

Fundamentals of Electrochemistry, Thermodynamics and Solid State Chemistry for fuel cells

August 22, 2011 | L.G.J. (Bert) de Haart

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 Aug 21 – 27, 2011
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Fundamentals of Electrochemistry, Thermodynamics and Solid State Chemistry for Fuel Cells

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**Fundamentals of Electrochemistry,
 Thermodynamics and Solid State Chemistry**

BdH, FZJ/IEK-9, Aug 22, 2011, sheet 2

Electrochemistry

Electrochemistry is the branch of physical chemistry

- dealing with the interrelation of chemical and electrical effects
or
- dealing with the study of chemical reactions as a results of the passage of current
(conversion of chemical energy into electrical energy and *vice versa*)

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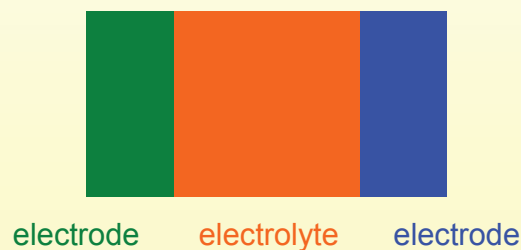
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– Principles of Electrochemistry (IEK-9)

Electrochemical cells

Electrochemistry occurs in **electrochemical cells**

Electrochemical cells in their most simple form consist of

- two electronic conductors → **electrodes**
both in contact with
- one ionic conductor (or solution) → **electrolyte**



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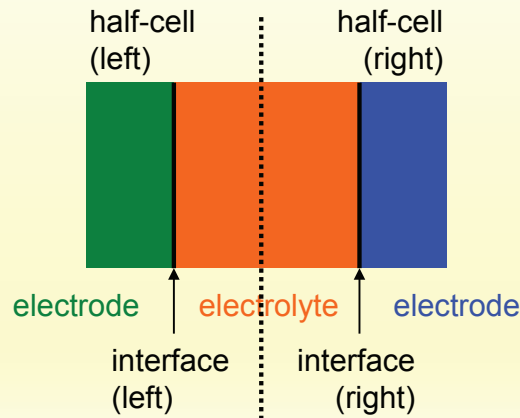
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Electrochemical cells: half-cells

In electrochemical cells **electrochemical reactions** occur at the **interfaces** between the electrolyte and the electrodes

Each electrode/electrolyte couple is referred to as **half-cell**; the electrochemical reaction occurring at its interface as **half-cell reaction**



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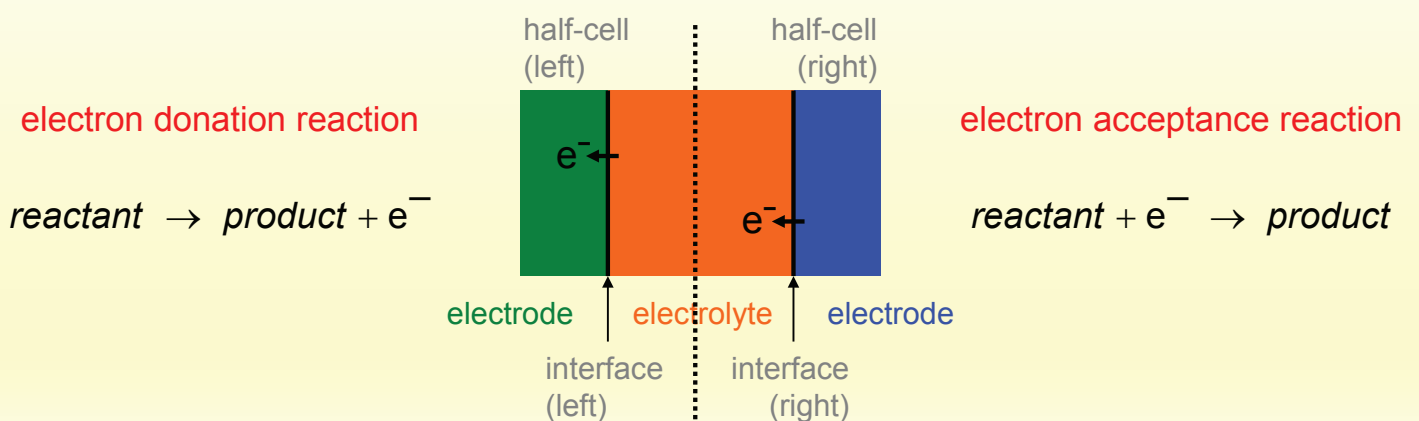
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Electrochemical cells: half-cell reactions

The electrochemical reactions at the electrode/electrolyte interfaces involve **electron transfer** between the electrode and the electrolyte (or species in solution)

There are two distinct types of half-cell reaction:

- the electrolyte (or species in solution) **donates** electron(s) to the electrode
- the electrolyte (or species in solution) **accepts** electron(s) from the electrode



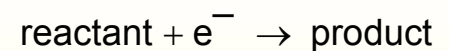
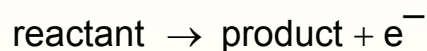
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Electrochemical cells: oxidation and reduction

electron donation reaction

electron acceptance reaction

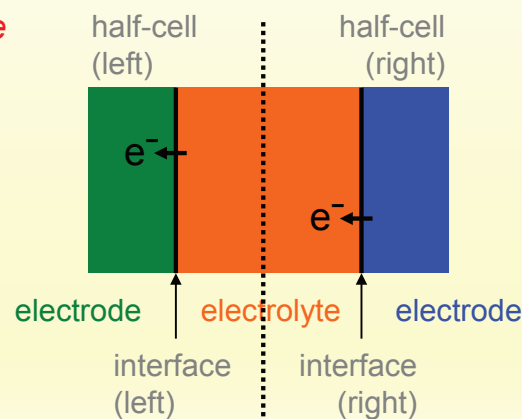


OXIDATION

- loss of electrons
- increase in *oxidation state*

REDUCTION

- gain of electrons
- decrease in *oxidation state*



Intermezzo: oxidation state

The definition⁽¹⁾ as listed by IUPAC (International Union of Pure and Applied Chemistry)

A measure of the degree of oxidation of an atom in a substance.

It is defined as **the charge an atom might be imagined to have** when electrons are counted according to an agreed-upon set of rules:

- (1) the oxidation state of a free element (un-combined element) is zero;
- (2) for a simple (monatomic) ion, the oxidation state is equal to the net charge on the ion;
- (3) hydrogen has an oxidation state of 1 and oxygen has an oxidation state of -2 when they are present in most compounds. (Exceptions to this are that hydrogen has an oxidation state of -1 in hydrides of active metals, e.g. LiH, and oxygen has an oxidation state of -1 in peroxides, e.g. H₂O₂);
- (4) the algebraic sum of oxidation states of all atoms in a neutral molecule must be zero, while in ions the algebraic sum of the oxidation states of the constituent atoms must be equal to the charge on the ion. For example, the oxidation states of sulfur in H₂S, S₈ (elementary sulphur), SO₂, SO₃, and H₂SO₄ are, respectively: -2, 0, +4, +6 and +6.

The higher the oxidation state of a given atom, the greater is its degree of oxidation; the lower the oxidation state, the greater is its degree of reduction.

(1) source: http://en.wikipedia.org/wiki/Oxidation_state

Intermezzo: oxidation state

CHEMIX - PERIODIC TABLE

Graphics Close

Atomic number
 Name
 Relative atomic mass u
 Melting point $^{\circ}C$
 Boiling point $^{\circ}C$
 Density g/cm^3
 Covalent radius $\cdot 10^{-10} m$
 Atomic radius $\cdot 10^{-10} m$
 Atomic volume cm^3/mol

First ionization potential V
 Specific heat capacity $Jg^{-1}K^{-1}$
 Electrical conductivity $\cdot 10^6 Ohm^{-1}cm^{-1}$
 Thermal conductivity $Wcm^{-1}K^{-1}$
 Electronegativity Pauling
 Heat of fusion kJ/mol
 Heat of vaporization kJ/mol
 Acid-base properties
 Number of stable isotopes

Electron configuration
 Oxidation states
 Phase $20^{\circ}C$
 Crystal structure 18/IIIA

Group	1/A	2/IIA	3/IIIB	4/IVB	5/VB	6/VI	7/VII	8/VIII	9/VIII	10/VIII	11/IB	12/IIB	13/IIIA	14/IVA	15/VA	16/VI	17/VIIA	18/VIIIA
1	2	3	4,3	5,4,3	3,2,6	2,3,4	2,3	2,3	2,3	2,1	2	3	4	4,2	3,3,5	2	1	
H	Li	Be	B	C	N	O	F	Ne										
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Na	Mg	Al	Si	P	S	Cl	Ar											
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Fr	Ra	Ac																
Lanthanides ->			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Actinides ->			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

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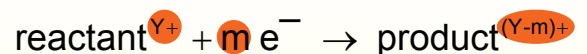
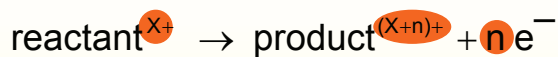
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Electrochemical cells: oxidation and reduction

electron donation reaction

more formal

electron acceptance reaction

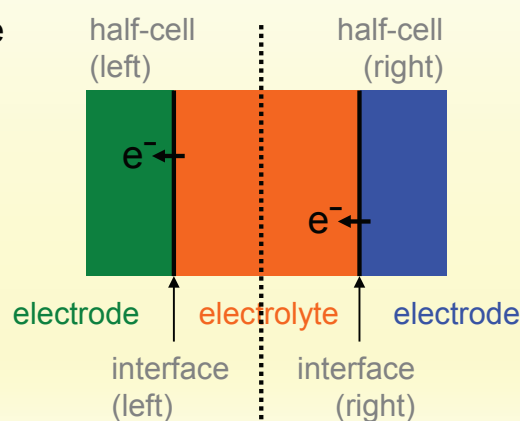


OXIDATION

- loss of electrons
- increase in oxidation state

REDUCTION

- gain of electrons
- decrease in oxidation state



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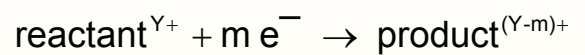
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Electrochemical cells: oxidation and reduction

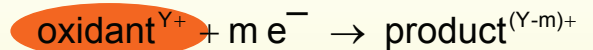
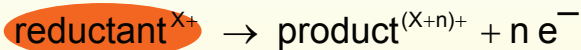
electron donation reaction

electron acceptance reaction



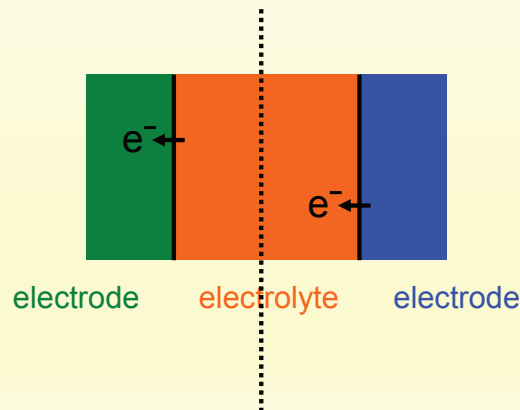
OXIDATION

REDUCTION



the **reductant** transfers electrons to another substance, and is, thus, oxidized itself. And, because it "donates" electrons it is also called an **electron donor**.

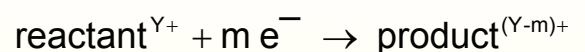
the **oxidant** removes electrons from another substance, and is, thus, reduced itself. And, because it "accepts" electrons, it is also called an **electron acceptor**.



Electrochemical cells: oxidation and reduction

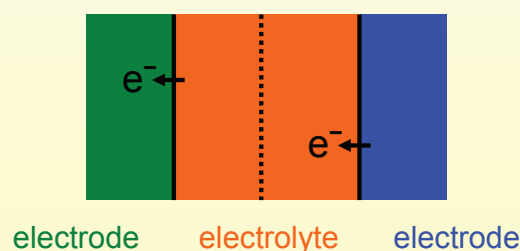
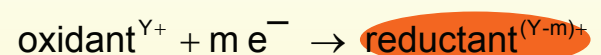
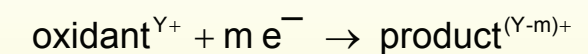
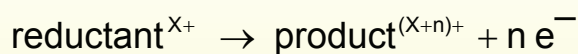
electron donation reaction

electron acceptance reaction



OXIDATION

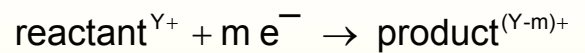
REDUCTION



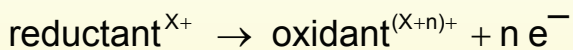
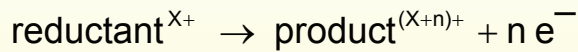
Electrochemical cells: anode and cathode

electron donation reaction

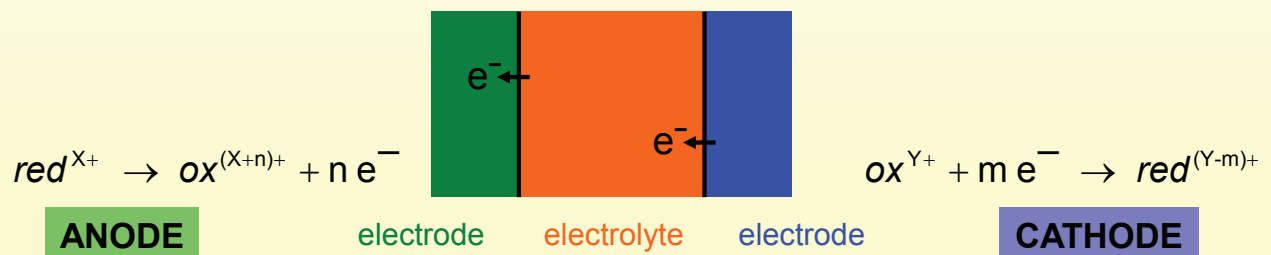
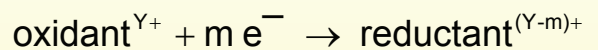
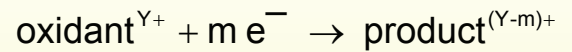
electron acceptance reaction



OXIDATION



REDUCTION



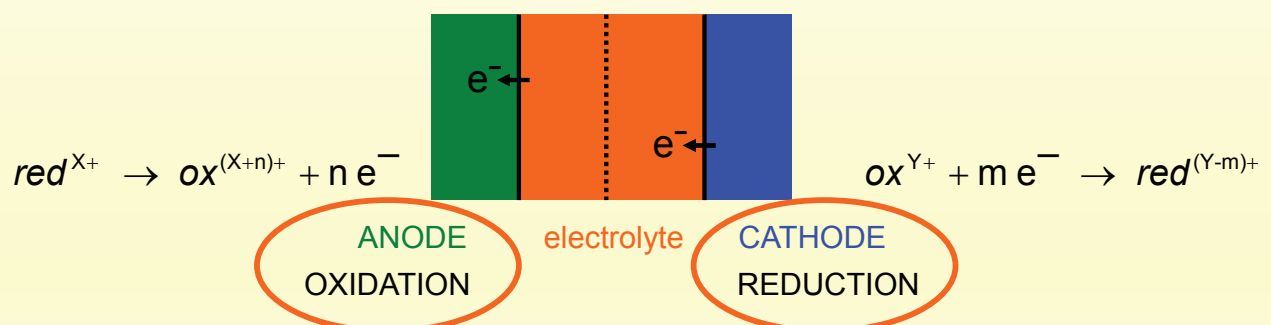
Electrochemical cells: anode and cathode

by definition:
oxidation at the anode reduction at the cathode

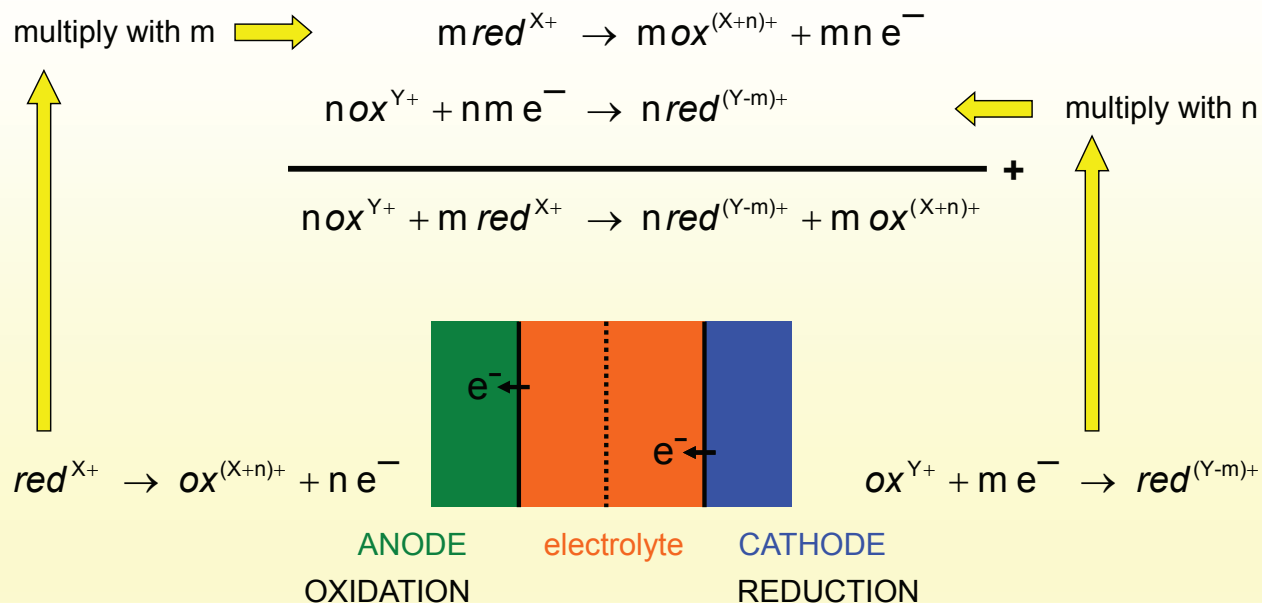
O A R C

two vowels

two consonants



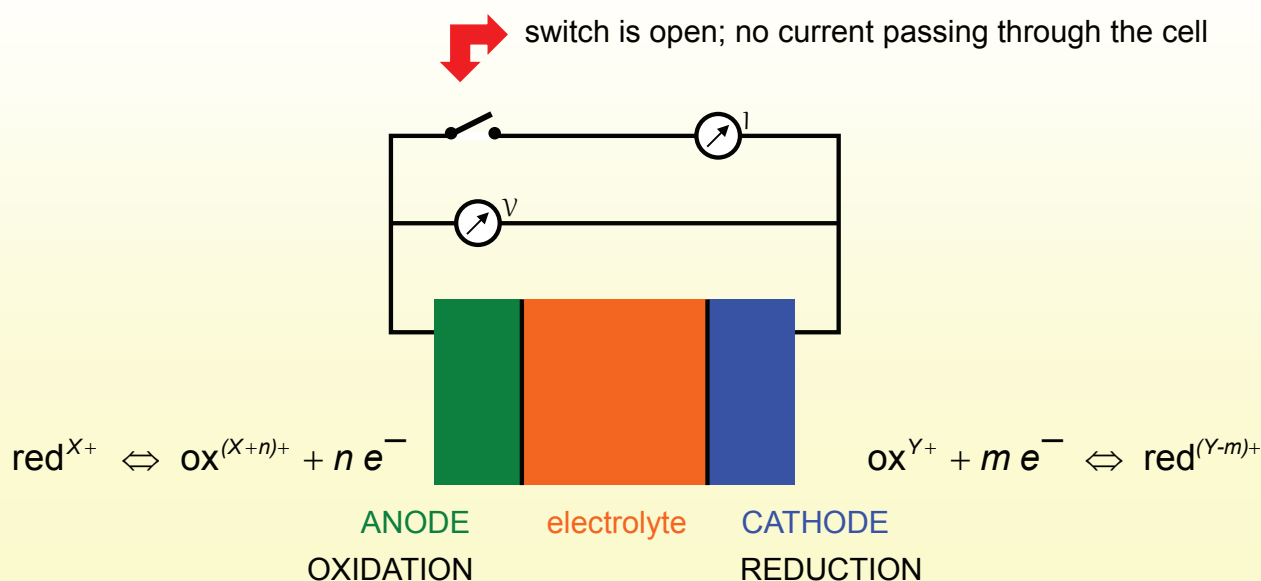
Electrochemical cells: net cell reaction



Electrochemical cells: cell potential

by convention (IUPAC):

$$\Delta E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$



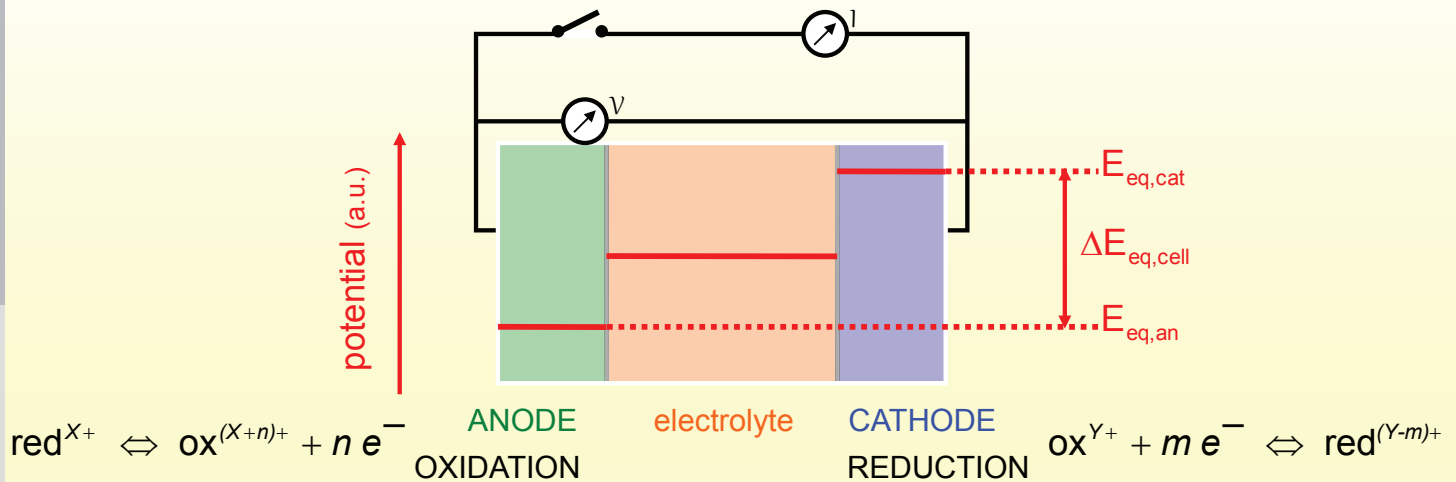
Electrochemical cells: cell potential

by convention (IUPAC):

$$\Delta E_{\text{eq,cell}} = E_{\text{eq,cathode}} - E_{\text{eq,anode}}$$

with E_{eq} electrode potential at current 0

↪ equilibrium at both electrode/electrolyte interfaces



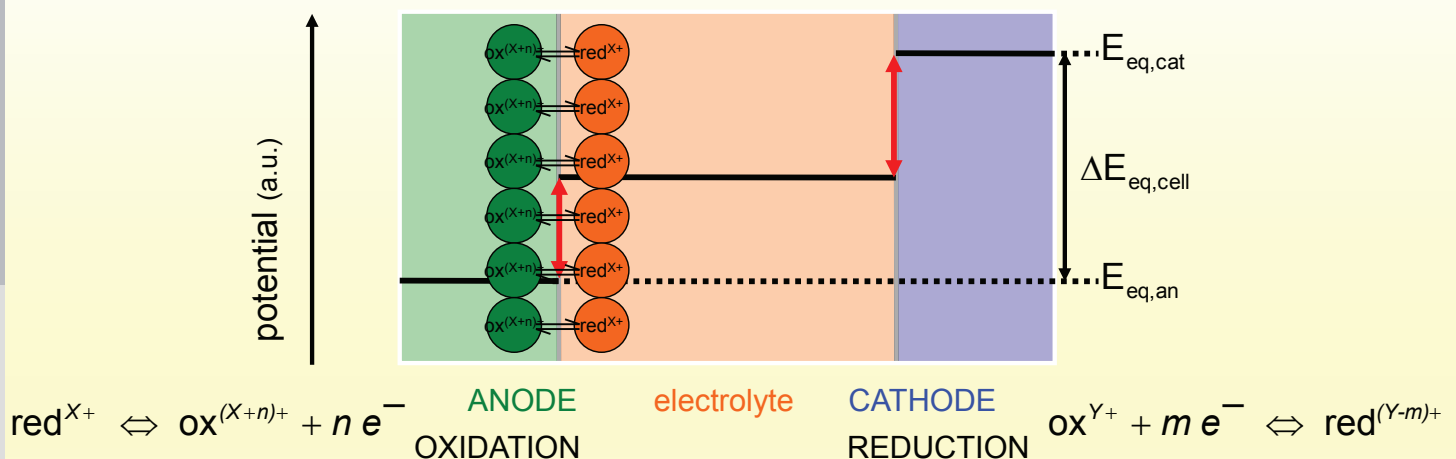
Electrochemical cells: cell potential

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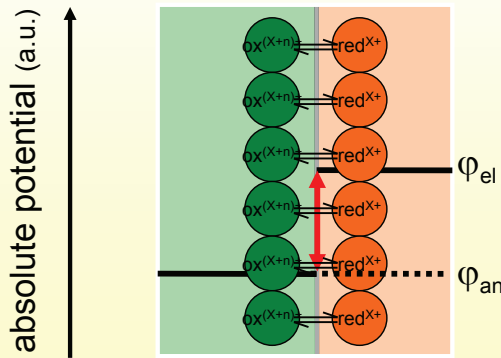
↪ equilibrium at both electrode/electrolyte interfaces



Electrochemical cells: electrode potential

electrochemical (thermodynamic) equilibrium at the anode/electrolyte interface:
the electrochemical potential $\tilde{\mu}_i$ of all species i must be equal in both phases (an,el)

$$(\tilde{\mu}_i)_{an} = (\tilde{\mu}_i)_{el} \quad \sum_i v_i \tilde{\mu}_i = 0 \quad v_i \text{ stoichiometric coefficients}$$



$$\tilde{\mu}_i = \underbrace{\mu_T^0 + RT \ln a_i}_{\text{chemical potential}} + \underbrace{nF\phi}_{\text{electrical potential}}$$

μ_T^0 chemical potential at standard conditions

a_i activity of species i

= 1 for solids

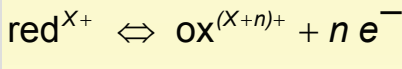
= $f_i c_i$ for solutions

f_i activity coefficient

= 1 for diluted solutions

c_i concentration

= p_i pressure for ideal gases



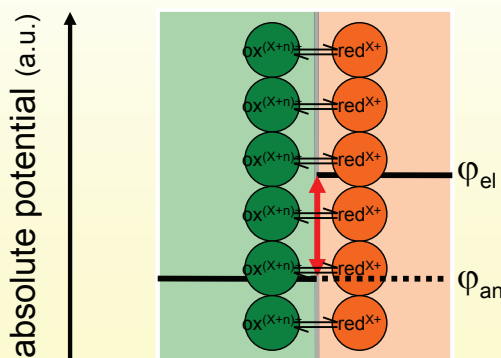
ANODE
OXIDATION

electrolyte

Electrochemical cells: electrode potential

electrochemical (thermodynamic) equilibrium at the anode/electrolyte interface:
the electrochemical potential $\tilde{\mu}_i$ of all species i must be equal in both phases (an,el)

$$(\tilde{\mu}_i)_{an} = (\tilde{\mu}_i)_{el} \quad \sum_i v_i \tilde{\mu}_i = 0 \quad v_i \text{ stoichiometric coefficients}$$



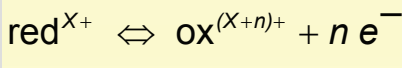
$$\tilde{\mu}_i = \mu_T^0 + RT \ln a_i + nF\phi$$

for the anodic oxidation reaction given here:

$$\begin{aligned} \mu_{T,red}^0 + RT \ln a_{red} + nF\phi_{el} \\ = \mu_{T,ox}^0 + RT \ln a_{ox} + nF\phi_{an} \end{aligned}$$

$$\phi_{an} - \phi_{el} = \frac{\mu_{T,ox}^0 - \mu_{T,red}^0}{nF} + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}}$$

$$\Delta\phi_{T,eq} = \Delta\phi_{T,eq}^0 + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}}$$

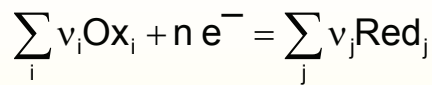


ANODE
OXIDATION

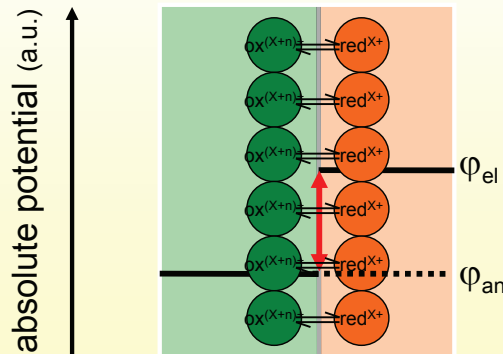
electrolyte

Electrochemical cells: electrode potential

in more general terms



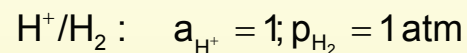
NOTE: now written as reduction reaction!



$$\Delta\varphi_{T,eq} = \Delta\varphi_{T,eq}^0 - \frac{RT}{nF} \ln \left[\frac{\prod_j a_{red,j}^{\nu_j}}{\prod_i a_{ox,i}^{\nu_i}} \right]$$

however instead of absolute potentials electrode potentials relative to a defined standard reference electrode are preferred

SHE: standard hydrogen electrode



$$E_{25^\circ\text{C},eq,\text{H}_2/\text{H}^+}^0 = 0 \text{ Volt}$$

$$E_{T,eq,ox/red} = E_{T,eq,ox/red}^0 - \frac{RT}{nF} \ln \left[\frac{\prod_j a_{red,j}^{\nu_j}}{\prod_i a_{ox,i}^{\nu_i}} \right]$$

Nernst potential

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Electrochemical cells: reduction potentials

standard reduction potentials (relative to SHE)
can be found in tables in most reference works

$$E_{T,eq,ox/red} = E_{T,eq,ox/red}^0 - \frac{RT}{nF} \ln \left[\frac{\prod_j a_{red,j}^{\nu_j}}{\prod_i a_{ox,i}^{\nu_i}} \right]$$

TABLE 1. Alphabetical Listing

Reaction	E°/V	Reaction	E°/V
$\text{Ac}^+ + 3 e^- \rightleftharpoons \text{Ac}$	-2.20	$\text{As} + 3 \text{H}^+ + 3 e^- \rightleftharpoons \text{AsH}_3$	-0.608
$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$	0.7996	$\text{As}_2\text{O}_3 + 6 \text{H}^+ + 6 e^- \rightleftharpoons 2 \text{As} + 3 \text{H}_2\text{O}$	0.234
$\text{Ag}^{2+} + e^- \rightleftharpoons \text{Ag}^+$	1.980	$\text{HAsO}_2 + 3 \text{H}^+ + 3 e^- \rightleftharpoons \text{As} + 2 \text{H}_2\text{O}$	0.248
$\text{Ag}(\text{ac}) + e^- \rightleftharpoons \text{Ag} + (\text{ac})^-$	0.643	$\text{AsO}_2^- + 2 \text{H}_2\text{O} + 3 e^- \rightleftharpoons \text{As} + 4 \text{OH}^-$	-0.68
$\text{AgBr} + e^- \rightleftharpoons \text{Ag} + \text{Br}^-$	0.07133	$\text{H}_2\text{AsO}_4 + 2 \text{H}^+ + 2 e^- \rightleftharpoons \text{HAsO}_4 + 2 \text{H}_2\text{O}$	0.560
$\text{AgBrO}_2 + e^- \rightleftharpoons \text{Ag} + \text{BrO}_2^-$	0.546	$\text{AsO}_4^{3-} + 2 \text{H}_2\text{O} + 2 e^- \rightleftharpoons \text{AsO}_2^- + 4 \text{OH}^-$	-0.71
$\text{Ag}_2\text{C}_2\text{O}_4 + 2 e^- \rightleftharpoons 2 \text{Ag} + \text{C}_2\text{O}_4^{2-}$	0.4647	$\text{At}_2 + 2 e^- \rightleftharpoons 2 \text{At}^-$	0.3
$\text{AgCl} + e^- \rightleftharpoons \text{Ag} + \text{Cl}^-$	0.22233	$\text{Au}^+ + e^- \rightleftharpoons \text{Au}$	1.692
$\text{AgCN} + e^- \rightleftharpoons \text{Ag} + \text{CN}^-$	-0.017	$\text{Au}^{2+} + 2 e^- \rightleftharpoons \text{Au}^+$	1.401
$\text{Ag}_2\text{CO}_3 + 2 e^- \rightleftharpoons 2 \text{Ag} + \text{CO}_3^{2-}$	0.47	$\text{Au}^{3+} + 3 e^- \rightleftharpoons \text{Au}$	1.498
$\text{Ag}_2\text{CrO}_4 + 2 e^- \rightleftharpoons 2 \text{Ag} + \text{CrO}_4^{2-}$	0.4470	$\text{Au}^{3+} + e^- \rightleftharpoons \text{Au}^+$	1.8
$\text{AgF} + e^- \rightleftharpoons \text{Ag} + \text{F}^-$	0.779	$\text{AuOH}^{2+} + \text{H}^+ + 2 e^- \rightleftharpoons \text{Au}^+ + \text{H}_2\text{O}$	1.32
$\text{Ag}[\text{Fe}(\text{CN})_6] + 4 e^- \rightleftharpoons 4 \text{Ag} + [\text{Fe}(\text{CN})_6]^{4-}$	0.1478	$\text{AuBr}_2^- + e^- \rightleftharpoons \text{Au} + 2 \text{Br}^-$	0.959
$\text{AgI} + e^- \rightleftharpoons \text{Ag} + \text{I}^-$	-0.15224	$\text{AuBr}_3 + 3 e^- \rightleftharpoons \text{Au} + 4 \text{Br}^-$	0.854
$\text{AgIO}_3 + e^- \rightleftharpoons \text{Ag} + \text{IO}_3^-$	0.354	$\text{AuCl}_2^- + 3 e^- \rightleftharpoons \text{Au} + 4 \text{Cl}^-$	1.002
$\text{Ag}_2\text{MoO}_4 + 2 e^- \rightleftharpoons 2 \text{Ag} + \text{MoO}_4^{2-}$	0.4573	$\text{Au}(\text{OH})_2 + 3 \text{H}^+ + 3 e^- \rightleftharpoons \text{Au} + 3 \text{H}_2\text{O}$	1.45
$\text{AgNO}_2 + e^- \rightleftharpoons \text{Ag} + 2 \text{NO}_2^-$	0.564	$\text{H}_2\text{BO}_3^- + 5 \text{H}_2\text{O} + 8 e^- \rightleftharpoons \text{BH}_4^- + 8 \text{OH}^-$	-1.24
$\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2 e^- \rightleftharpoons 2 \text{Ag} + 2 \text{OH}^-$	0.342	$\text{H}_2\text{BO}_3^- + \text{H}_2\text{O} + 3 e^- \rightleftharpoons \text{B} + 4 \text{OH}^-$	-1.79
$\text{Ag}_2\text{O}_2 + \text{H}_2\text{O} + 2 e^- \rightleftharpoons 2 \text{Ag} + 2 \text{OH}^-$	0.739	$\text{H}_2\text{BO}_2 + 3 \text{H}^+ + 3 e^- \rightleftharpoons \text{B} + 3 \text{H}_2\text{O}$	-0.8698
$\text{Ag}^{2+} + 2 e^- \rightleftharpoons \text{Ag}^+$	1.9	$\text{B}(\text{OH})_3 + 7 \text{H}^+ + 8 e^- \rightleftharpoons \text{BH}_4^- + 3 \text{H}_2\text{O}$	-0.481
$\text{Ag}^{2+} + e^- \rightleftharpoons \text{Ag}^+$	1.8	$\text{Ba}^{2+} + 2 e^- \rightleftharpoons \text{Ba}$	-2.912
$\text{Ag}_2\text{O}_2 + 4 \text{H}^+ + e^- \rightleftharpoons 2 \text{Ag} + 2 \text{H}_2\text{O}$	1.802	$\text{Ba}^{2+} + 2 e^- \rightleftharpoons \text{Ba}(\text{Hg})$	-1.570
$2 \text{Ag}_2\text{O} + \text{H}_2\text{O} + 2 e^- \rightleftharpoons \text{Ag}_2\text{O} + 2 \text{OH}^-$	0.607	$\text{Ba}(\text{OH})_2 + 2 e^- \rightleftharpoons \text{Ba} + 2 \text{OH}^-$	-2.99
$\text{AgOCN} + e^- \rightleftharpoons \text{Ag} + \text{OCN}^-$	0.41	$\text{Be}^{2+} + 2 e^- \rightleftharpoons \text{Be}$	-1.847
$\text{Ag}_2\text{S} + 2 e^- \rightleftharpoons 2 \text{Ag} + \text{S}^{2-}$	-0.691	$\text{Be}_2\text{O}_3 + 3 \text{H}_2\text{O} + 4 e^- \rightleftharpoons 2 \text{Be} + 6 \text{OH}^-$	-2.63

source:
Vanýsek, Petr (2007). "Electrochemical Series",
in Handbook of Chemistry and Physics: 88th
Edition (Chemical Rubber Company).

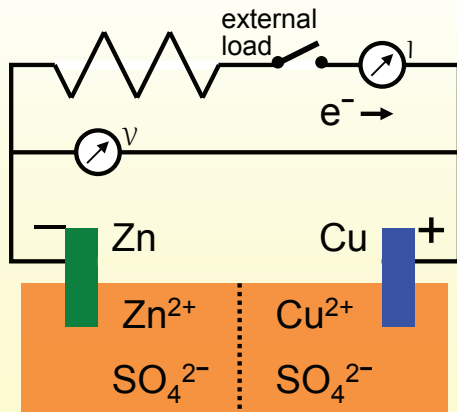
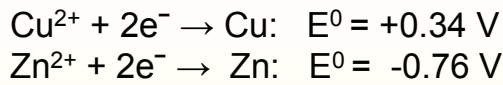
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– Principles of Electrochemistry (IEK-9)

Electrochemical cells: reduction potentials

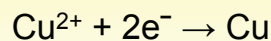
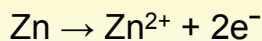
an example



ANODE electrolyte CATHODE

OXIDATION

REDUCTION



$$E_{T,\text{eq,ox/red}} = E_{T,\text{eq,ox/red}}^{\circ} - \frac{RT}{nF} \ln \left[\frac{\prod_j a_{\text{red},j}^{\nu_j}}{\prod_i a_{\text{ox},i}^{\nu_i}} \right]$$

$$E_{\text{Cu/Cu}^{2+}} = E_{\text{Cu/Cu}^{2+}}^{\circ} - \frac{RT}{2F} \ln \left[\frac{1}{c_{\text{Cu}^{2+}}} \right]$$

$$E_{\text{Zn/Zn}^{2+}} = E_{\text{Zn/Zn}^{2+}}^{\circ} - \frac{RT}{2F} \ln \left[\frac{1}{c_{\text{Zn}^{2+}}} \right]$$

$$\Delta E_{\text{eq,cell}} = E_{\text{eq,cathode}} - E_{\text{eq,anode}}$$

$$\Delta E_{\text{eq,cell}} = +0.34 - (-0.76) - \frac{RT}{2F} \ln \left[\frac{c_{\text{Zn}^{2+}}}{c_{\text{Cu}^{2+}}} \right]$$

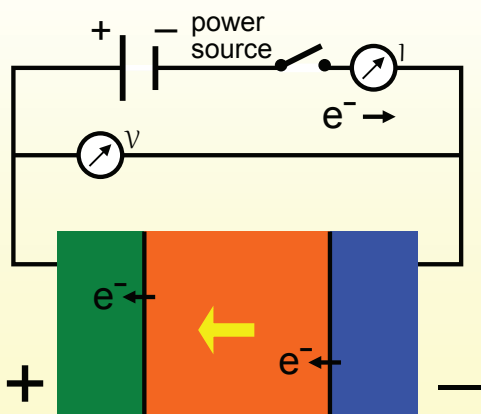
$$= +1.1 - \frac{RT}{2F} \ln \left[\frac{c_{\text{Zn}^{2+}}}{c_{\text{Cu}^{2+}}} \right]$$

$\Delta E_{\text{eq,cell}}^{\circ} > 0 \rightarrow$ a spontaneous reaction!

Electrochemical cells: electrolytic and galvanic cells

$\Delta E_{\text{eq,cell}} < 0$ electrolytic cell

- needs to be electrically driven
- not spontaneous



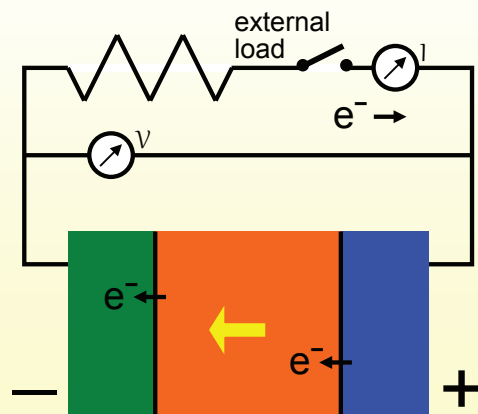
ANODE electrolyte CATHODE

OXIDATION

REDUCTION

$\Delta E_{\text{eq,cell}} > 0$ galvanic cell

- produces electrical energy
- spontaneous



ANODE electrolyte CATHODE

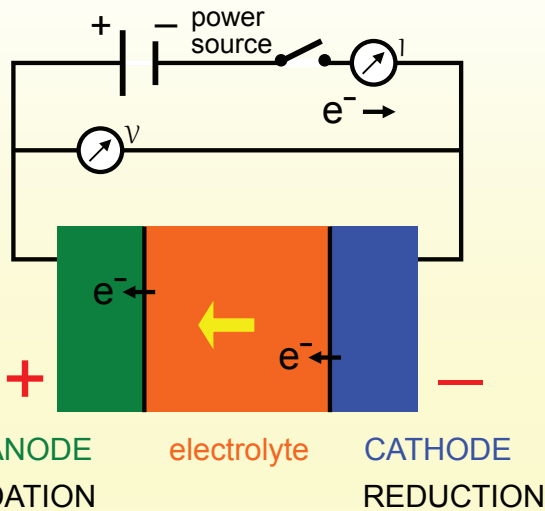
OXIDATION

REDUCTION

Electrochemical cells: electrolytic and galvanic cells

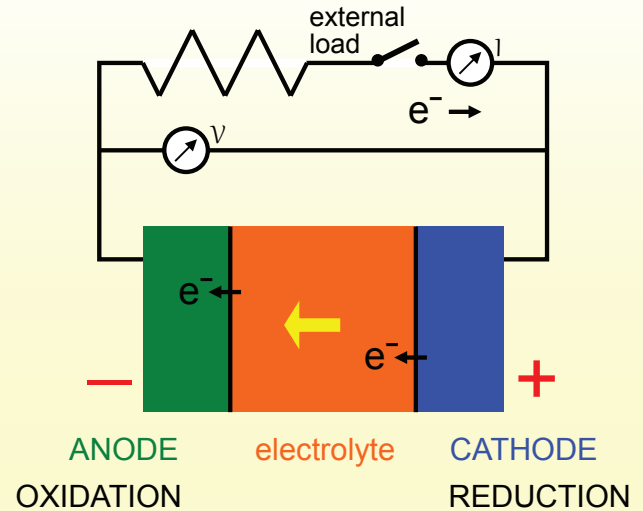
$\Delta E_{eq,cell} < 0$ electrolytic cell

- needs to be electrically driven
- not spontaneous



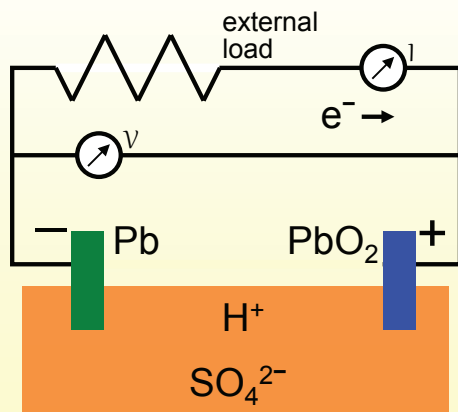
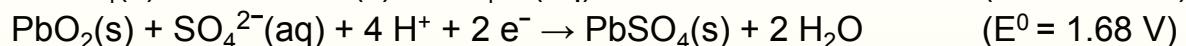
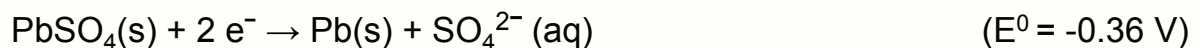
$\Delta E_{eq,cell} > 0$ galvanic cell

- produces electrical energy
- spontaneous



Electrochemical cells: galvanic cells

an example: the lead acid battery consists of Pb and PbO₂ electrodes in sulphuric acid

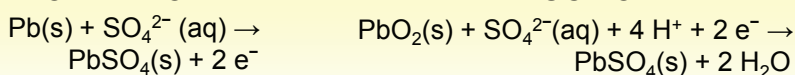


during **discharging** (electricity production)
PbSO₄ is formed on both electrodes

$$\Delta E_{eq,cell} = E_{eq,cathode} - E_{eq,anode}$$

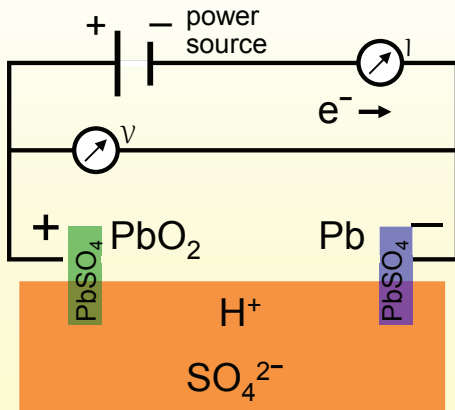
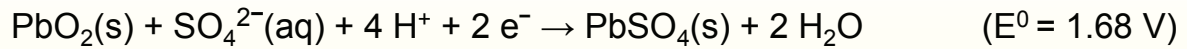
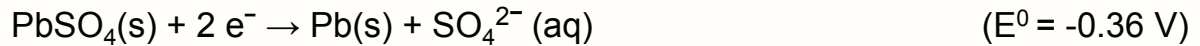
$$\begin{aligned} \Delta E_{eq,cell}^0 &= E_{\text{PbO}_2/\text{PbSO}_4}^0 - E_{\text{PbSO}_4/\text{Pb}}^0 \\ &= 1.68 - (-0.36) \text{ Volt} \\ &= 2.04 \text{ Volt} \end{aligned}$$

ANODE electrolyte **CATHODE**
OXIDATION REDUCTION



Electrochemical cells: galvanic cells

an example: the lead acid battery consists of Pb and PbO₂ electrodes in sulphuric acid



during **charging** an external power source has to apply a voltage higher than 2.04 V

$$\Delta E_{\text{eq,cell}} = E_{\text{eq,cathode}} - E_{\text{eq,anode}}$$

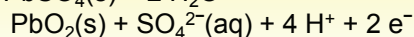
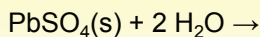
$$\begin{aligned} \Delta E_{\text{eq,cell}}^0 &= E_{\text{PbSO}_4/\text{Pb}}^0 - E_{\text{PbO}_2/\text{PbSO}_4}^0 \\ &= -0.36 - (1.68) \text{ Volt} \\ &= -2.04 \text{ Volt} \end{aligned}$$

ANODE

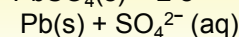
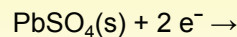
electrolyte

CATHODE

OXIDATION



REDUCTION



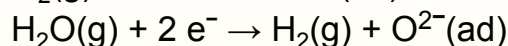
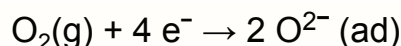
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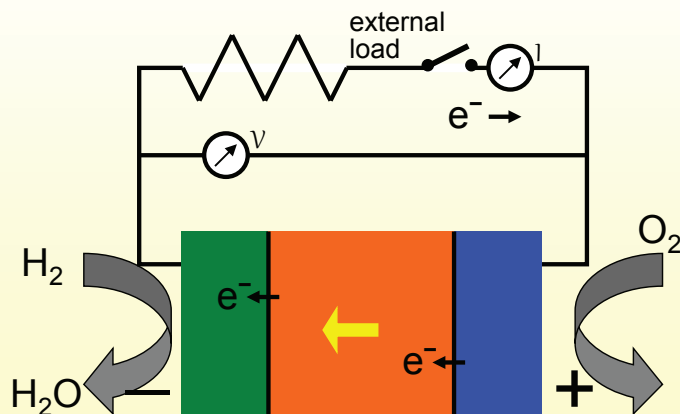
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Electrochemical cells: galvanic cells

another example: the (solid oxide) fuel cell



no standard reduction potentials
(relative to SHE) available



$$\Delta E_{\text{eq,cell}} = E_{\text{eq,cathode}} - E_{\text{eq,anode}}$$

$$\Delta E_{0,\text{cell}} = E_{\text{O}_2/\text{O}^{2-}}^0 - \frac{RT}{2F} \ln \frac{1}{p_{\text{O}_2}^{1/2}} +$$

$$- \left(E_{\text{H}_2/\text{H}_2\text{O}}^0 - \frac{RT}{2F} \ln \frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \right)$$

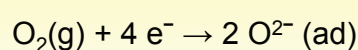
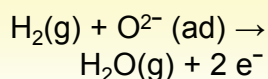
$$\Delta E_{\text{eq,cell}} = \left(E_{\text{O}_2/\text{O}^{2-}}^0 - E_{\text{H}_2/\text{H}_2\text{O}}^0 \right) - \frac{RT}{2F} \ln \frac{p_{\text{H}_2\text{O}}^{1/2}}{p_{\text{O}_2} p_{\text{H}_2}}$$

ANODE

electrolyte

CATHODE

OXIDATION



REDUCTION

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Electrochemical cells and thermodynamics

$$\Delta U = U_2 - U_1 = Q - W$$

$$G = H - TS$$

in fuel cells:

volume work	W_V	$W_V = p\Delta V$
electrical work	W_E	$W_E = nF \Delta E$
heat transfer	Q	$Q = T\Delta S$

$$H = U + pV$$

$$\begin{aligned} \Delta G_{T,p} &= \Delta H_{T,p} - T\Delta S_{T,p} \\ &= \Delta U_{T,p} + p\Delta V_{T,p} - T\Delta S_{T,p} \end{aligned}$$

$$\Delta U = T\Delta S - p\Delta V - nF \Delta E$$

$$\Delta U_{T,p} = \Delta G_{T,p} - p\Delta V_{T,p} + T\Delta S_{T,p}$$

$$\Delta G_{T,p} = -nF \Delta E_{T,p}$$

$$\Delta E_{T,p} = \frac{-\Delta G_{T,p}}{nF}$$

Fuel cells: Nernst, standard and heating voltage

$$\Delta E_{\Delta G}^0 = \frac{-\Delta G^0}{2F} \quad \text{standard voltage (all activities =1)}$$

measure for the available energy

for ΔG^0 and ΔH^0

$$\Delta E_{\Delta H}^0 = \frac{-\Delta H^0}{2F} \quad \text{heating voltage (based on enthalpy)}$$

measure for the maximum energy

values at 25 °C and 1 bar

can be found in
thermodynamic tables
in most reference works

$$\Delta E_{\text{Nernst}} = \Delta E_{\Delta G}^0 - \frac{RT}{2F} \ln \frac{p_{\text{H}_2\text{O}}}{p_{\text{O}_2}^{1/2} p_{\text{H}_2}} \quad \text{for} \quad \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$$

Nernst voltage or Open Circuit Voltage (OCV)

deviation from the standard voltage (concentration dependence)

Fuel cells: Nernst, standard and heating voltage

$$\Delta E_{\Delta G}^0 = \frac{-\Delta G^0}{2F}$$

temperature dependence:

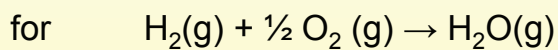
$$\Delta G_T = \Delta H_T - T\Delta S_T$$

$$\Delta E_{\Delta H}^0 = \frac{-\Delta H^0}{2F}$$

by useful approximation:

ΔH and ΔS are temperature independent

$$\Delta G_T = \Delta G^0 - (T - (273 + 25))\Delta S^0$$

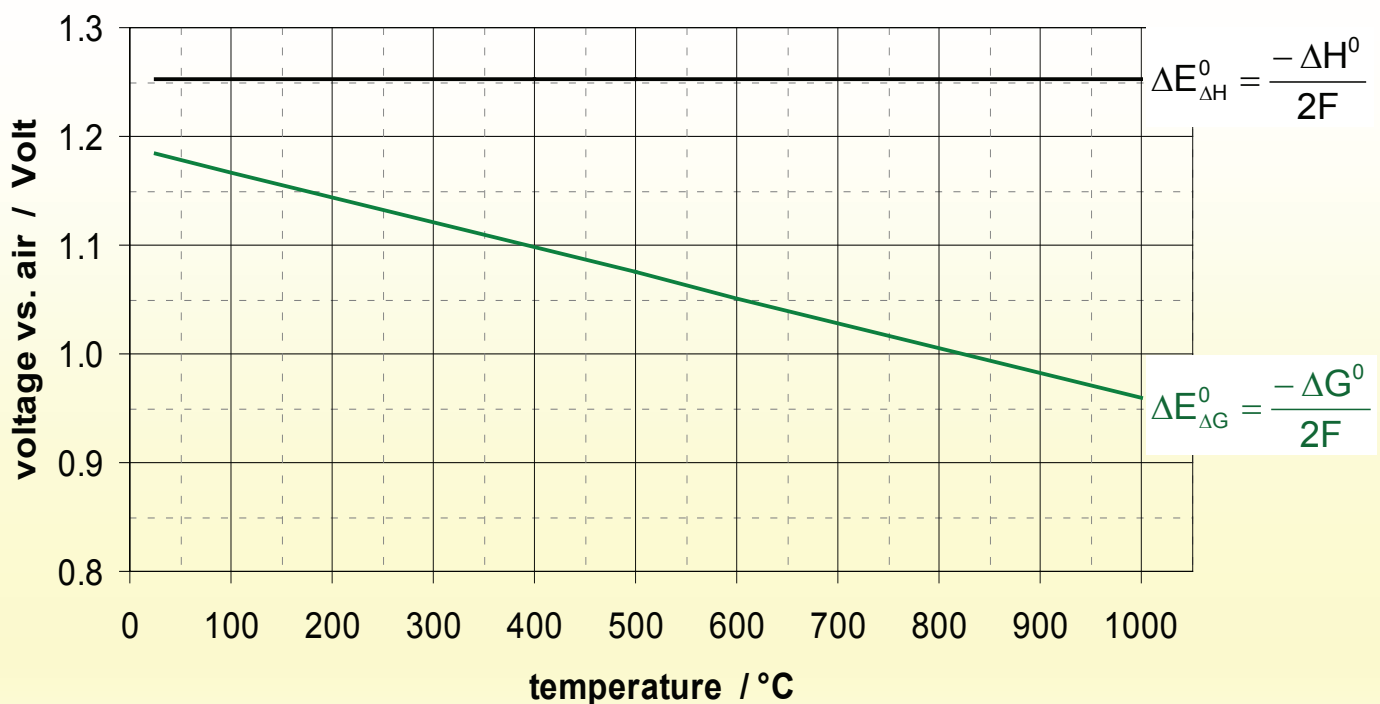


	ΔE^0	25 °C	800 °C
ΔG^0	= - 228.4 kJ/mol	1.184 V	1.006 V
ΔH^0	= - 241.8 kJ/mol	1.253 V	1.253 V
ΔS^0	= - 44.4 J/(mol K)		

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Fuel cells: Nernst, standard and heating voltage



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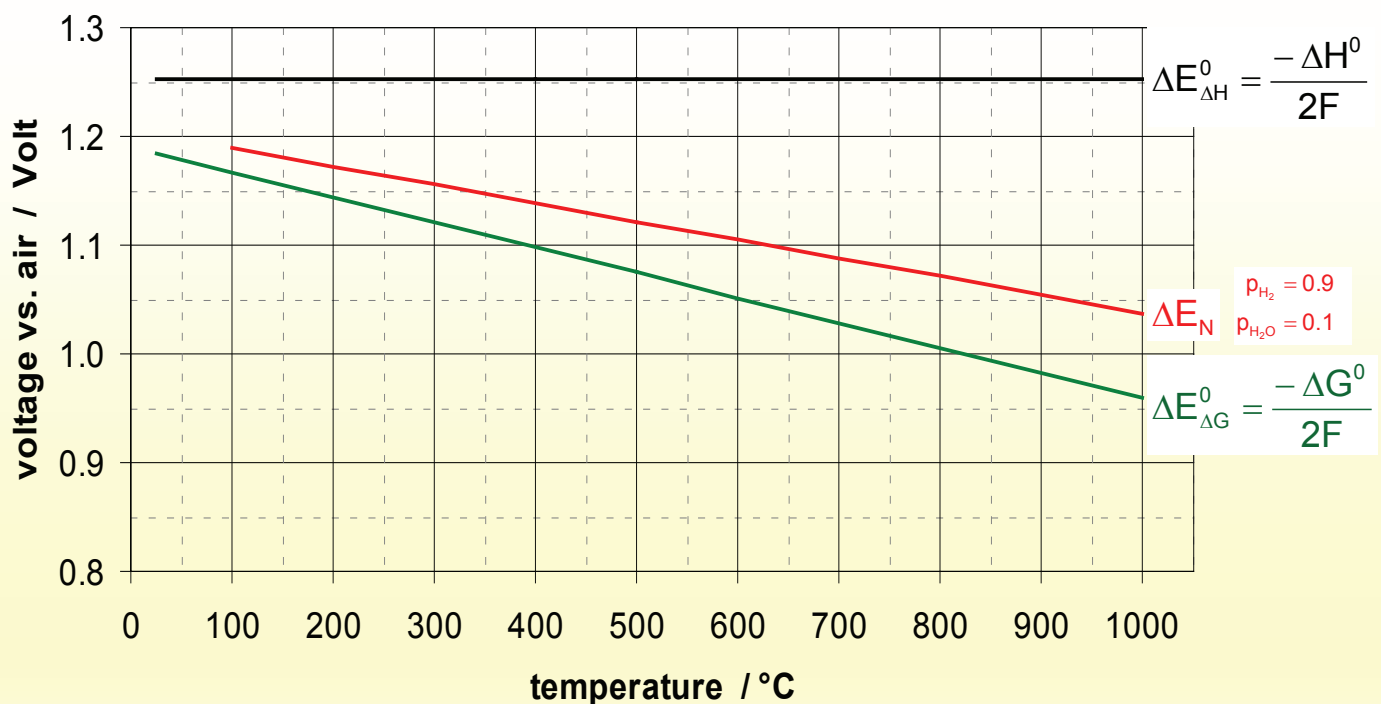
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Fuel cells: Nernst, standard and heating voltage

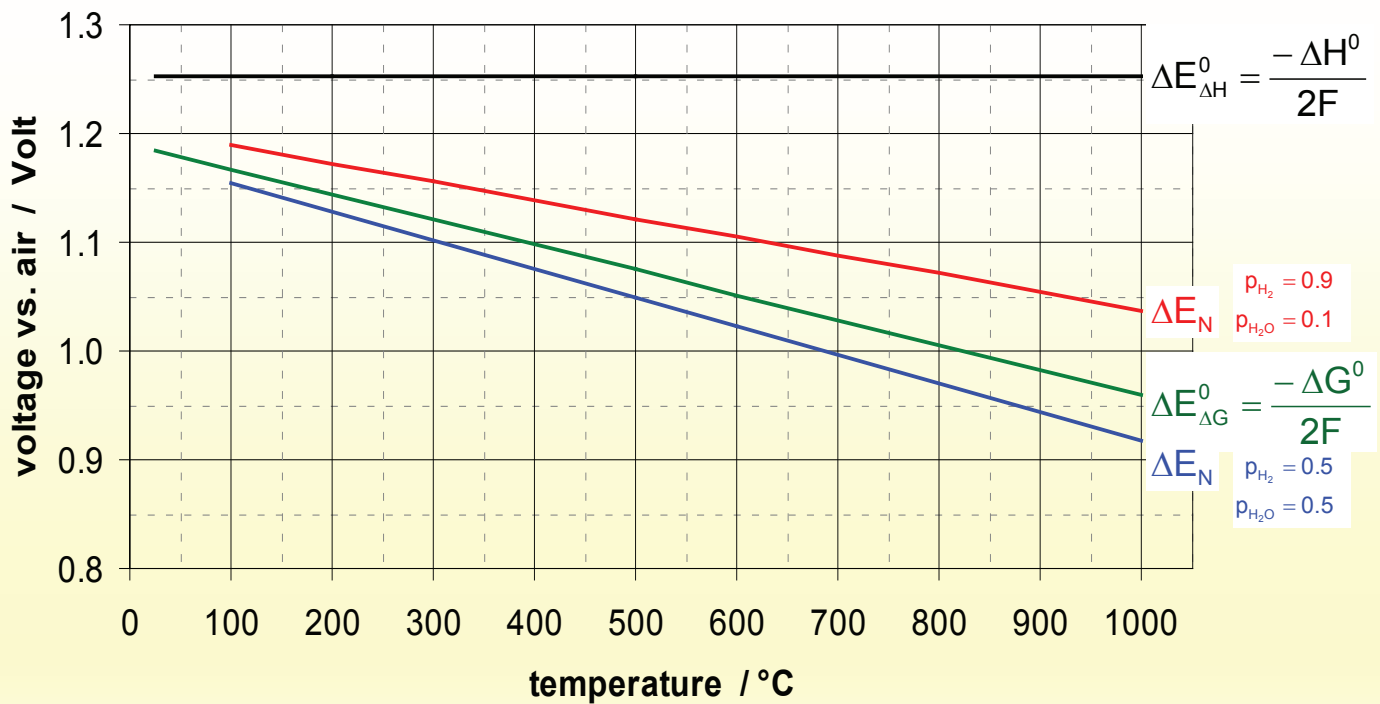
$$\Delta E_{\text{Nernst}}(T) = \Delta E_{\Delta G}^0(T) - \frac{RT}{2F} \ln \frac{p_{\text{H}_2\text{O}}}{p_{\text{O}_2}^{1/2} p_{\text{H}_2}}$$

	ΔE^0		
	25 °C	800 °C	
$\Delta E_{\Delta G}^0$	1.184 V	1.006 V	
$\Delta E_{\Delta H}^0$	1.253 V	1.253 V	
ΔE_N	1.202 V	1.071 V	for $p_{\text{H}_2} = 0.9$; $p_{\text{H}_2\text{O}} = 0.1$; $p_{\text{O}_2} = 0.21\text{bar}$ $p_{\text{H}_2} = 0.5$; $p_{\text{H}_2\text{O}} = 0.5$; $p_{\text{O}_2} = 0.21\text{bar}$
	1.174 V	0.970 V	

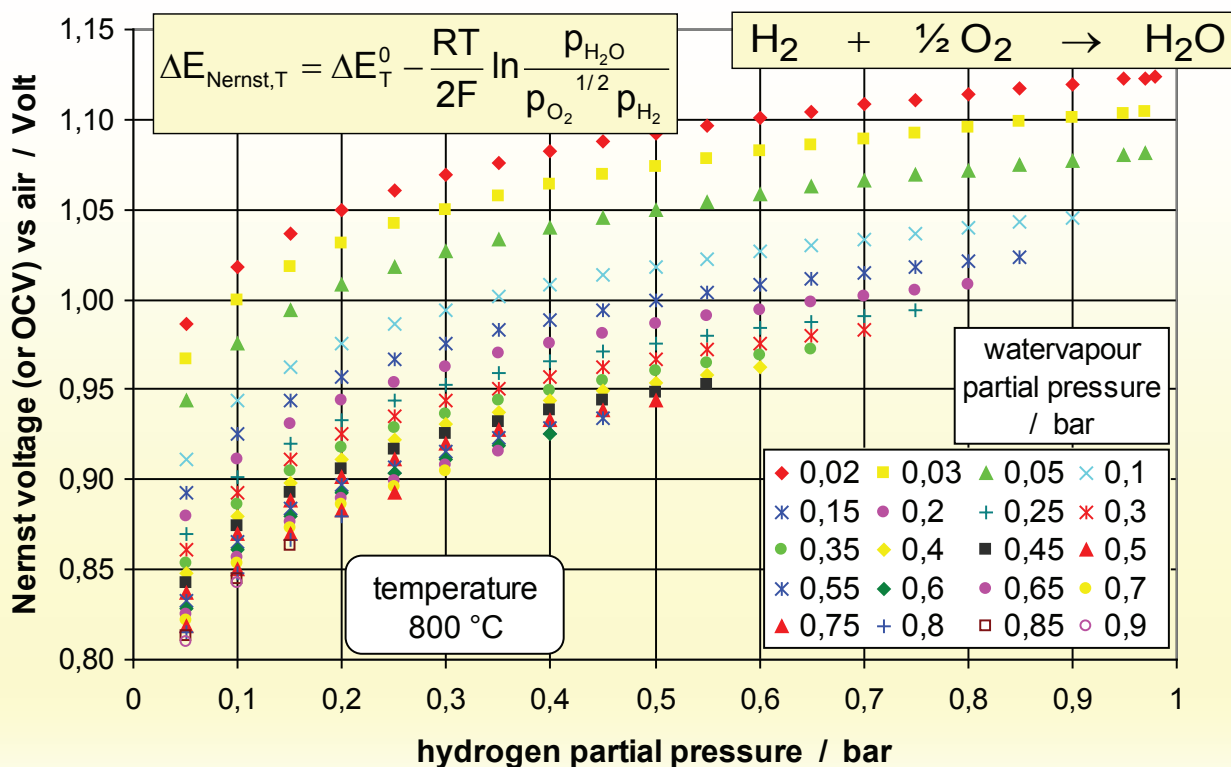
Fuel cells: Nernst, standard and heating voltage



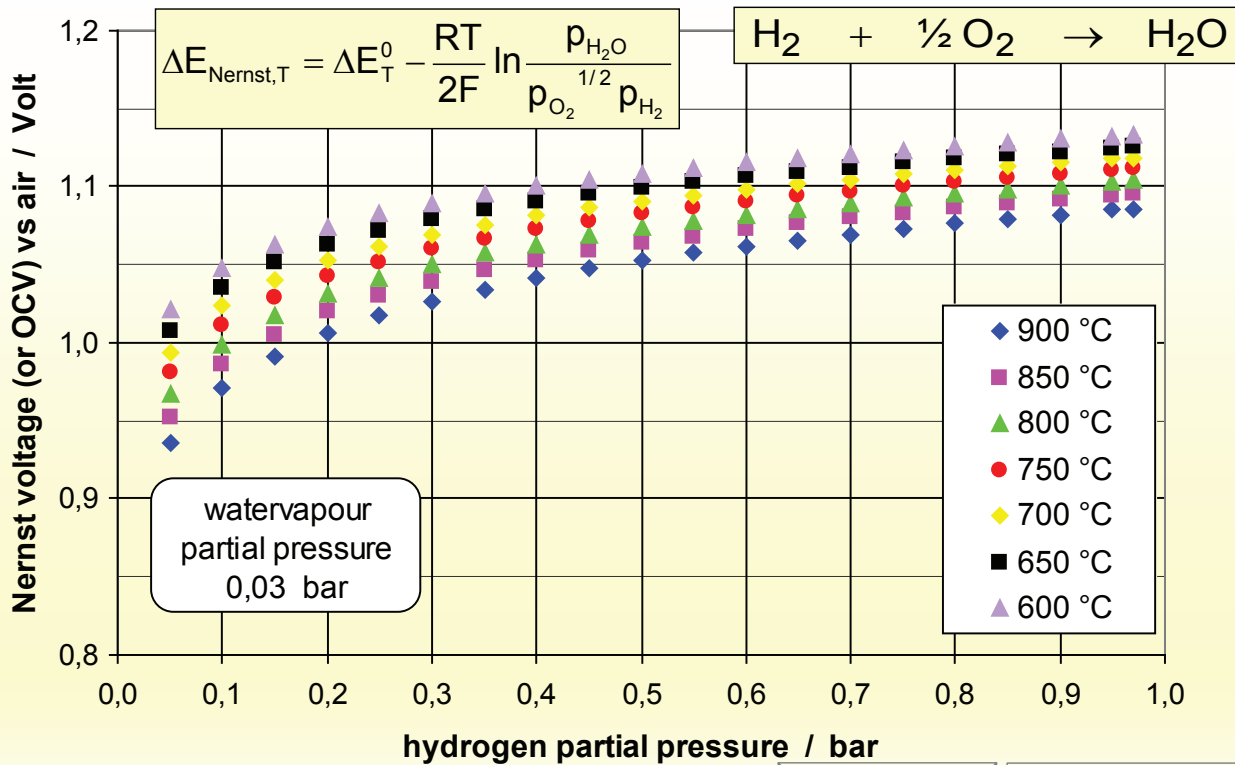
Fuel cells: Nernst, standard and heating voltage



Fuel cells: Nernst voltage



Fuel cells: Nernst voltage




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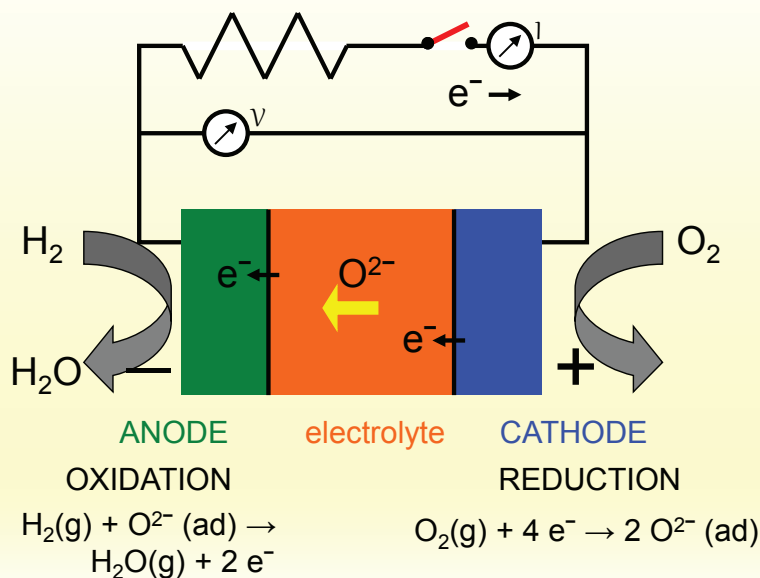
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– Principles of Electrochemistry (IEK-9)

Fuel cells

well...
let's start doing some actual work

 the switch is closed; current is passing through the cell



- transport of electric charge
- via ions in the electrolyte
 - via electrons in the outer circuit
 - via charge transfer across the electrode/electrolyte interfaces

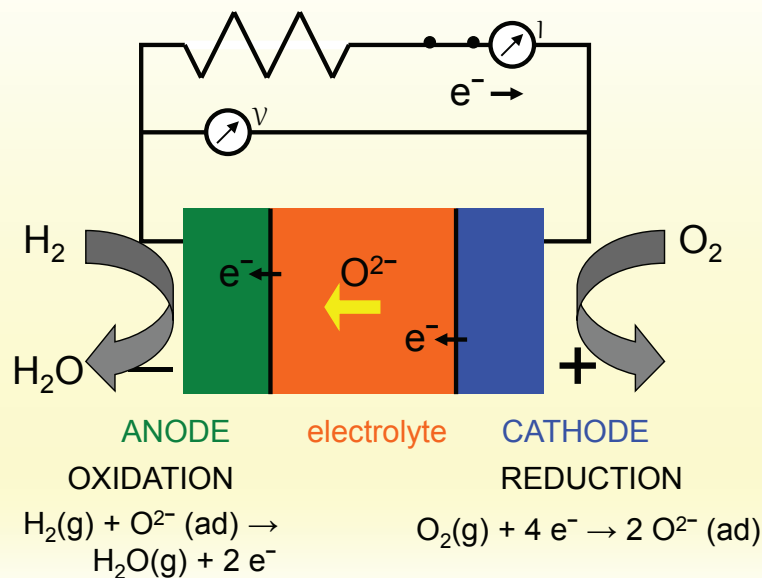
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– Principles of Electrochemistry (IEK-9)

Fuel cells: charge transport or electric current

transport of electric charge via charge transfer across the electrode/electrolyte interfaces



- implies the occurrence of electrochemical reactions at the interfaces
- the current corresponds to the rates of the reactions
- the current corresponds to the consumption of fuel

$$I = \text{total current [A]}$$

$$j = I/A = \text{current density [A/cm}^2\text{]}$$

$$A = \text{effective electrode area [cm}^2\text{]}$$

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Intermezzo: Faraday constant

the total charge Q transported by one mol of electrons is given by:

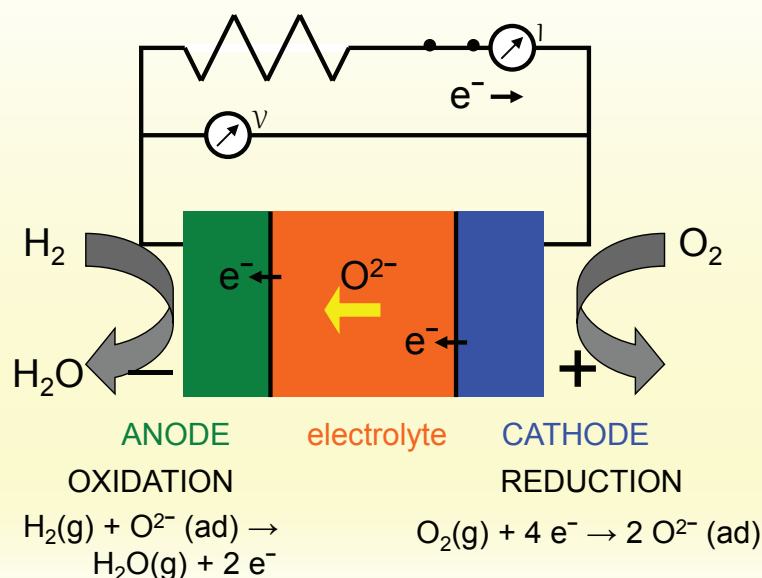
$$Q = N_A \cdot e$$

with N_A Avogadro constant = $6.022 \times 10^{23} \text{ mol}^{-1}$
 e elementary charge = $1.602 \times 10^{-19} \text{ C}$

$$Q = 96485 \text{ C mol}^{-1}$$

this is the
Faraday constant

$$F = 96485 \text{ C mol}^{-1} \\ = 96485 \text{ A s mol}^{-1}$$



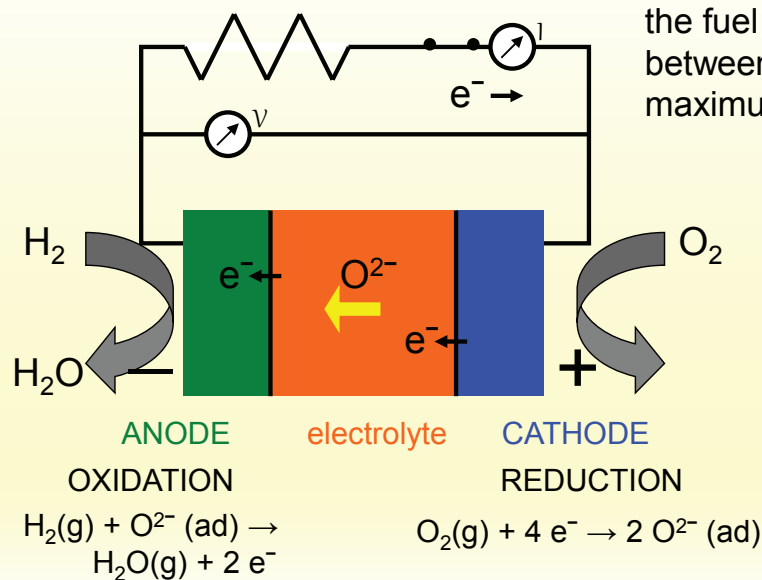
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Fuel cells: fuel utilisation u_F

the maximum current that can be drawn from a hydrogen supply \dot{n}_{H_2} (in [mol/s])

is given by $I_{max} = 2F\dot{n}_{H_2}$ ($n = 2$)

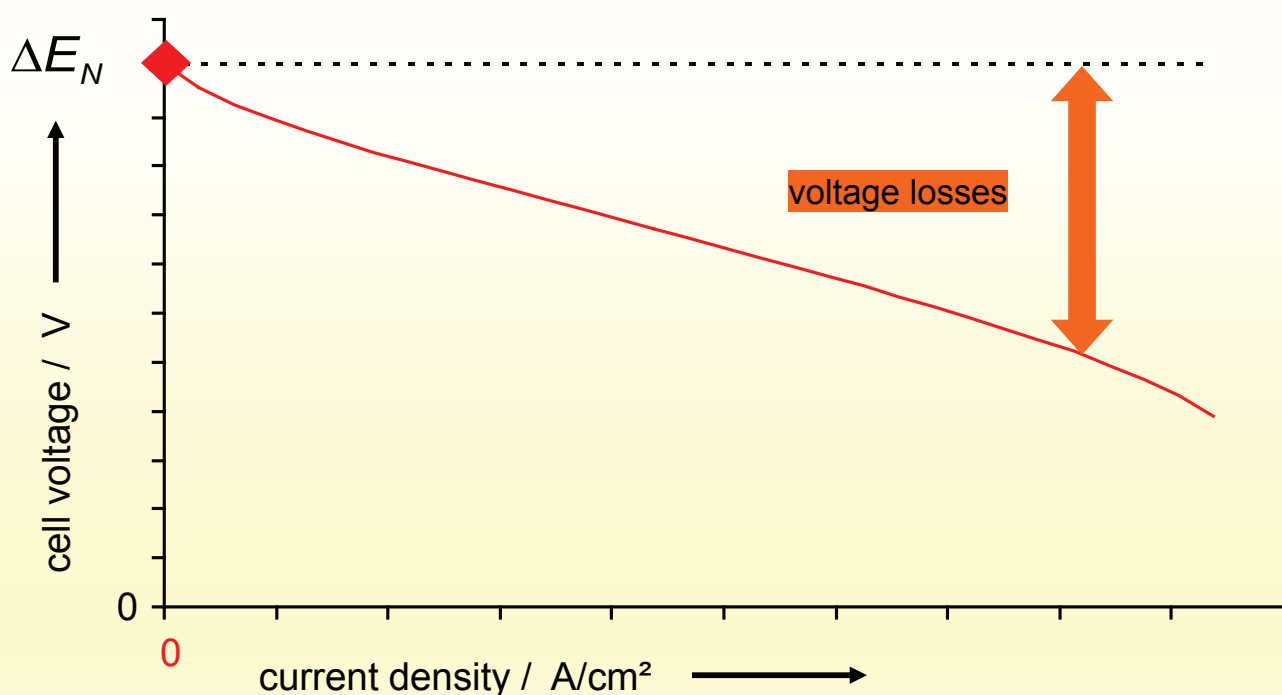


the fuel utilisation u_F is defined as the ratio between the actual current drawn (I) and the maximum current (I_{max}) that can be reached

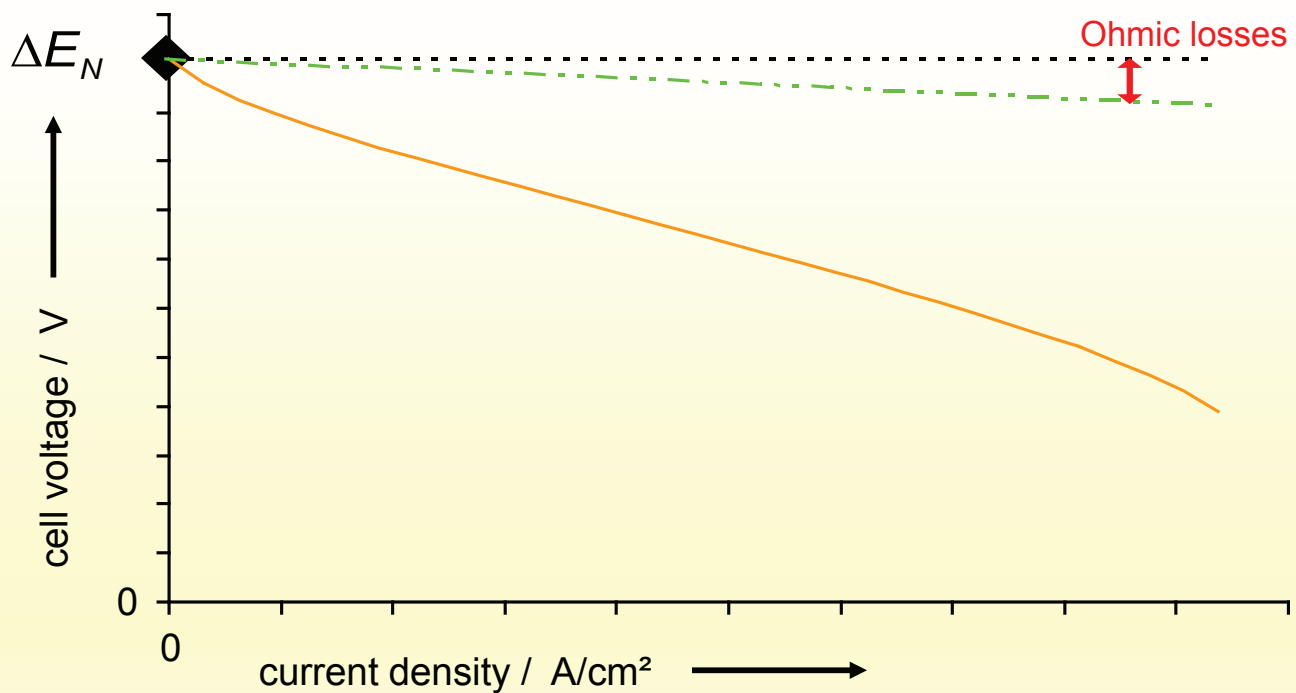
$$u_F = \frac{Z \cdot I}{I_{max}} = \frac{Z \cdot I}{2F\dot{n}_{H_2}}$$

where Z is the number of cells in a stack

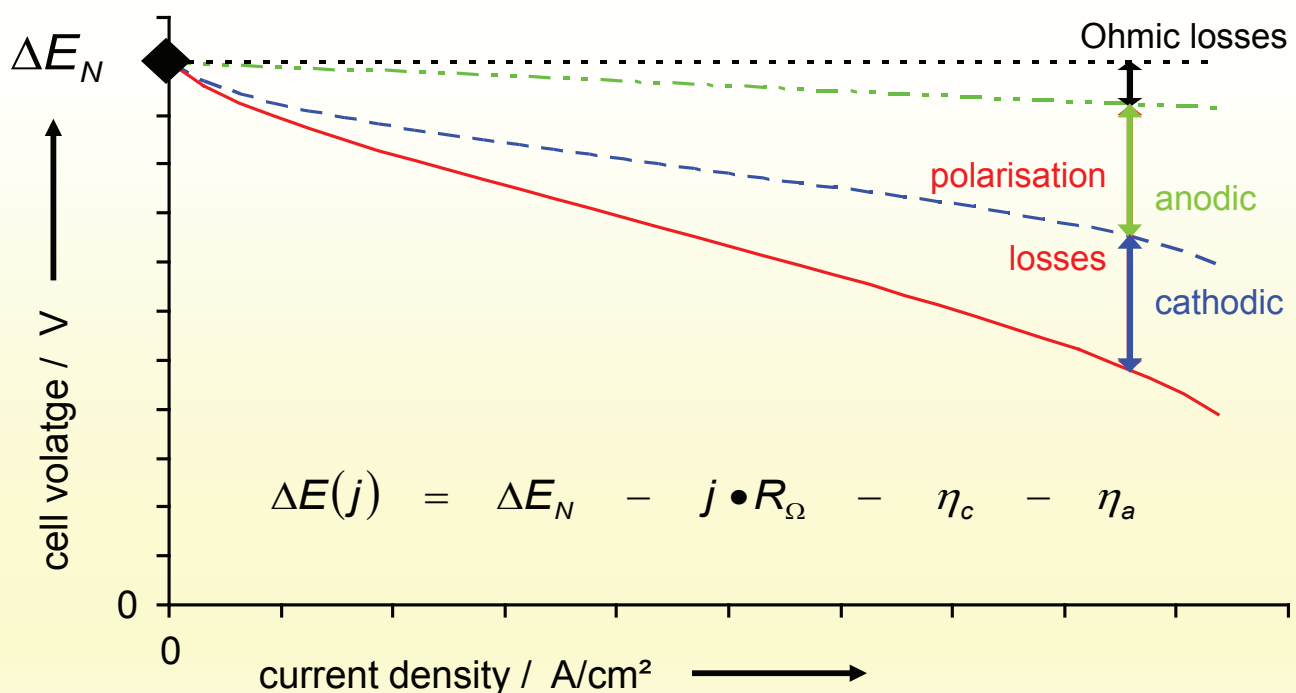
Fuel cells: operation characteristic (IV-curve)



Fuel cells: operation characteristic (IV-curve)



Fuel cells: operation characteristic (IV-curve)



Fuel cells: operation characteristic (IV-curve)

$$\Delta E(j) = \Delta E_N - j \cdot R_\Omega - |\eta_c| - \eta_a$$

$$R_\Omega = R_E + R_C + R_A + R_{contacts}$$

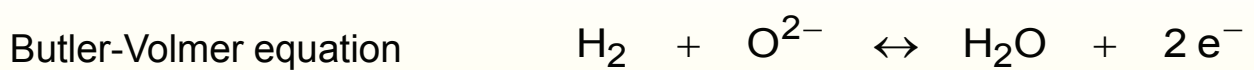
materials: specific conductivity
design: geometric sizes

$|\eta_c|, \eta_a$ charge transfer
diffusion
adsorption/desorption
reaction

materials: combination electrode/electrolyte
design: triple phase boundary

Fuel cells: operation characteristic (IV-curve)

$|\eta_c|, \eta_a$ charge transfer polarisation



$$j = j_{0,\text{H}_2} p_{\text{H}_2}^r p_{\text{H}_2\text{O}}^s \left[\exp\left(\alpha_a \frac{nF}{RT} \eta_a\right) - \exp\left(-\alpha_c \frac{nF}{RT} \eta_a\right) \right]$$

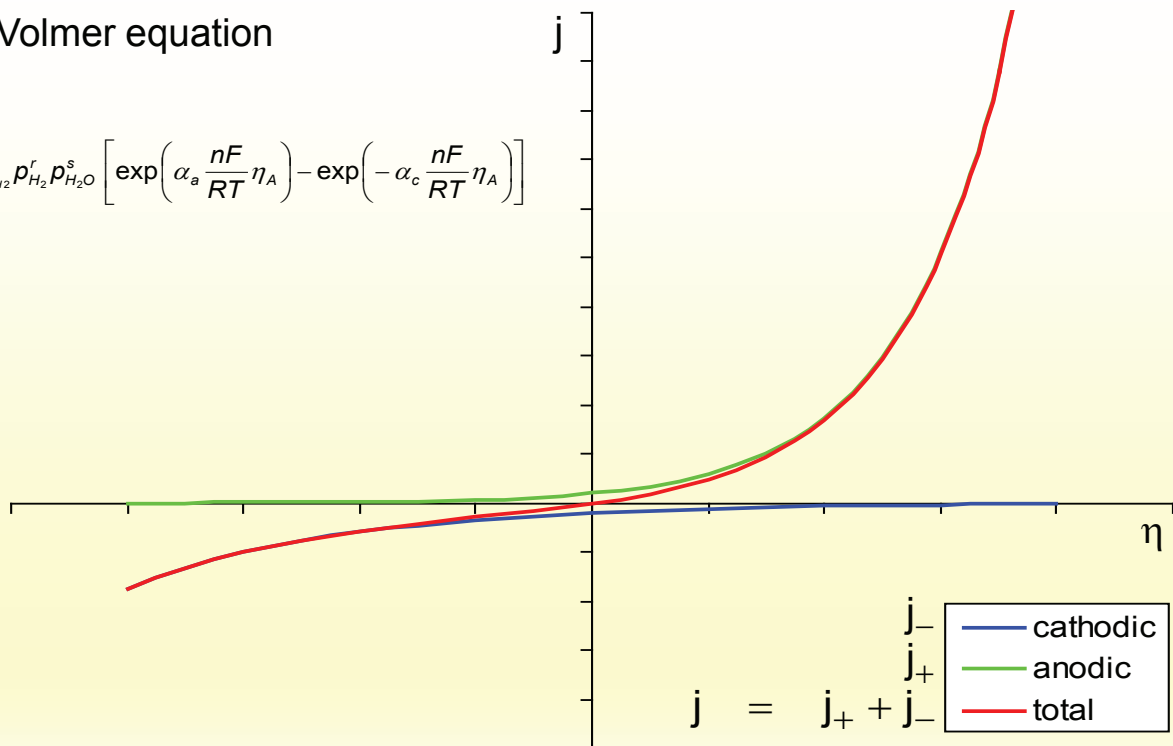
$$j = j_{0,\text{H}_2} p_{\text{H}_2}^r p_{\text{H}_2\text{O}}^s \exp\left(\alpha_a \frac{nF}{RT} \eta_a\right) - j_{0,\text{H}_2} p_{\text{H}_2}^r p_{\text{H}_2\text{O}}^s \exp\left(-\alpha_c \frac{nF}{RT} \eta_a\right)$$

$$j = j_+ + j_-$$

Fuel cells: operation characteristic (IV-curve)

Butler-Volmer equation

$$j = j_{0,H_2} p_{H_2}^r p_{H_2O}^s \left[\exp\left(\alpha_a \frac{nF}{RT} \eta_A\right) - \exp\left(-\alpha_c \frac{nF}{RT} \eta_A\right) \right]$$



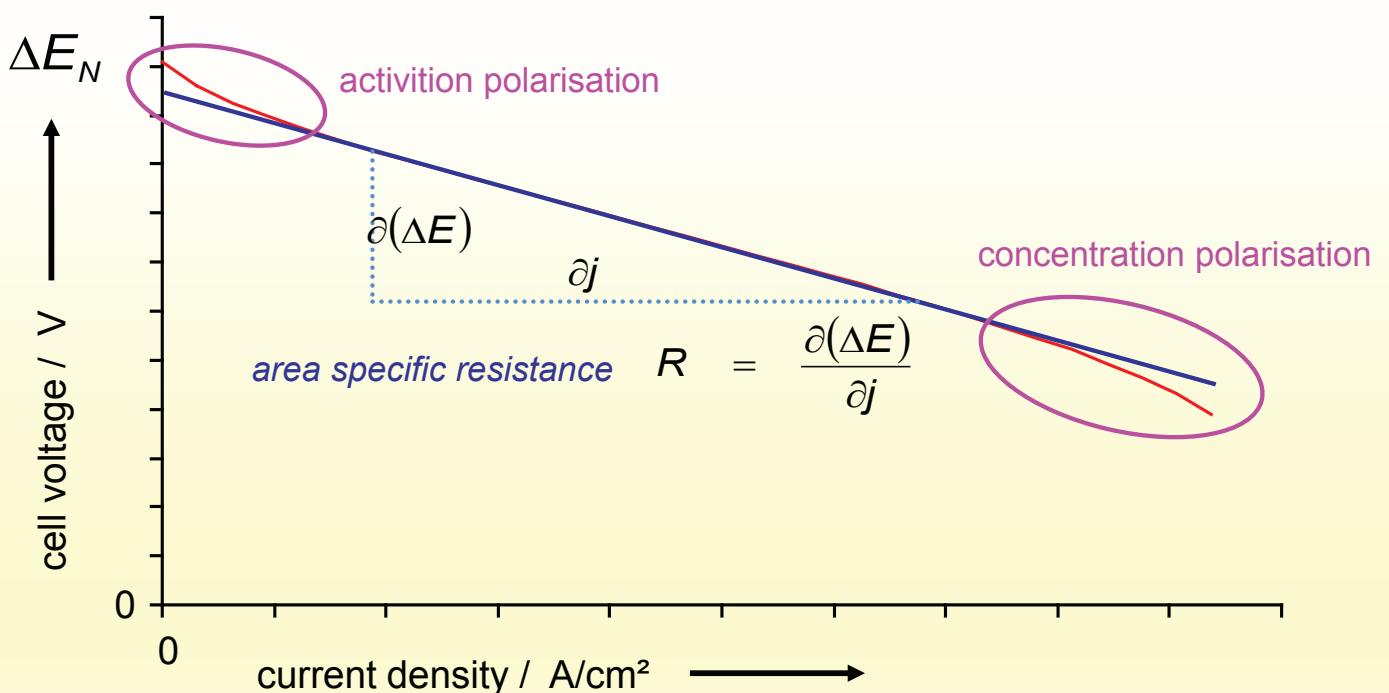
$$j = j_+ + j_-$$

- cathodic
- anodic
- total

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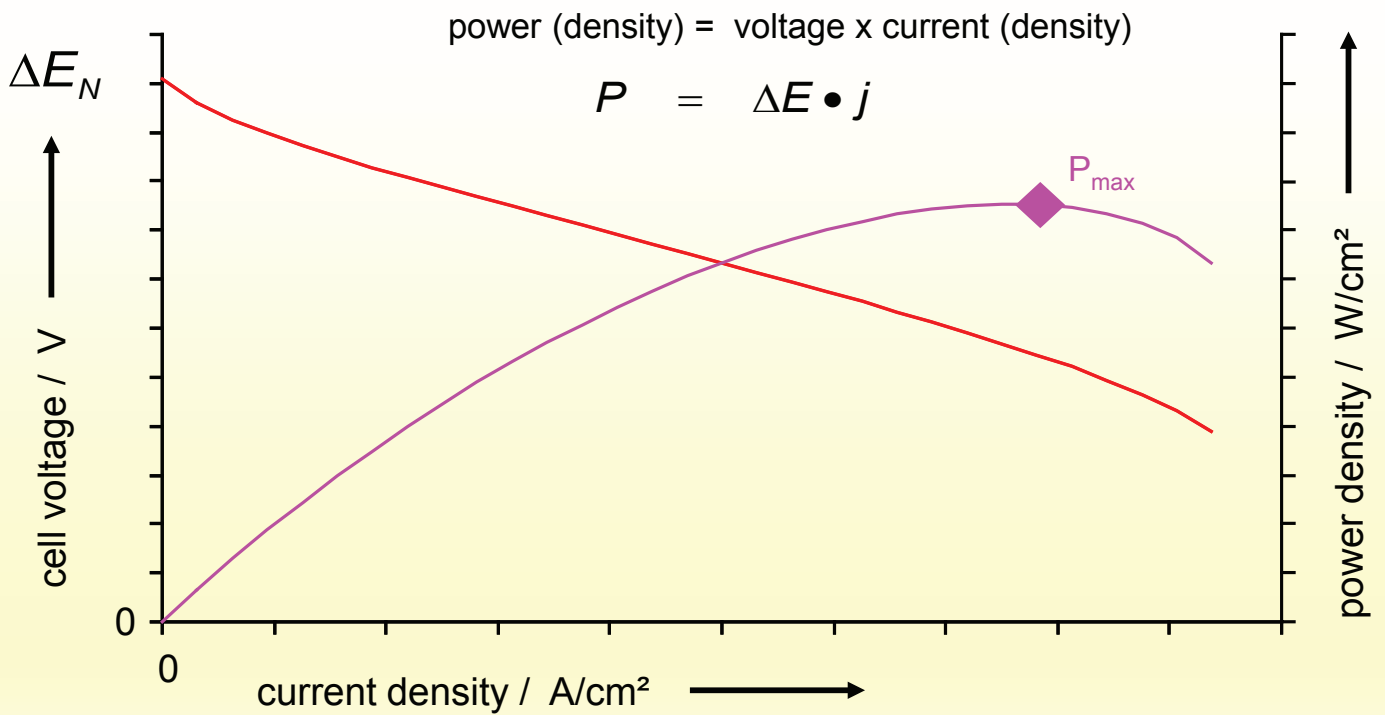
Fuel cells: operation characteristic (IV-curve)



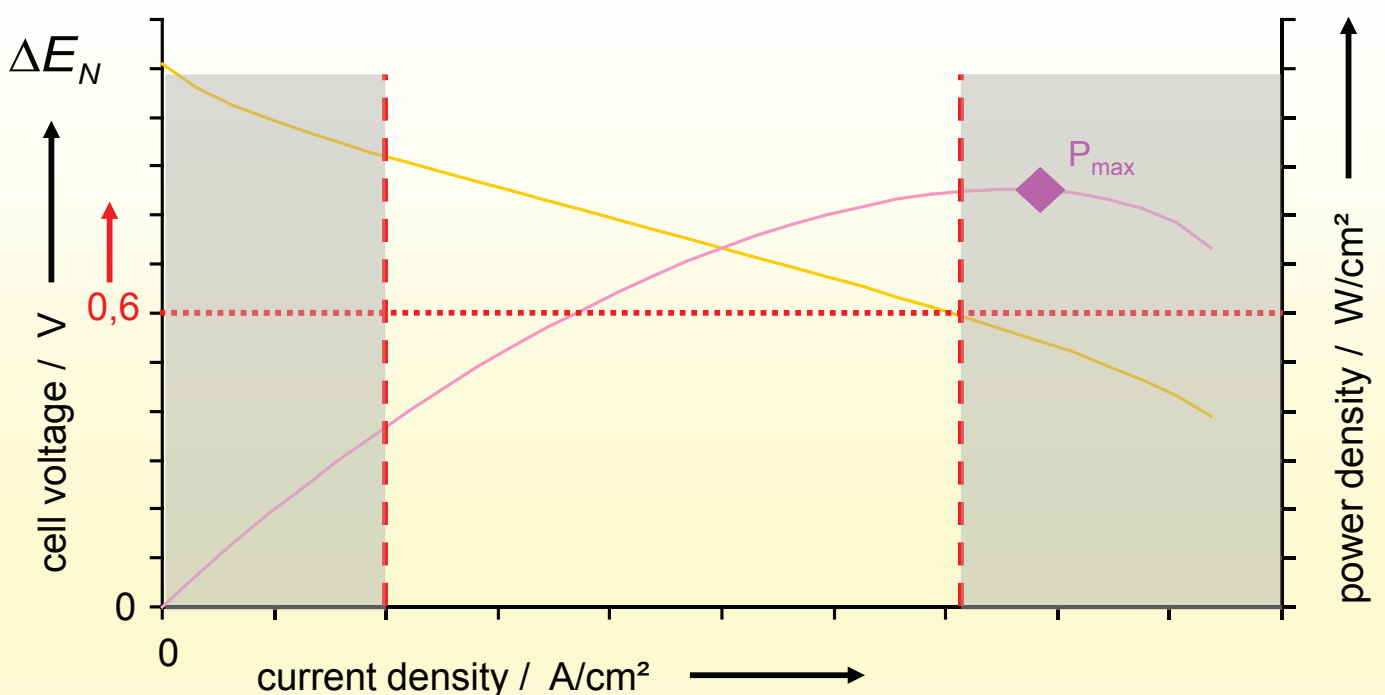
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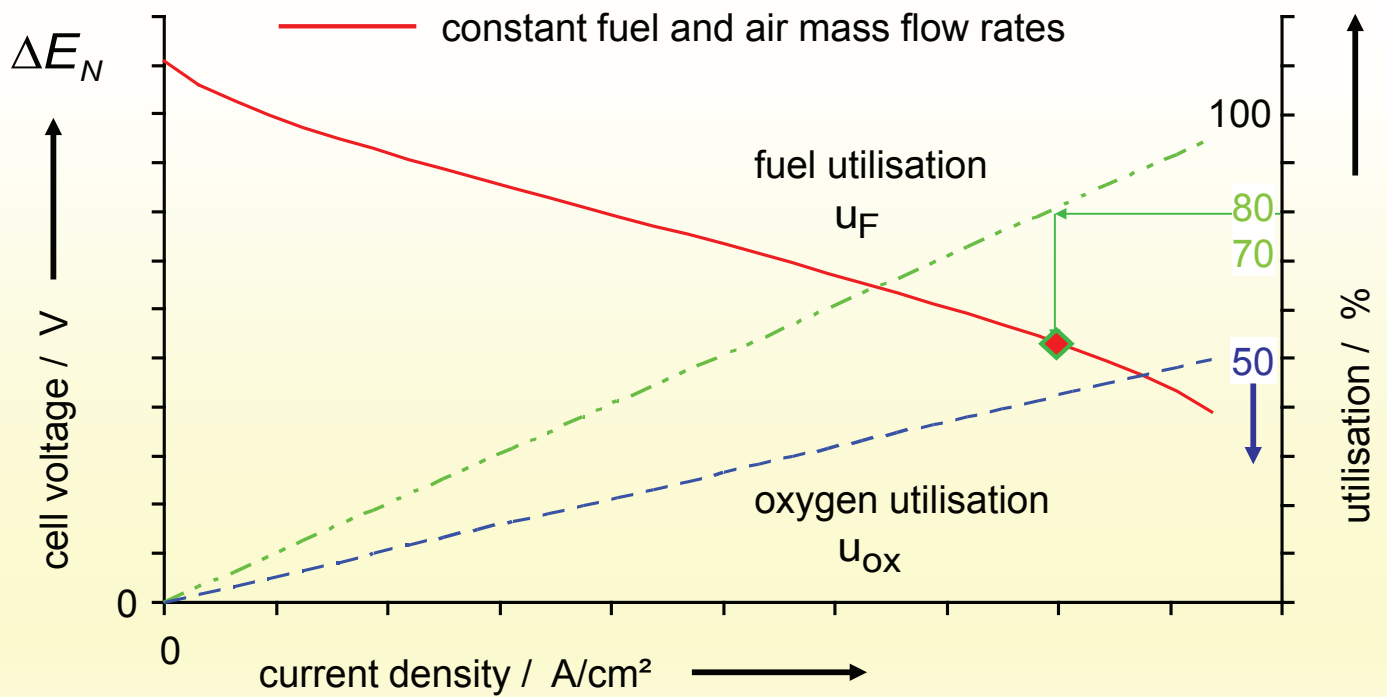
Fuel cells: operation characteristic (IV-curve)



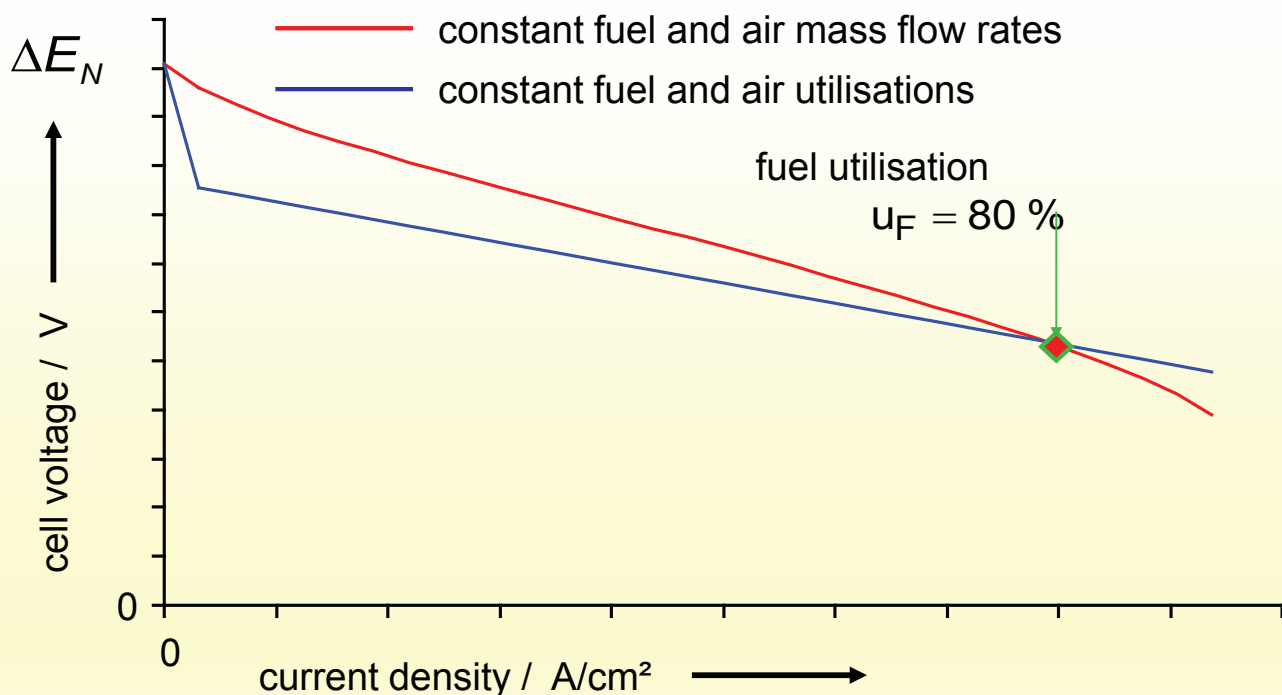
Fuel cells: operation characteristic (IV-curve)



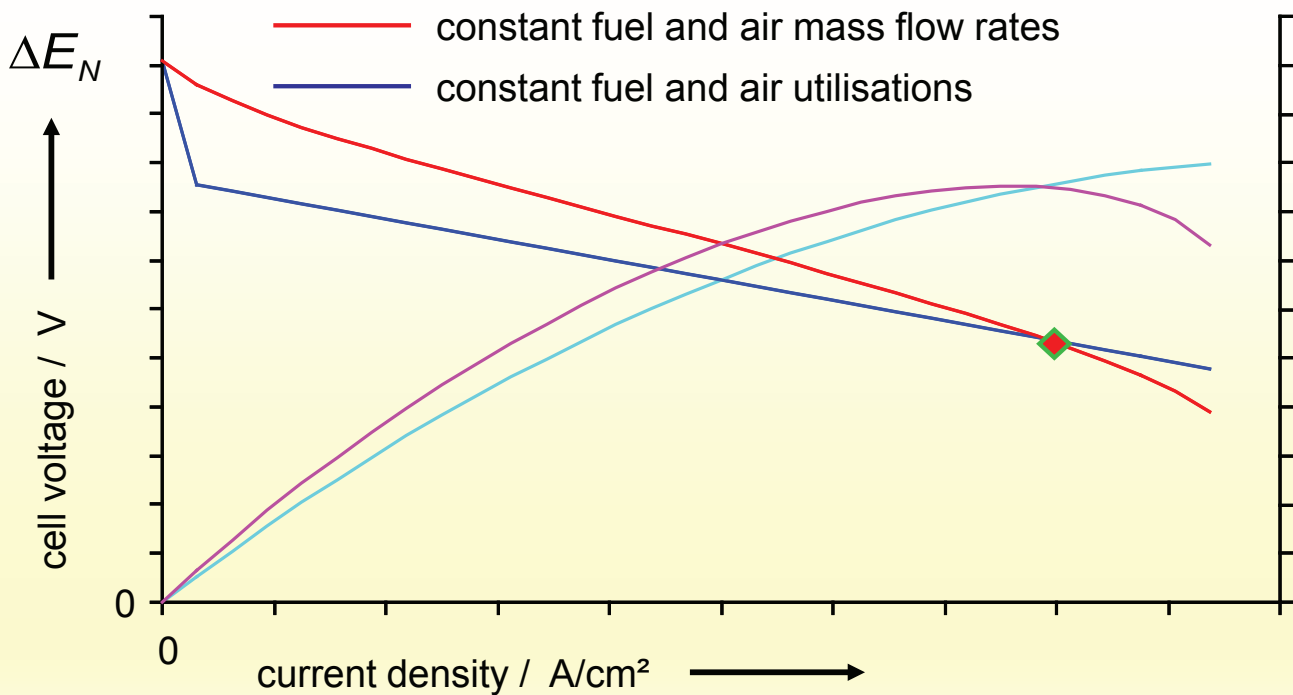
Fuel cells: operation characteristic (IV-curve)



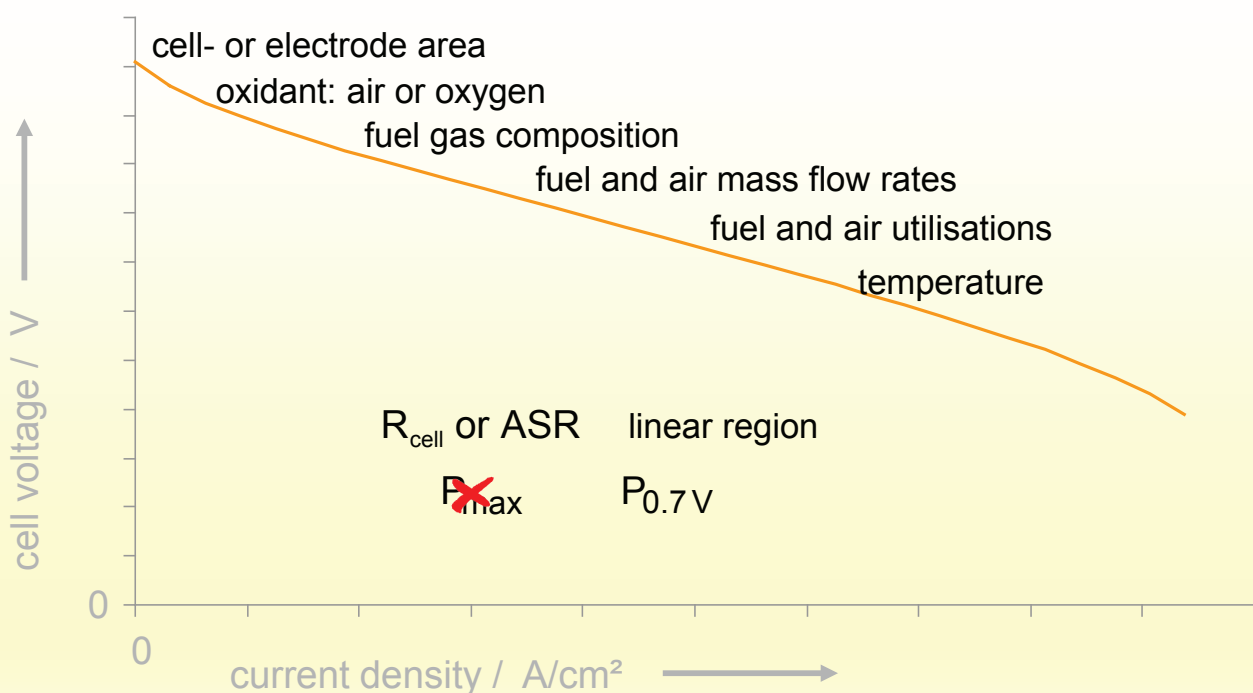
Fuel cells: operation characteristic (IV-curve)



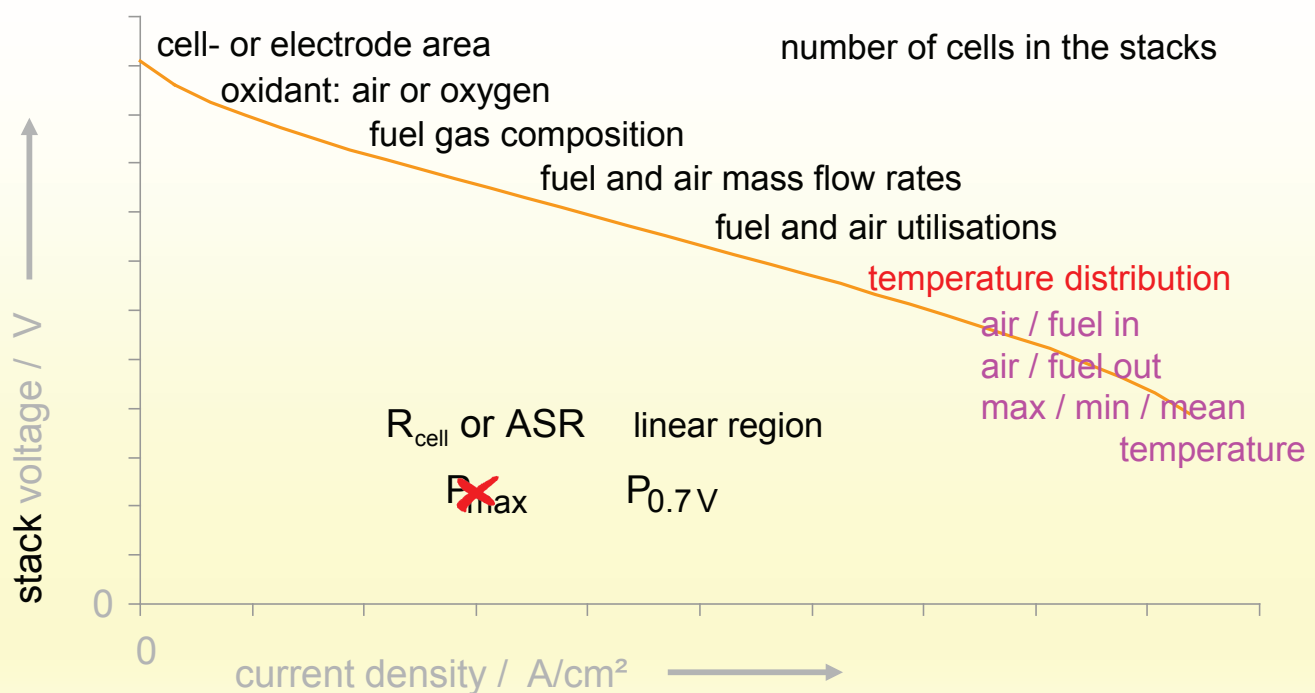
Fuel cells: operation characteristic (IV-curve)



Fuel cells: operation characteristic (IV-curve) of cells



Fuel cells: operation characteristic (IV-curve) of stacks



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Fuel cells: efficiency

the 'ideal' thermodynamic efficiency is given by:

$$\eta_{\text{id}} = \frac{\Delta G^0_{\text{T}}}{\Delta H^0} = \frac{\Delta E_{\Delta G}}{\Delta E_{\Delta H}}$$

ratio between the available energy (Gibbs free energy change of the cell reaction; ΔG) and the maximum energy (enthalpy change of the cell reaction; ΔH)

for	$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$	ΔE^0	
		25 °C	800 °C
ΔG^0	= - 228.4 kJ/mol	1.184 V	1.006 V
ΔH^0	= - 241.8 kJ/mol	1.253 V	1.253 V
ΔS^0	= - 44.4 J/(mol K)	94 %	80 %

In here the so-called lower heating value (LHV) is used; the product water is in the gaseous phase. This is common practice in power plant technology. When the condensation, respectively evaporation of water is taken into account, the higher heating value (HHV) has to be used.

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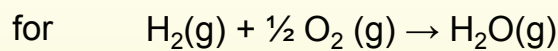
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Fuel cells: efficiency

the voltage efficiency is given by:

$$\eta_{\Delta E} = \frac{\Delta E(j)}{\Delta E_{\Delta G}}$$

ratio between the voltage under current load and the standard voltage; effect of the real gas compositions (Nernst voltage) and potential losses



$$\Delta G^0 = -228.4 \text{ kJ/mol} \quad 800 \text{ }^\circ\text{C} \quad \Delta E_{\Delta G} = 1.006 \text{ V}$$

$\Delta E(j)$	0.900 V	0.800 V	0.700 V
$\eta_{\Delta E}$	89 %	80 %	70 %

Fuel cells: efficiency

the electrical stack efficiency is given by:

$$\begin{aligned} \eta_{el} &= \eta_{id} \cdot \eta_{\Delta E} \\ &= \frac{\Delta E_{\Delta G}}{\Delta E_{\Delta H}} \cdot \frac{\Delta E(j)}{\Delta E_{\Delta G}} \\ &= \frac{\Delta E(j)}{\Delta E_{\Delta H}} \end{aligned}$$

the effective stack efficiency is given by:

$$\begin{aligned} \eta_{eff,st} &= \eta_{el} \cdot u_F \\ &= \frac{\Delta E(j)}{\Delta E_{\Delta H}} \cdot u_F \end{aligned}$$

with the fuel utilisation as given before:

$$u_F = \frac{Z \cdot I}{I_{max}} = \frac{Z \cdot I}{2F \dot{n}_{\text{H}_2}}$$

takes into account the fuel gas leaving the stack (not consumed) as well as leakages in the stack

SOFC: basic characteristics and requirements

the Solid Oxide Fuel Cell (SOFC) is characterised by / requires

- a ceramic oxygen-ion conductor as the electrolyte
- requires operating temperatures above 600 °C
- non-noble metal and metal oxides as catalysts for the electrochemical reactions
- allows the use of carbon (as carbon monoxide CO and methane CH₄) containing fuels
- requires catalysts for methane/steam reforming in/at the fuel electrode
- produces useable heat in the off-gas, next to electricity

SOFC: materials in history

- 1937 Bauer and Preis: first fuel cell on the basis of a zirconia electrolyte
 - ↪ even today (yttria stabilised) zirconia (YSZ) most commonly used as electrolyte

- 1960s first period with intense activities (industry) in SOFC research (mainly electrolyte materials) (military, space, transport)
 - ↪ Sr-doped LaMnO_3 cathode and Ni/YSZ anode used in combination with YSZ
 - ↪ ceramic LaCrO_3 as interconnect material

- 1980s second period with intense activities (industry) in SOFC research (electrode materials, stacks and systems)
 - ↪ electrolyte supported cells, still mainly YSZ
 - ↪ metallic Cr-based interconnect materials

- 1990s increased activities (universities, research centres) in SOFC research (EU, NEDO and SECA programmes)
 - ↪ anode supported cells, still mainly YSZ

- 2000s ↪ ferritic steel based interconnect materials

SOFC: requirements for the components / materials

	electrolyte	anode	cathode	interconnect	sealing
conductivity	ionic purely	electronic additional ionic advantageous	electronic additional ionic advantageous	electronic purely	insulator
thermal expansion		adapted to electrolyte and interconnect	adapted to electrolyte and interconnect	adapted to electrolyte	adapted to electrolyte and interconnect
thermo-chemical	stable in oxidising and reducing atmospheres	stable in reducing atmospheres	stable in oxidising atmospheres	stable in oxidising and reducing atmospheres	stable in oxidising and reducing atmospheres
	stable in contact with anode, cathode, sealing and interconnect	stable in contact with electrolyte and interconnect	stable in contact with electrolyte and interconnect	stable in contact with anode, cathode and sealing	stable in contact with electrolyte and interconnect
micro-structure	impermeable for hydrogen	porous open	porous open	impermeable for hydrogen	impermeable for hydrogen

SOFC: electrolyte materials

ionic conductivity in solids

- by movement of ions in the lattice, e.g. Ag^+ in AgI driven by
 - chemical potential gradient (diffusion)
 - electrical potential gradient (migration)

recall:

electrochemical potential

$$\tilde{\mu}_i = \underbrace{\mu_T^0 + RT \ln a_i}_{\text{chemical potential}} + \underbrace{nF\phi}_{\text{electrical potential}}$$

- by movement of (oxygen) ions in the metal oxide lattice
 - ↳ enhanced by (the creation of) point defects

SOFC: electrolyte materials

point defects in metal oxides

Kröger-Vink notation for point defects

Lattice species	Symbol	Effective charge (electron units)
Metal and oxygen ions on normal sites	M_M^x or O_O^x	Uncharged
Metal interstitial ion	$M_i^{\bullet\bullet}$	2 positive
Oxygen interstitial ion	$O_i^{\prime\prime}$	2 negative
Metal vacancy	$V_M^{\prime\prime}$	2 negative
Oxygen vacancy	$V_O^{\bullet\bullet}$	2 positive
Higher valency cation (donor)	D_M^{\bullet}	1 positive
Lower valency cation (acceptor)	A_M^{\prime}	1 negative
Conduction electron	e^{\prime}	1 negative
Electron hole	h^{\bullet}	1 positive

SOFC: electrolyte materials

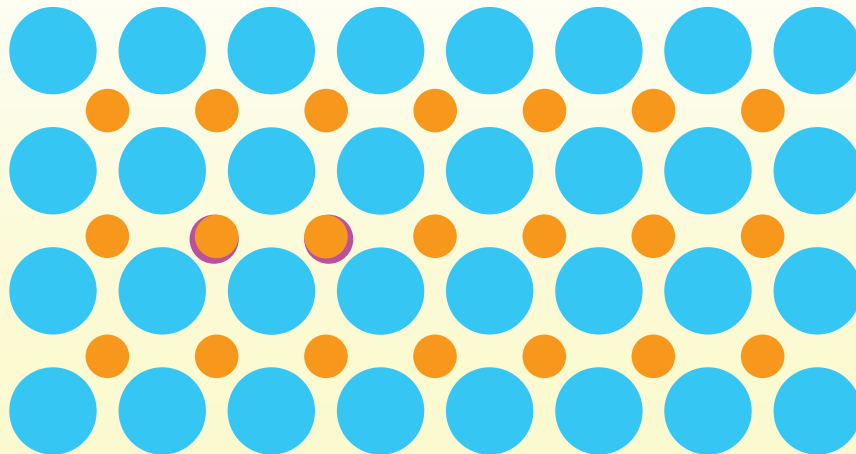
point defects in metal oxides

MeO₂
e.g. ZrO₂

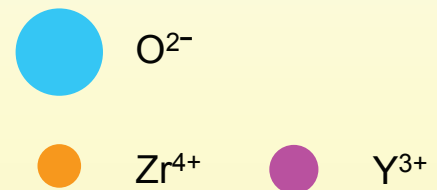
substitution
with Y₂O₃

take out 2 Zr⁴⁺
and 4 O²⁻

2 Y³⁺-ions will replace
2 Zr⁴⁺-ions on their lattice sites



because of charge neutrality:
only 3 O²⁻-ions are available
for 4 O²⁻-lattice sites, leaving
one sites unoccupied:
an oxygen vacancy is created



SOFC: electrolyte materials

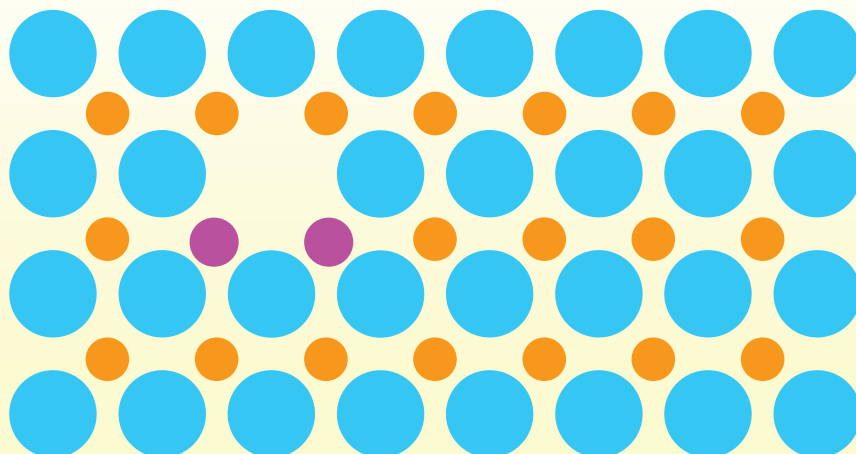
point defects in metal oxides

MeO₂
e.g. ZrO₂

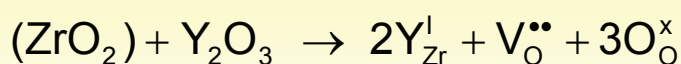
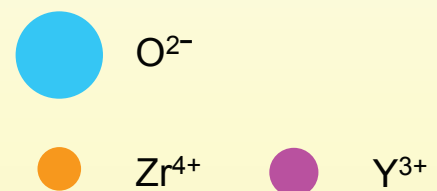
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SOFC: electrolyte materials

point defects in metal oxides

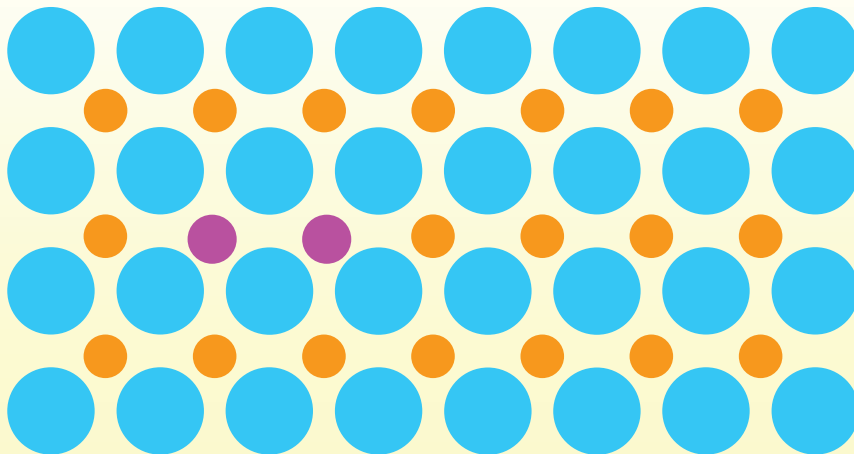
MeO_2
e.g. ZrO_2

substitution
with Y_2O_3

take out 2 Zr^{4+}
and 4 O^{2-}

2 Y^{3+} -ions will replace
2 Zr^{4+} -ions on their lattice sites

because of charge neutrality:
only 3 O^{2-} -ions are available
for 4 O^{2-} -lattice sites, leaving
one sites unoccupied:
an oxygen vacancy is created



O^{2-}

Zr^{4+}

Y^{3+}

← migration of oxygen ion
migration of oxygen ion vacancy →

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SOFC: electrolyte materials

ionic conductivity in metal oxides

- conductivity = concentration x charge x mobility
 - 8...9 mol% Y_2O_3 in ZrO_2 creates high concentration of oxygen vacancies
 - ↪ higher amounts lead to clustering (immobility)
 - mobility is thermally activated
 - ↪ high temperature required for high conductivity
- metal ions which can have multiple valences (oxidation states) should be avoided in solid electrolytes:
 - reduction at low oxygen partial pressures creates electrons
 - oxidation at high partial pressures creates electron-holes
 - ↪ electrons and electron-holes have higher mobility's

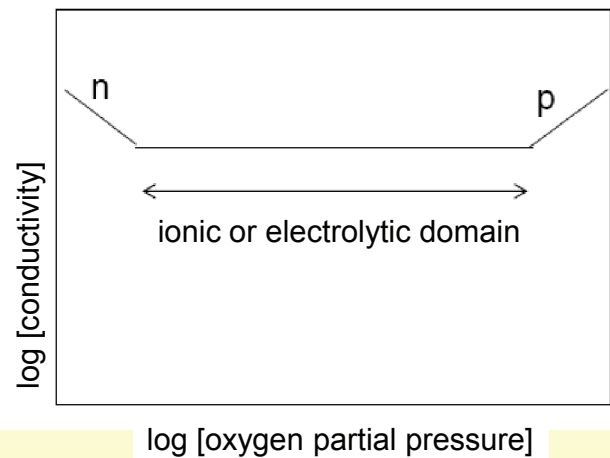
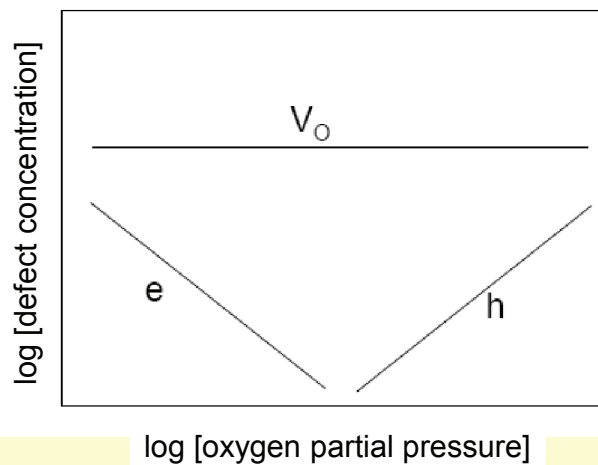
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SOFC: electrolyte materials

ionic conductivity in metal oxides



over the range of oxygen partial pressure in SOFCs
the ionic transfer number needs to be close to 1 (> 0.99)

SOFC: electrolyte materials

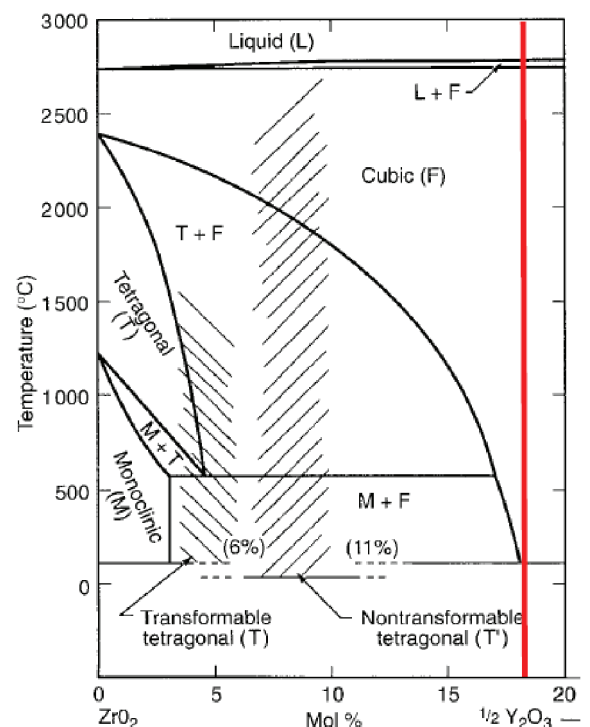
ionic conductivity in solids

- 9 mol% yttria stabilised zirconia (9YSZ)
to fully stabilise the cubic phase
 - ↪ 10 mol% YSZ good alternative,
increased stability of the cubic phase,
but lower conductivity
 - ↪ 3 mol% YSZ good alternative,
higher strength of the tetragonal phase,
but lower conductivity

alternative dopants

- Sc^{3+}
 - ↪ gives higher conductivity,
but is more expensive
(because of poor availability)

8 mol% yttria stabilised zirconia commonly preferred



SOFC: electrolyte materials

ionic conductivity in solids

alternatives to zirconia

- doped ceria, e.g. Gd-doped CeO_2 ; high ionic conductivity
 - ↳ n-type electronic conduction dominant in SOFC fuel environment above 570°C caused by $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$
 - also lattice expansion in reduced environment leads to mechanical problems
- doped gallates, e.g. $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$; high ionic conductivity
 - ↳ difficult to process, unstable at higher temperatures
- doped bismuth oxides; e.g. $\text{Bi}_{0.8}\text{Er}_{0.2}\text{O}_{1.5}$; high ionic conductivity
 - ↳ unstable at higher temperatures, high reactivity with other cell components

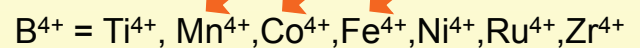
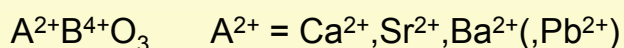
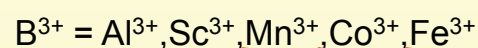
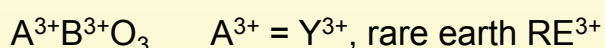
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SOFC: cathode materials

- high temperature in combination with
- highly oxidising atmospheres
require either
 - noble metals
 - ↳ are too expensive or too volatile (Ag)
 - or
 - electronic conducting metal oxides
 - ↳ (transition) metal ions which can have multiple valences (oxidation states)
e.g. in perovskites ABO_3



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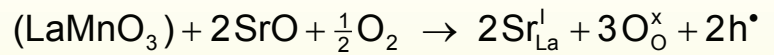
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SOFC: cathode materials

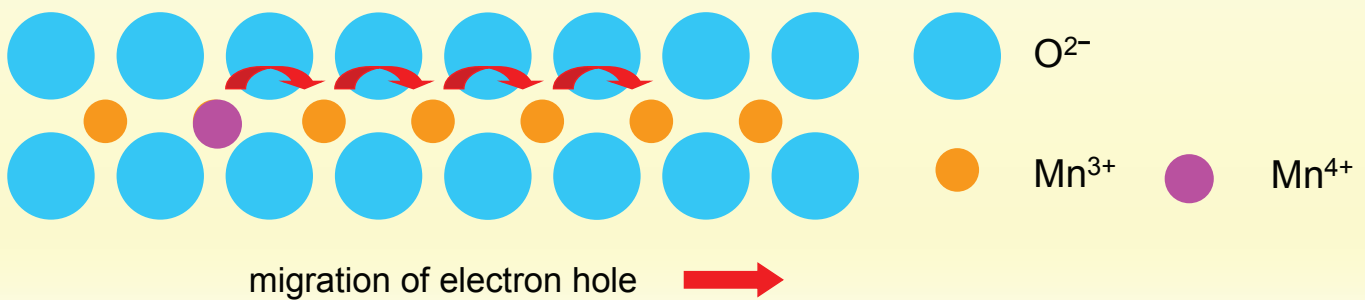
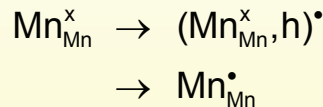
electronic conductivity in metal oxides

$\text{La}^{3+}\text{Mn}^{3+}\text{O}_3$ substitution of La^{3+} by Sr^{2+}

because of charge neutrality
electron holes are created



the electron hole can be regarded
as temporary Mn^{4+} ion:
 Mn^{3+} is oxidised to Mn^{4+}



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SOFC: cathode materials

electronic conductivity in metal oxides

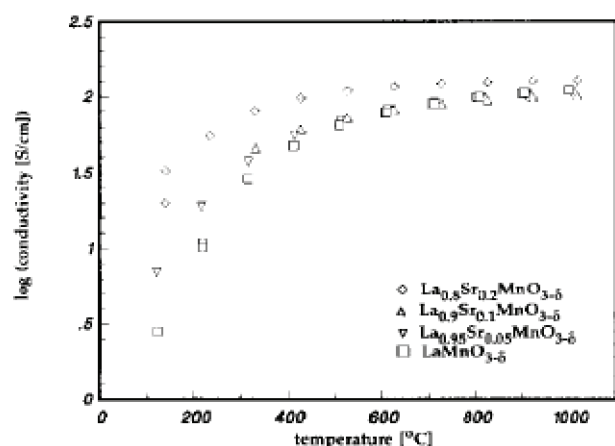


Fig. 2. Electrical conductivity of pure and strontium-doped lanthanum manganite, in air at atmospheric pressure, as a function of temperature.

E. O. Ahlgren, F. W. Poulsen, *Solid State Ionics* 86-88 (1996) 1173-1178

source:
Chania_cathodes_2008.ppt /
08.08 / © IEF-1 / Tietz

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SOFC: cathode materials

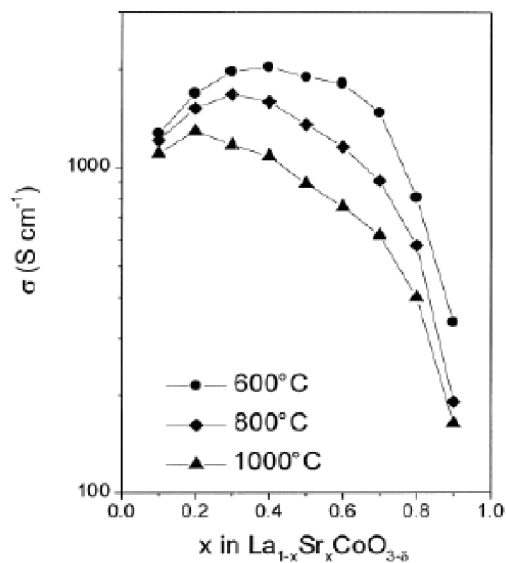


Fig. 2. Electrical conductivity of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ as a function of Sr content.

A. Petric, P. Huang, F. Tietz, *Solid State Ionics*, 135 (2000) 719-728

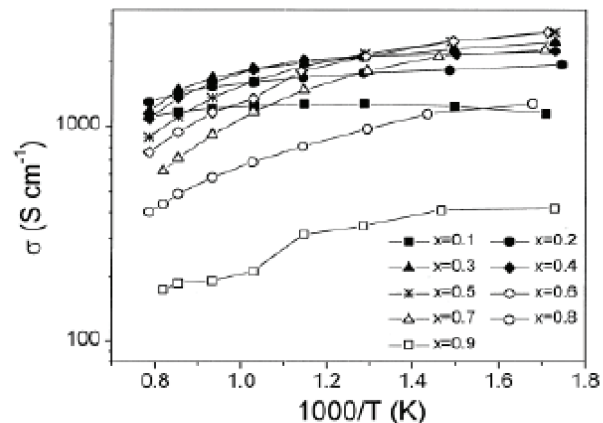


Fig. 1. Arrhenius plots of electrical conductivity of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$.

A. Petric, P. Huang, F. Tietz, *Solid State Ionics*, 135 (2000) 719-728

source:

Chania_cathodes_2008.ppt / 08.08 / © IEF-1 / Tietz

SOFC: cathode materials

selection $(\text{La,Sr})(\text{Mn,Fe,Co})\text{O}_3$ depends on:

- conductivity
 - ↳ highest for $(\text{La,Sr})\text{CoO}_3$, reasonable for $(\text{La,Sr})\text{MnO}_3$, too low for $(\text{La,Sr})\text{FeO}_3$
- thermal expansion coefficient
 - ↳ reasonable for $(\text{La,Sr})\text{MnO}_3$ with Sr-content between 0.15 and 0.35
 - ↳ too high for $(\text{La,Sr})\text{CoO}_3$, reasonable for $(\text{La,Sr})(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_3$
- chemical stability (oxygen deficiency)
 - ↳ reasonable down to oxygen partial pressures of 10^{-5} bar
- reactivity (with YSZ)
 - ↳ reasonable for $(\text{La,Sr})\text{MnO}_3$, further suppressed by slight A-site deficiency
 - ↳ $(\text{La,Sr})(\text{Co,Fe})\text{O}_3$ reacts to form strontium zirconate (insulator)
 - ↳ suppressed by a $(\text{Ce,Gd})\text{O}_2$ (CGO) diffusion barrier layer
- electrochemical activity
 - ↳ highest for $(\text{La,Sr})\text{CoO}_3$, $(\text{La,Sr})(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_3$
 - ↳ reasonable for $(\text{La,Sr})\text{MnO}_3$,
 - ↳ improved by mixing with YSZ

SOFC: anode materials

- high temperature in combination with
 - highly reducing atmospheres require
 - noble metals
 - ↳ are too expensive or too volatile (Ag)
 - or
 - electronic conducting metal oxides
 - ↳ (transition) metal ions which can have multiple valences (oxidation states) e.g. in perovskites ABO_3
- doped $SrTiO_3$
- or
 - transition metals stable over a wide range of reducing oxygen partial pressures, e.g. Ni, Fe, Co, Cu
 - ↳ Ni is preferred: shows the largest stability range (lowest risk of oxidation) has the highest electrochemical activity for the hydrogen oxidation reaction (even over the noble metals)

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SOFC: anode materials

Ni has

- the tendency to sinter at operating temperature
 - ↳ decrease of porosity, loss of activity
- a thermal expansion coefficient not comparable to YSZ

therefore

- Ni particles are dispersed in a matrix of YSZ particles
 - ↳ to match the thermal expansion coefficient
 - ↳ to prevent the sintering of the nickel particles

 Ni/YSZ **cermet** (*ceramic metal*)

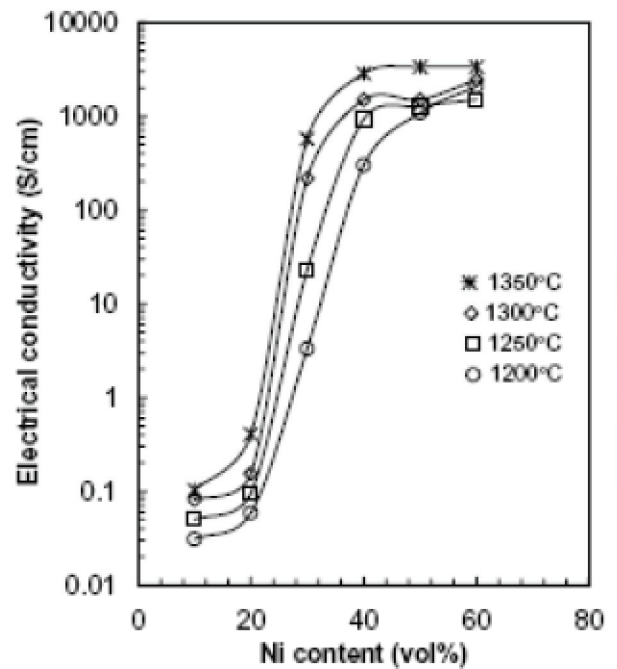
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SOFC: anode materials

Ni/YSZ cermet

- Ni amount has to be above 40 vol% (percolation threshold) to keep the high metallic conductivity upright
- Ni and YSZ particle size (distribution) has to be well balanced to keep the micro structure upright
- manufactured out of a mixture of NiO and YSZ; reduction of NiO to Ni on first operation of the fuel cell



source:
Alan Atkinson, SOFC Anodes, Chania 2008