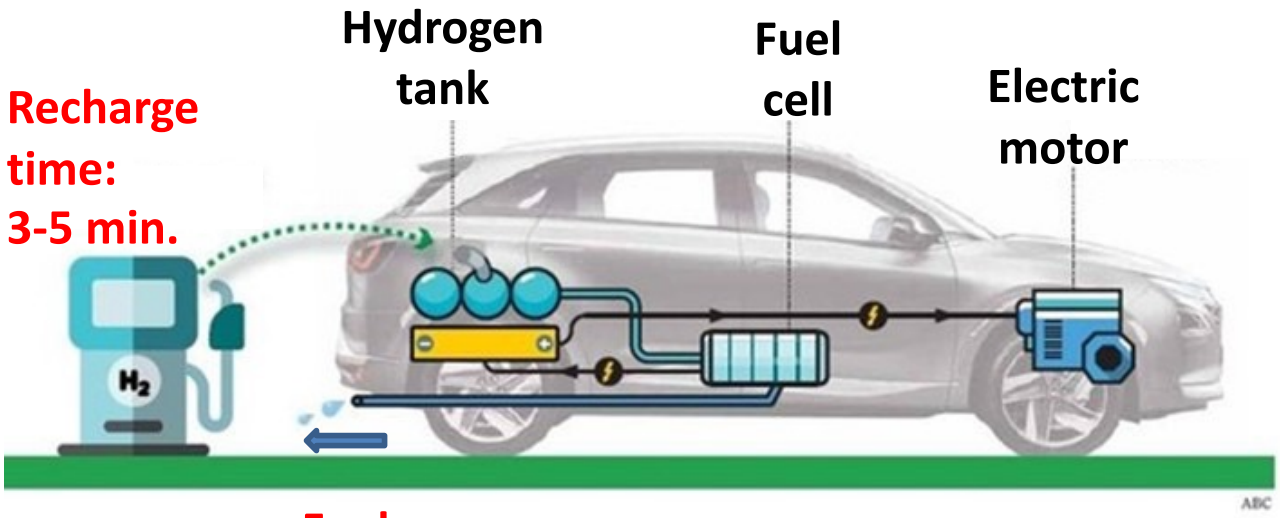
Possible causes for failure:

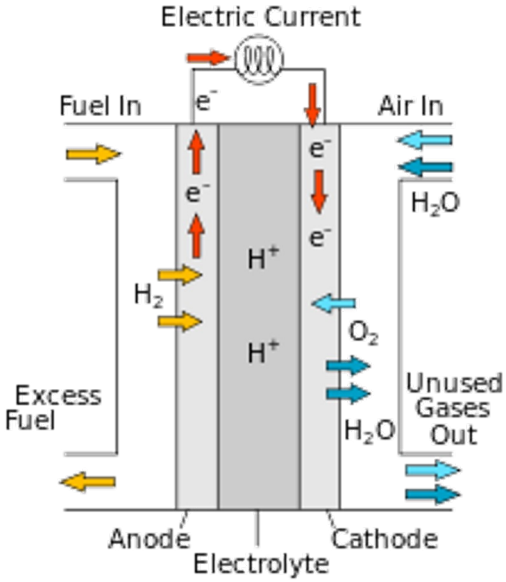
- Battery is too thin (separator failure)
- Lithium “needles” (dendrites) extend from electrodes and puncture the separator



Fuel cells

Extracting electrical energy from a fuel





Engineering use of electrochemistry

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  - Production of Al, Cl_2, H_2, NaOH, …
- Energy conversion / storage
  - Batteries, fuel cells, water electrolysis
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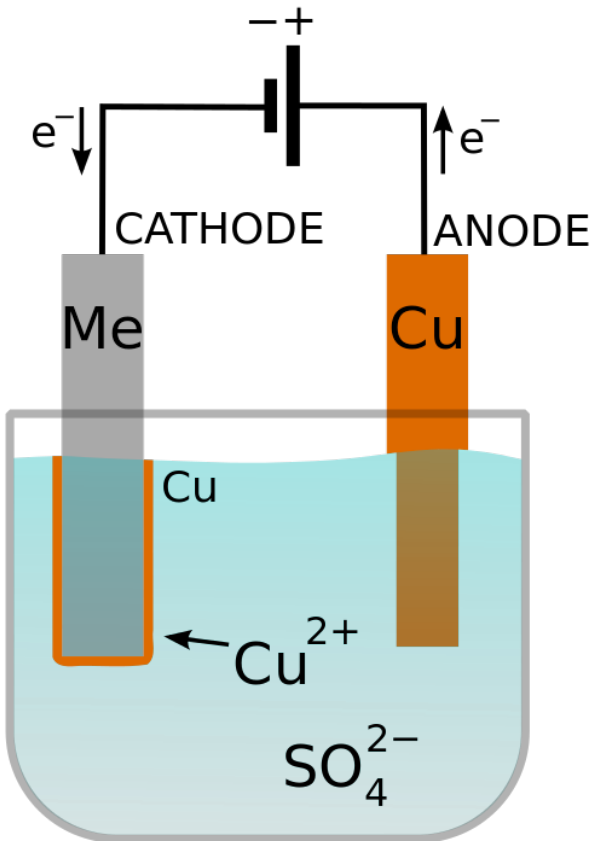
Surface treatments by metal electrodeposition

Principle of electrodeposition

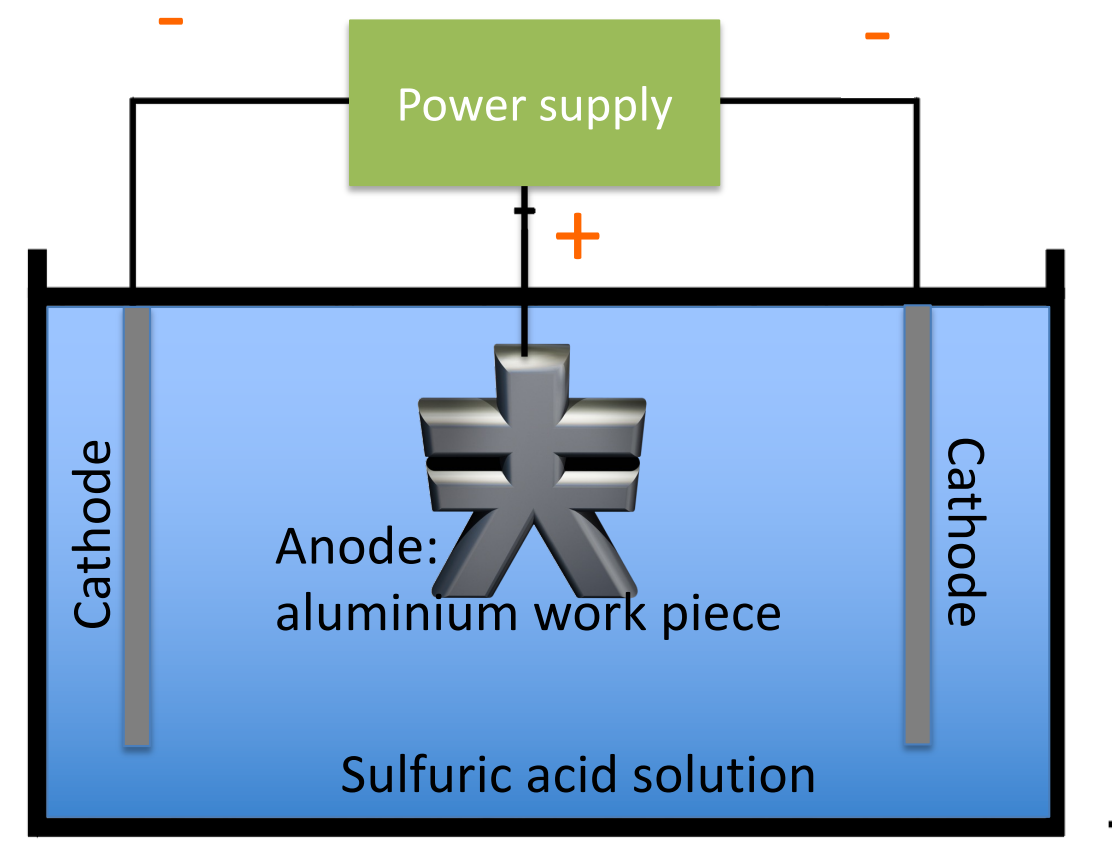


Cathode:
Cu^{2+} + 2 e -> Cu

Anode:
Cu -> Cu^{2+} + 2 e

Examples of electrodeposition

Surface treatments by metal anodizing (formation of a metal oxide surface film)



Car fitting component: anodized aluminum

Cathode

$2\ H^+ + 2e \rightarrow H_2$

Anode

$2\ Al + 3\ H_2O \rightarrow Al_2O_3 + 6\ H^+ + 6e$

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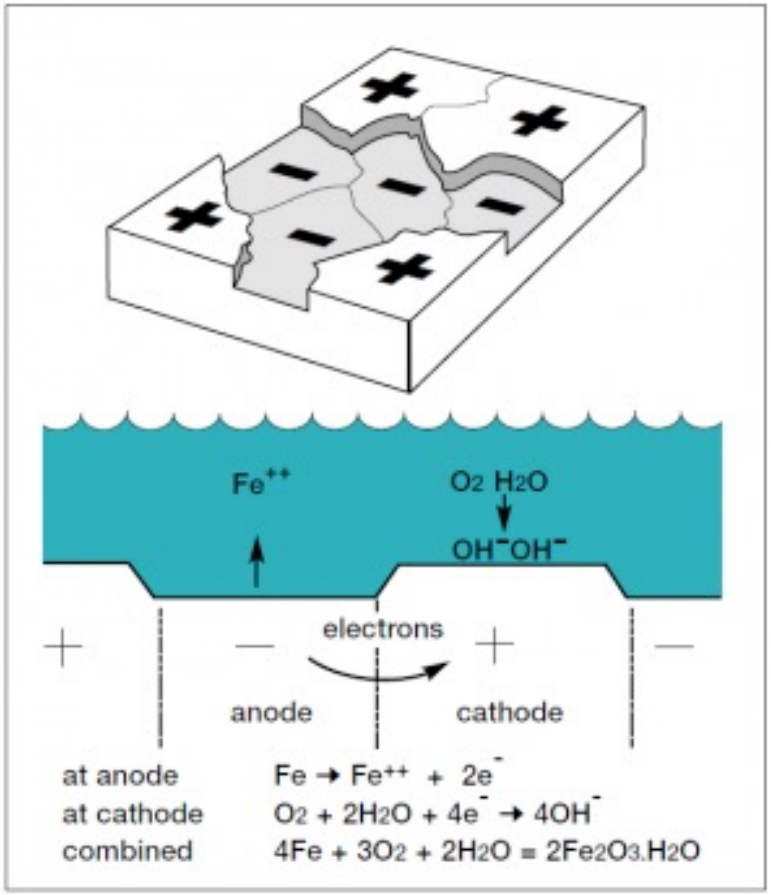
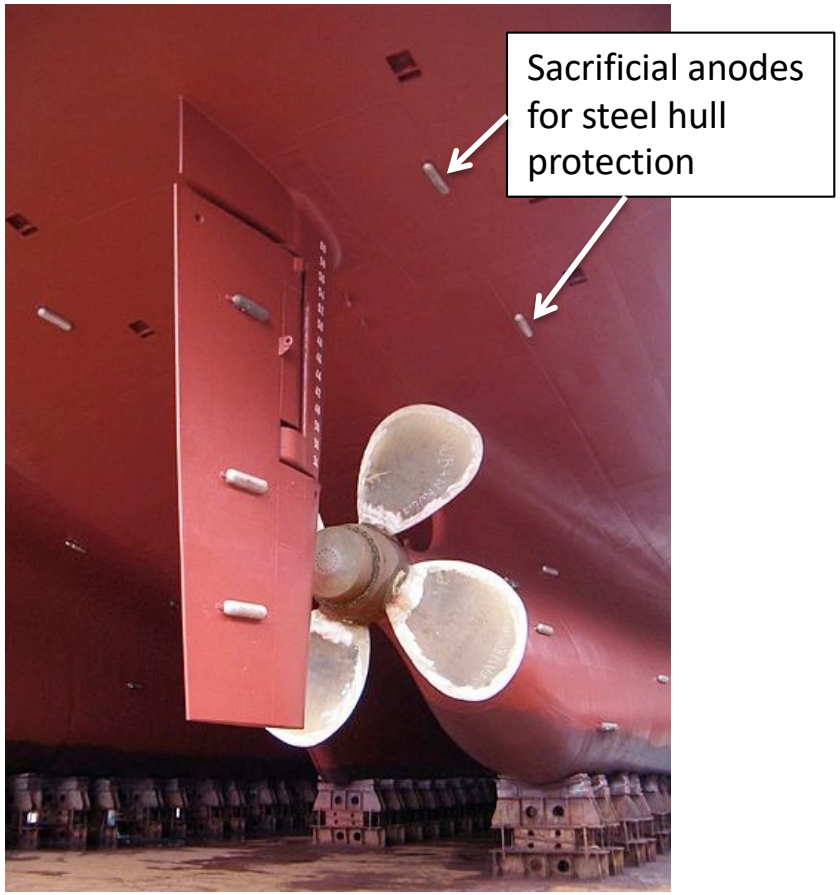
Corrosion

Corrosion mechanisms

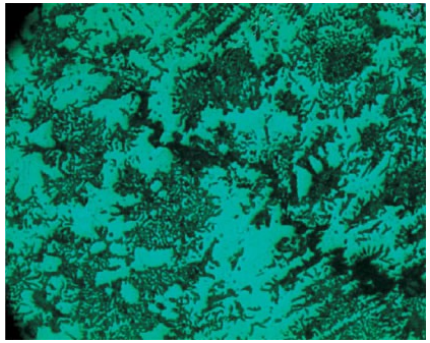


Corrosion protection

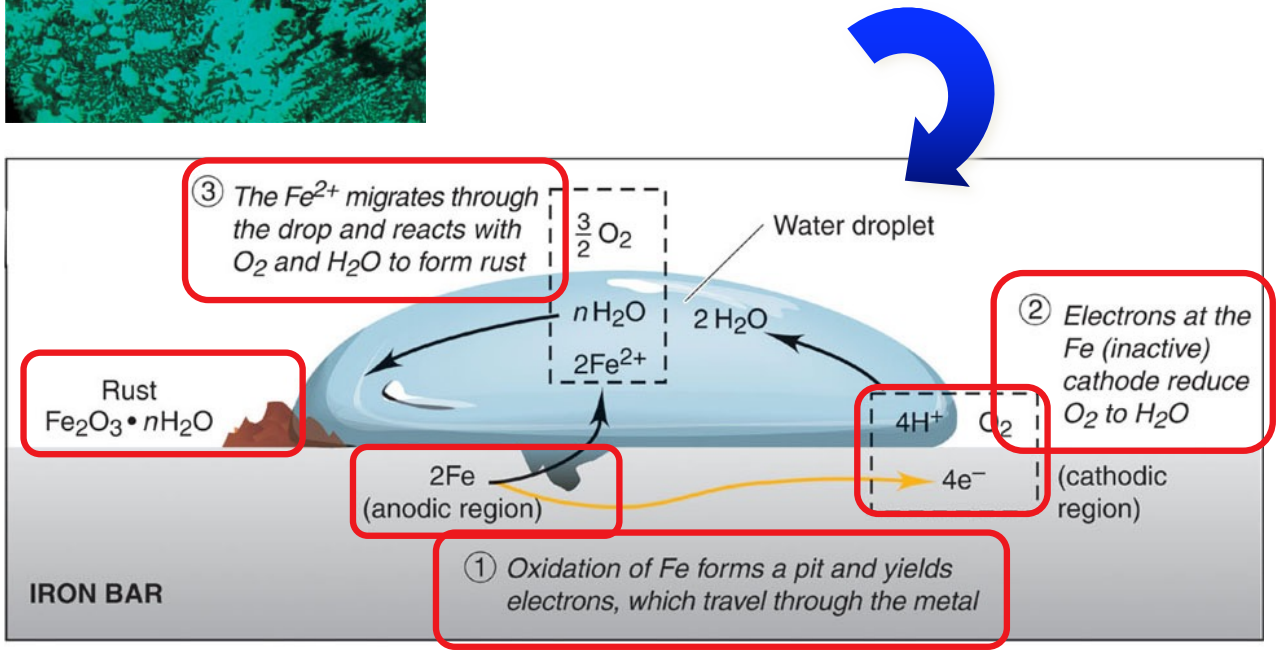


Corrosion

Conversion of metals to metal oxides.



Corrosion of Fe is essentially a miniature electrochemical cell



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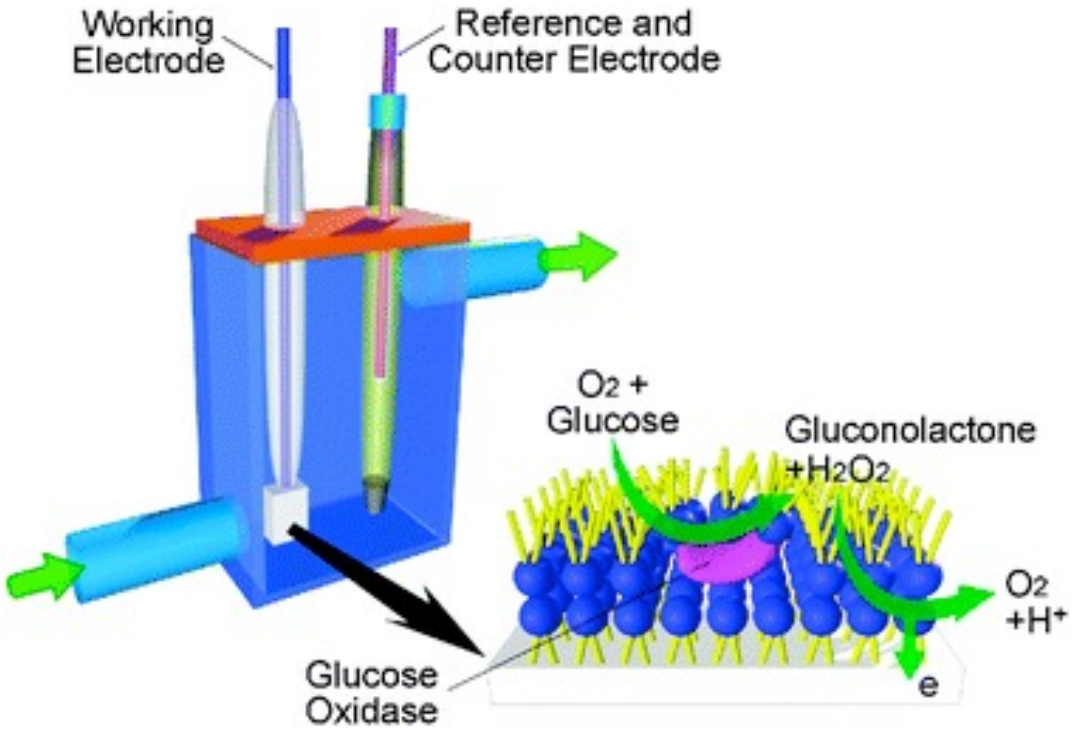
  - **Sensors** for pH, glucose, pollutants (e.g. NOx, H_2S,..)
- …

Glucose sensor based on electrochemical oxidation of hydrogen peroxide



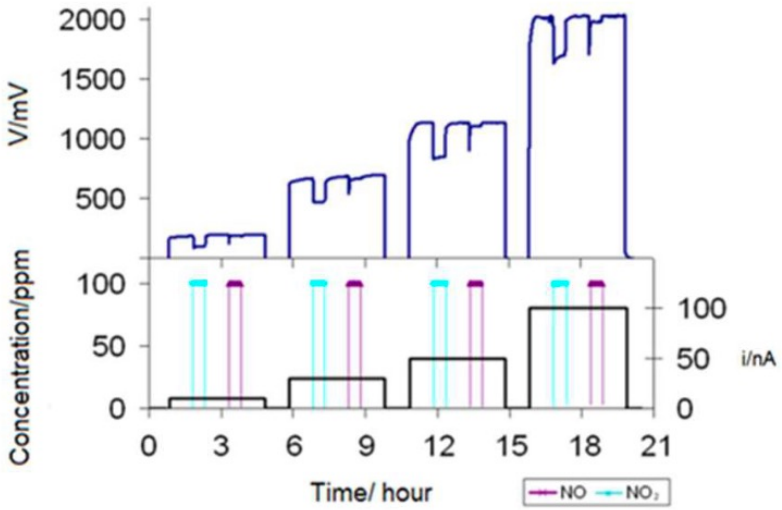
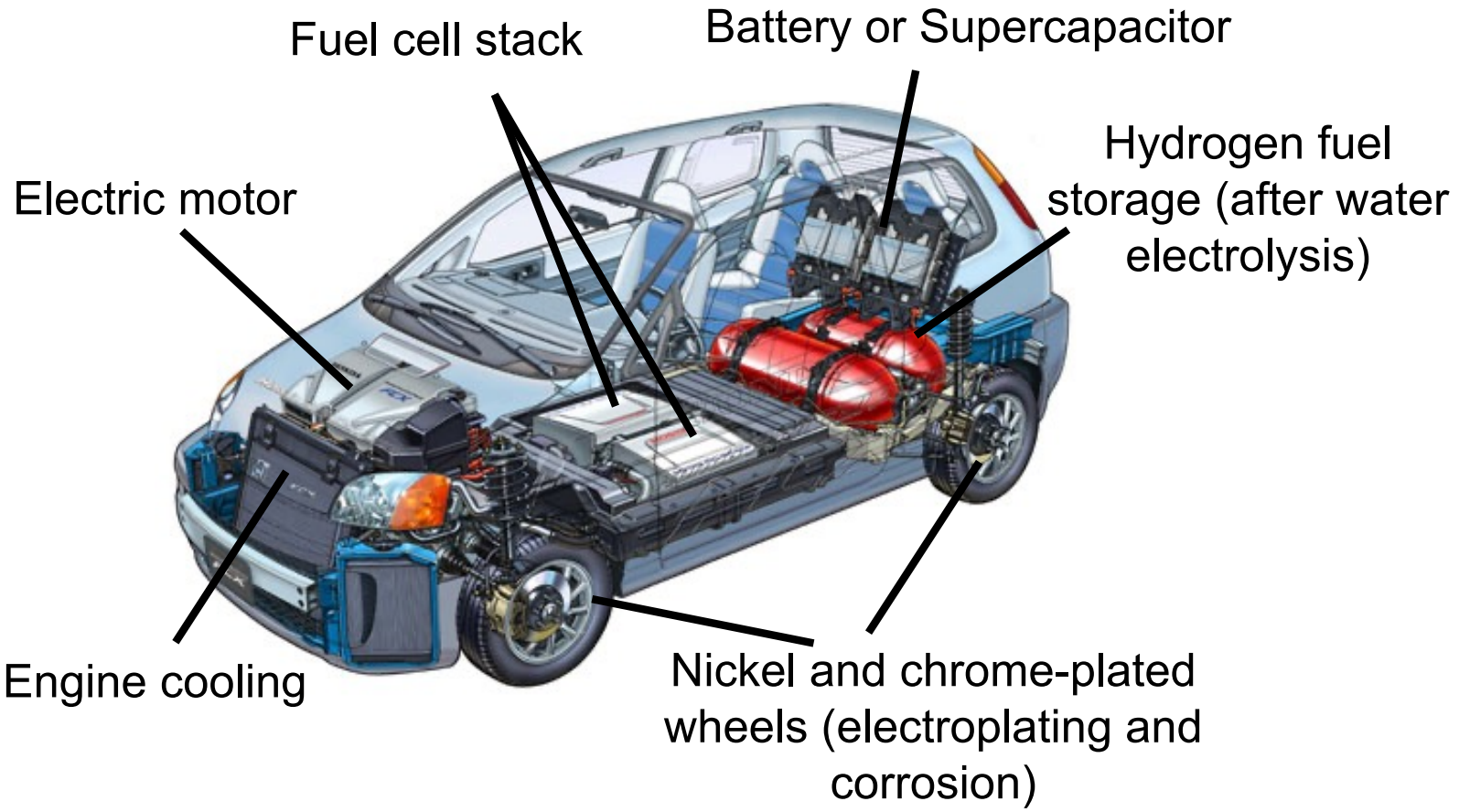


Fig. 2. Sensor response (ΔV /mV) at 450°C to 100ppm NO_2/NO (O_2 12vol.%, H_2O 2vol.%) at different polarizations (i /nA).

Other examples :

- NO_2-sensor for engine exhaust https://www.sciencedirect.com/science/article/pii/S187770581633421X
- Lambda-sensor (O_2) for 3-way cat regulation for gasoline engines

Multiple combined applications of electrochemistry



Other related courses

- Electrosynthesis (CHE407)
- **Energy storage and conversion**
- **Surface treatments**
- Analysis and measurement, Environment (CHE407)
- Corrosion (MX Bachelor)
- Thermodynamics (CH-241, MSE-204, ..)
- Transport phenomena (ChE-301)
- Chemical kinetics (CH-342)
- **Fuel Cells & Engines (ME-551)**

Follow up in practice (lab)

- To apply your knowledge:
  - **Semester projects** at GEM lab (EPFL-Sion), see gem.epfl.ch (J Van herle)
  - **Master project** at GEM lab or elsewhere
    - with or without industry partner
  - Semester job (1-2 days/week), summer internship (possible to be full time) etc.
    - employed at GEM lab

Take home message

- Electrochemistry and its applications are a vast and highly relevant field, with massive impact
  - electricity will (partly) replace combustion processes
  - electrolytic industries (metal extraction)
- Very interdisciplinary
- Voltage and current are precise tuning handles, instead of heat (thermal processing), to control chemical reactions of interest