

# Electrochemistry for materials technology

## 1. Introduction

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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
  - Membr. 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 Comninellis, 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 from 2024

- This class in 2024 merged students from **MSE-441** (Electrochemistry for Materials – MX section) and **CHE-407** (Electrochemical Engineering – Prof A. Boghossian)
- Monday, 14h-16h: Lectures. In addition: **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
- 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-08	Intro	Electrochemistry general / examples	J Van herle	Y
2024-Sep-15	1	Electrode Potential / Thermodynamics	J Van herle	Y
2024-Sep-22	holiday			
2024-Sep-29	2	Electrode Kinetics	J Van herle	Y
2024-Oct-06	3	Batteries	J Van herle	Y
2024-Oct-13	4	Batteries	J Van herle	Y
2024-Oct-20	break			
2024-Oct-27	5	Fuel Cells	J Van herle	Q & A
2024-Nov-03	6	Electrolysis	J Van herle	Y
2024-Nov-10	7	Electrolysis / Electricity storage	J Van herle	Y
2024-Nov-17	8	Electrodeposition 1	Cédric Frantz	Y
2024-Nov-24	9	Electrodeposition 2	Cédric Frantz	Y
2024-Dec-01	10	Electrodeposition 3	Cédric Frantz	Y
2024-Dec-08	11	Electrochemical methods (instrumentation)	C. Frantz / J. Van herle	Y
2024-Dec-15	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**.



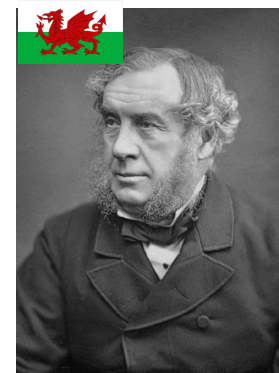
**Johann W.  
Ritter**



**John Daniell   Michael  
Faraday**

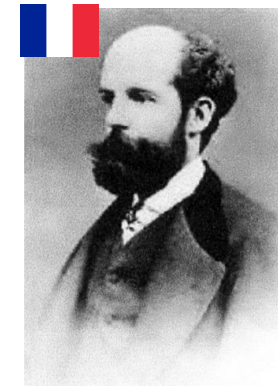
**1832:** Faraday's laws of electro-chemistry.

**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**

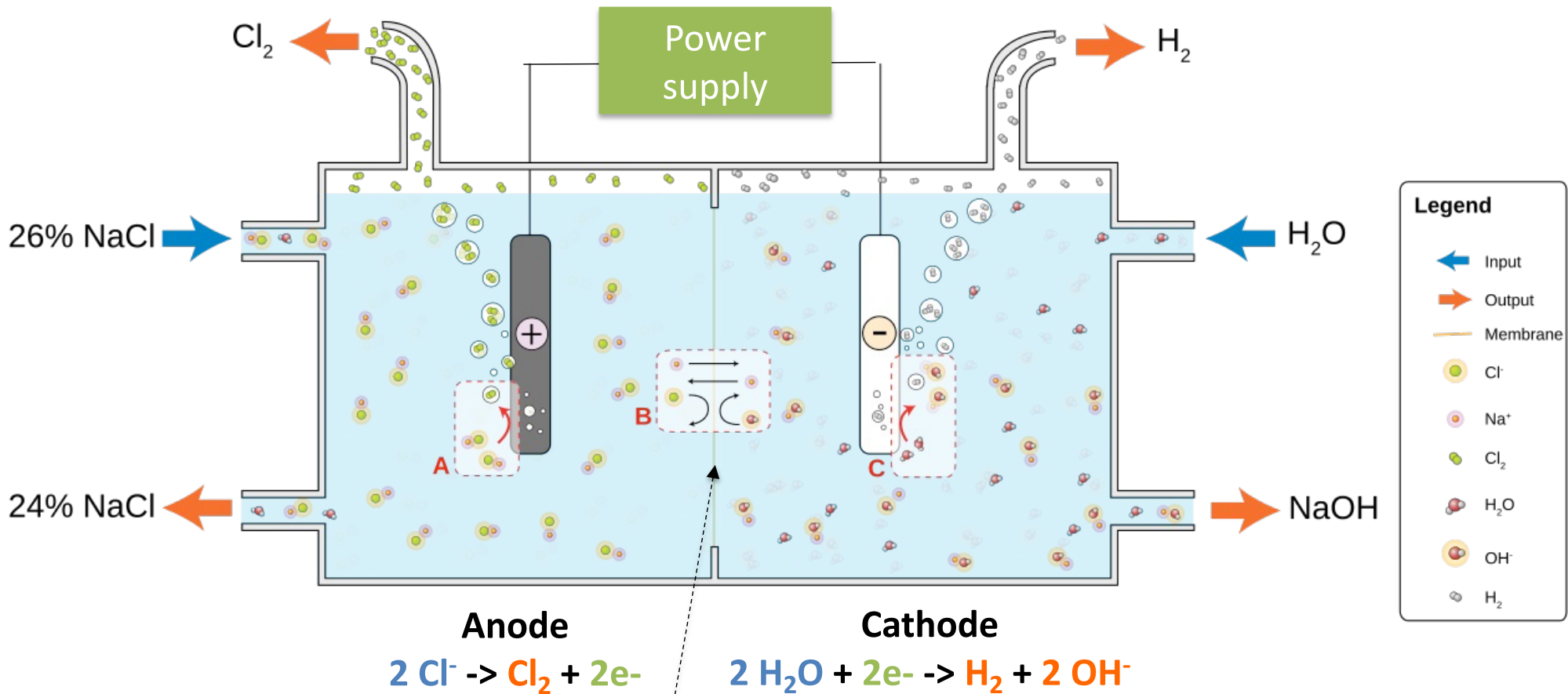
# Engineering use of electrochemistry

- **Electrosynthesis** (electricity used as **separation** process)
  - Large scale production of Al, Cl<sub>2</sub>, H<sub>2</sub>, 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
- ...

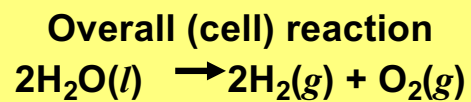
# Electrosynthesis of Cl<sub>2</sub>, H<sub>2</sub> and NaOH by electrolysis of NaCl solutions and water

=> Exercise 1 today

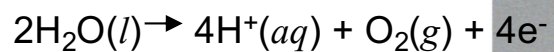
650 large plants worldwide (consuming ≈ 0.5 % of world electricity)



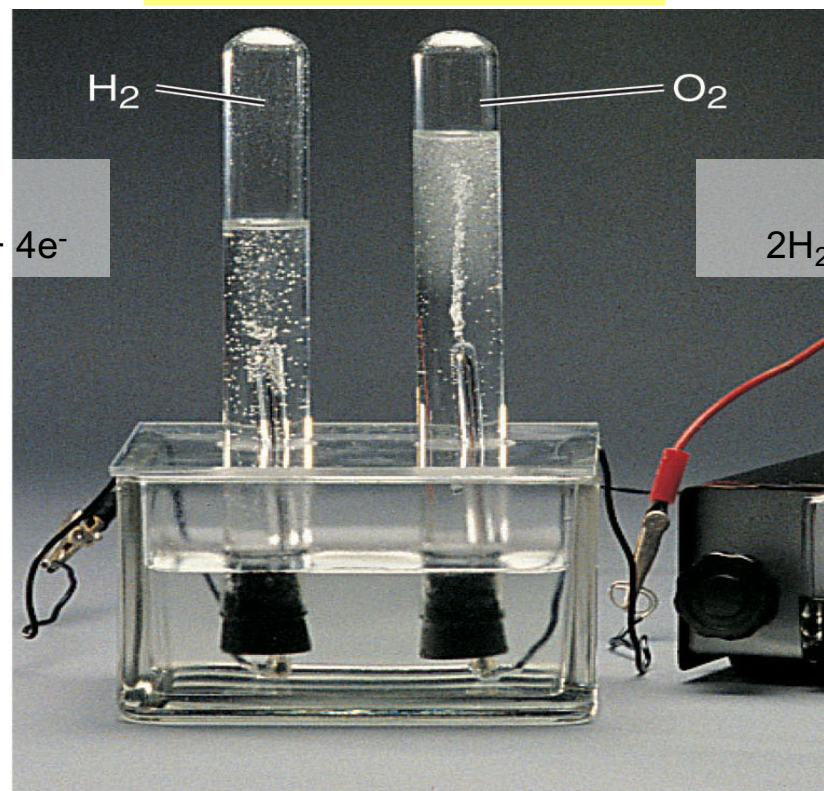
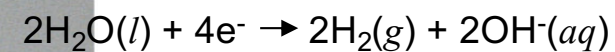
# Lab-scale water electrolysis



Oxidation half-reaction



Reduction half-reaction



# Industrial scale water electrolysis => H<sub>2</sub>

150 MWe: it has been done before !



**Norsk Hydro's 30,000 Nm<sup>3</sup>/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<sub>2</sub>/day

Questions:

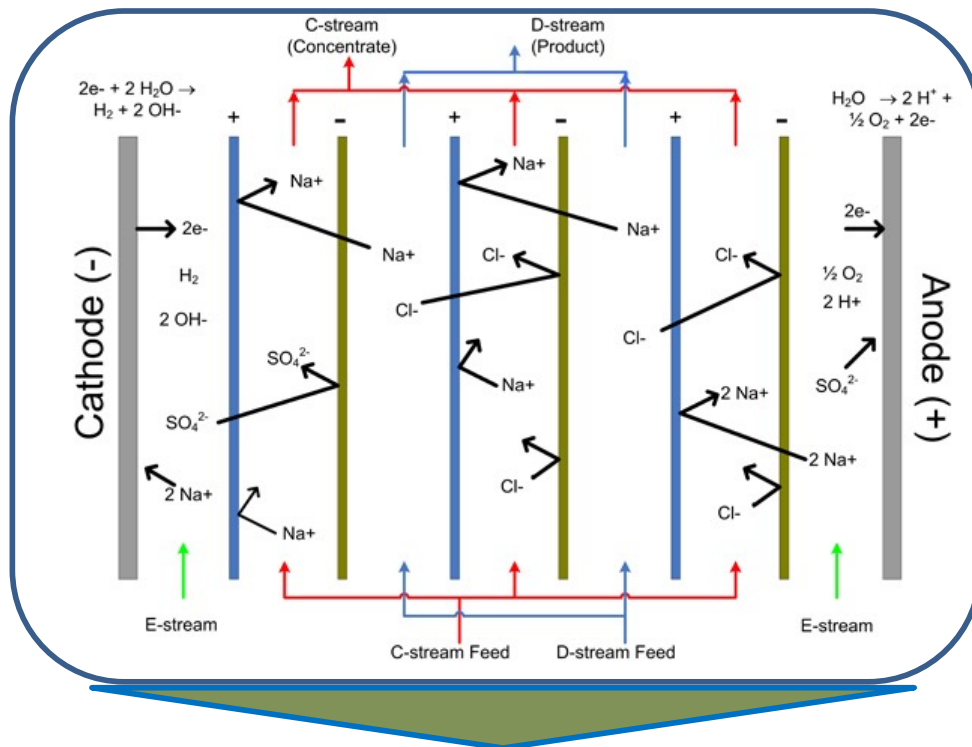
- 1) Verify correspondence between 30'000 m<sup>3</sup> H<sub>2</sub>/h and 70 t H<sub>2</sub>/ day.
- 2) Estimate the efficiency of this plant.

# Examples of separation process:

use electricity to separate or extract desired products.

## Electrodialysis

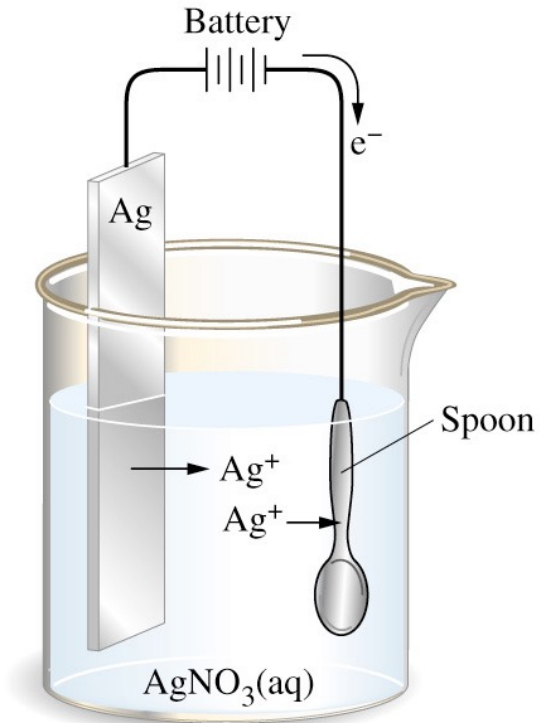
(transport of salt ions across membrane)



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

## Electroplating

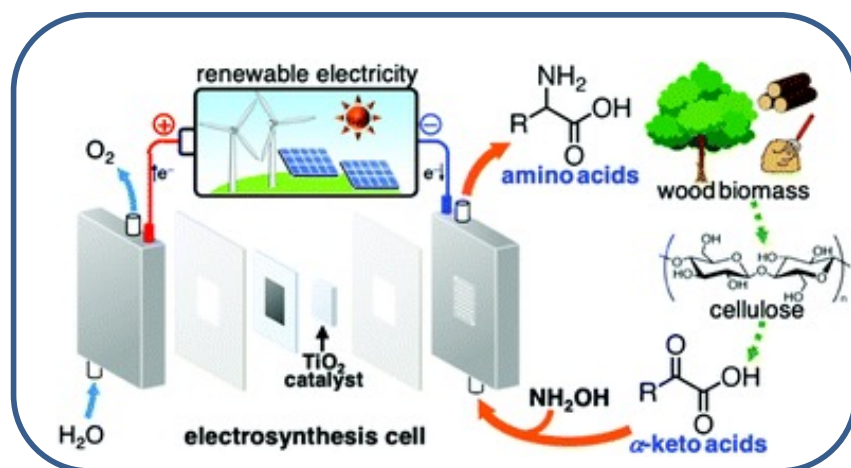
(coating surface with another metal)



# 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.

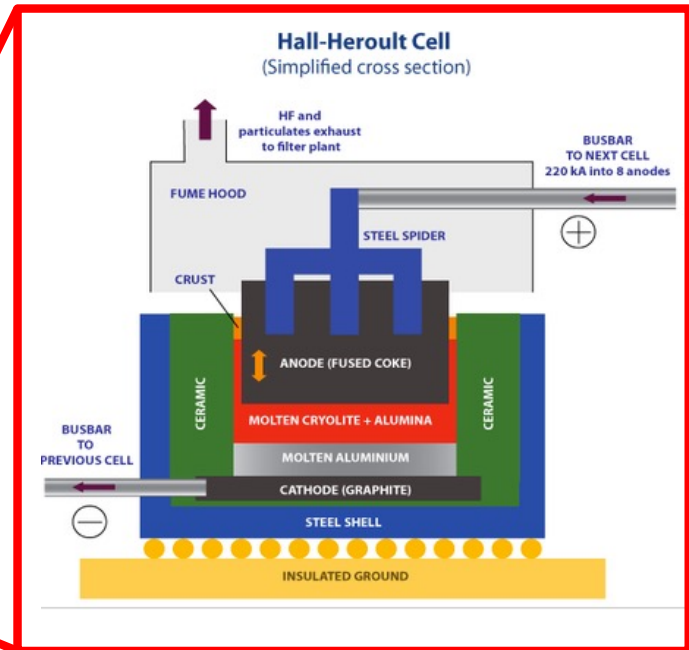
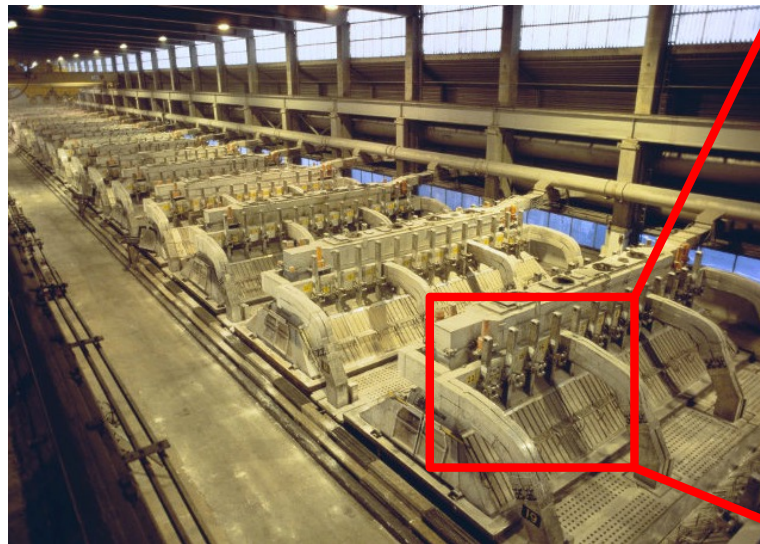
=> accurate regulation of **voltage** and **current** allow for precise **control** of the desired reactions/products (other than thermal processes can do)

# Example of separation process:

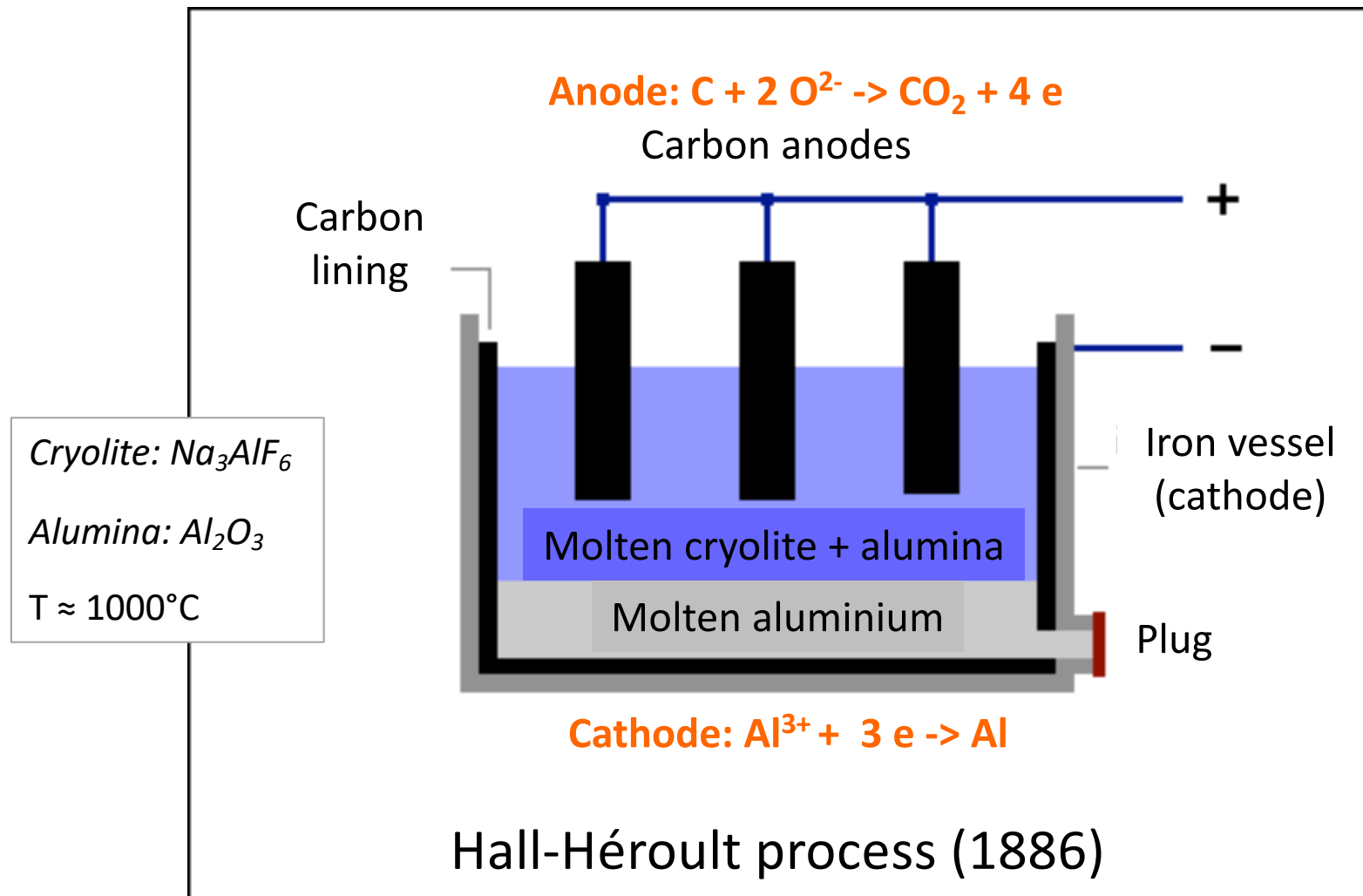
## Electrowinning/electroextraction

e.g. Al metal from  $\text{Al}_2\text{O}_3$  oxide (bauxite)

(electrodeposition of metals from their liquefied ores)



# Aluminium production through the electrolysis of aluminium molten salt

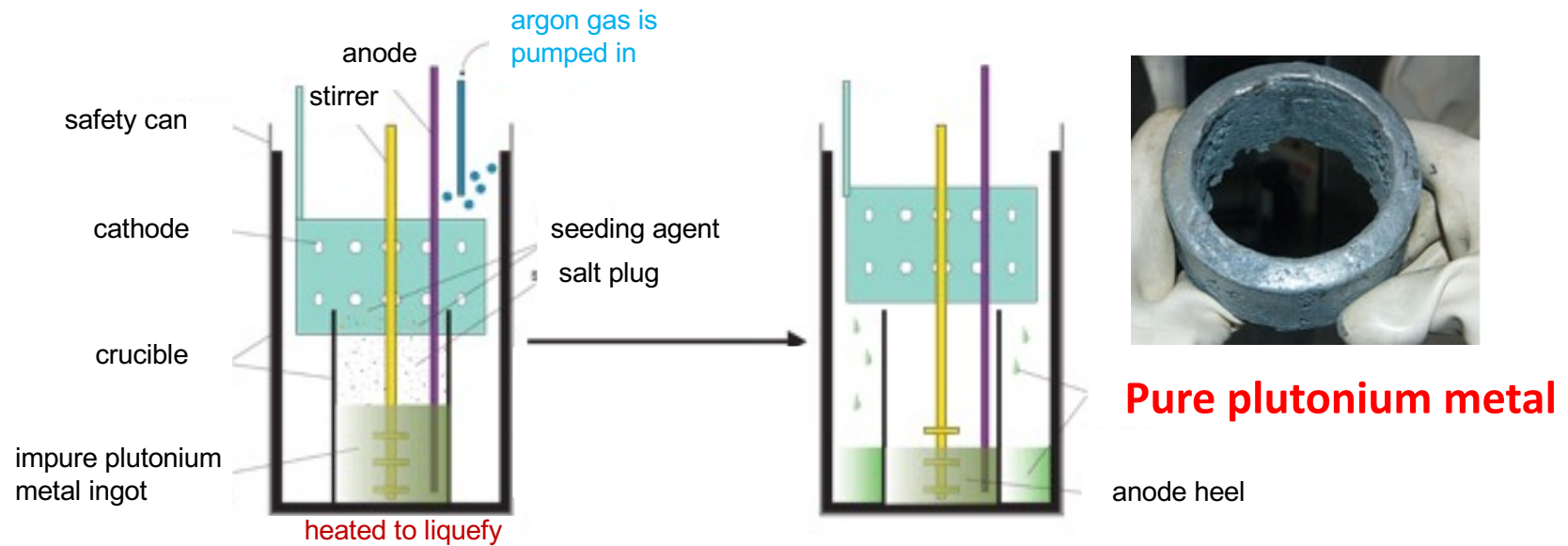


≈ 4 % of the world's electricity goes into aluminium extraction !

# Example of separation process:

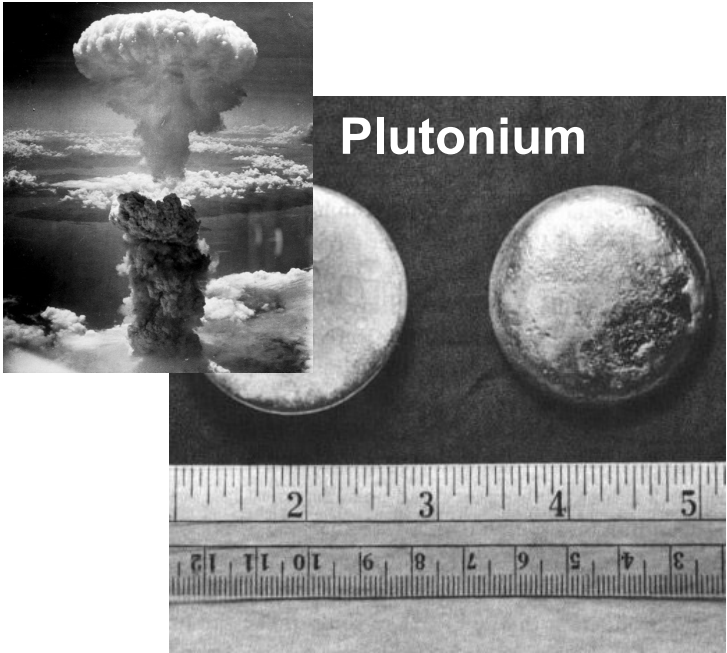
## Electrorefining

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

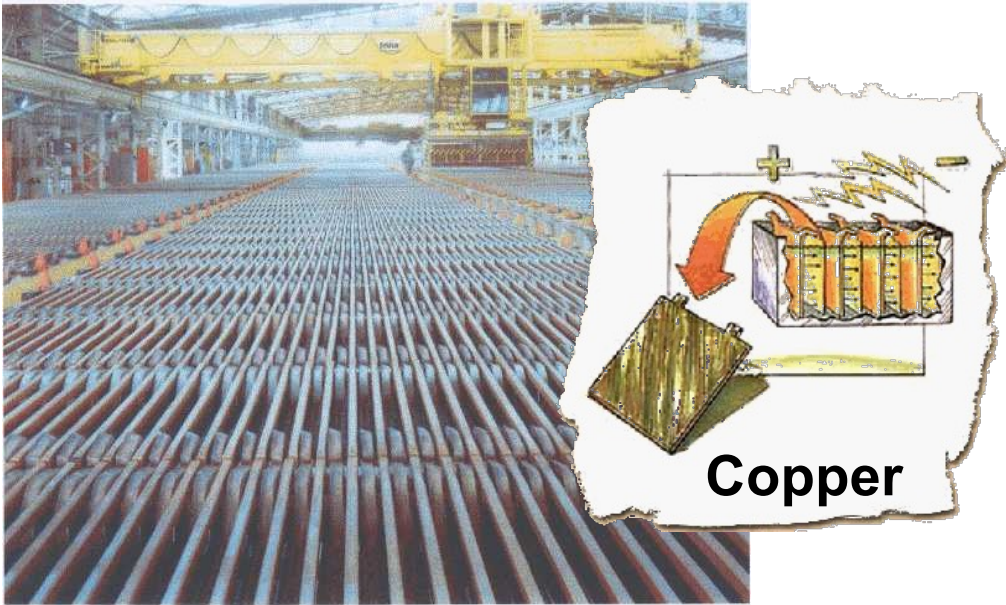


# Electrorefining

Small amounts...



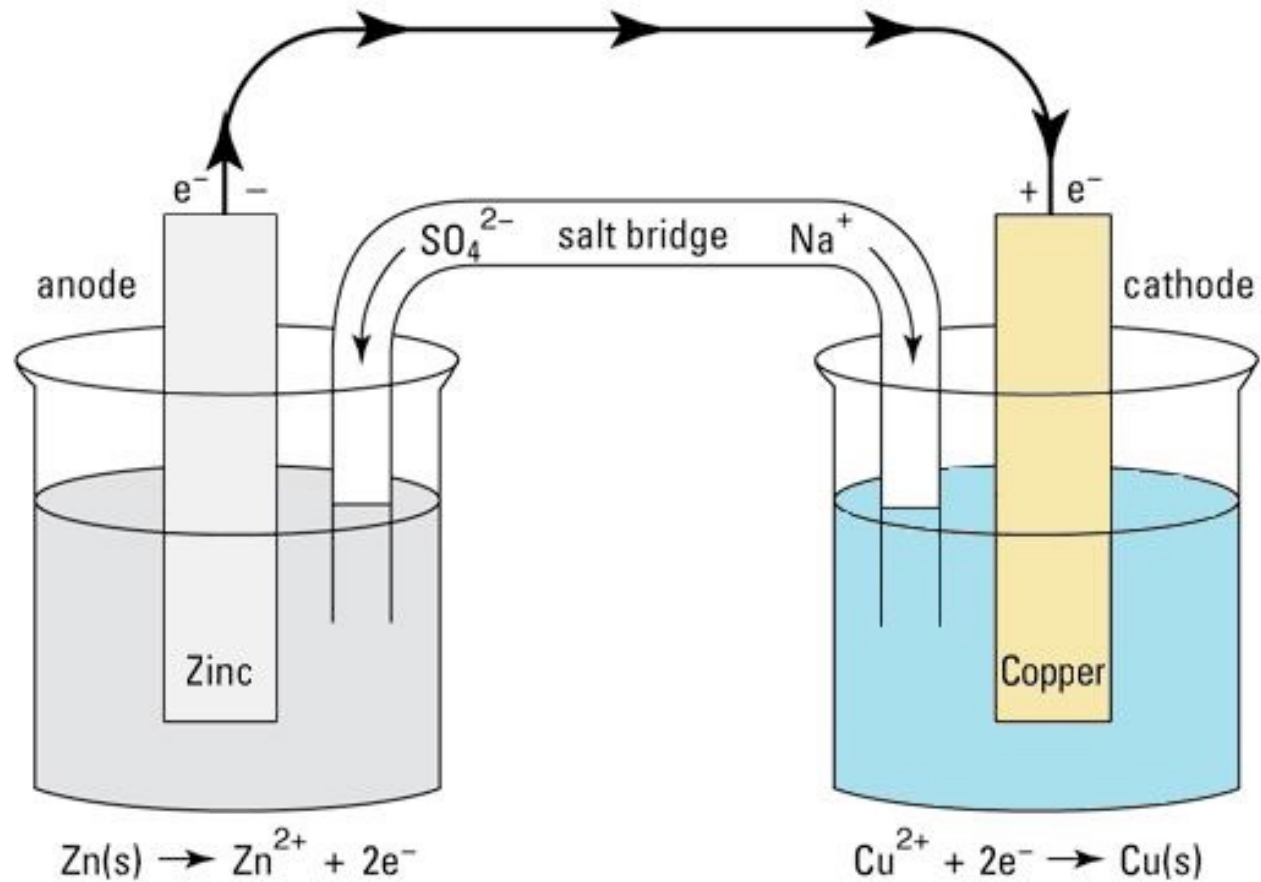
..to large amounts



# Engineering use of electrochemistry

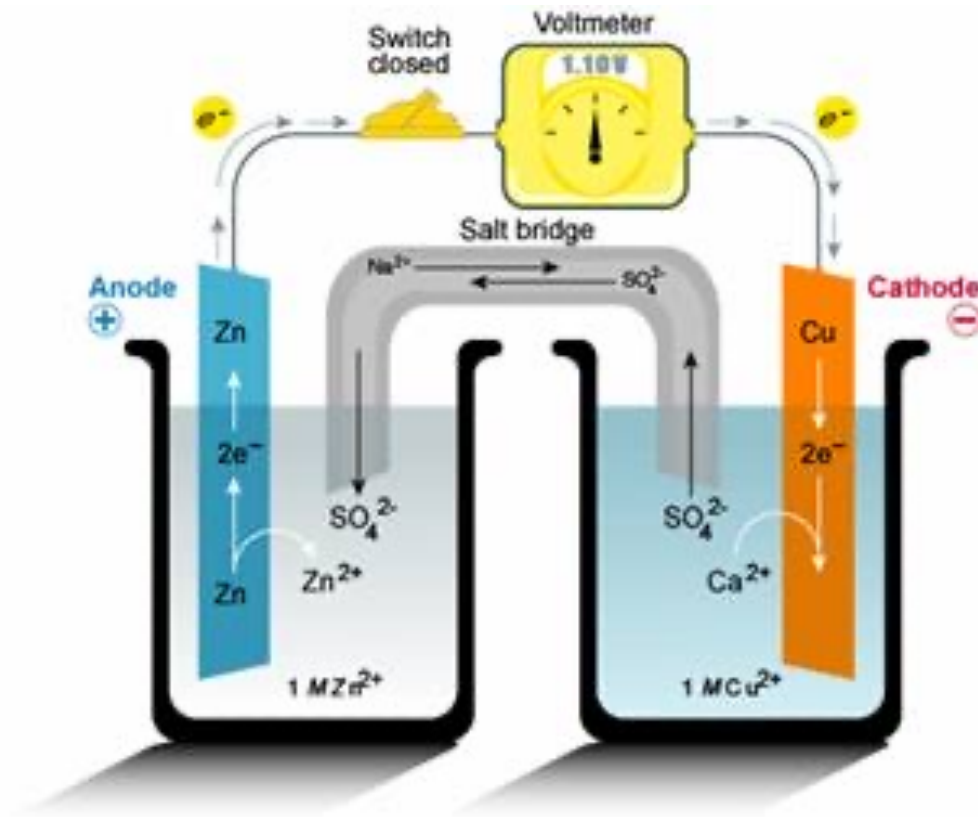
- Electrosynthesis (electricity used as separation process)
  - Production of Al, Cl<sub>2</sub>, H<sub>2</sub>, NaOH, ...
- Energy conversion / storage
  - Batteries, fuel cells, water electrolysis
- Surface treatments
  - Coatings, anodic films, polishing, electroforming, ...
- Corrosion
  - Mechanisms, protection
- Analysis and measurement
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- ...

# Chemical to electrical energy conversion: the Daniell cell

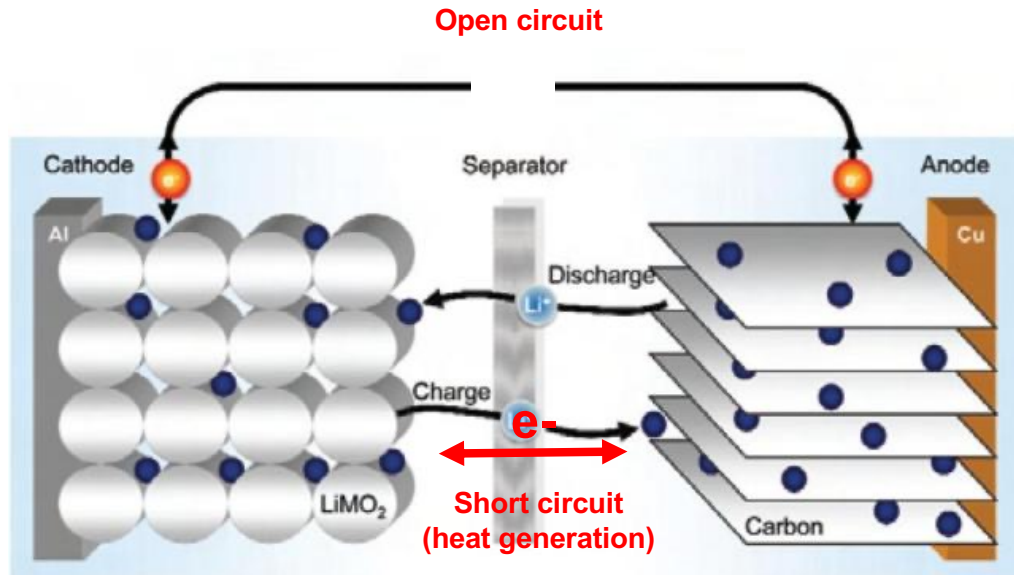


# Batteries

Storing electricity in the form of chemical energy

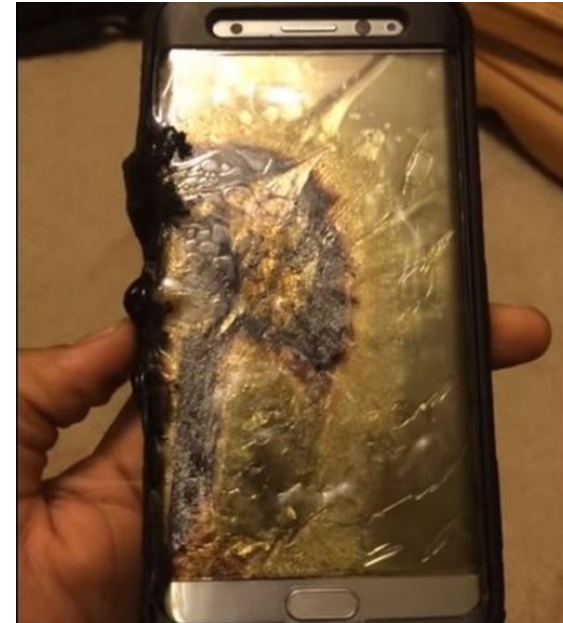


# Batteries



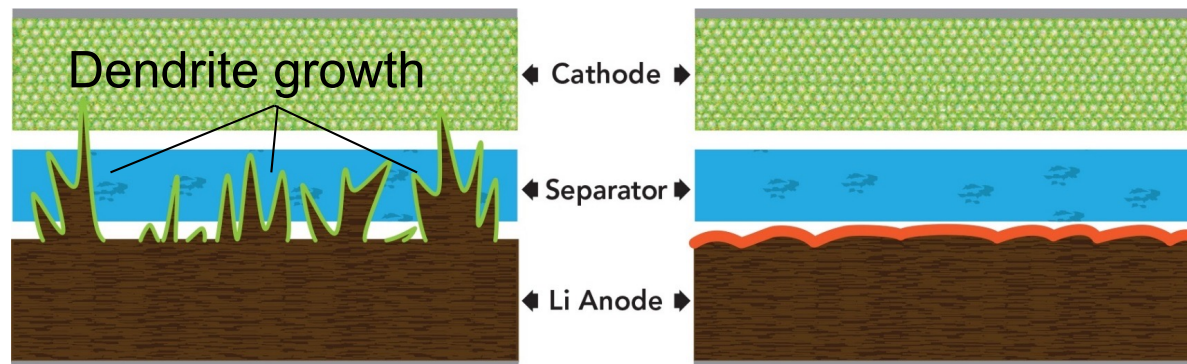
Li ion solution dissolved in **organic solvent (flammable!)**

Failure:



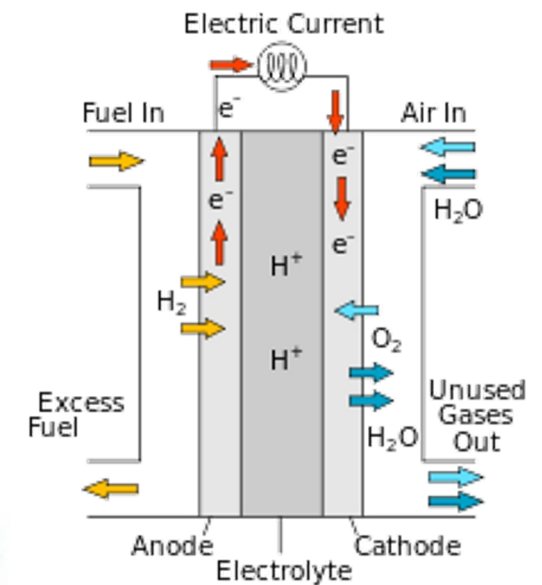
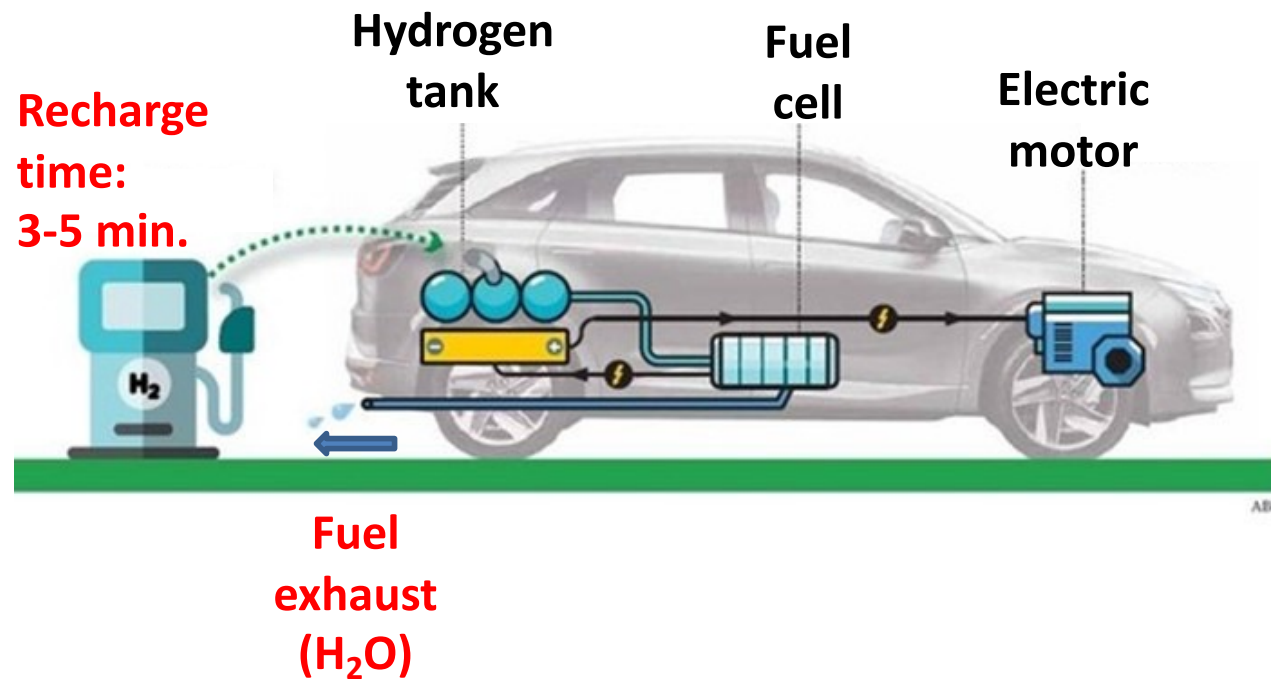
Possible causes for failure:

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



# Fuel cells

Extracting electrical energy from a fuel



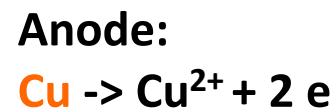
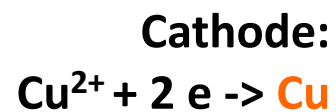
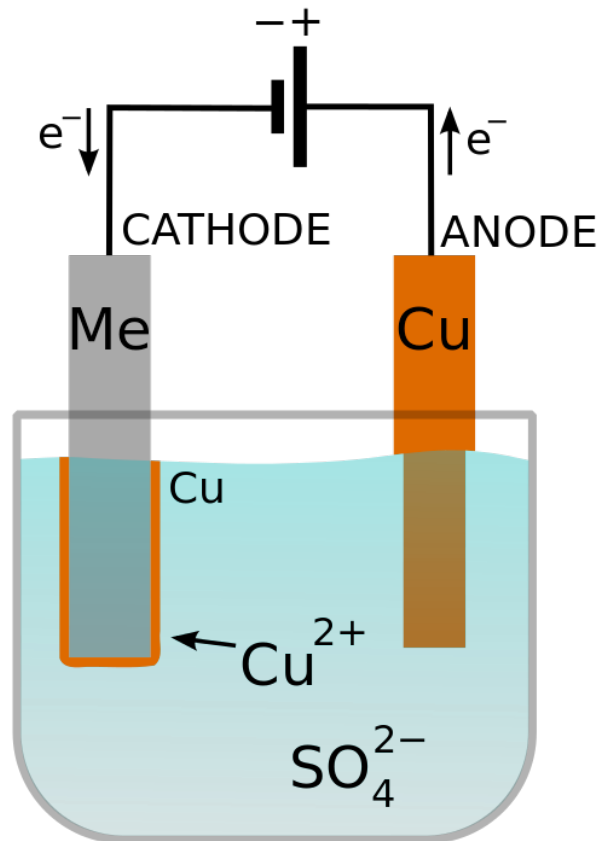
# Engineering use of electrochemistry

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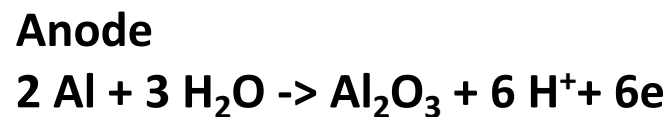
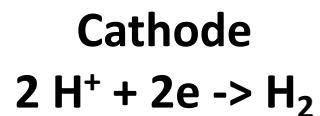
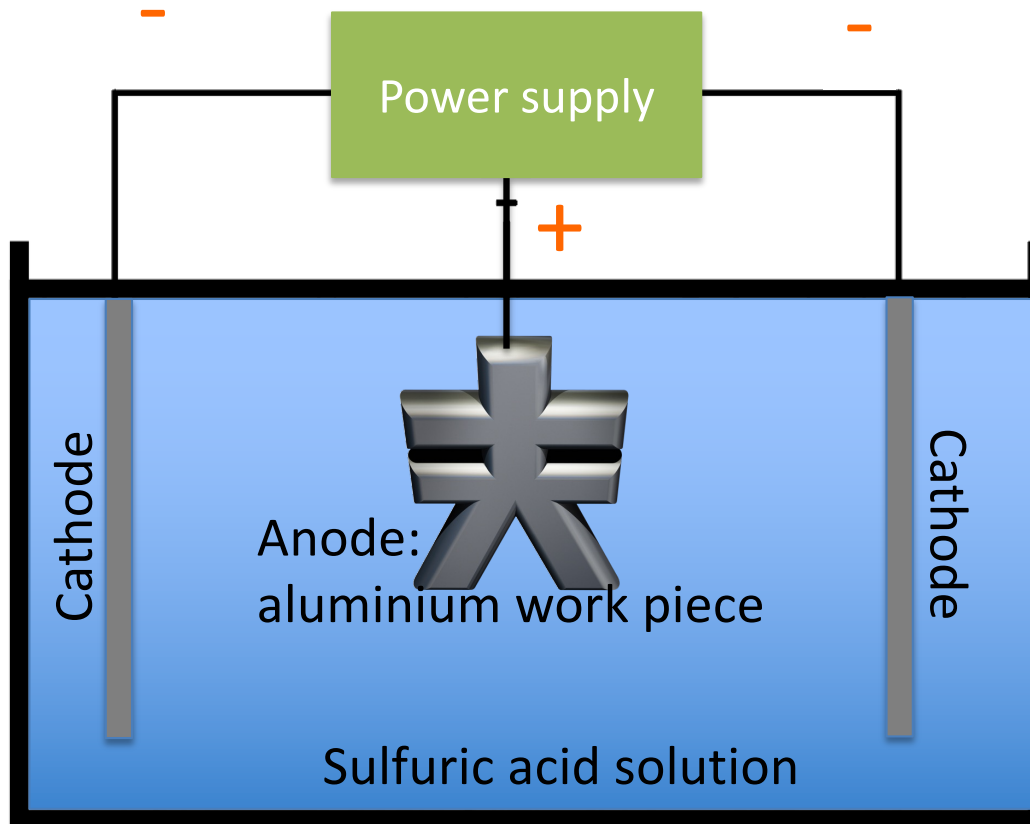
# Surface treatments by metal electrodeposition

Principle of electrodeposition

Examples of electrodeposition



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



*Car fitting component:  
anodized aluminum*

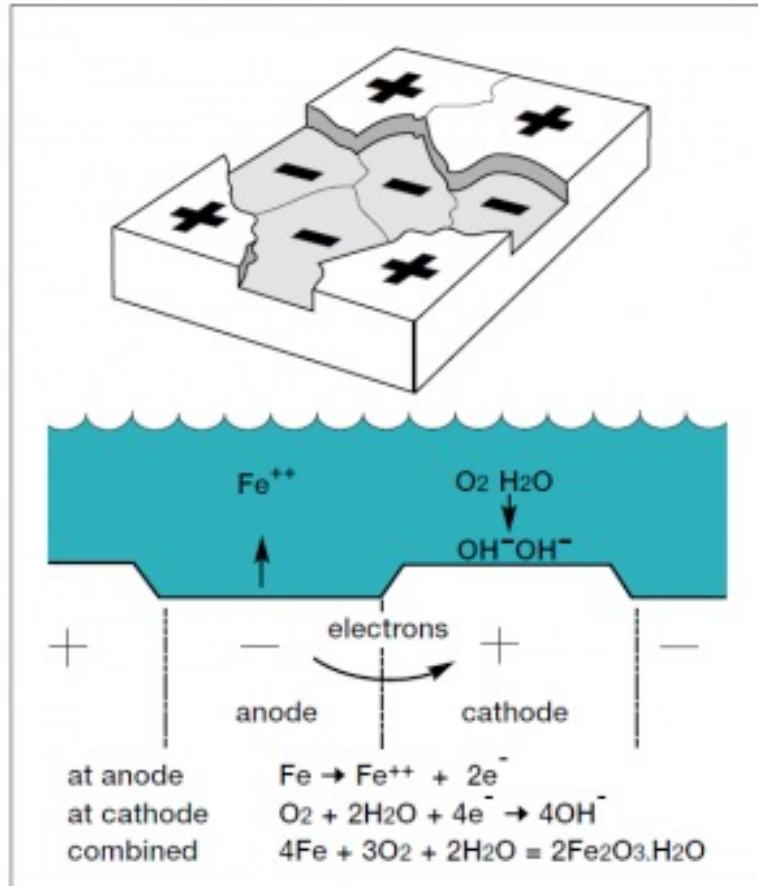


# Engineering use of electrochemistry

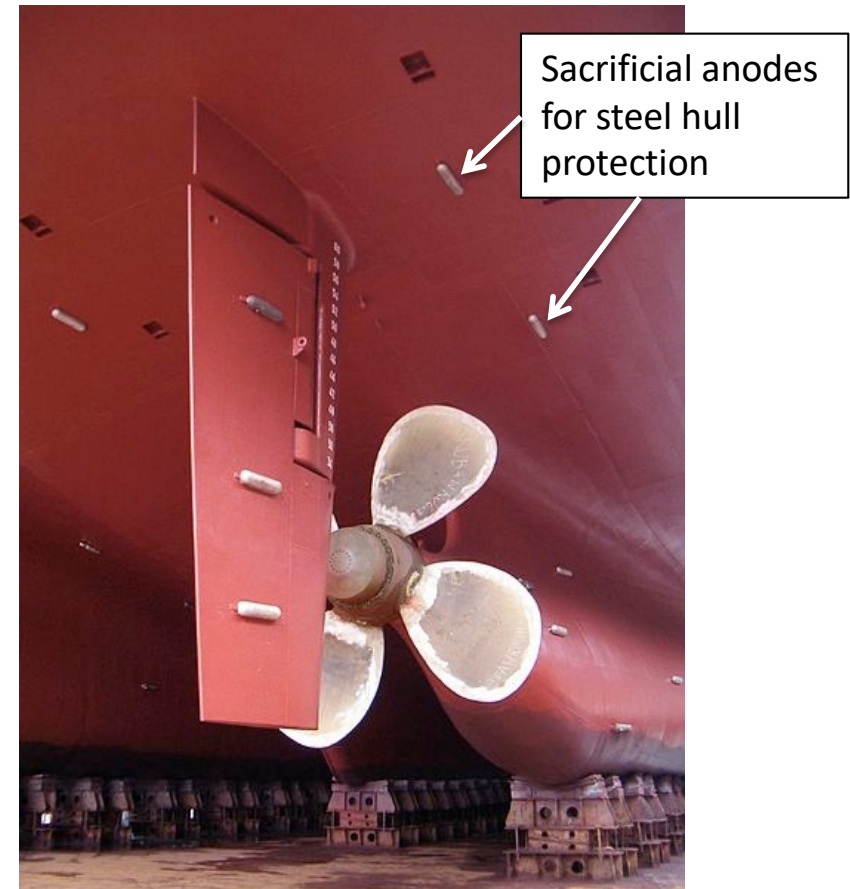
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# Corrosion

## Corrosion mechanisms

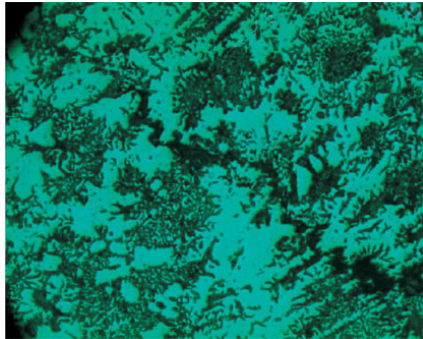


## Corrosion protection

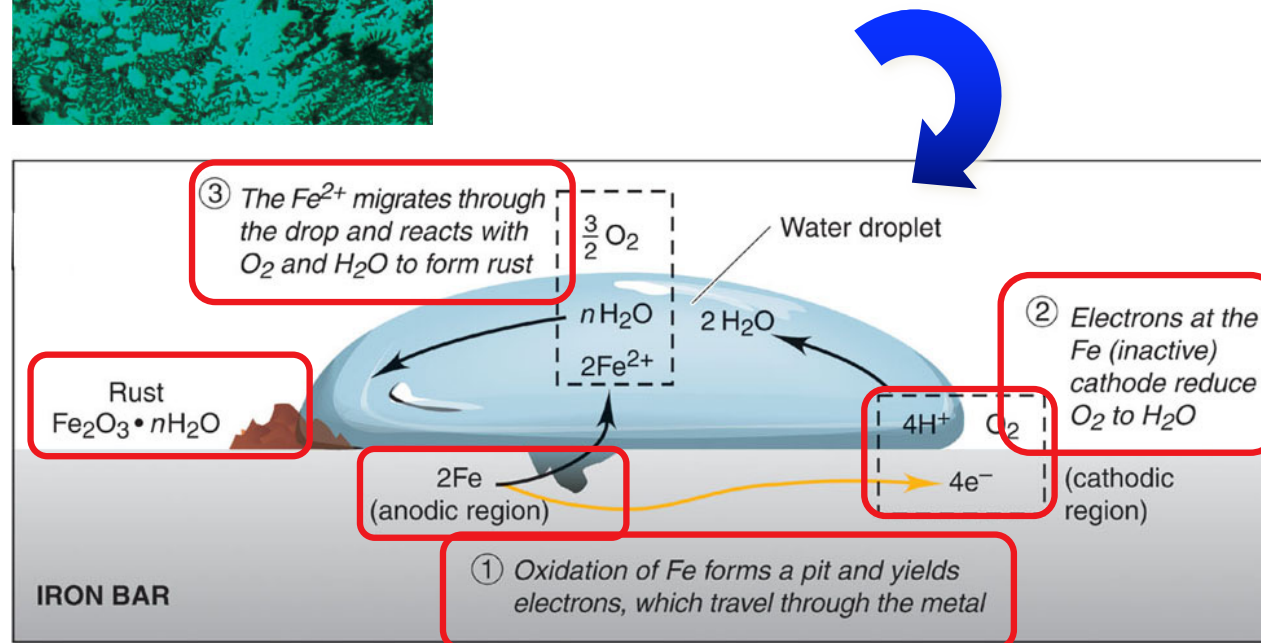


# Corrosion

Conversion of metals to metal oxides.



Corrosion of Fe is essentially a miniature electrochemical cell



# Engineering use of electrochemistry

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- Surface treatments
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- Corrosion
  - Mechanisms, protection
- Analysis and measurement
  - **Sensors** for pH, glucose, pollutants (e.g. NO<sub>x</sub>, H<sub>2</sub>S,..)
- ...

# Glucose sensor based on electrochemical oxidation of hydrogen peroxide

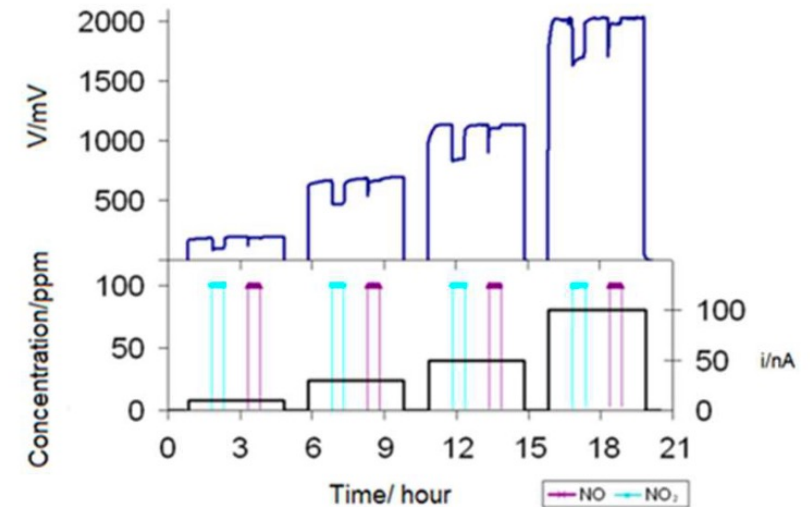
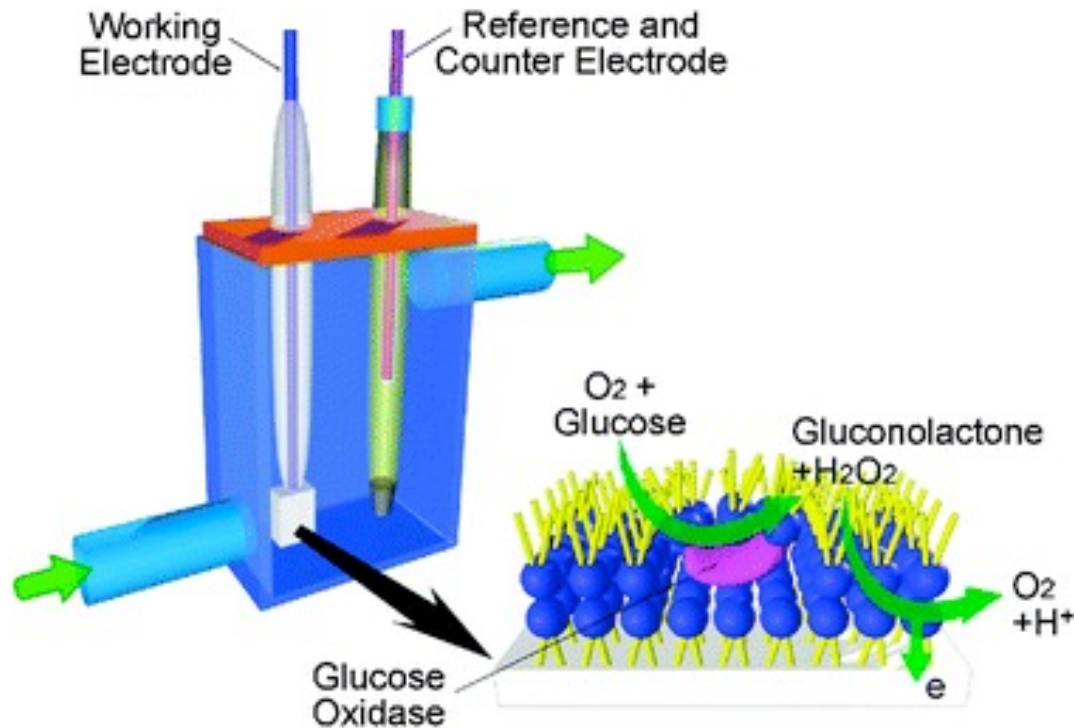


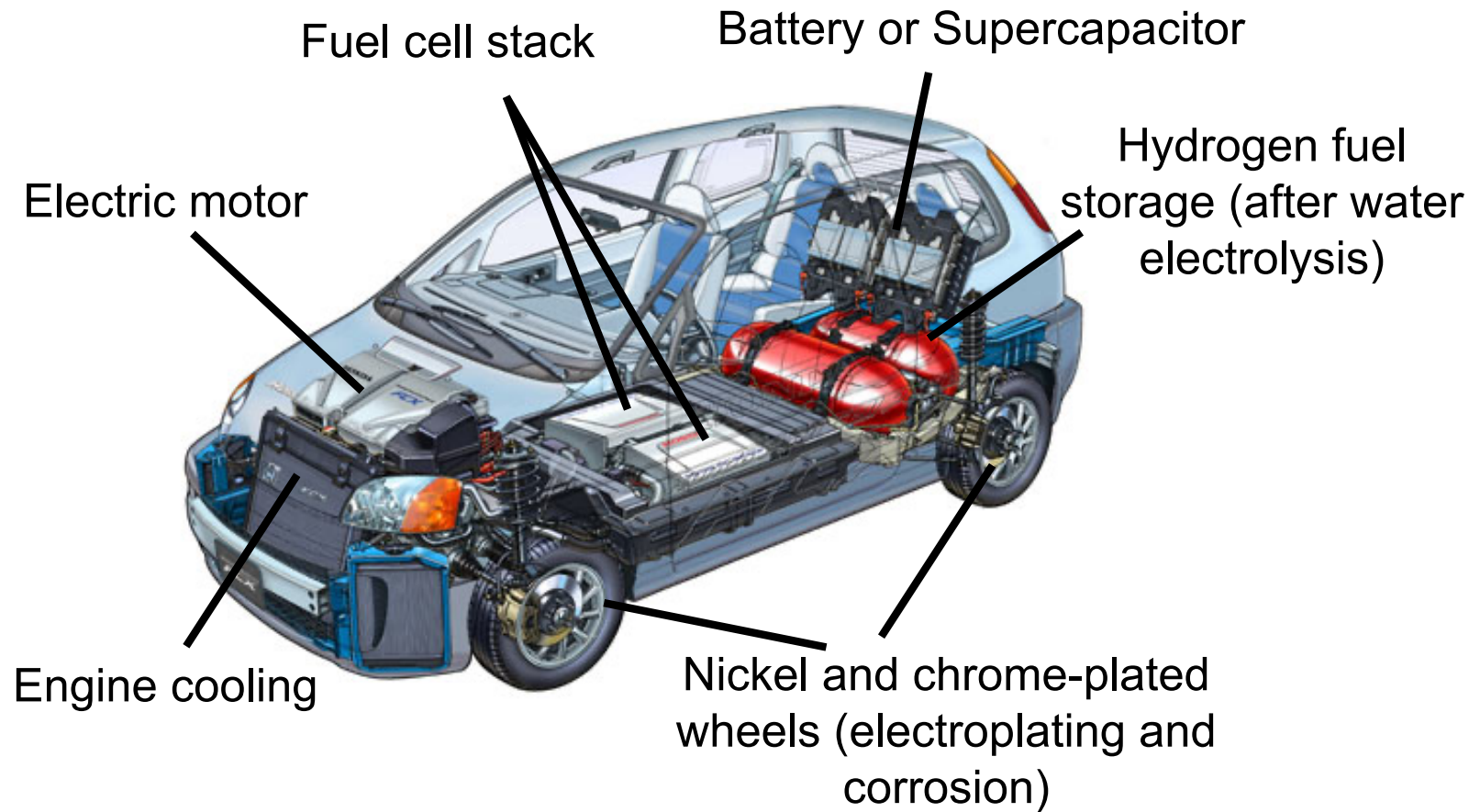
Fig. 2. Sensor response ( $\Delta V / mV$ ) at  $450^{\circ}C$  to 100ppm NO<sub>2</sub>/NO (O<sub>2</sub> 12vol.%, H<sub>2</sub>O 2vol.%) at different polarizations (i / nA).



Other examples :

- NO<sub>2</sub>-sensor for engine exhaust <https://www.sciencedirect.com/science/article/pii/S187770581633421X>
- Lambda-sensor (O<sub>2</sub>) for 3-way cat regulation for gasoline engines

# Multiple combined applications of electrochemistry



# Other related courses

- ~~Electrosynthesis (CHE407)~~
- **Energy storage and conversion**
- **Surface treatments**
- 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](http://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