



Electrochemistry

A science with many potentials

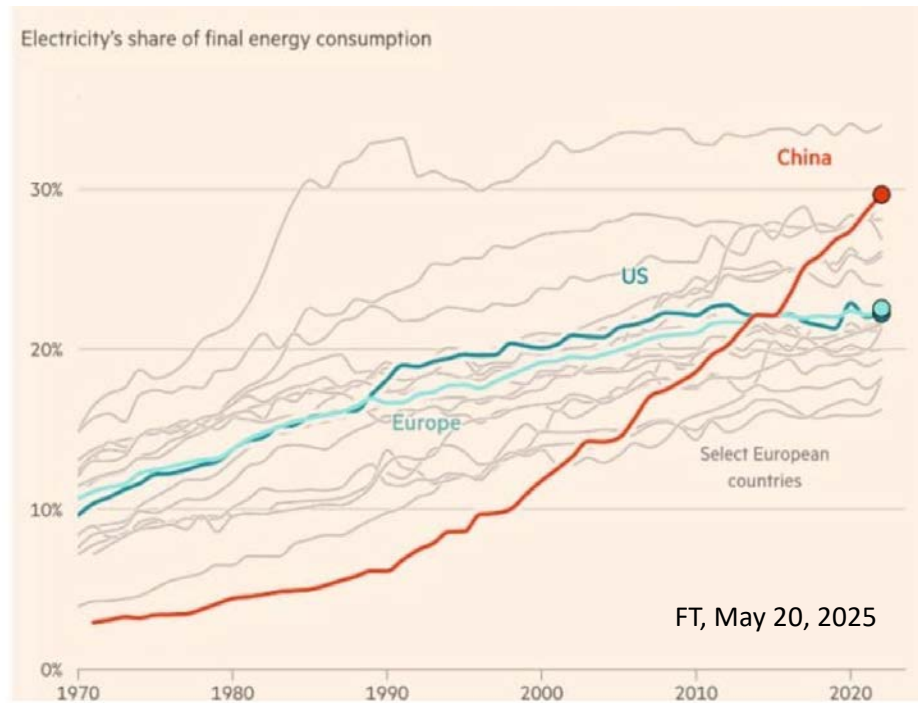
Prof. Hubert Girault

11.09.2025

EPFL

Electrification : The major challenge of the 21st century

Electrochemistry is a core science of electrification



Challenges:

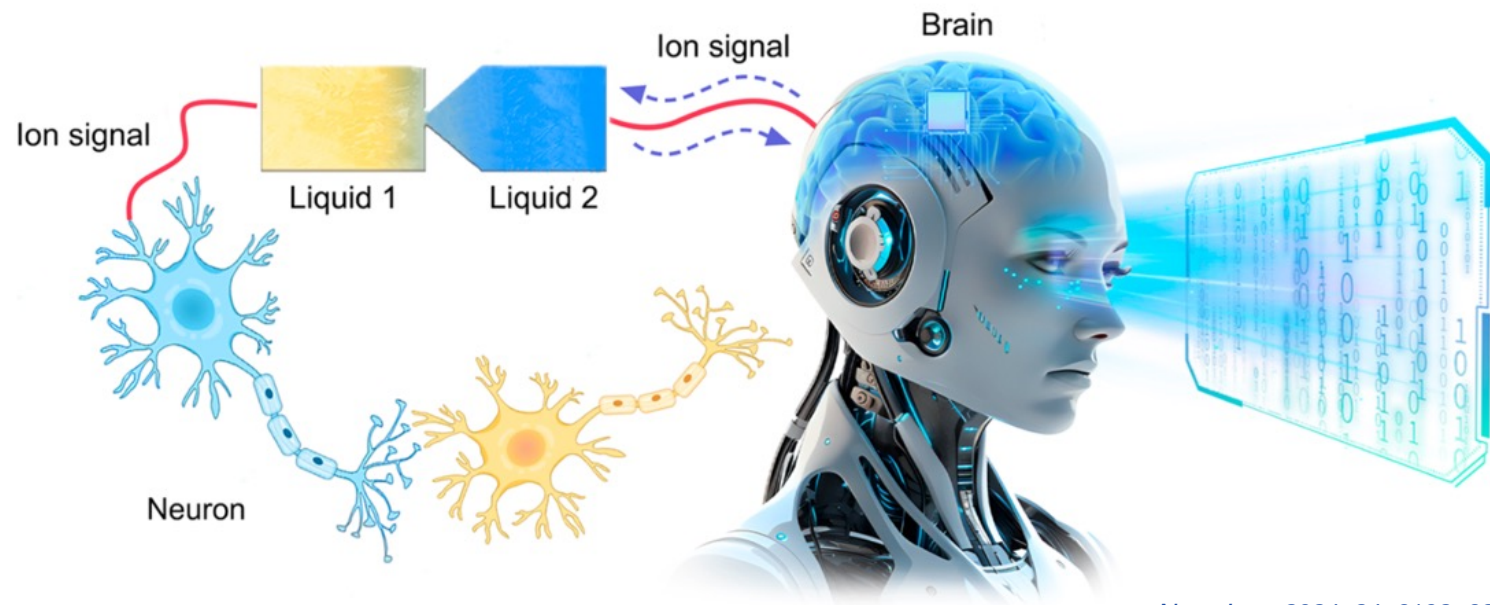
Renewable energy storage

Green hydrogen production

Powering AI

- China leads the world in electrification, with a 30% electrification rate—far ahead of the U.S. and EU at ~22%—dominating sectors like transport and industry.

Iontronics



Nano Lett. 2024, 24, 6192–6200

When electrochemistry at liquid-liquid interfaces meets ion transport in nanofluidics, the ionic computer becomes feasible.

The human brain consumes about **20 W** of power on average... as a dim light bulb.

- **Energy source:** The brain gets its energy from glucose, delivered via the bloodstream.
- **Oxygen consumption:** It uses about **20% of the body's oxygen supply**, despite being only about 2% of the body's mass.



One Graphic Processing Unit , e.g.
NVIDIA A100 s consumes 300 to 400 W

A neuron consumes about 10
picowatts during active firing. With ~86
billion neurons, the brain's total power
usage (~20 watts) makes sense.

Plan



Potentials and redox reactions

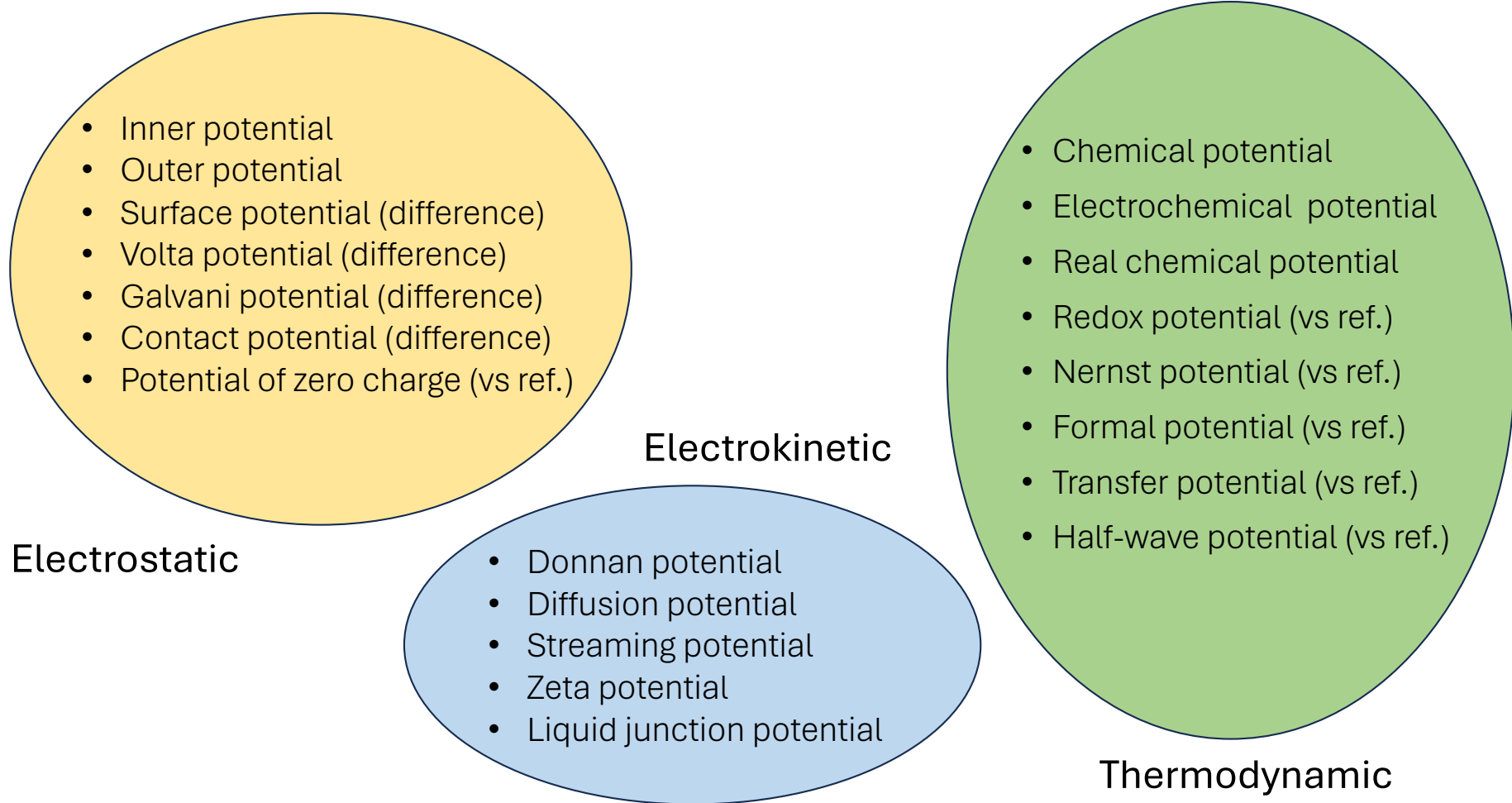


Li-ion battery

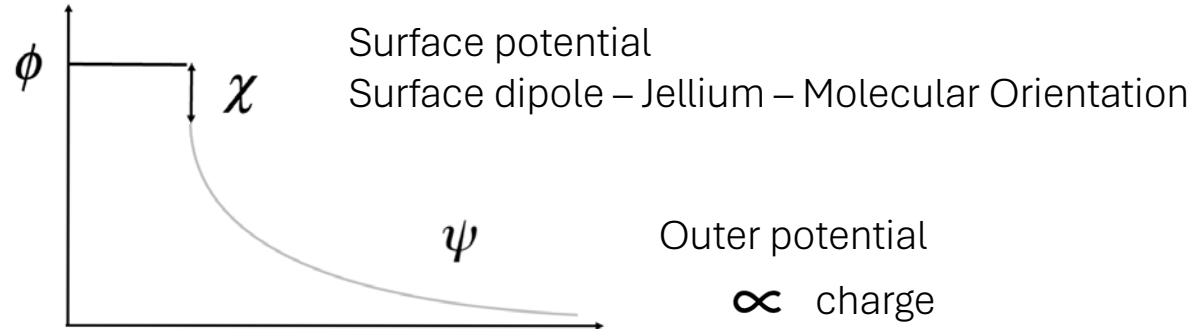
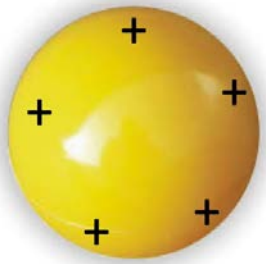


Water electrolysis

Potentials in electrochemistry



Inner Potential



The inner potential is constant for a given phase, neutral by definition $\phi = \chi + \psi$

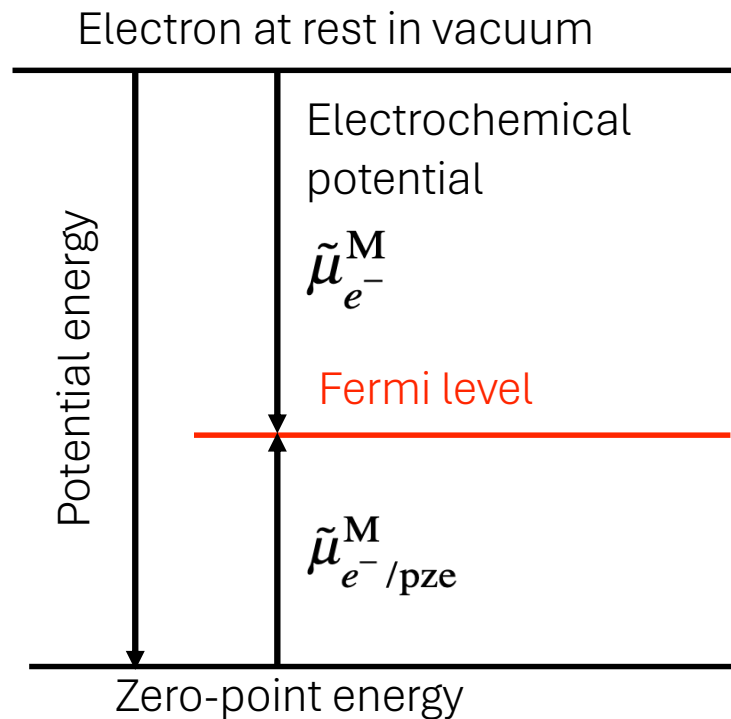
Electrochemical Potential

$$\tilde{\mu}_i = \mu_i^\ominus + RT \ln a_i + z_i F \phi$$

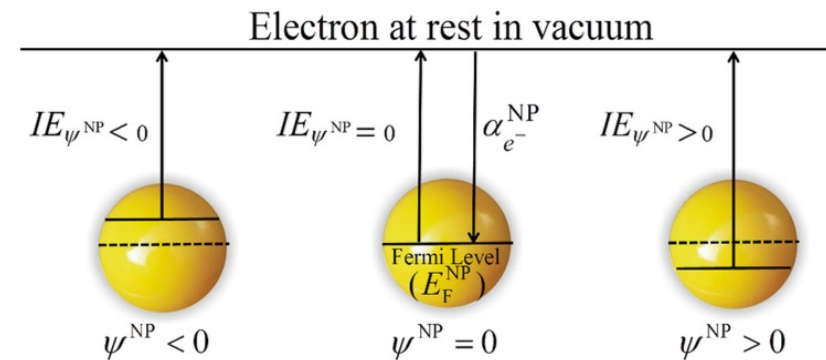
Work to transfer a charged species from vacuum to a phase

Electrochemical potential of an electron in a metal

$$\tilde{\mu}_{e^-}^M = \mu_{e^-}^M - F\phi^M = (\mu_{e^-}^M - F\chi^M) - F\psi^M = \alpha_{e^-}^M - F\psi^M$$

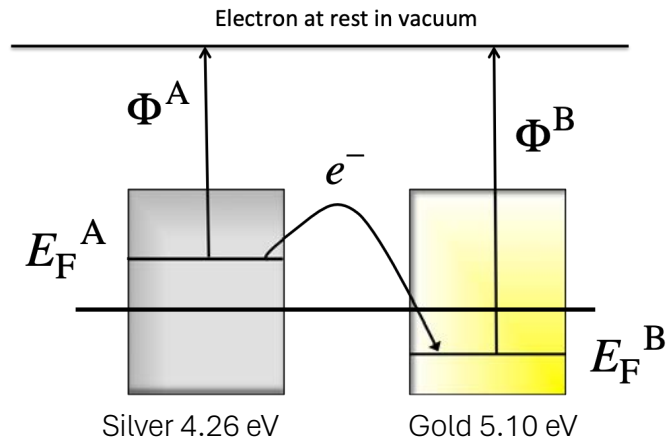


Work function $\Phi^M = -\alpha_{e^-}^M$



The Fermi level varies with the charge

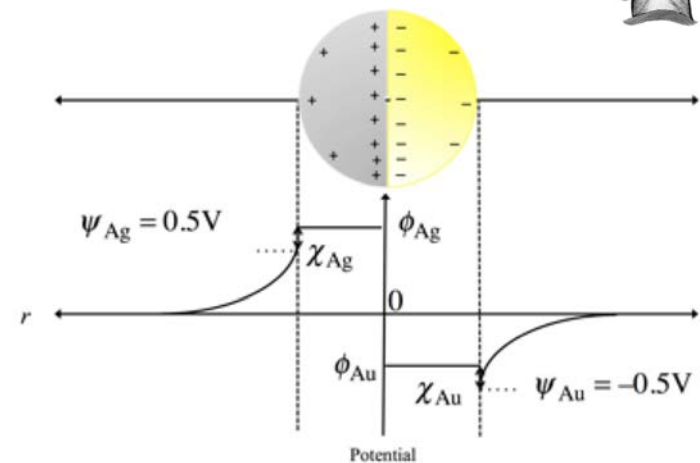
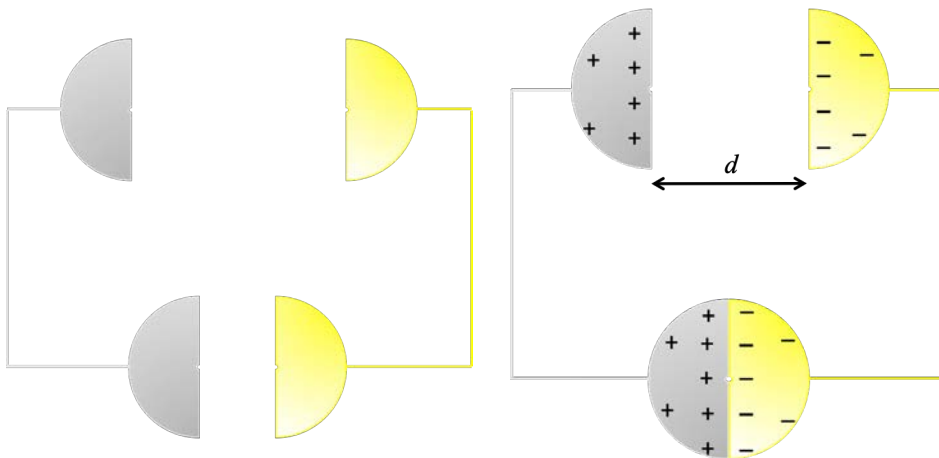
Contact potential (difference)



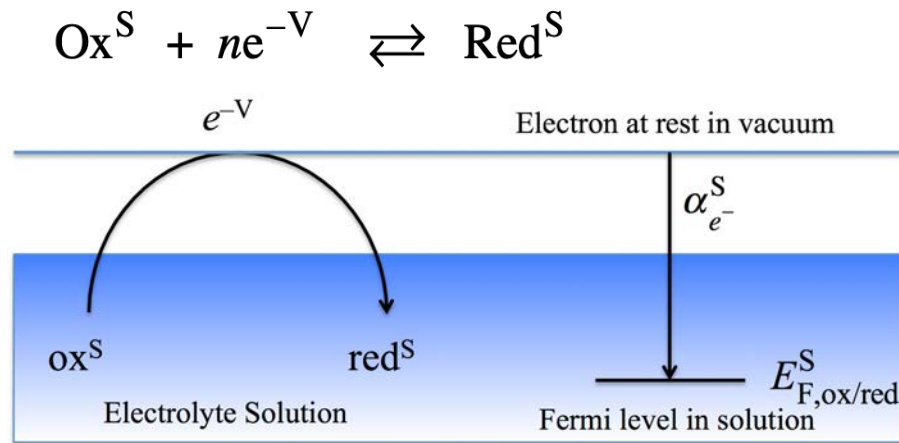
Electronic equilibrium
Volta potential difference

$$\psi^B - \psi^A = [\alpha_{e^-}^B - \alpha_{e^-}^A] / e = [\Phi^A - \Phi^B] / e$$

Janus particle



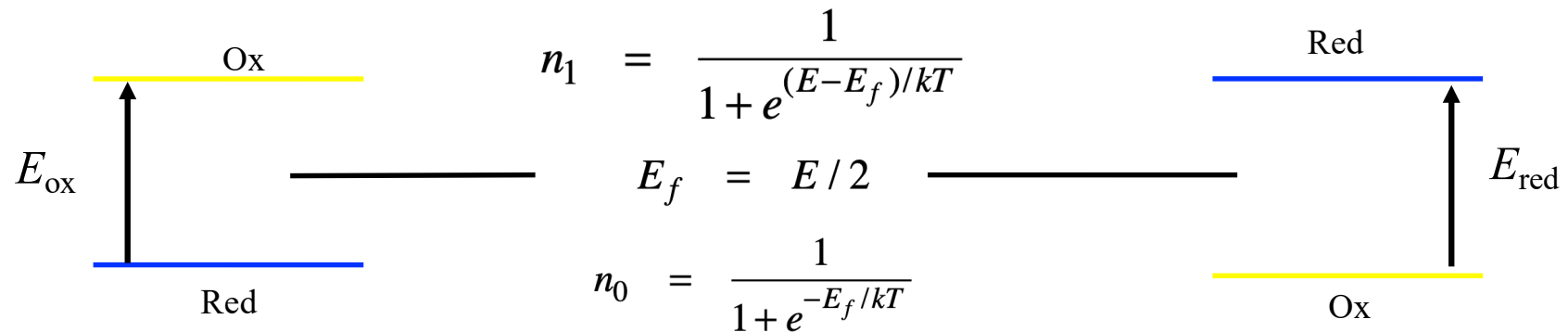
Fermi level for a redox couple in solution



$$\begin{aligned}
 \left[E_{\text{ox/red}}^{\ominus} \right]_{\text{abs}} &= -\frac{\Delta \tilde{G}_r^{\ominus}}{nF} = \frac{\tilde{\mu}_{\text{ox}}^{\ominus,S} - \tilde{\mu}_{\text{red}}^{\ominus,S}}{nF} \\
 &= \frac{\alpha_{\text{ox}}^{\ominus,S} - \alpha_{\text{red}}^{\ominus,S}}{nF} + \psi^S
 \end{aligned}$$

$$-\alpha_{e^-}^S = e \left[E_{\text{ox/red}} \right]_{\text{AVS}, \psi^S=0}^S = \alpha_{\text{ox}}^S - \alpha_{\text{red}}^S$$

Two state Fermi-Dirac statistics





Zeitschrift für Physikalische Chemie Neue Folge, Bd. 26, S. 223 – 247 (1960)

Über den Ablauf von Redoxreaktionen an Metallen und an Halbleitern

I. Allgemeines zum Elektronenübergang zwischen einem Festkörper und einem Redoxelektrolyten

Von

H. GERISCHER

Max-Planck-Institut für Metallforschung, Stuttgart

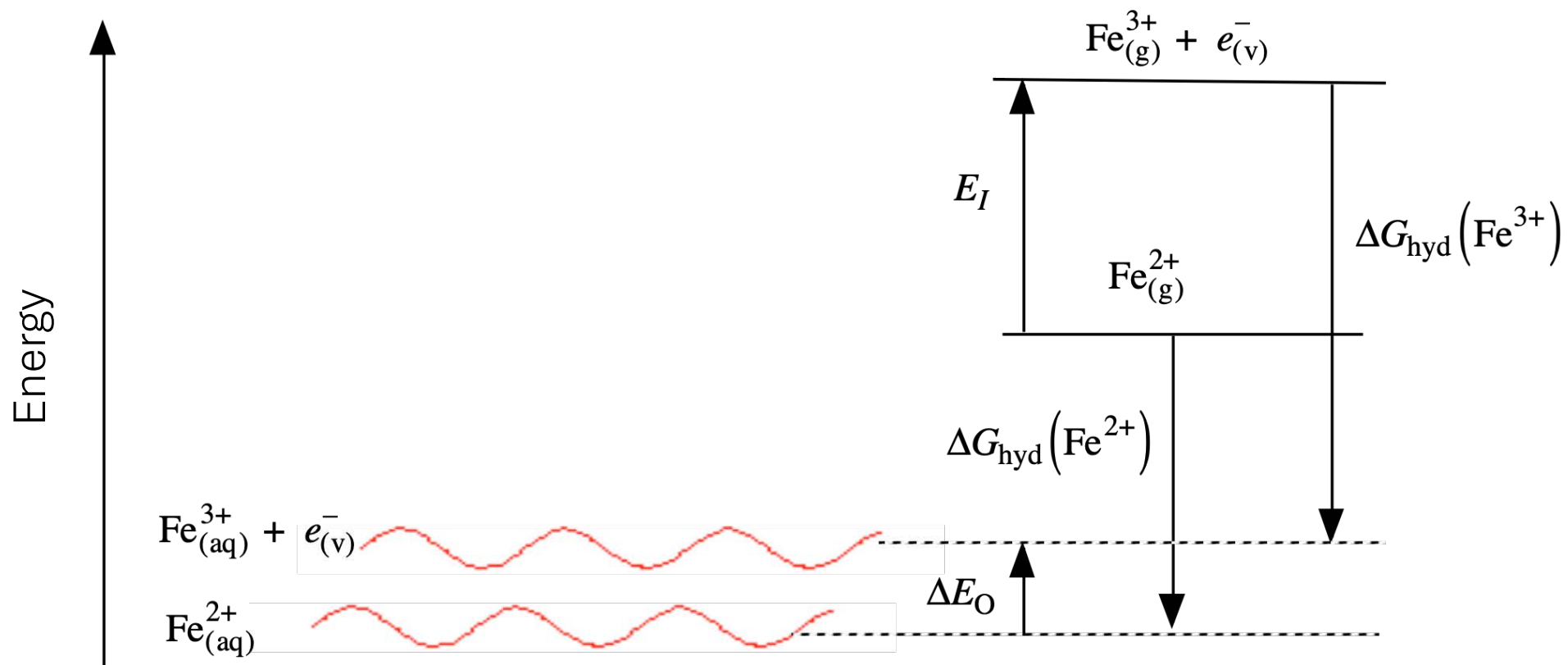
Mit 7 Abbildungen im Text

(Eingegangen am 10. Mai 1960)

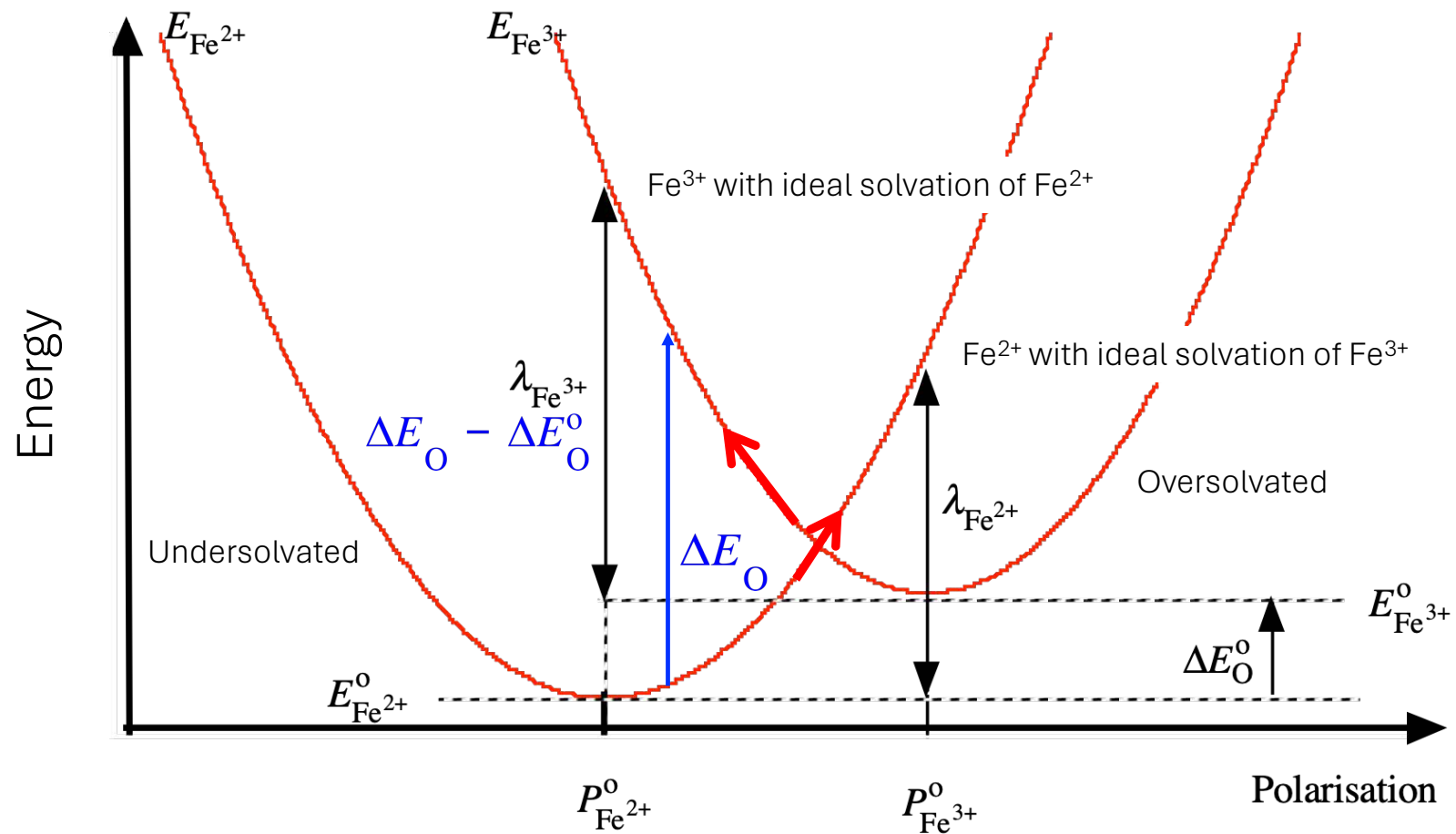
Redox reactions at metals and semiconductors

General information on electron transfer between a solid
and a redox electrolyte

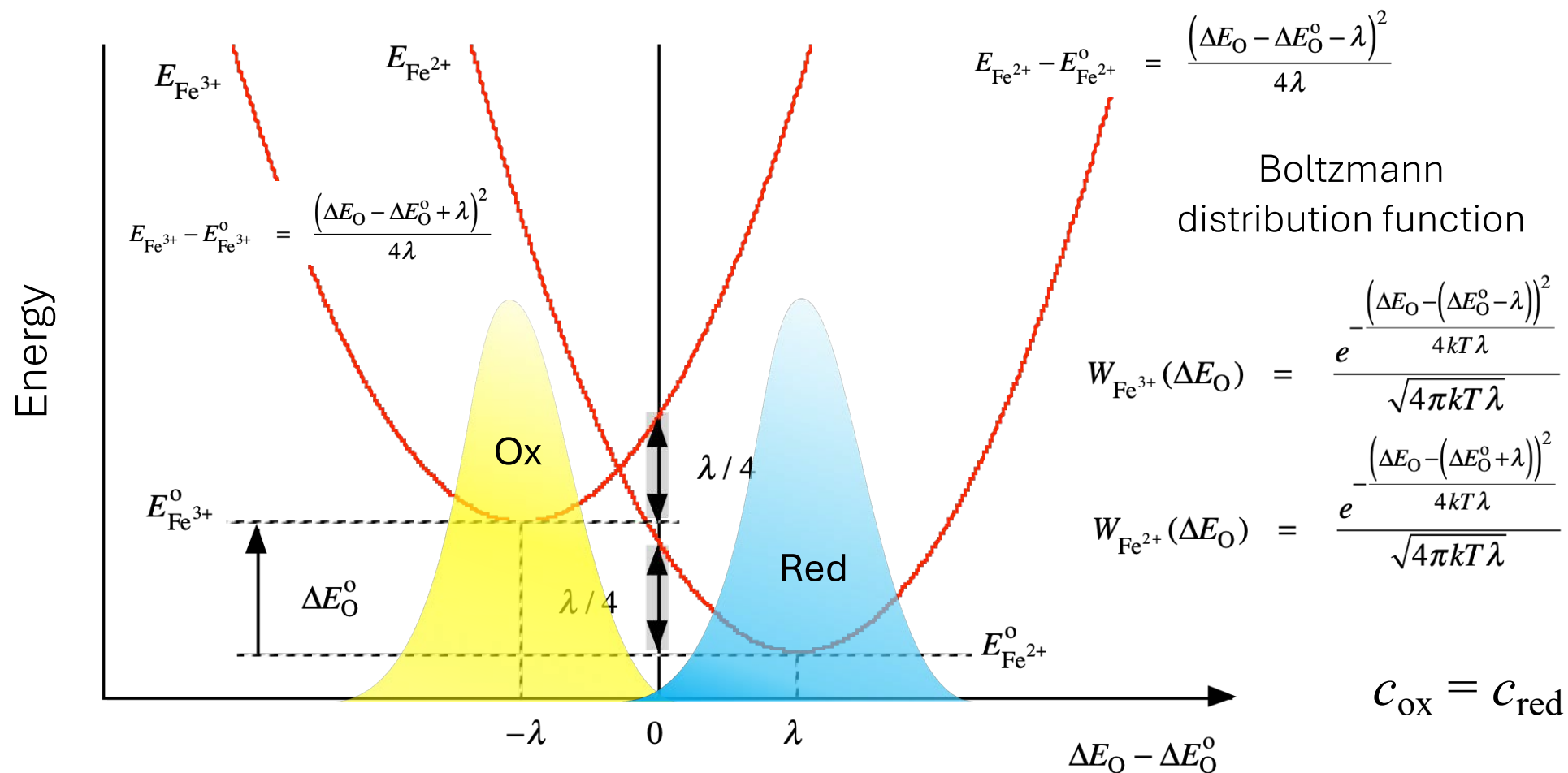
Oxidation energy in solution



Solvent re-organisation energy



Ion energy – Oxidation energy diagram



Distribution function

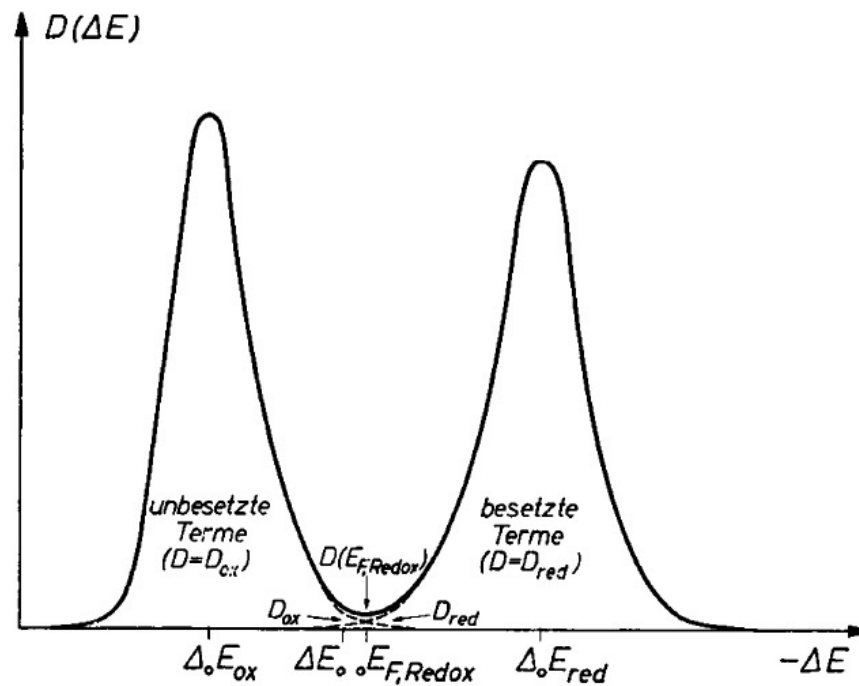
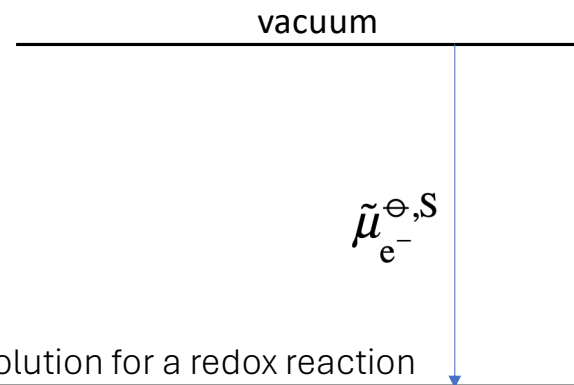
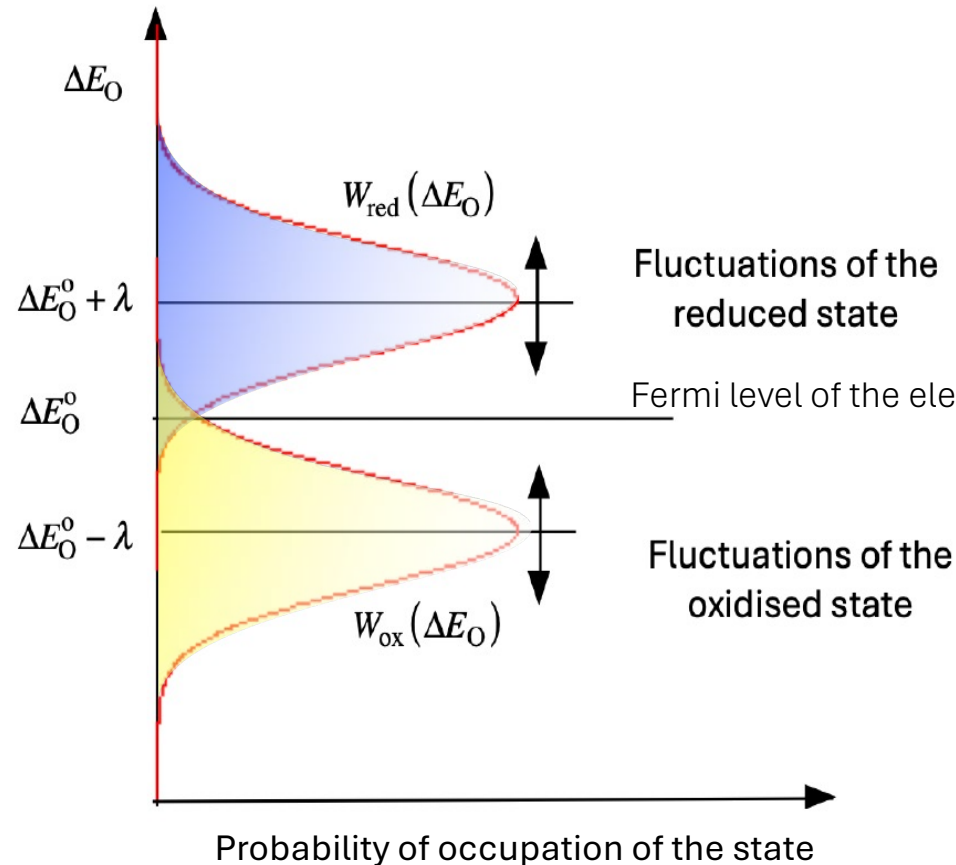


Abb. 3. Verteilungsfunktion der Energieterme für Elektronen im Redoxelektrolyten bei $c_{ox} = c_{red}$ (schematisch)

Distribution function of the energy terms for electrons in the redox electrolyte at $c_{ox} = c_{red}$ (schematic)"

Gerischer diagram for oxidation



$$E_{\text{abs}} = \left[E_{\text{ox/red}}^{\ominus} \right]_{\text{abs}} + \frac{RT}{F} \ln \left(\frac{c_{\text{ox}}}{c_{\text{red}}} \right)$$

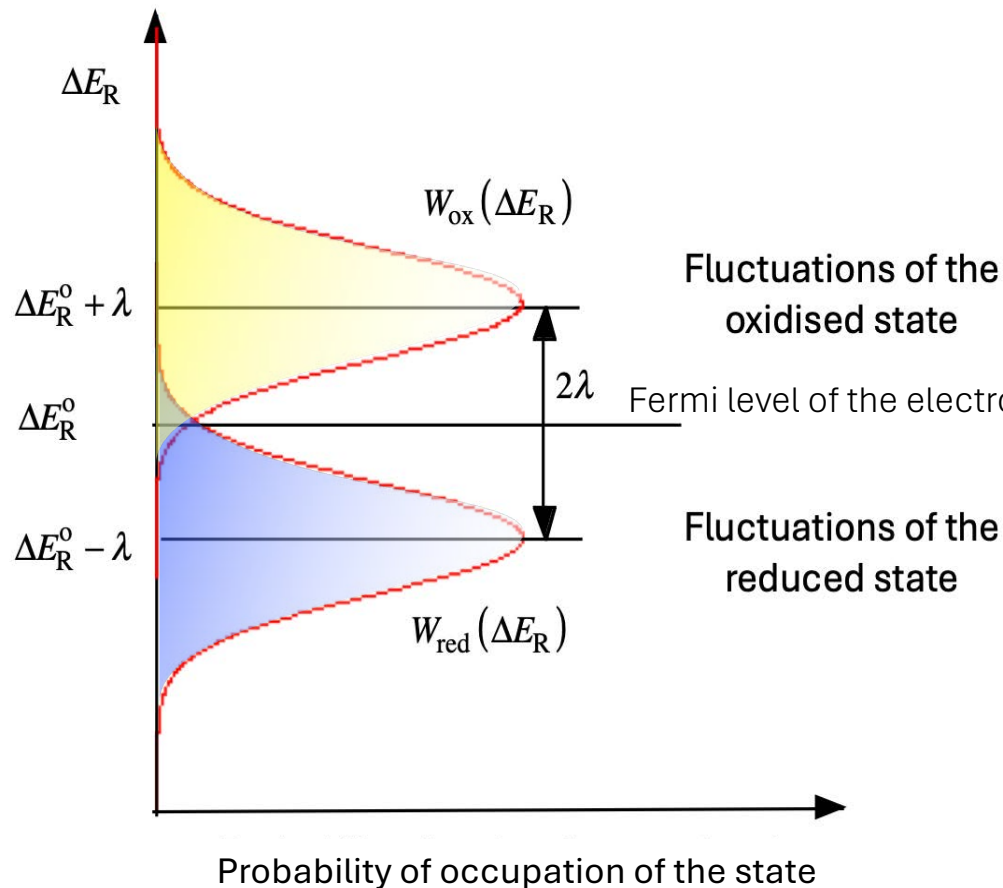
W. Nernst



1889
Habilitation
Thesis
Electromotive
force

1864-1941

Gerischer diagram for reduction



vacuum

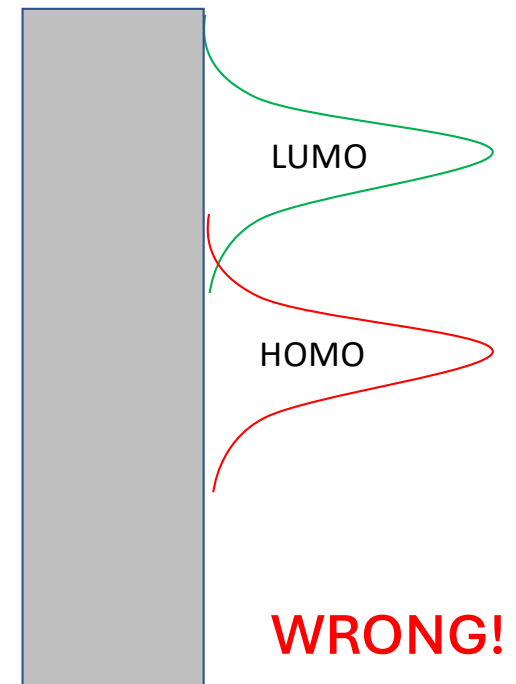
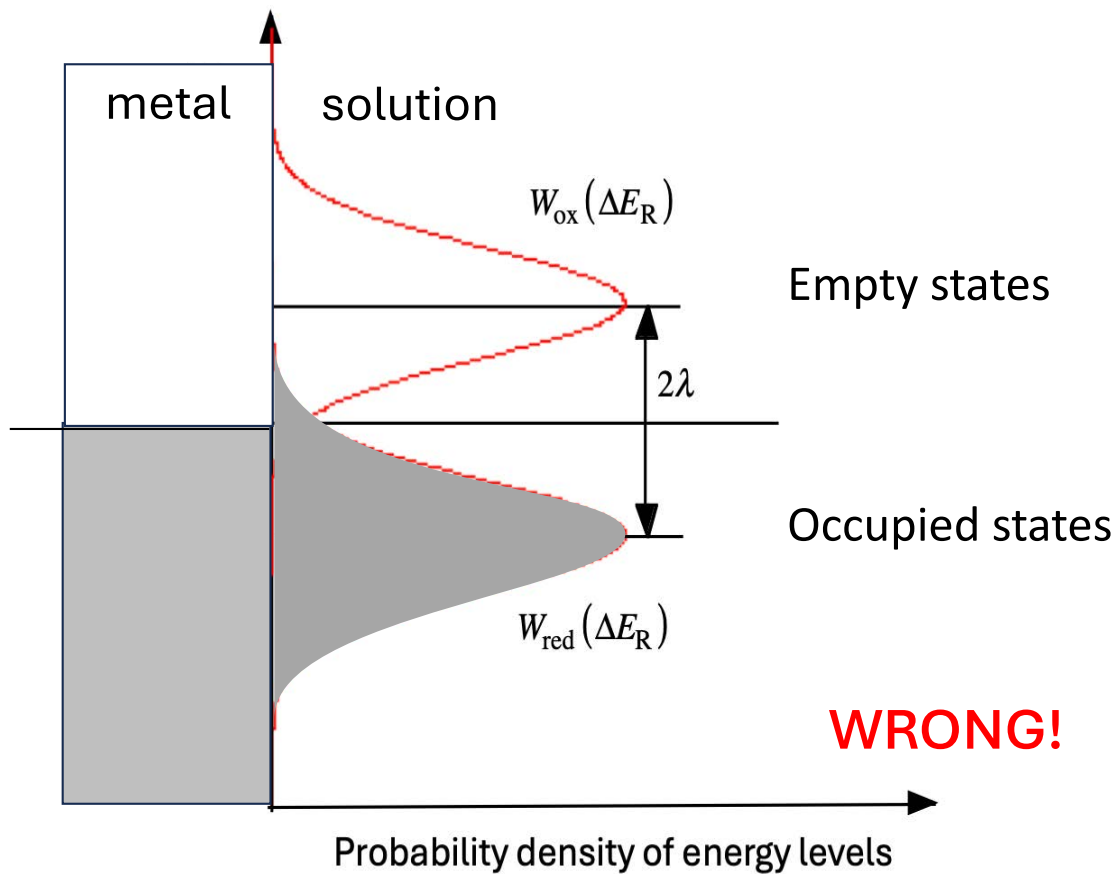
$\tilde{\mu}_{e^{-}}^{\ominus, S}$

Fermi level of the electron in solution for a redox reaction

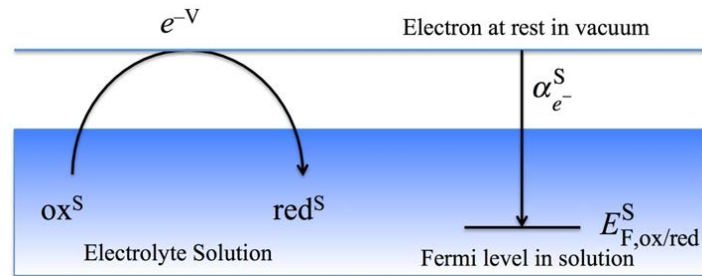
$$E_{\text{abs}} = \left[E_{\text{ox/red}}^{\ominus'} \right]_{\text{abs}} + \frac{RT}{F} \ln \left(\frac{c_{\text{ox}}}{c_{\text{red}}} \right)$$

Lost in translation...

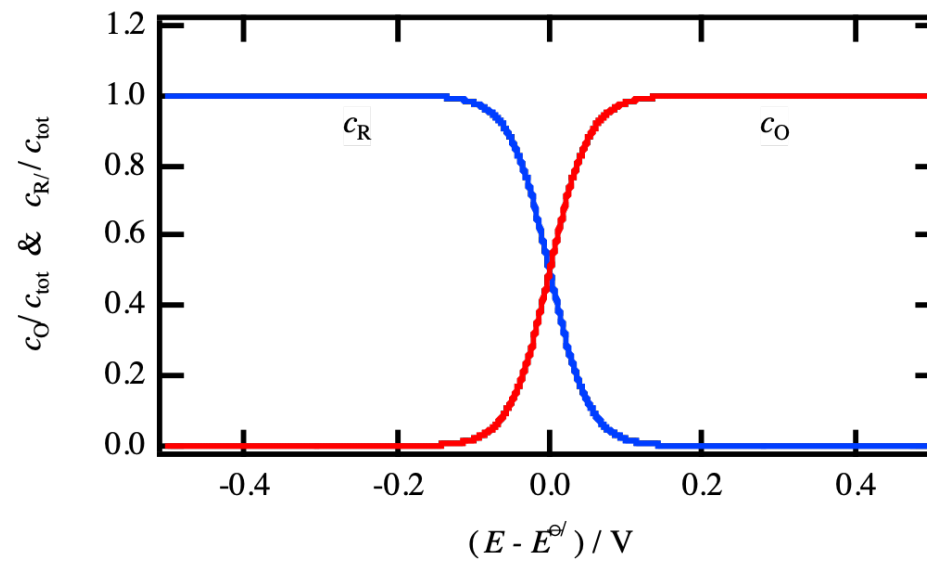
Misconception on the Gerischer diagram



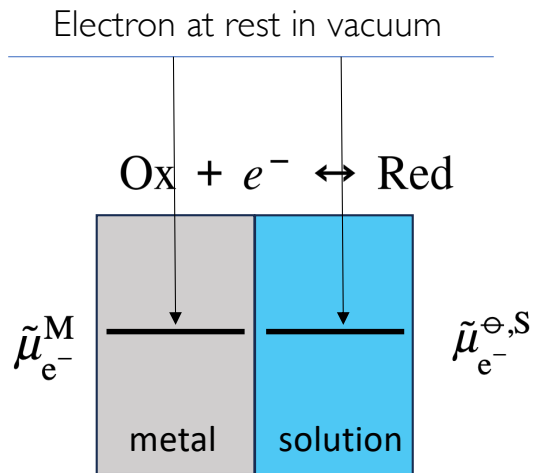
Nernst equation . Two state Fermi-Dirac statistics



$$E_{\text{abs}} = \left[E_{\text{ox/red}}^{\ominus} \right]_{\text{abs}} + \frac{RT}{F} \ln \left(\frac{c_{\text{ox}}}{c_{\text{red}}} \right)$$



Electron transfer reactions



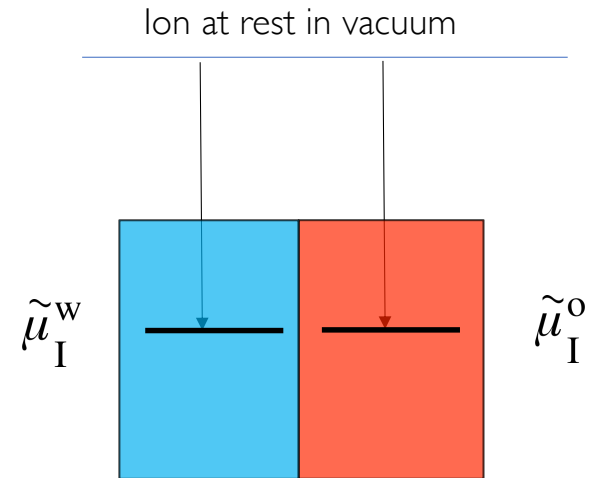
At equilibrium

$$\text{with } \tilde{\mu} = \mu^{\ominus} + RT \ln a + zF\phi$$

$$E_{\text{abs}} = \left[E_{\text{ox/red}}^{\ominus} \right]_{\text{abs}} + \frac{RT}{F} \ln \left(\frac{c_{\text{ox}}}{c_{\text{red}}} \right)$$

Nernst equation for electron transfer

Ion transfer reactions



$$\Delta_o^w \phi = \phi^w - \phi^o = \Delta_o^w \phi_i^{\ominus} + \frac{RT}{z_i F} \ln \left(\frac{a_i^o}{a_i^w} \right)$$

Nernst equation for ion transfer

Plan



Potentials and redox reactions

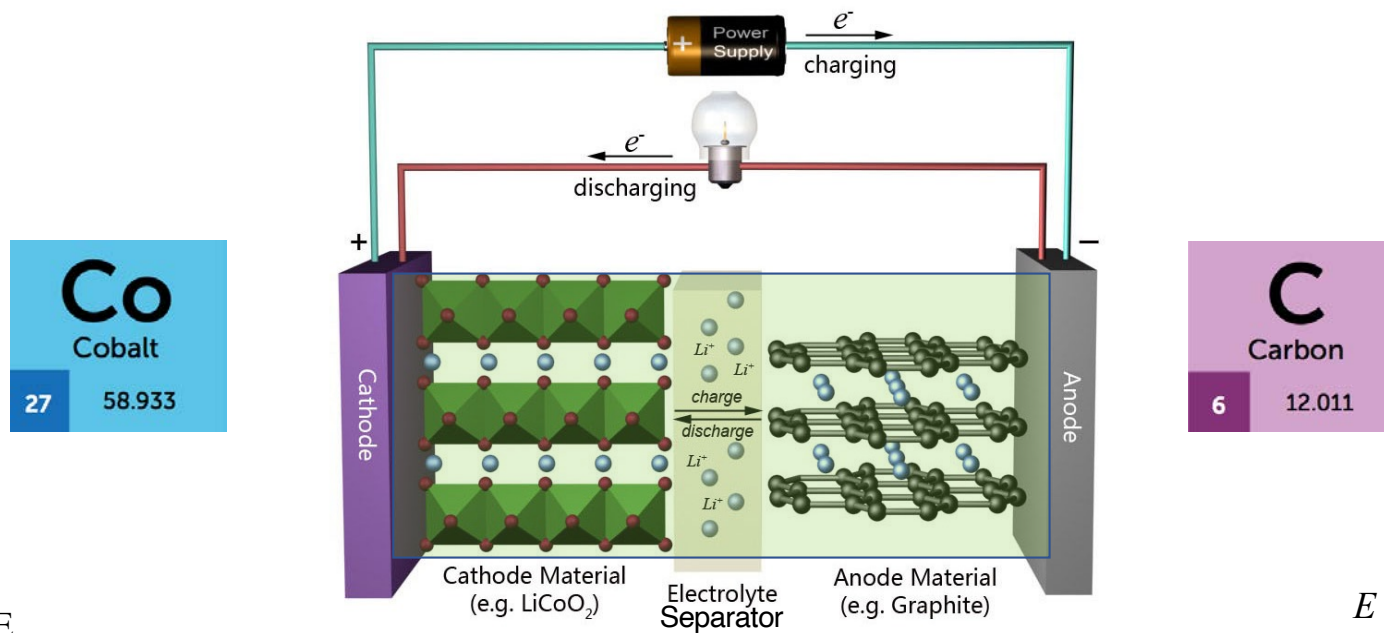


Li-ion battery

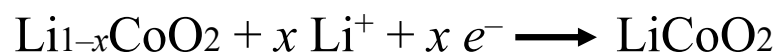


Water electrolysis

Intercalation reactions

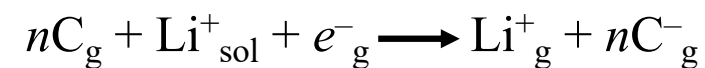
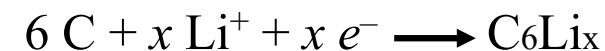


$$E = 0.9 \text{ V vs SHE}$$



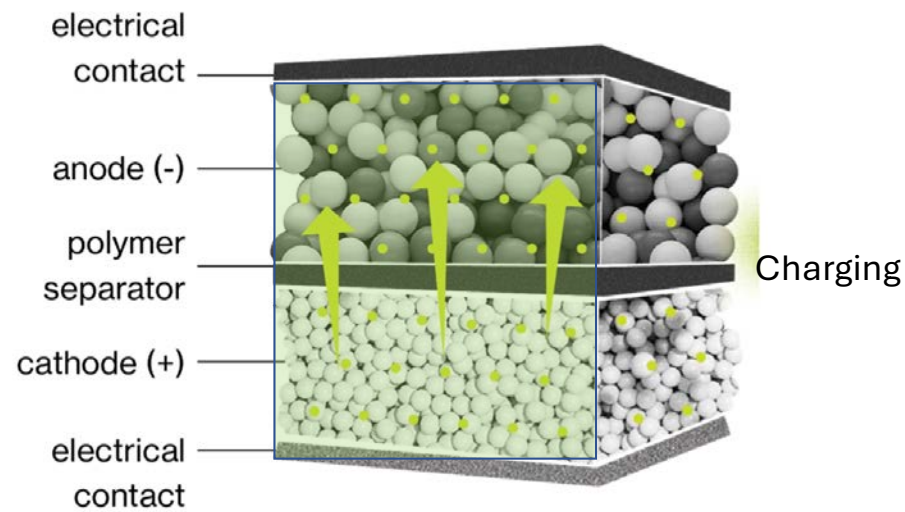
Discharging

$$E = -2.9 \text{ V vs SHE}$$



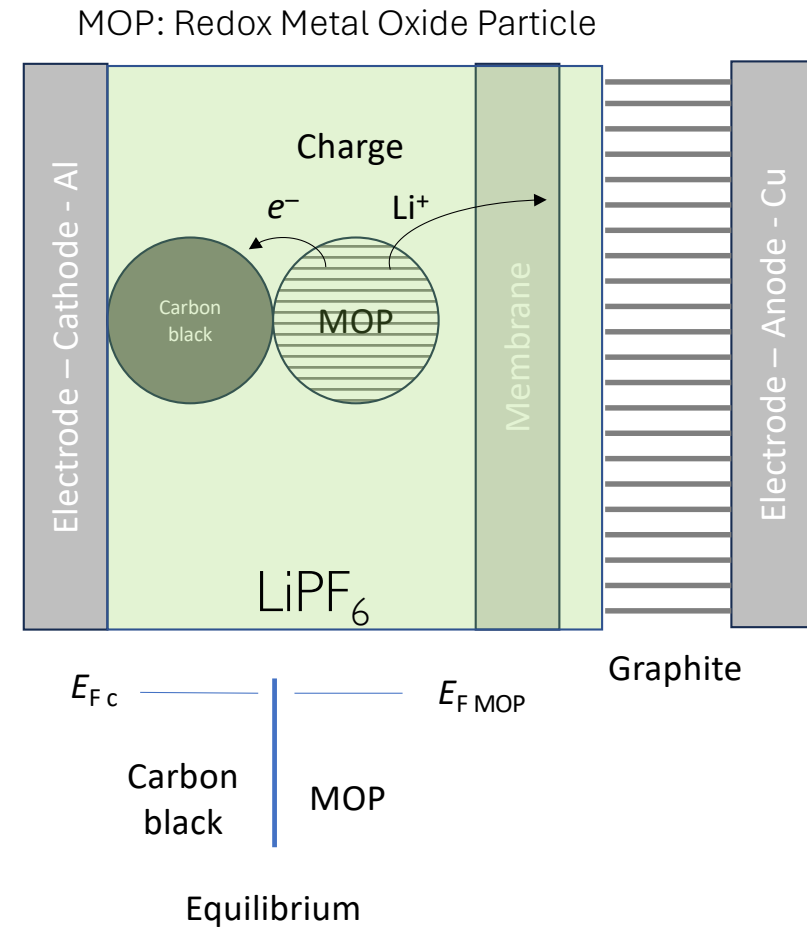
Charging

Lithium-ion battery with graphite anode

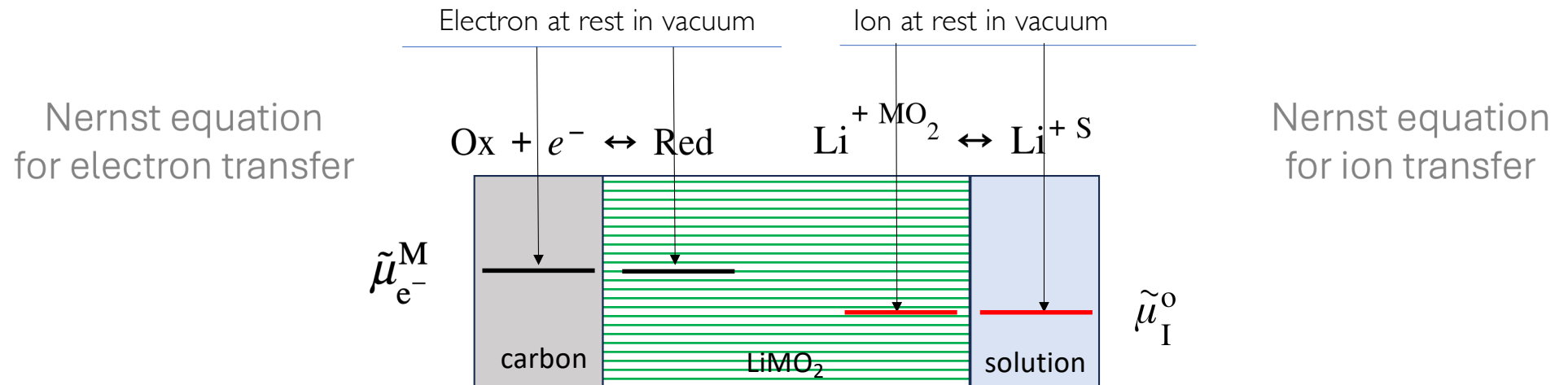


Powder and coating technologies

<https://mineralprices.com/novel-lithium-metal-batteries-will-drive-the-switch-to-electric-cars/>



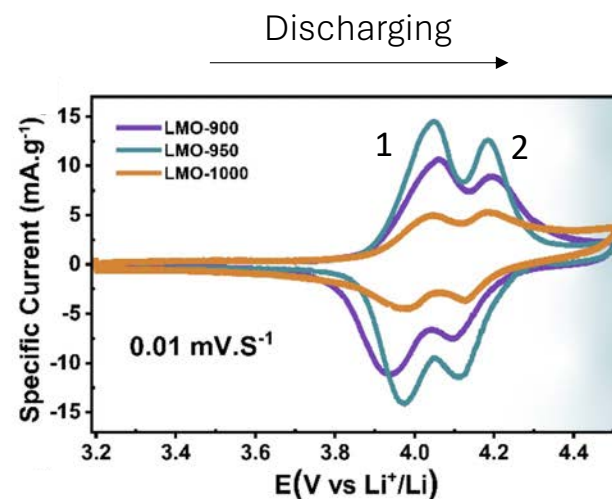
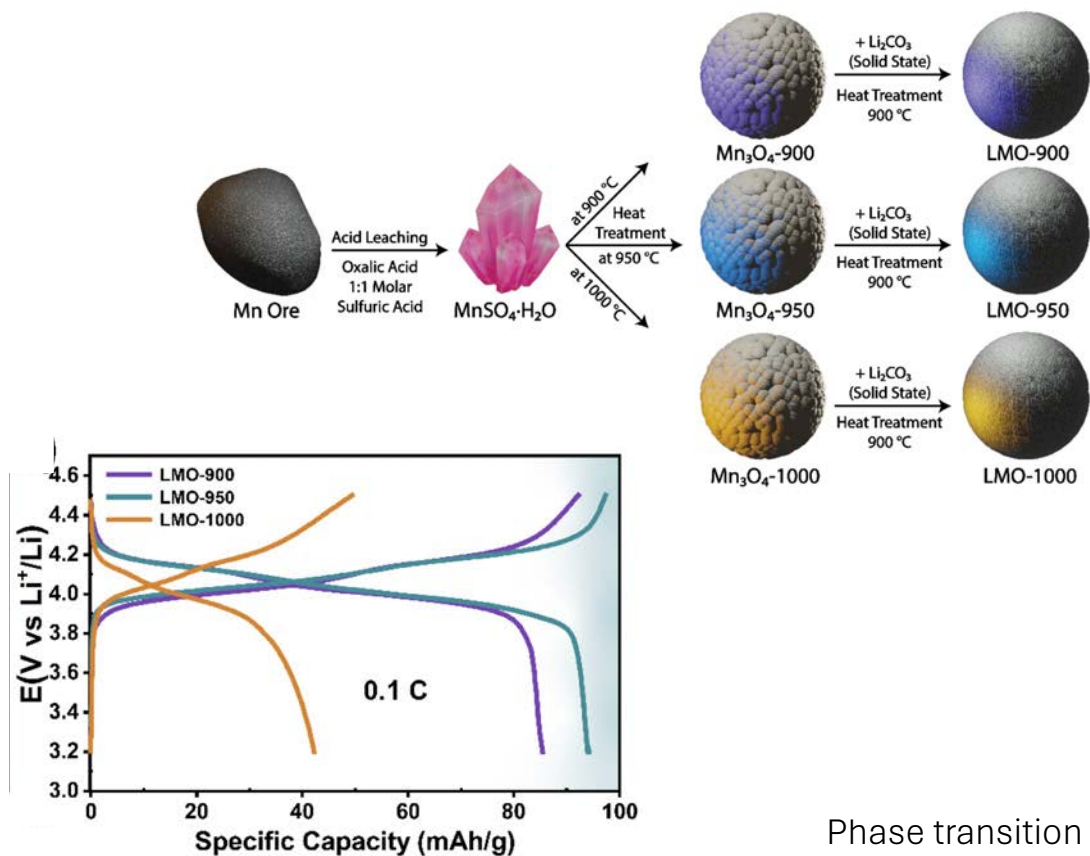
Insertion reactions



The redox solid phase should remain electroneutral inside



Lithium Manganese Oxide -LMO

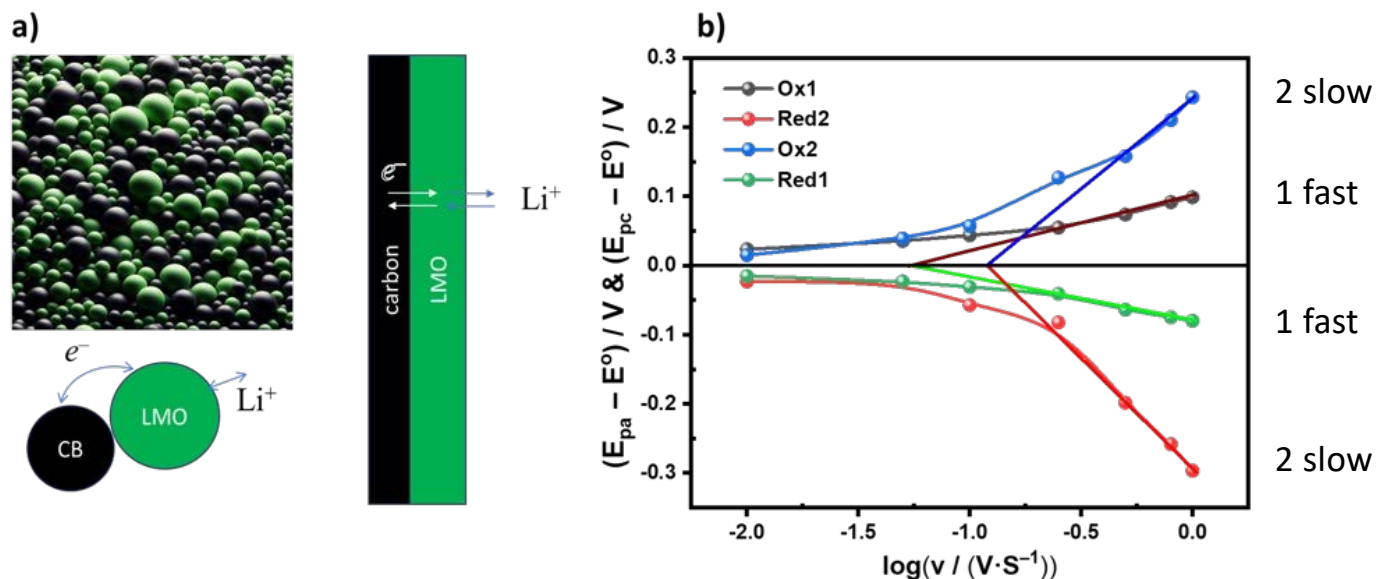


Ox2/Red 2: $\text{MnO}_2/\text{Li}_{0.5}\text{Mn}_2\text{O}_4$

Ox1/Red 1: $\text{Li}_{0.5}\text{Mn}_2\text{O}_4/\text{LiMn}_2\text{O}_4$

Phase transition at $x=0.5$
From tetrahedral to octahedral sites

Thin layer voltammetry - LMO



Thin-layer constant

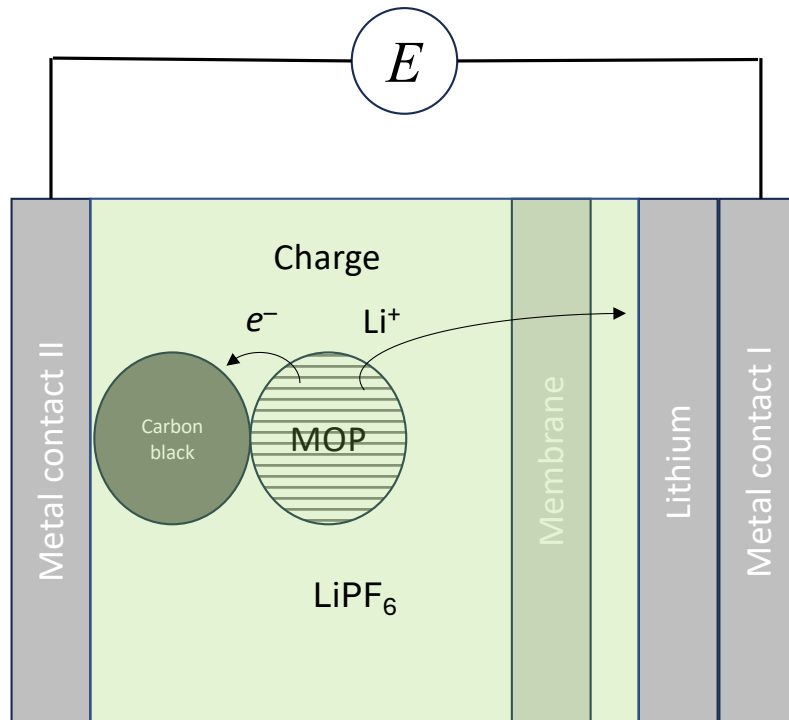
$$K_{\text{cm}} = \frac{RTA k^{\ominus}}{nFvV} = \frac{RTk^{\ominus}}{nFv\delta}$$

Laviron equation

$$E_{\text{pa}} = E^{\ominus'} + \frac{RT}{\alpha nF} \ln \left(\frac{\alpha}{K_{\text{cm}}} \right) = \left[E^{\ominus'} + \frac{RT}{\alpha nF} \ln \left(\frac{\alpha nF \delta}{RTk^{\ominus}} \right) \right] + \frac{RT}{\alpha nF} \ln v$$

$$E_{\text{pc}} = E^{\ominus'} - \frac{RT}{(1-\alpha)nF} \ln \left(\frac{1-\alpha}{K_{\text{cm}}} \right)$$

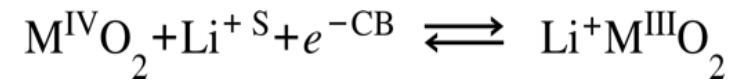
Nernst equation for an insertion reaction



$$\left[E_{M^{IV}/M^{III}} \right]_{Li^+/Li} = \phi^{MC^{II}} - \phi^{MC^I} =$$

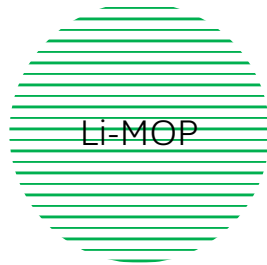
$$(\phi^{MC^{II}} - \phi^{CB}) + (\phi^{CB} - \phi^S) + (\phi^S - \phi^{Li}) + (\phi^{Li} - \phi^{MC^I})$$

Insertion reaction equilibrium

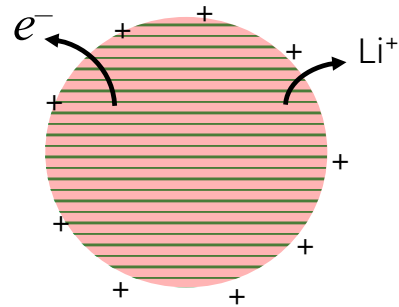
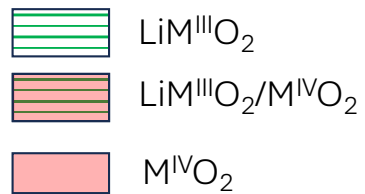


$$\tilde{\mu}_{M^{IV}}^{MOP} + \tilde{\mu}_{Li^+}^S + \tilde{\mu}_{e^-}^{CB} = \tilde{\mu}_{M^{III}}^{MOP} + \tilde{\mu}_{Li^+}^{MOP}$$

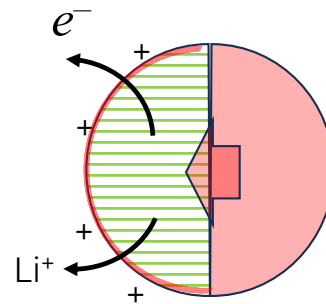
Metal Oxide Particle oxidation



Lithiated metal oxide particle



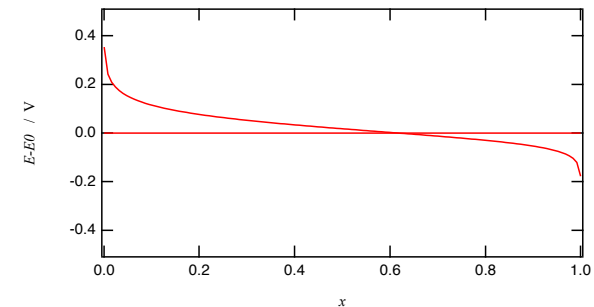
Solid solution oxidation



Biphasic oxidation

Nernst equation

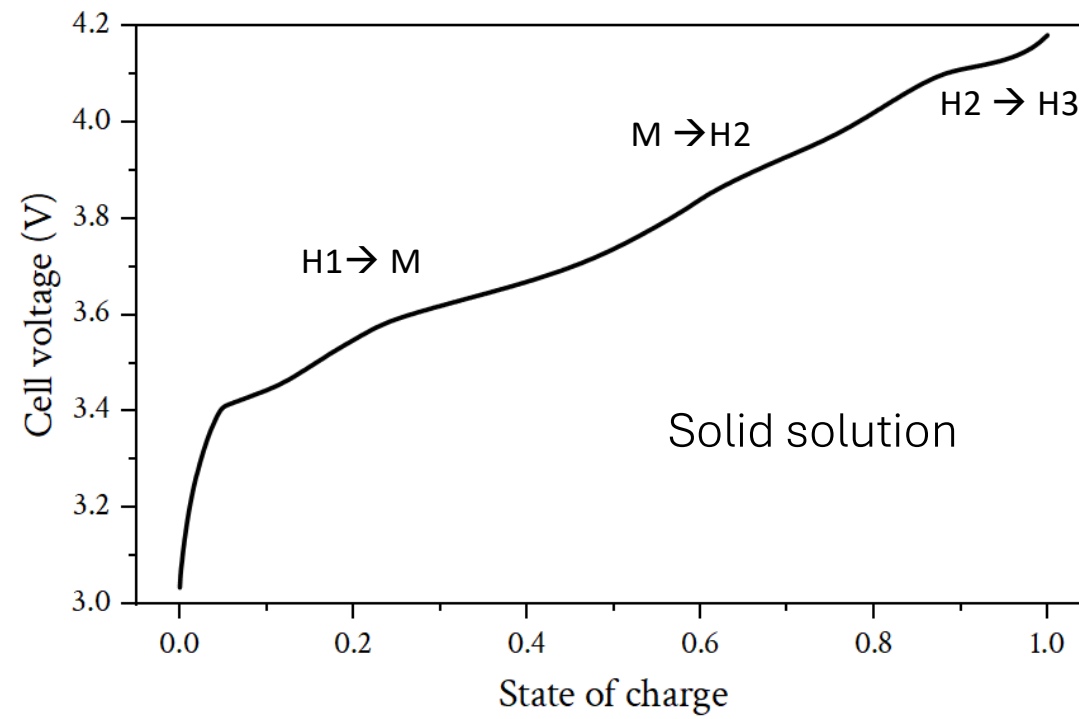
$$\left[E_{\text{M}^{\text{IV}}/\text{M}^{\text{III}}} \right]_{\text{Li}^+/\text{Li}} = \left[E_{\text{M}^{\text{IV}}/\text{M}^{\text{III}}}^{\circ} \right]_{\text{Li}^+/\text{Li}} + \frac{RT}{F} \ln \left[\frac{1-x}{x^2} \right]$$



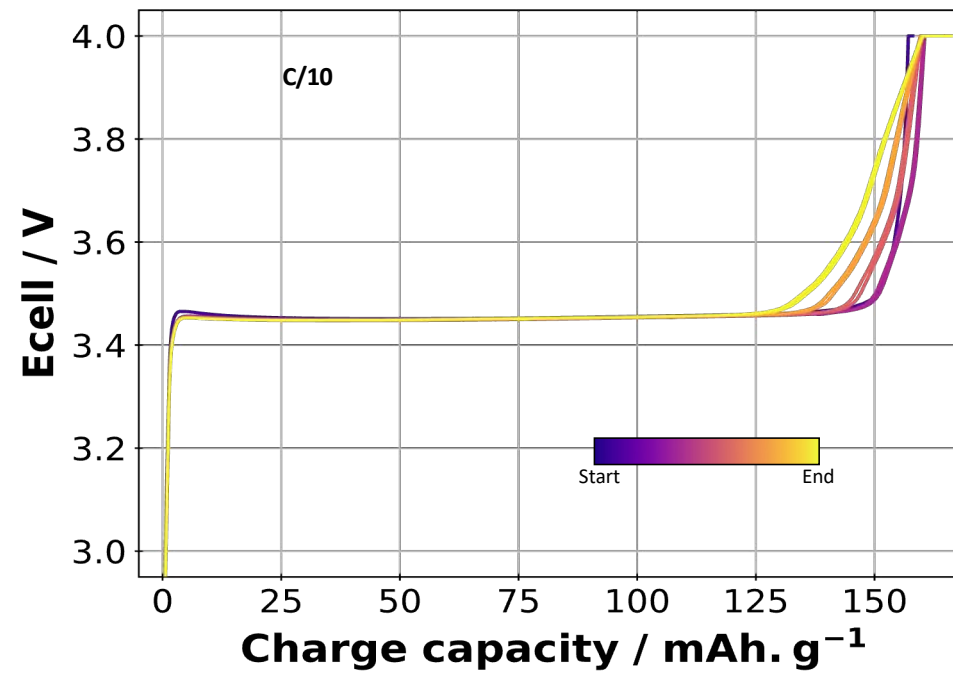
Constant potential

$$\left[E_{\text{M}^{\text{IV}}/\text{M}^{\text{III}}} \right]_{\text{Li}^+/\text{Li}} = \left[E_{\text{M}^{\text{IV}}/\text{M}^{\text{III}}}^{\circ} \right]_{\text{Li}^+/\text{Li}}$$

NMC811 vs Graphite



LFP vs Li



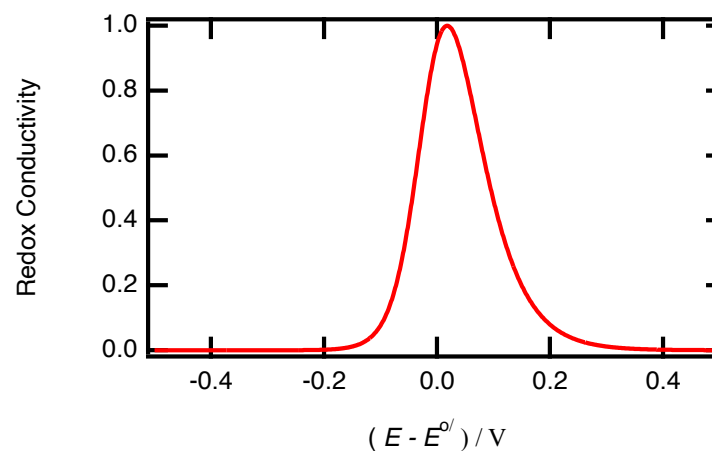
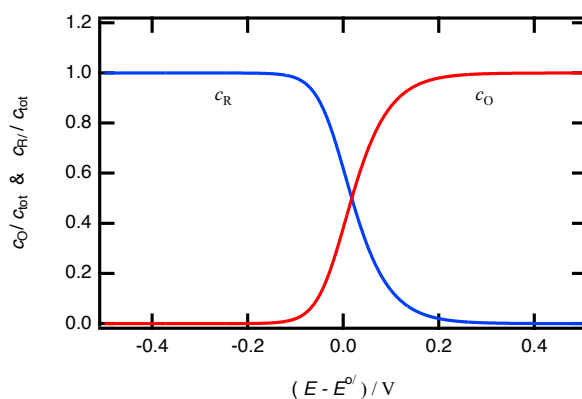
Biphasic solids

Courtesy Arno Villalbi, LEPMI

Redox conductivity in solid solutions

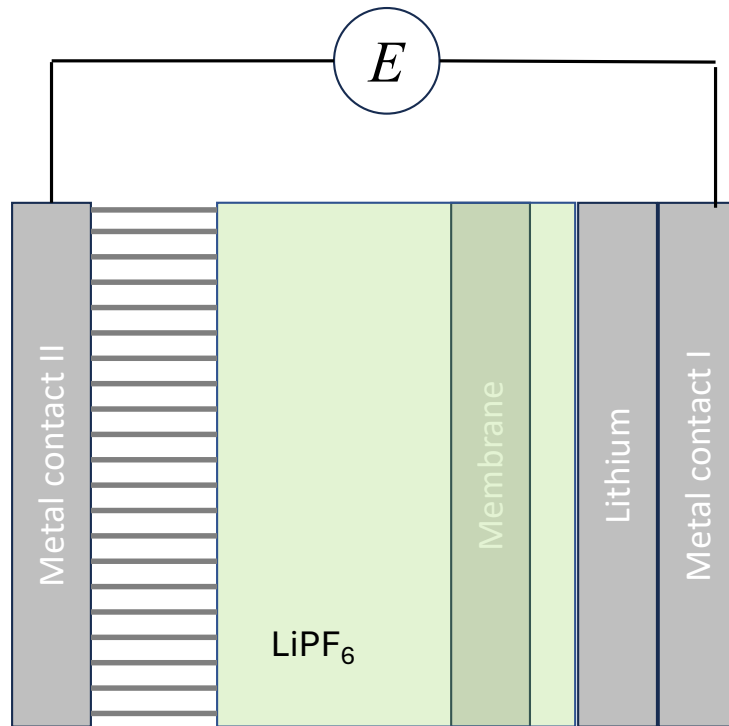
Electron hopping

$$D_e = k_{\text{ex}} c_{\text{redox}}^{\text{tot}} \Delta x^2$$

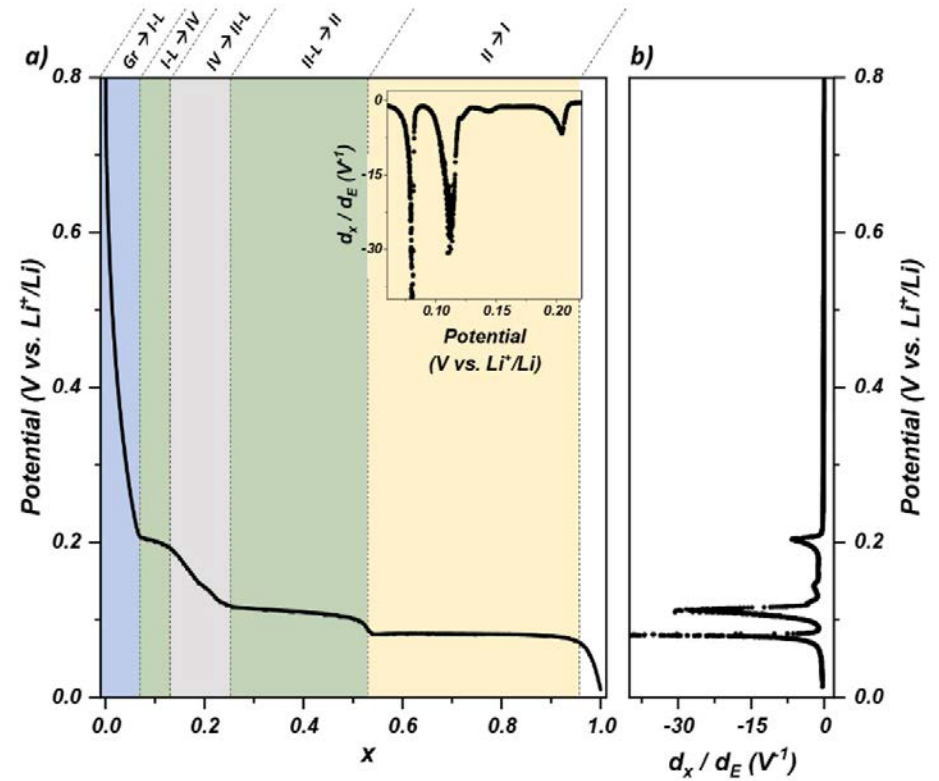


$$\sigma_{\text{redox}} = \frac{F^2 D_e}{RT} c_{\text{red}} \left(1 - \frac{c_{\text{red}}}{c_{\text{redox}}^{\text{tot}}} \right) = \frac{F^2 D_e}{RT} c_{\text{redox}}^{\text{tot}} x(1-x)$$

"Graphite Anode"

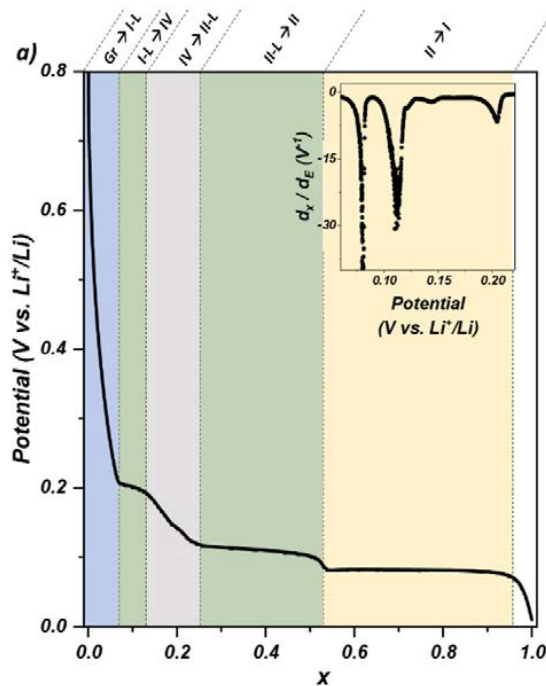


Graphite



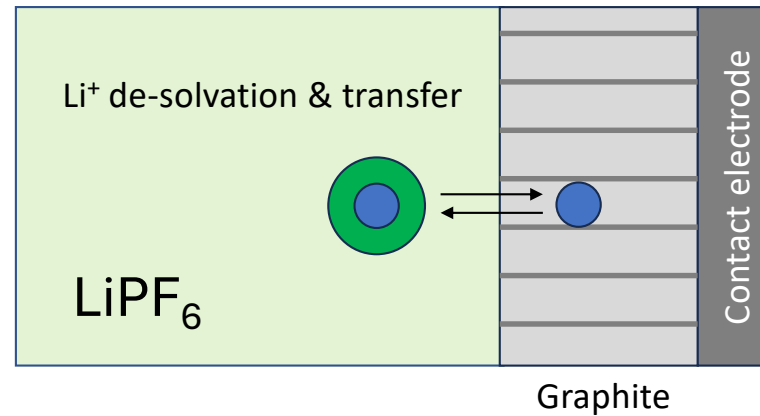
$$[E]_{\text{vs Li}^+/\text{Li}} = \phi^{\text{M}^{\text{II}}} - \phi^{\text{M}^{\text{I}}} = (\phi^{\text{G}} - \phi^{\text{S}}) + \left(\mu_{\text{Li}} - \mu_{\text{Li}^+}^{\text{o,S}} - \mu_{e^-}^{\text{G}} \right) / F - \frac{RT}{F} \ln a_{\text{Li}^+}^{\text{S}}$$

First blue zone ($x < 0.08$)



Cell potential

Ion transfer reaction : Solid solution I-L



Nernst equation
for ion transfer reactions

$$\phi^G - \phi^S = (\mu_{\text{Li}^+}^{\text{o},\text{S}} - \mu_{\text{Li}^+}^{\text{o},\text{G}}) / F + \frac{RT}{F} \ln \left(\frac{a_{\text{Li}^+}^{\text{S}}}{a_{\text{Li}^+}^{\text{G}}} \right)$$

$$[E]_{\text{vs Li}^+/\text{Li}} = (\mu_{\text{Li}} - \mu_{\text{Li}^+}^{\text{o},\text{G}} - \mu_{e^-}^{\text{G}}) / F - \frac{RT}{F} \ln a_{\text{Li}^+}^{\text{G}}$$

Potentiometric titration of silver with precipitation



Example determination

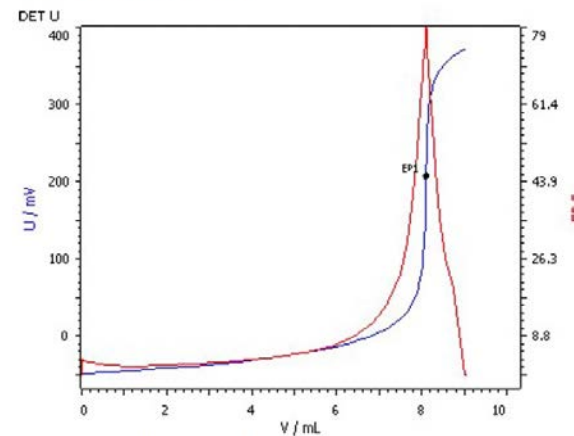
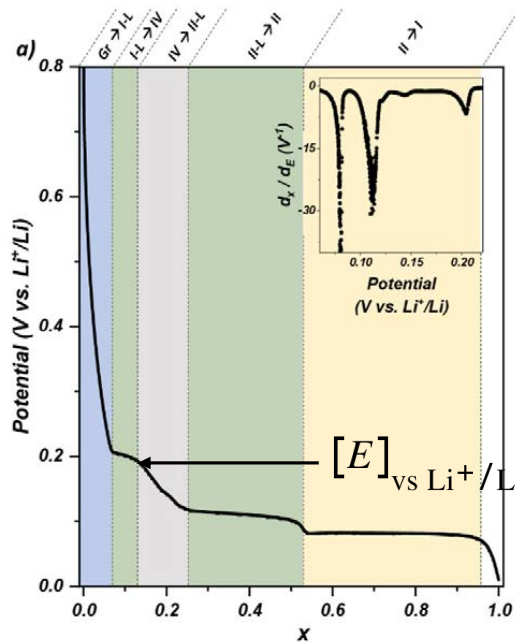


Fig. 1: Titration curve of fine silver according to EN ISO 11427

- Dissolve sample in nitric acid.
- Titrate with KCl
- AgCl precipitates
- Measure the Nernst potential of a silver electrode vs a reference electrode

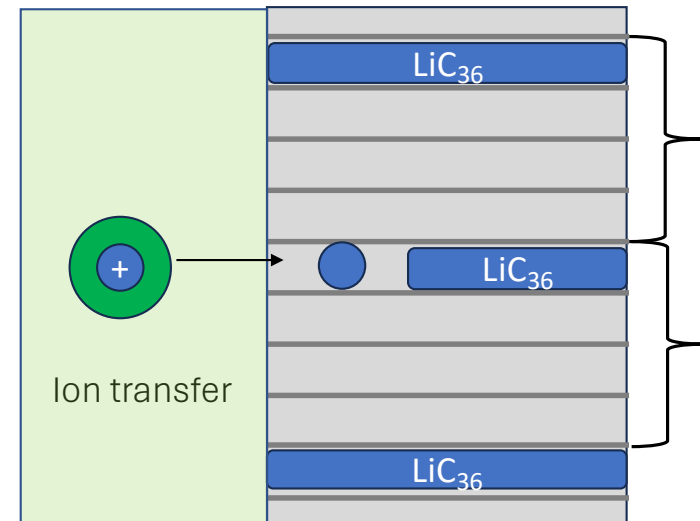
First green zone : Precipitation of LiC_{36}

$$0.08 < x < 0.16$$



$$[E]_{\text{vs Li}^+/\text{Li}} = (\mu_{\text{Li}} - \mu_{\text{LiC}_{36}} + 36 \mu_{\text{C}}^{\text{G}}) / F$$

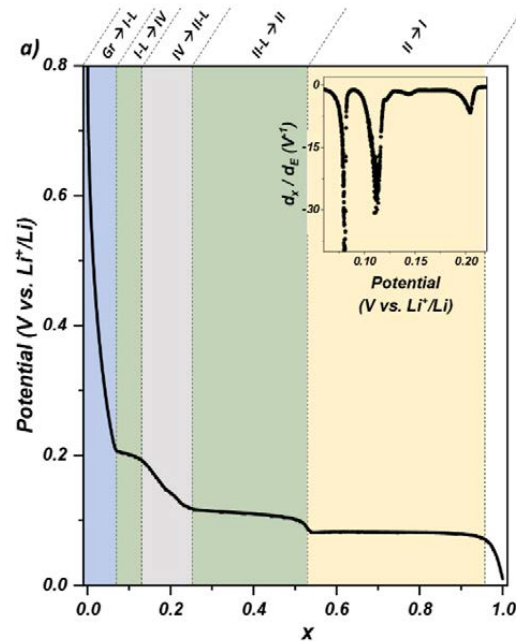
Titration of C_6 sites
Precipitation of LiC_{36}



1L to Stage 4 Biphasic solid solution-solid

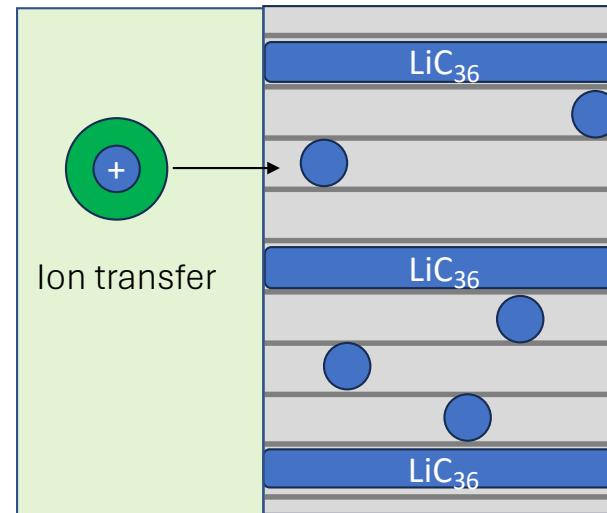


Grey zone : New solid solution 2L ($0.16 < x < 0.25$)



Nernst equation for ion transfer reactions

2L Solid solution formation



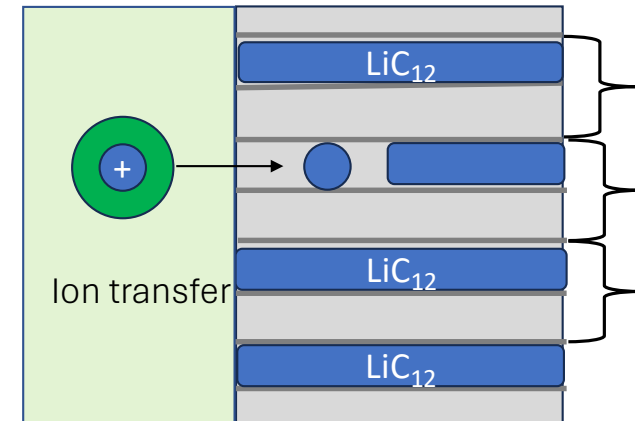
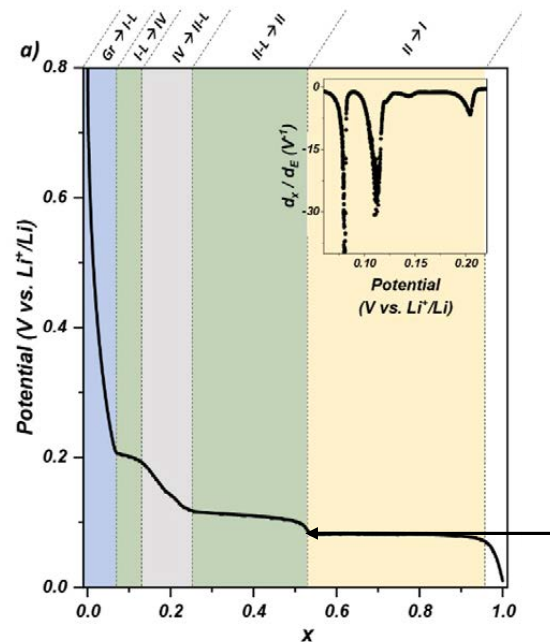
Stage 4 to 2L

$$\phi^G - \phi^S = (\mu_{\text{Li}^+}^{\text{o,S}} - \mu_{\text{Li}^+}^{\text{o,G}}) / F + \frac{RT}{F} \ln \left(\frac{a_{\text{Li}^+}^S}{a_{\text{Li}^+}^G} \right)$$

Second green zone : Precipitation of LiC_{12}

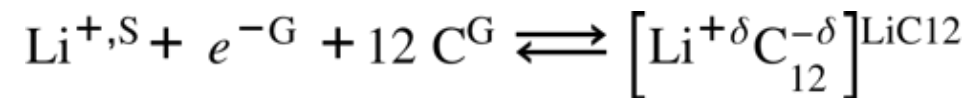
$$0.25 < x < 0.52$$

Titration of C_6 sites
Precipitation of LiC_{12}

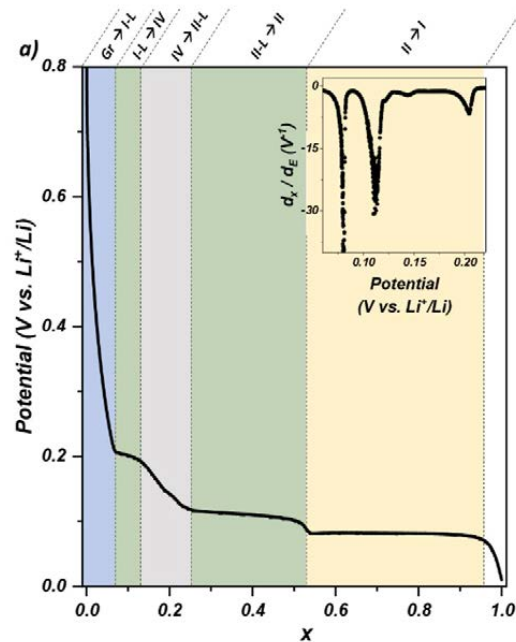


$$[E]_{\text{vs Li}^+/\text{Li}} = (\mu_{\text{Li}} - \mu_{\text{LiC}_{12}} + 12 \mu_{\text{C}}^{\text{G}}) / F$$

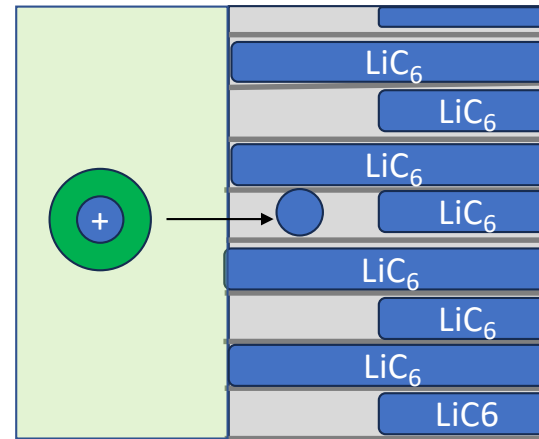
2L to Stage 2 Biphasic solid solution-solid



Yellow zone : Formation of LiC_6 $0.52 < x < 0.95$

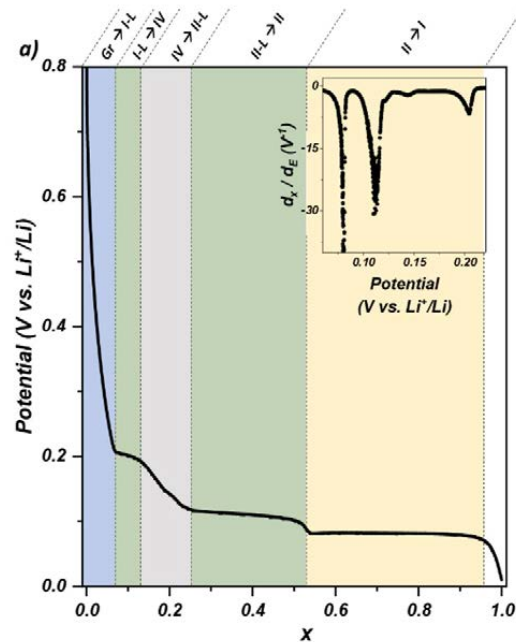


Li^+ addition on LiC_{12} to form LiC_6 domains

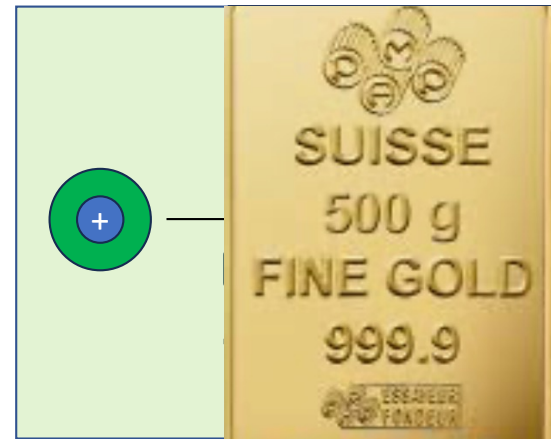


Stage 2 to Stage1: Biphasic solid-solid lithium insertion

Yellow zone : Formation of LiC_6 $0.52 < x < 0.95$

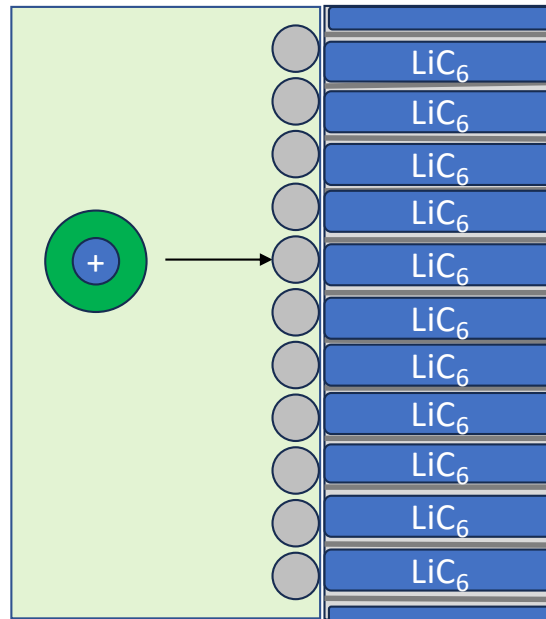


Li^+ addition on LiC_{12} to form LiC_6 domains



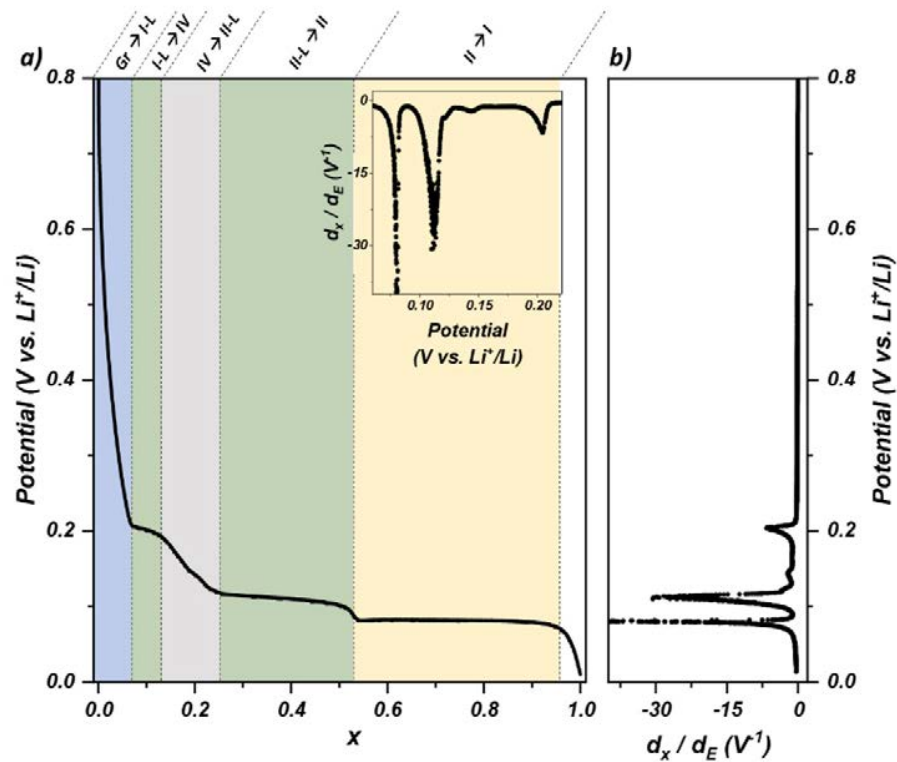
Stage 2 to Stage1: Biphasic solid-solid lithium insertion

Under potential lithium metal deposition
 $0.95 < x < 1.0$



Under potential deposition of
Li metal on LiC_6

Potentiometric titration of graphite



Electronic charge

1. Adsorption of solvated lithium on negatively charged graphite and intercalation of bare ions to form a solid solution I-L
2. Precipitation of LiC_{36}
3. Intercalation of bare ions to form a solid solution II-L
4. Precipitation of LiC_{12}
5. Intercalation to form LiC_6 by a solid/solid reaction
6. Electroplating of Li metal on LiC_6 .

Conclusion

“Cathode material” : Redox reactions with ion insertion.
Redox conductivity in solid solutions

Energy &
Environmental
Science



PERSPECTIVE

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Cite this: *Energy Environ. Sci.*,
2025, 18, 1658

The redox aspects of lithium-ion batteries†

Pekka Peljo, *^{ae} Claire Villevieille^b and Hubert H. Girault *^{cd}

Graphite : No redox reactions as neither lithium nor carbon change their degree of oxidation. “Volumic capacitor”

Definitions- IUPAC Gold book

oxidation

Online use... ▼



<https://doi.org/10.1351/goldbook.O04362>

1. The complete, net removal of one or more electrons from a molecular entity (also called 'de-electronation').
2. An increase in the oxidation number of any atom within any substrate.
3. Gain of oxygen and/or loss of hydrogen of an organic substrate.

reduction

Online use... ▼



<https://doi.org/10.1351/goldbook.R05222> [Copy](#)

The complete transfer of one or more electrons to a molecular entity (also called 'electronation'), and, more generally, the reverse of the processes described under oxidation (2) and (3).

Conclusion : *Stricto sensu* graphite is not an anode as long as lithium plating does not occur

Batteries are devices that store energy to later be converted into electricity using chemical reactions. During discharge of a battery, the anode undergoes an oxidation reaction, which produces electrons, and the cathode undergoes a reduction reaction, which absorbs electrons.

In 1746–1748, Benjamin Franklin experimented with charging Leyden jars in series and developed a system involving 11 panes of glass with thin lead plates glued on each side and then connected together. He used the term "**electrical battery**" to describe his electrostatic battery in a 1749 letter about his electrical research in 1748. It is possible that Franklin's choice of the word battery was inspired by the humorous wordplay at the conclusion of his letter, where he wrote, among other things, about a salute to electrical researchers from a battery of guns. This is the first recorded use of the term electrical battery. Wikipedia

Plan



Potentials and redox reactions



Li-ion battery



Water electrolysis



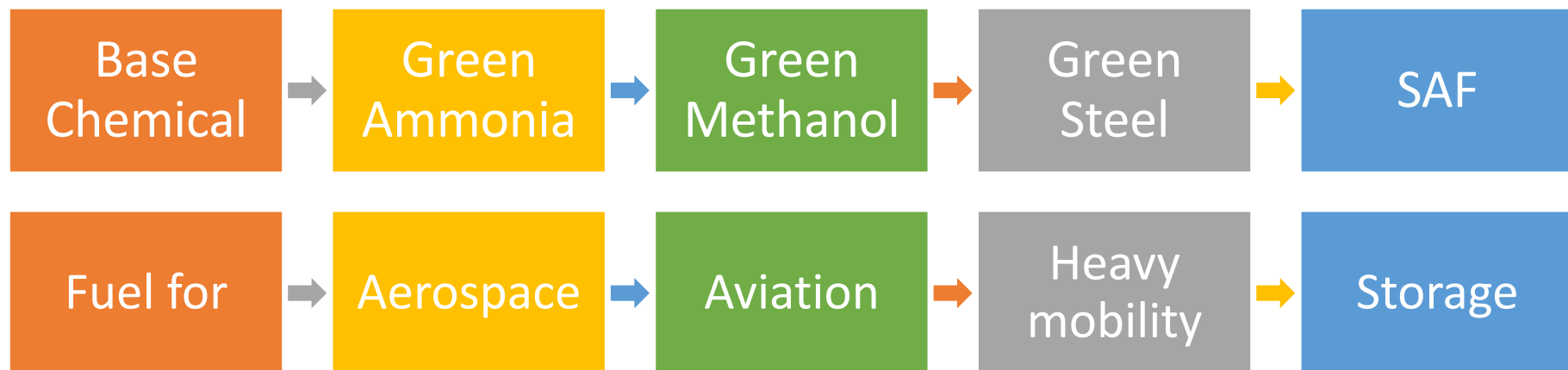
Hydrogen !

**Green Hydrogen Hype Is Giving Way
to Reality**

December 23, 2024

Bloomberg

Hydrogen : Electron storage molecule !



Can play a major role in electric grid regulation.

Being paid to produce hydrogen and remove electrons from the grid !

Different electrolysis technologies for different markets

Hydrogen production in 1899

Schmidt, O. (1899)

Apparat zur Elektrolyse von Wasser. Patent DE 111,131,
Jun.13, 1899.

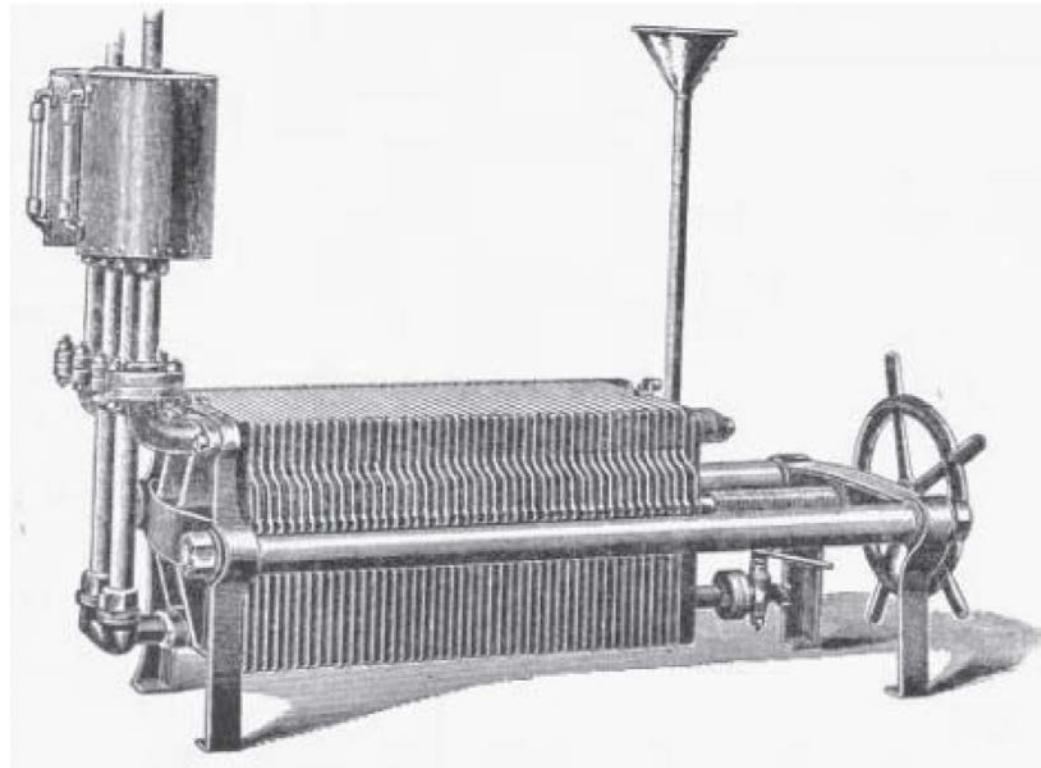
Bipolar filter-press electrolyser with
asbestos cloth diaphragm

2.5 V per cell

Current ranging from 15 A to 150 A

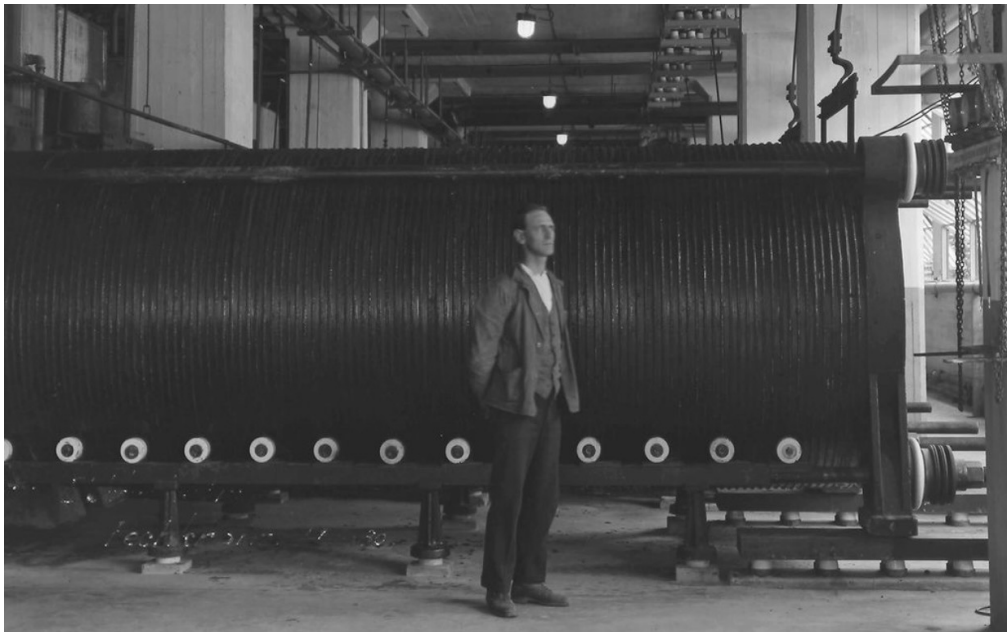
Oerlikon, Zurich, Switzerland

Voltage control (no thyristors yet...)
Dynamos

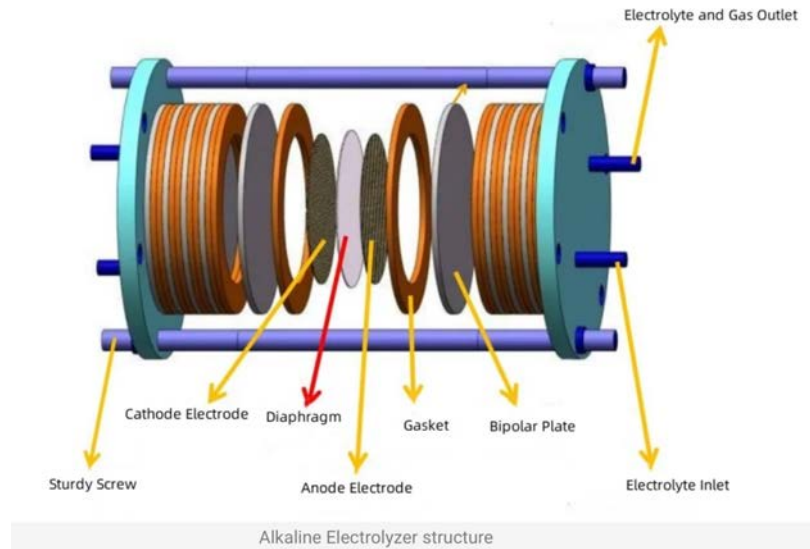


Hydrogen production in 1905: Norsk Hydro

The Vemork power plant, had six floors housing more than 300 Pechkranz electrolyzers. The stacks consisted of 140 cells operated at 2.5 kA with approx. 2.5V/cell (262.5 MW). The plant could produce 43500 Nm³ of hydrogen in one hour (3.9 tons H₂/h compared to 5.2 today).



Alkaline electrolyzers today



Incremental progresses

Still mainly bipolar electrodes

Still circular electrodes (mostly..)

Still operating at up to 30 bars and 80°C

Membranes :

PPS with inorganic fillers

Ion solvating membrane

Catalysts :

Nickel based

PGM

Key drawbacks:

Bubbles

Plant corrosion

Key advantages:

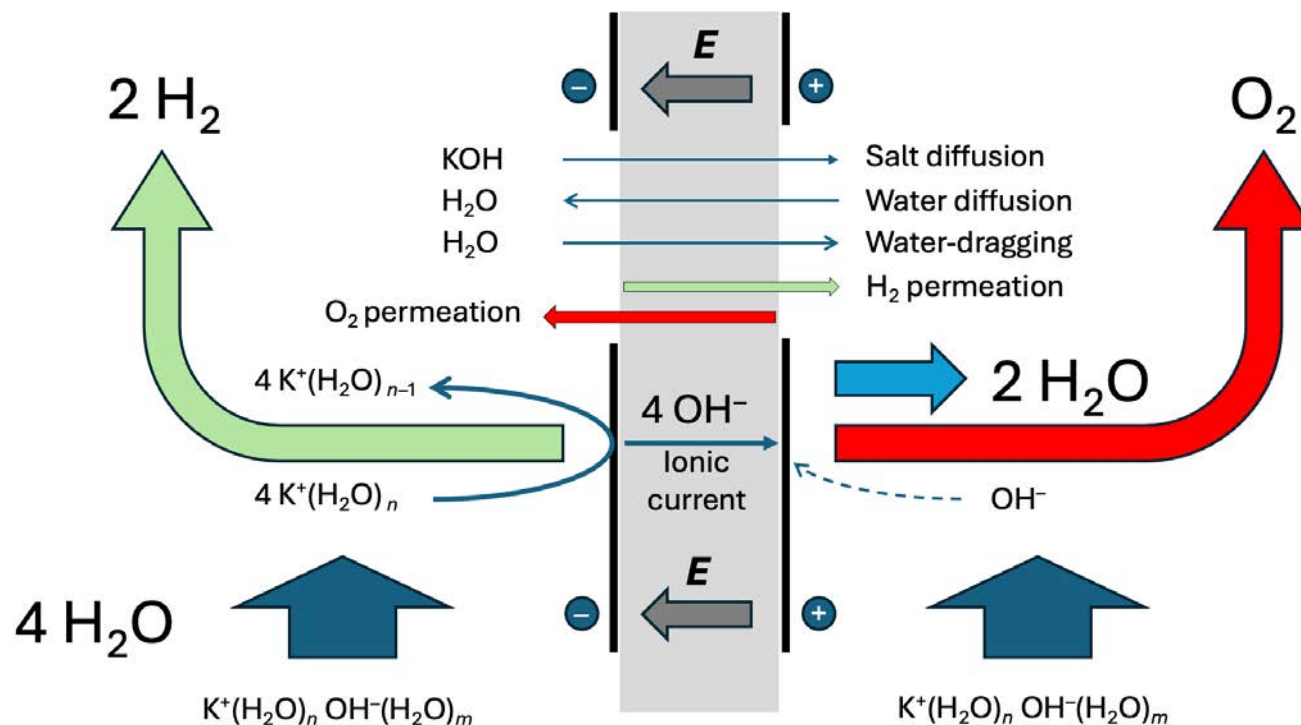
Robust and proven

All in all, a chemical plant...

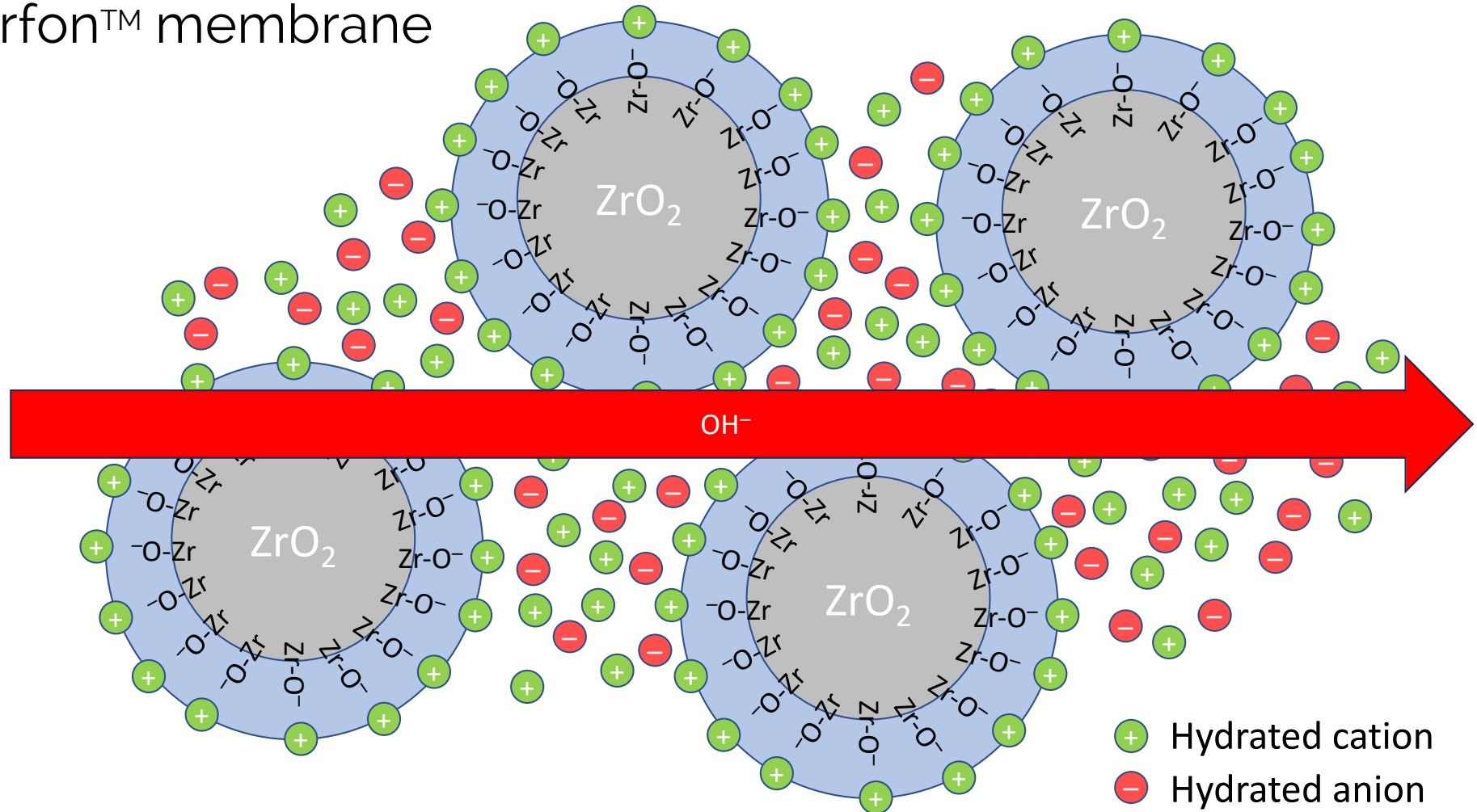
to operate at steady-state



Alkaline water electrolysis: Where is the water?



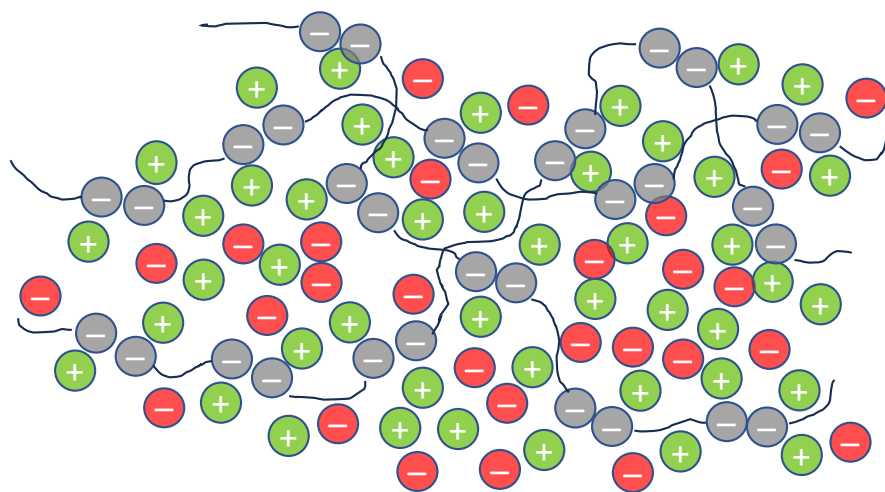
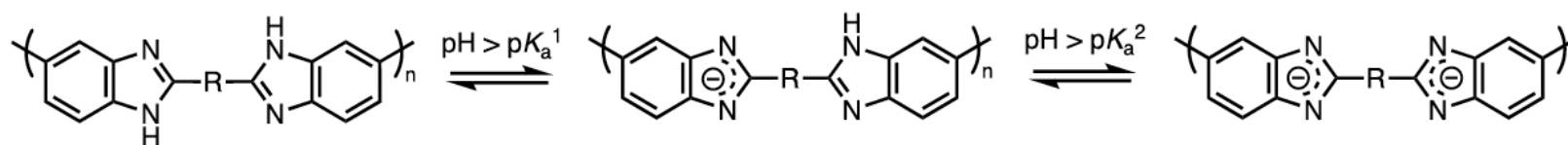
Zirfon™ membrane






Ion solvating membrane

Polybenzimidazole

polybenzimidazolides



-  De-protonated PBI
-  Hydrated cation
-  Hydrated anion

By Global Times

Published: Aug 08, 2023 09:27 PM



Sinopec
Solar to Hydrogen

300 MW solar
618 GWh/year
2000 hours/year

20'000
tonnes H₂/year

52 electrolyzers
13 from :
Cockerill JingLi
Longi
PERIC



The photo shows the green hydrogen demonstration project in Kuqa city, Northwest China's Xinjiang Uygur Autonomous Region on July 11, 2023. The project marks the first one in China utilizing photovoltaic power to directly generate hydrogen on a large scale with a total investment of 3 billion yuan (\$416.66 million) and can help reduce carbon dioxide emissions by 485,000 tons annually.

Photo: VCG



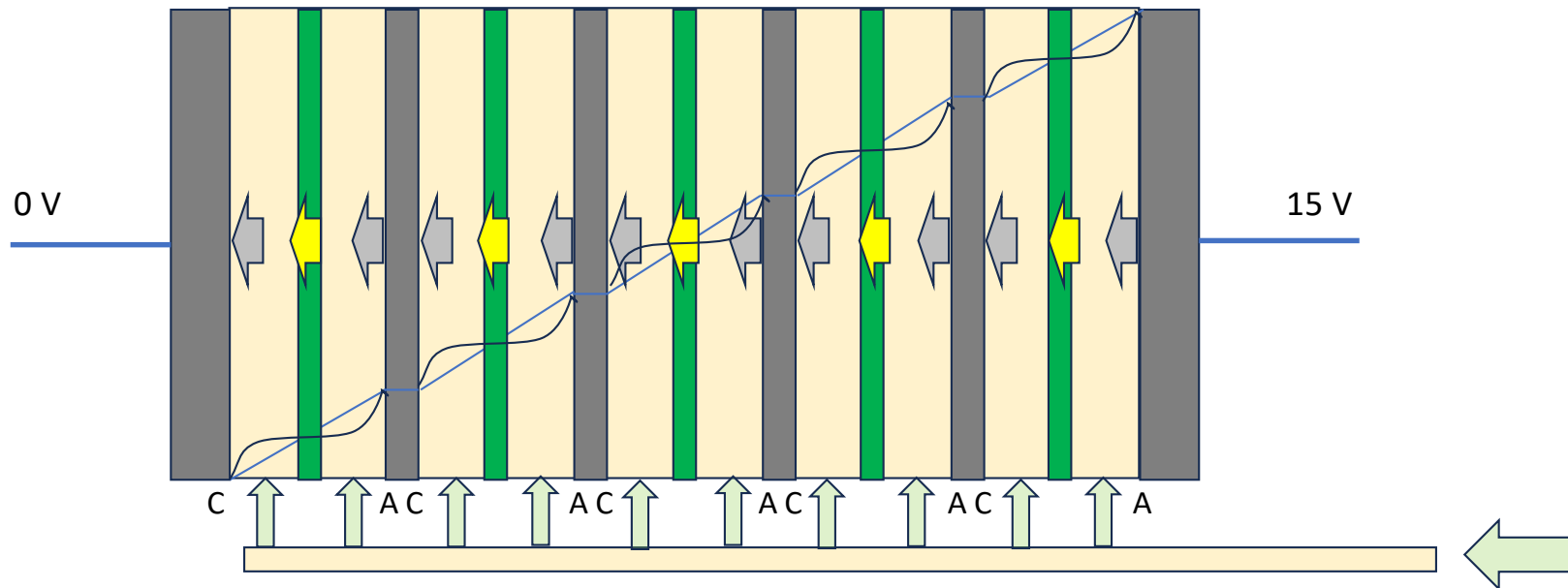
EXCLUSIVE | World's largest green hydrogen project 'has major problems due to its Chinese electrolyzers': BNEF

All the electrolyzers at Sinopec's 260MW Kuqa facility in China — made by three prominent manufacturers — have safety issues related to renewable-energy fluctuations, says analyst

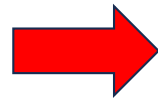
<https://www.hydrogeninsight.com/production/exclusive-worlds-largest-green-hydrogen-project-has-major-problems-due-to-its-chinese-electrolyzers-bnef/2-1-1566679>

11 December 2023 8:57 GMT *UPDATED* 12 December 2023 13:35 GMT

Bipolar stack

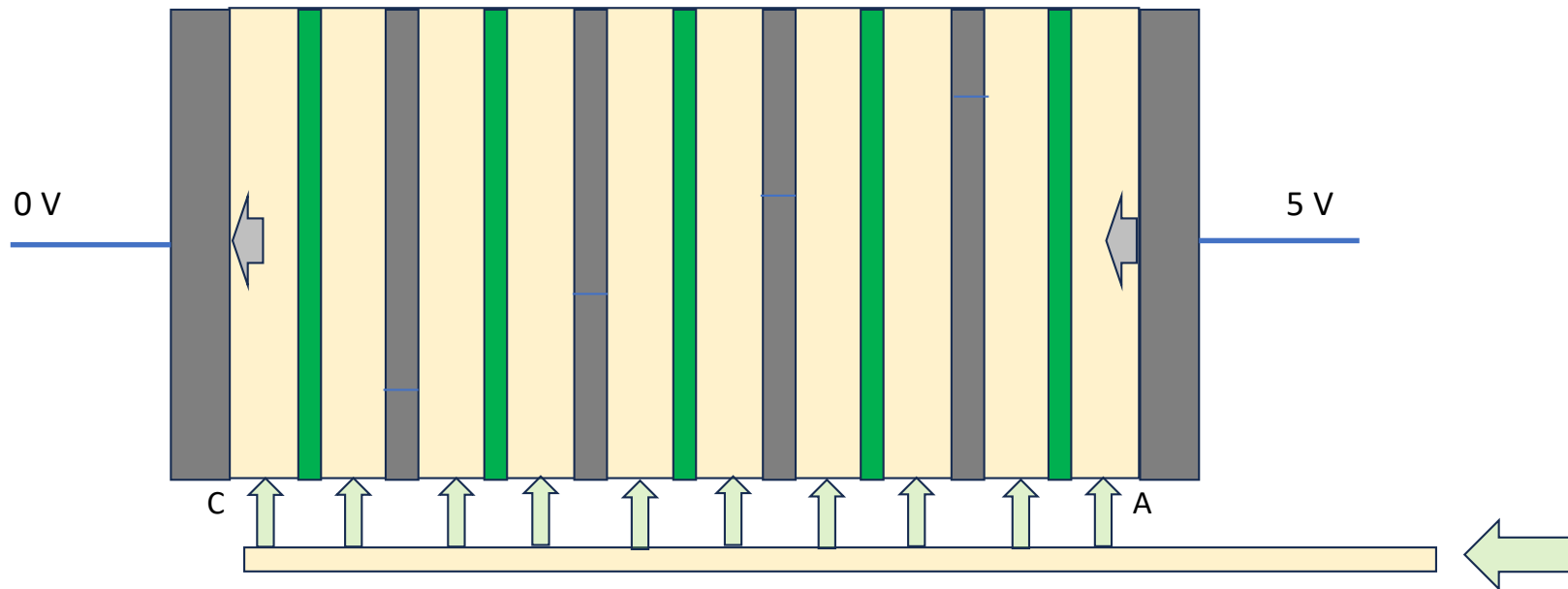


Continuity of current
Electroneutrality



- No control of individual cell voltage
- Inhomogeneous membrane resistance
- Inhomogeneous current distribution on a single bipolar plate

Bipolar stack – Shunt current



What happens when the stack voltage drops to 5 V?

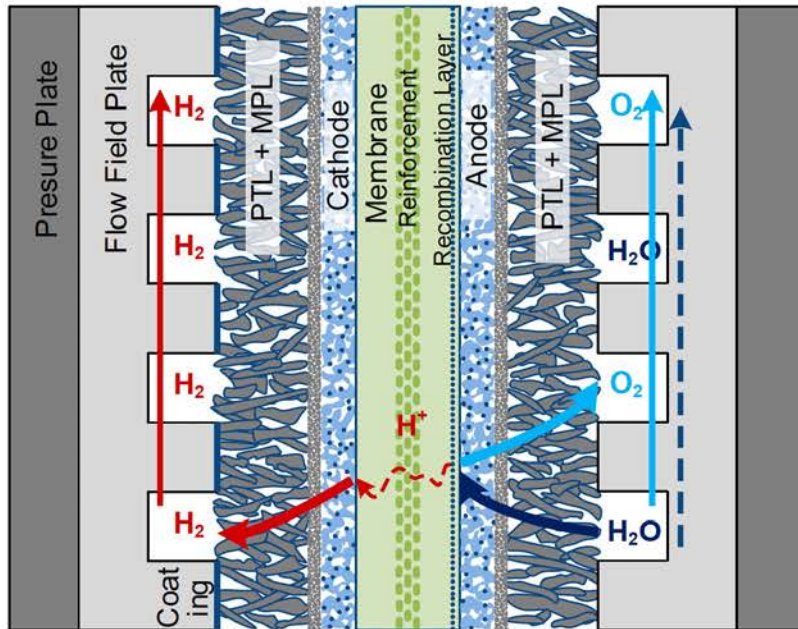
PEM water electrolysis



October 17, 2023

THE  TIMES

PEM electrolysis : Is it sustainable?



Cross section of an advanced PEM electrolysis cell

PTL: Porous Transport Layer (GDL in fuel cell)

MPL: MicroPorous Layer

Incremental progresses

Still bipolar electrodes

Still rectangular electrodes (mostly..)

Still operating at up to 30 bars and 60°C

Membranes :

Still Nafion analogs..PFAS

Catalysts :

Still PGM, e.g. IrO₂

Ionomers

Key advantages:

Compact

Clean

Flexible

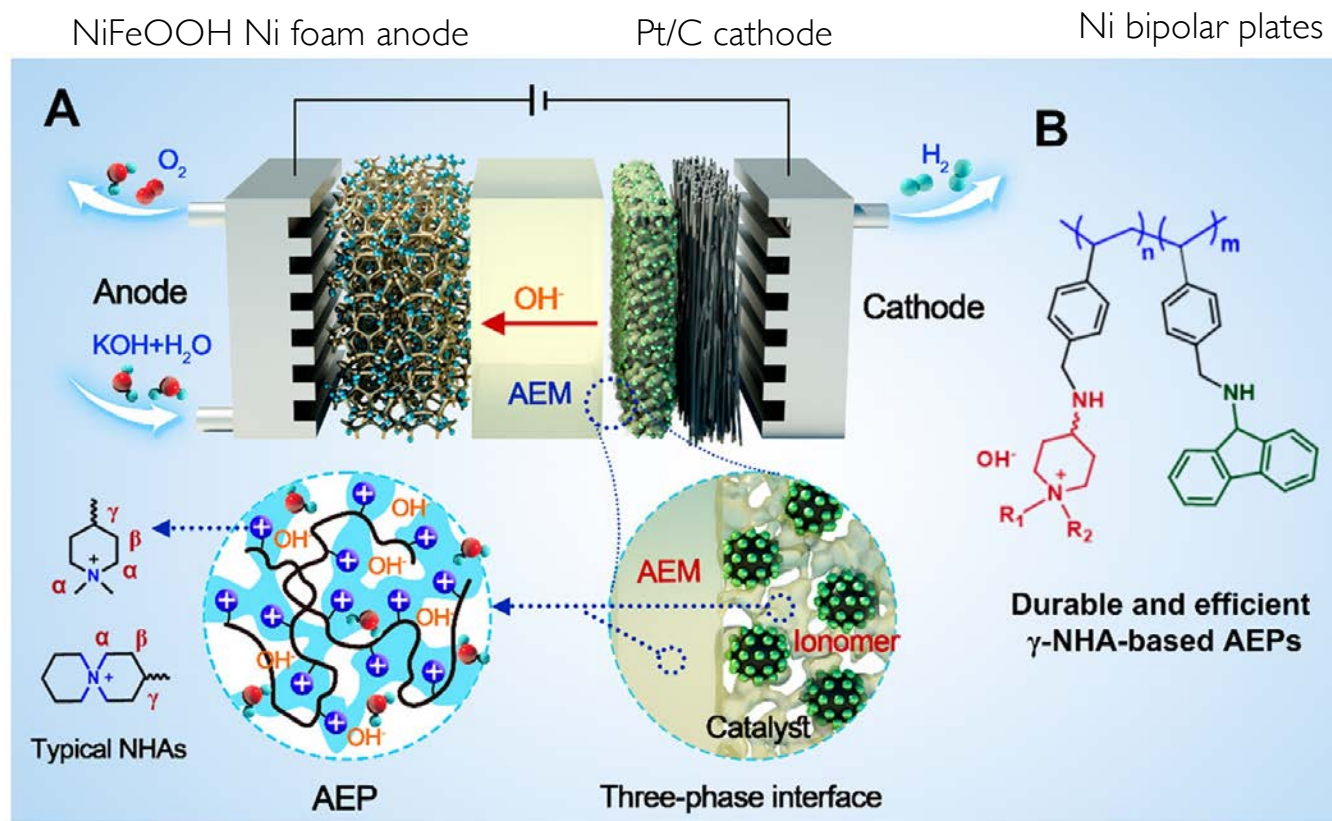
Key drawbacks :

Acidic environment

High oxidation potentials

Nanoparticles dissolution and precipitation

Robust Piperidinium-Enriched Polystyrene Ionomers for Anion Exchange Membrane Fuel Cells and Water Electrolyzers



Xile Hu



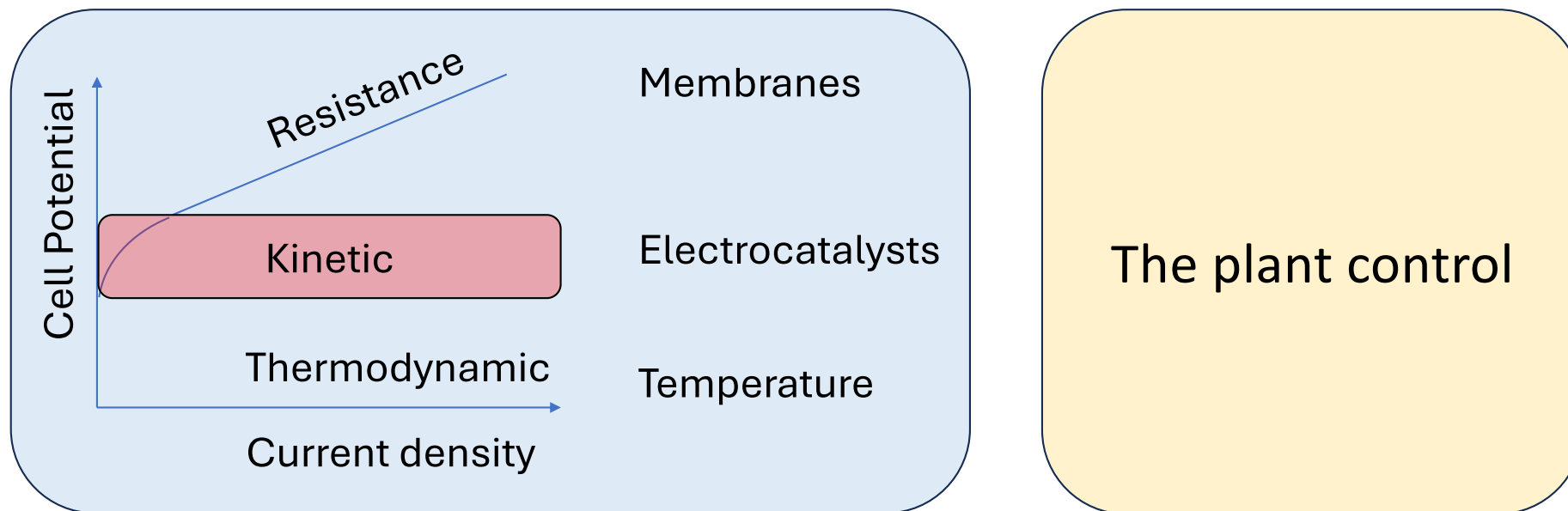
NovaMea

The cell can be run stably at 2 or 3 A · cm⁻² over 1,100 h in 1 M KOH

ACS Energy Lett. 2023, 8, 4043–4051

EPFL

Water electrolysis : What to improve?



Alkaline electrolyzers for large systems ($> 5\text{MW}$)
PEM electrolyzers for intermittent systems ($< 5\text{MW}$)

AEM electrolyzers may replace PEM electrolyzers



Conclusion

Electrochemistry is a fundamental science at the heart of the electrification of our modern societies.

It has important applications in:

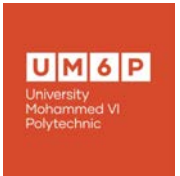
- Iontronics
- Energy storage
- Hydrogen production
- Chemical production e.g. Chlorine
- Electrometallurgy e.g. Aluminium
- Production of acids and bases for extractive industries
- ...

From fundamental science to race track...





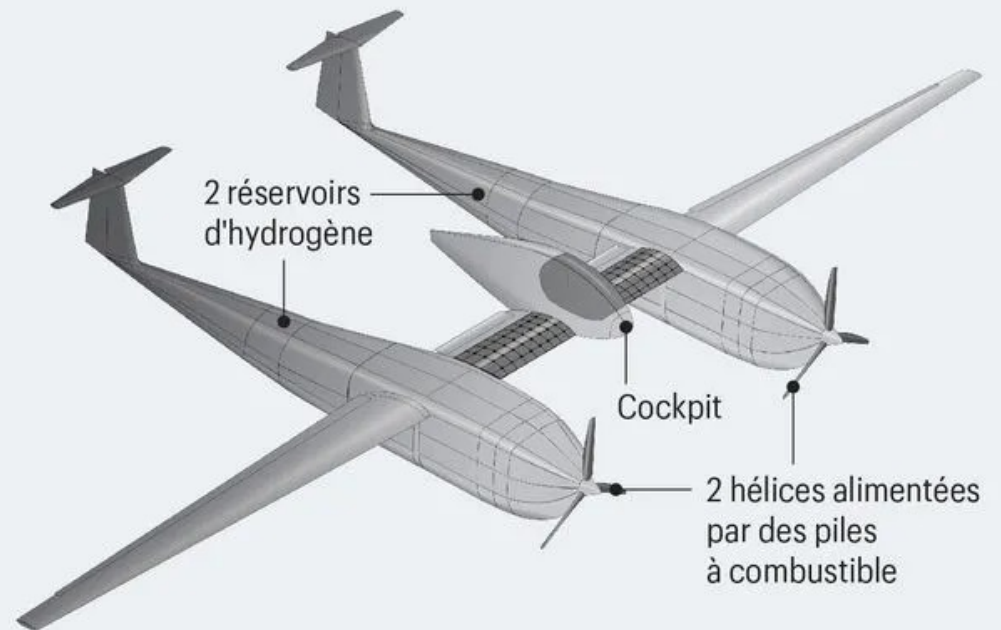
CLIMATE IMPULSE



Science

À quoi va ressembler Climate Impulse

Le nouvel engin volant alimenté à l'hydrogène de Bertrand Piccard



Thank you!

Acknowledgements:

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Prof. Claire Villevieille, CNRS

11-09-2024

