Electrical Conduction in Ionic Solids and Polymers
Conduction in Ionic Materials

Conduction
an electric current results from the motion of electrically charged particles

electronic conduction
a current arises from the flow of electrons

ionic conduction
a current produced by the motion of charged ions

$$\sigma_{total} = \sigma_{electronic} + \sigma_{ionic}$$

The total conductivity of an ionic material is equal to the sum of both electronic and ionic contributions.

Mobility μ_i

$$\mu_i = \frac{n_i e D_i}{kT}$$

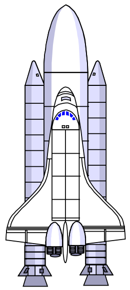
n_i : the valence coefficient of a particular ion
D_i : the diffusion coefficient of a particular ion

The ionic contribution to the total conductivity increases with increasing temperature.

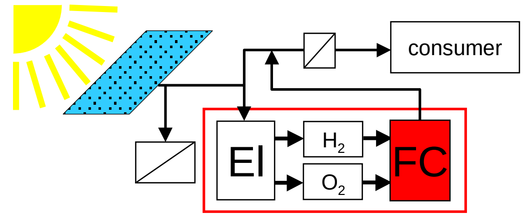
Fuel Cells for Direct Electrochemical Energy Conversion
Fuel Cell Applications

decentralized power supply

space travel



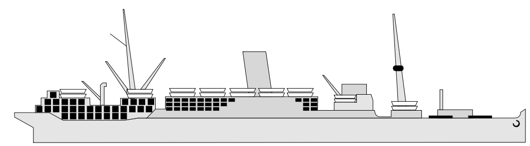
solar energy storage



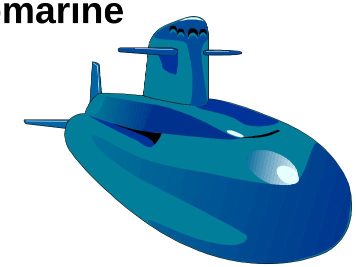
Fuel Cells

possible applications
for electrical
energy production

cargo ship



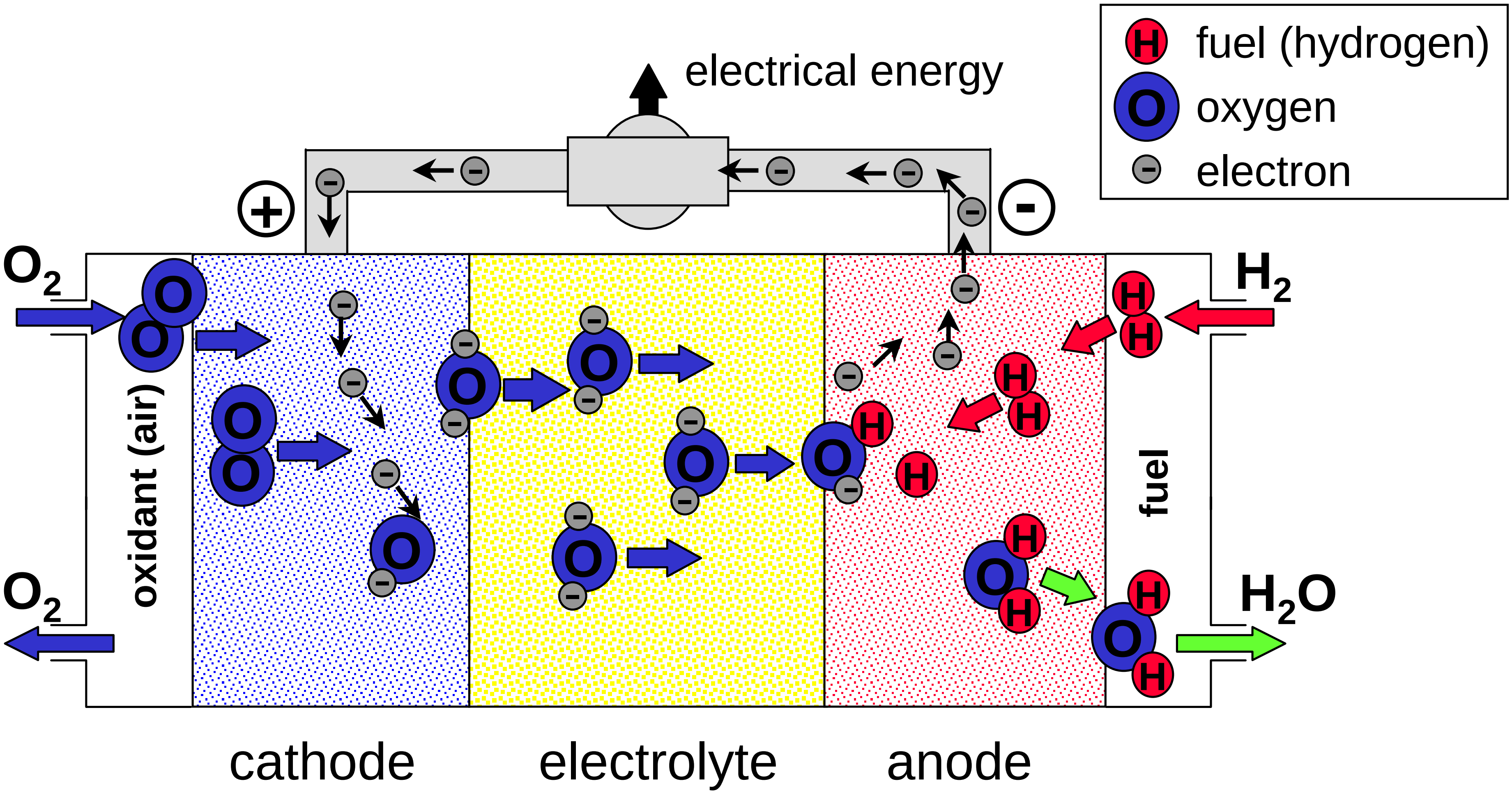
submarine



bus and train

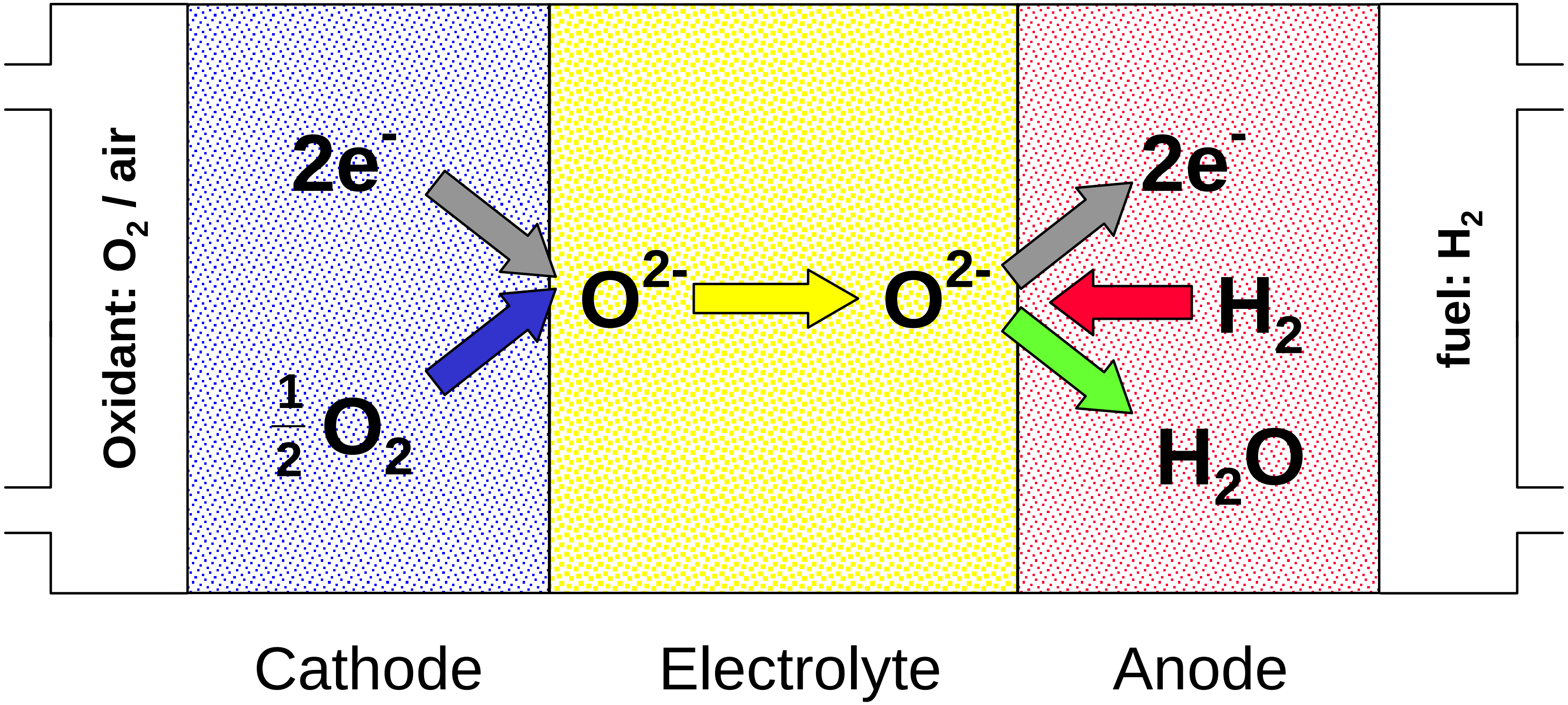
motor vehicles

Solid Oxide Fuel Cell
Principle of operation

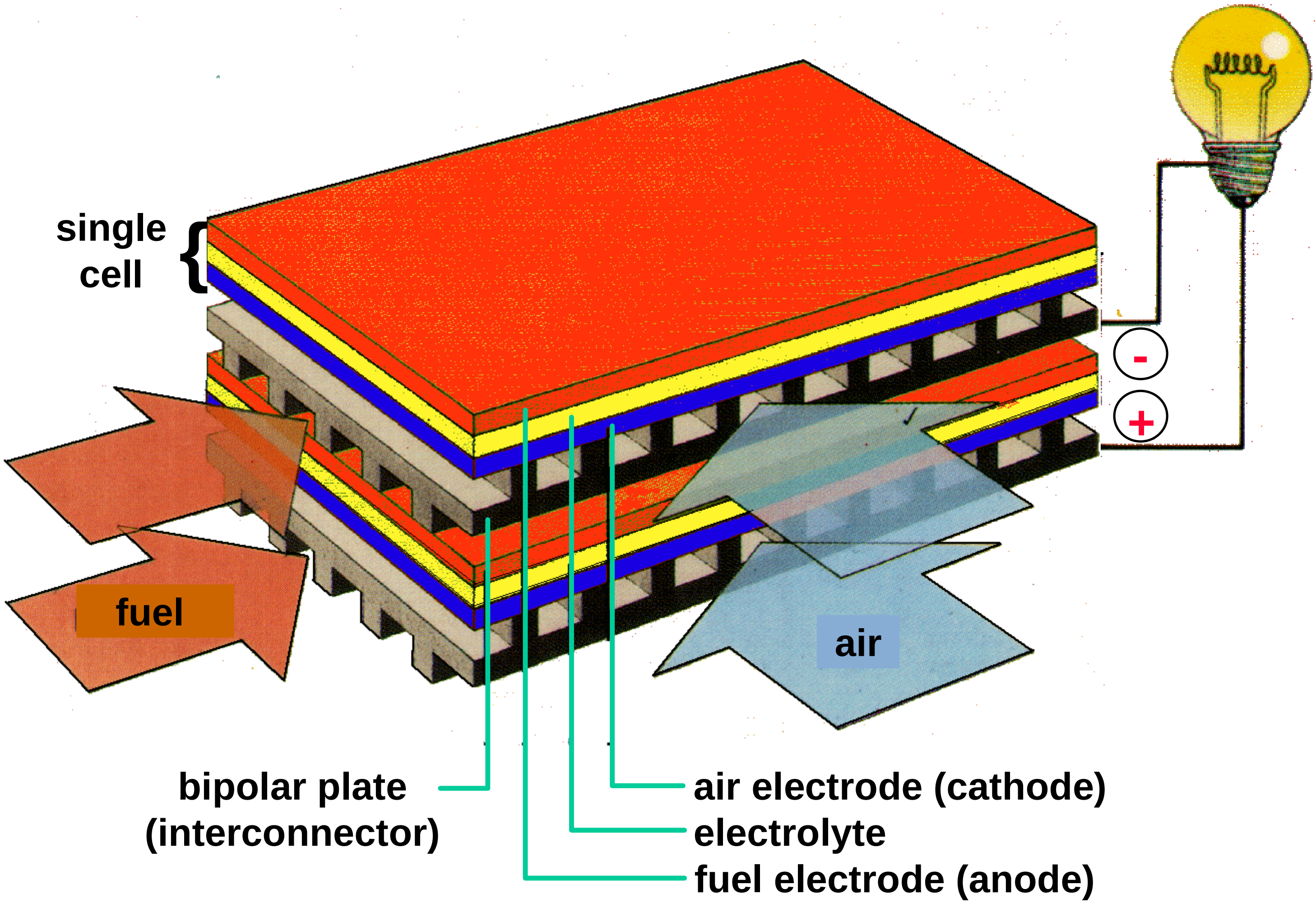


Fuel Cell Reactions
Cathode and Anode Reactions

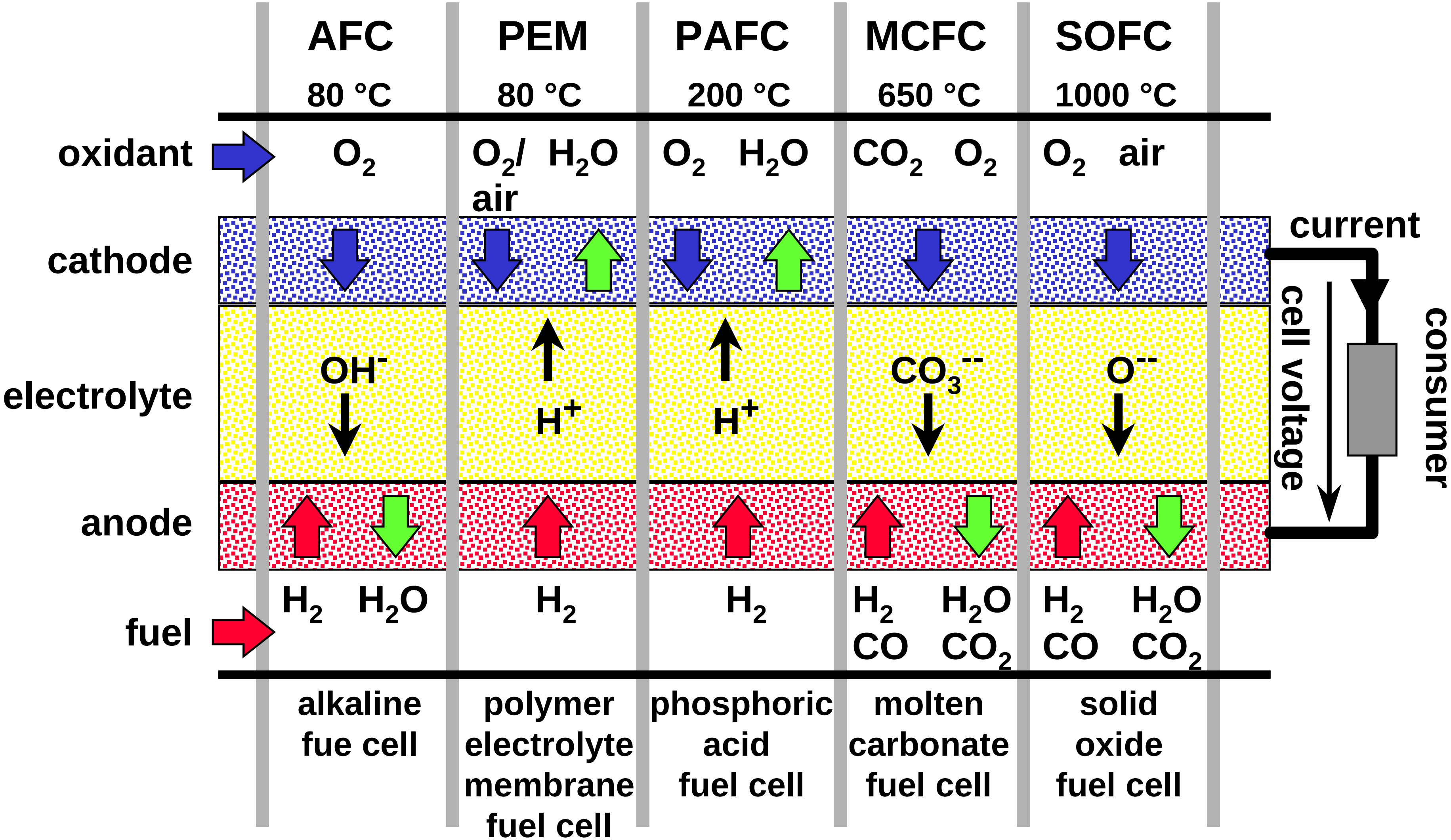
$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \qquad O^{2-} + H_2 \rightarrow H_2O + 2e^-$$



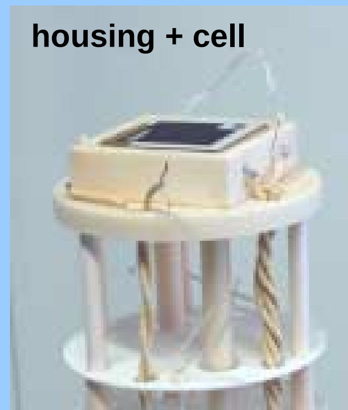
Schematic diagram of a planar cell design

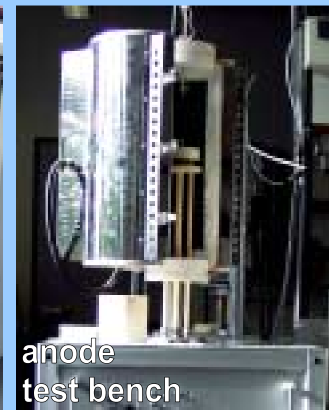


Types of Fuel Cells



Testing Equipment for SOFC single cells

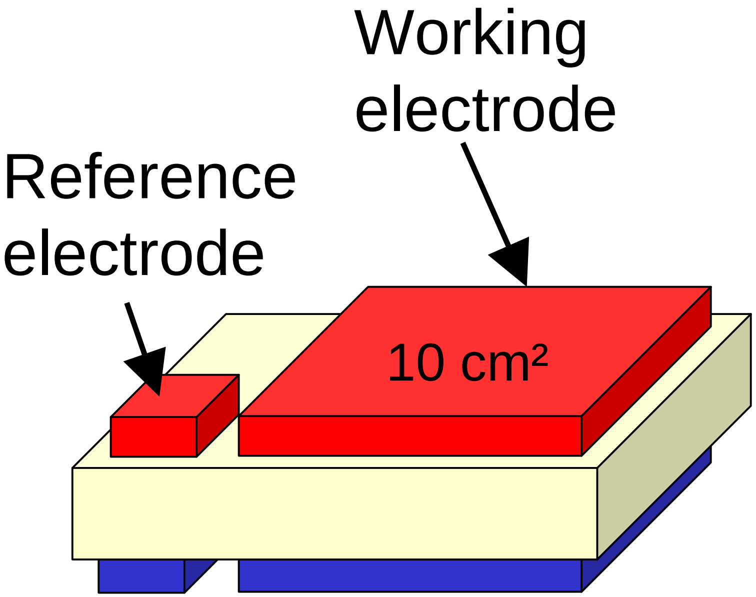




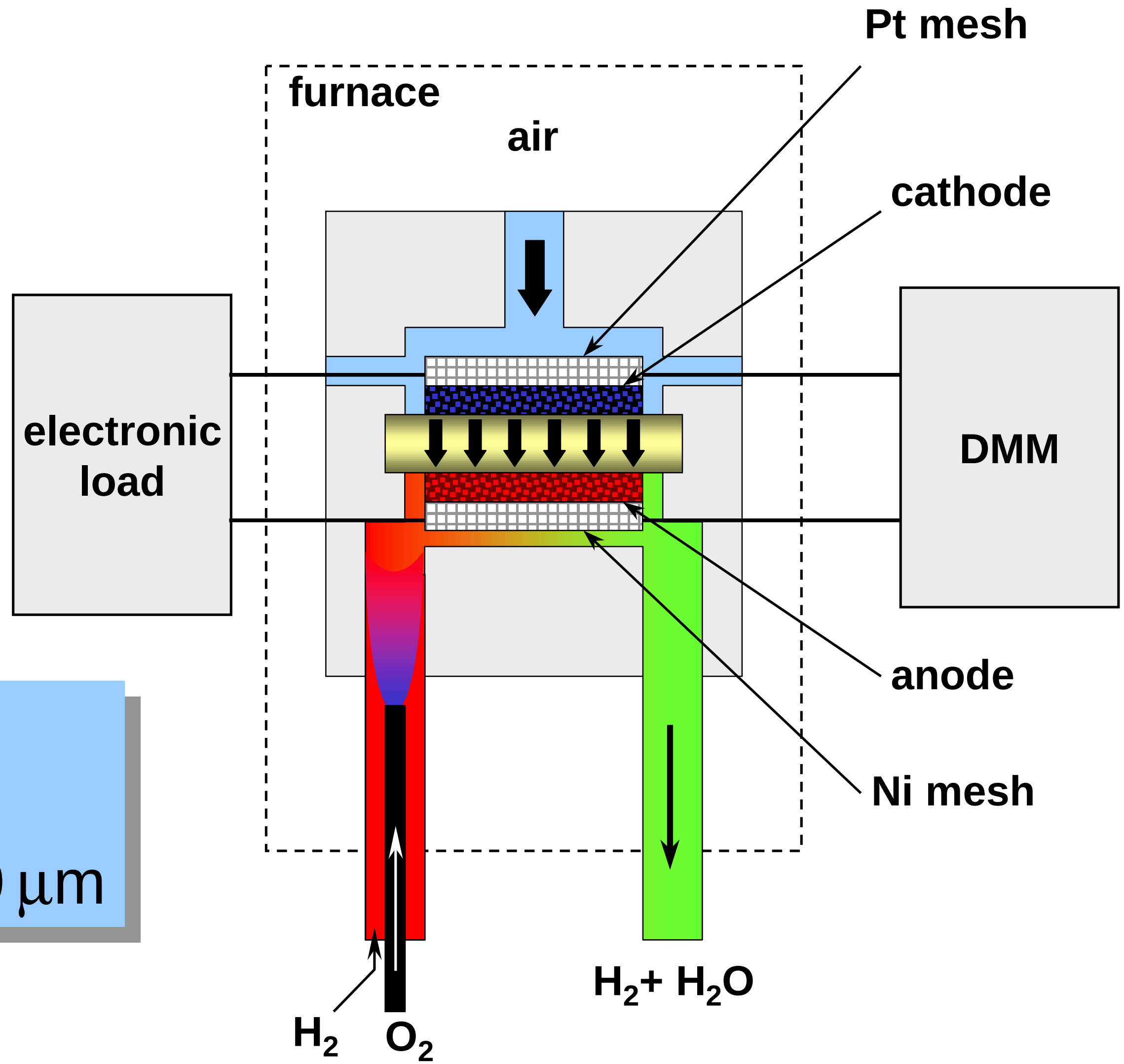
Single Cell Types
- planar single cells
- electrolyte or electrode supported
- electrode area: 1 ... 16 cm²

Testing conditions
- temperature: 500 ... 1000 °C
- fuel: H_2/H_2O, CO/CO_2, CH_4
- fuel utilization up to 100 %
- oxidant: air, O_2/N_2
- cell current: 10 mA ... 20 A
- in situ impedance spectroscopy

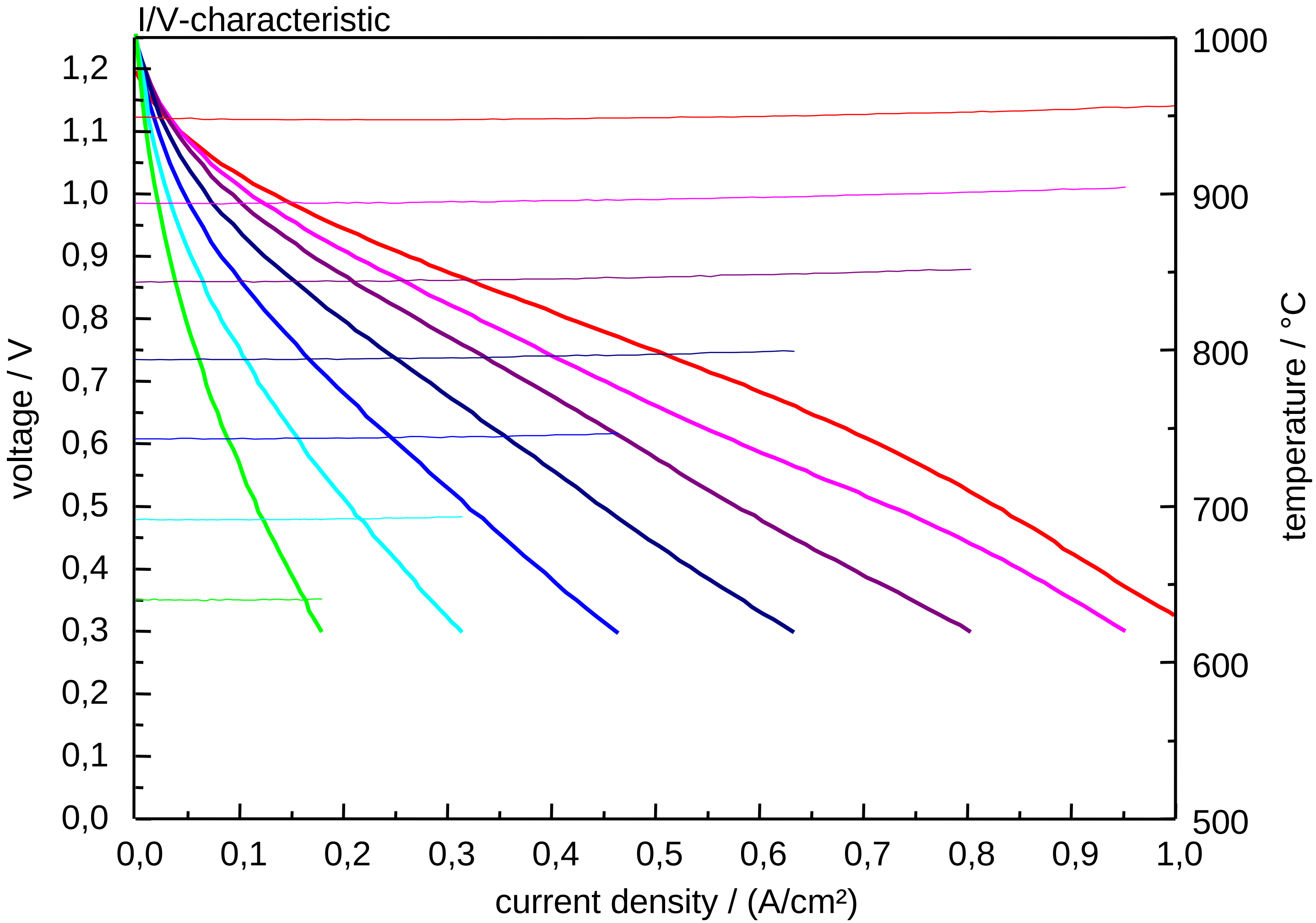
Cell design and measurement setup



anode: Ni-YSZ, 30 µm
electrolyte: YSZ, 150 µm
cathode: $La_{0.75}Sr_{0.2}MnO_3$, 30 µm



Performance of electrolyte supported Single Cells
State of the Art Materials

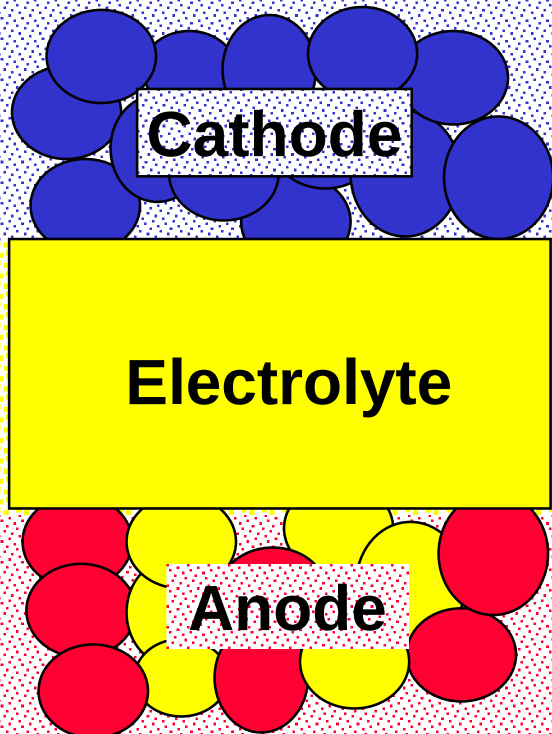


Z 1.4
St. 2.4.1
K: ULSM
E: TZ8Y, 0,15 mm
A: 75N-Z St.2
oxidant: air, 0.5 l/min
fuel: H_2, 0.5 l/min

Electrical Conduction in Ionic Solids and Polymers
Material and structure characteristics request by a single cell of SOFC

Thermal mechanical Characteristics

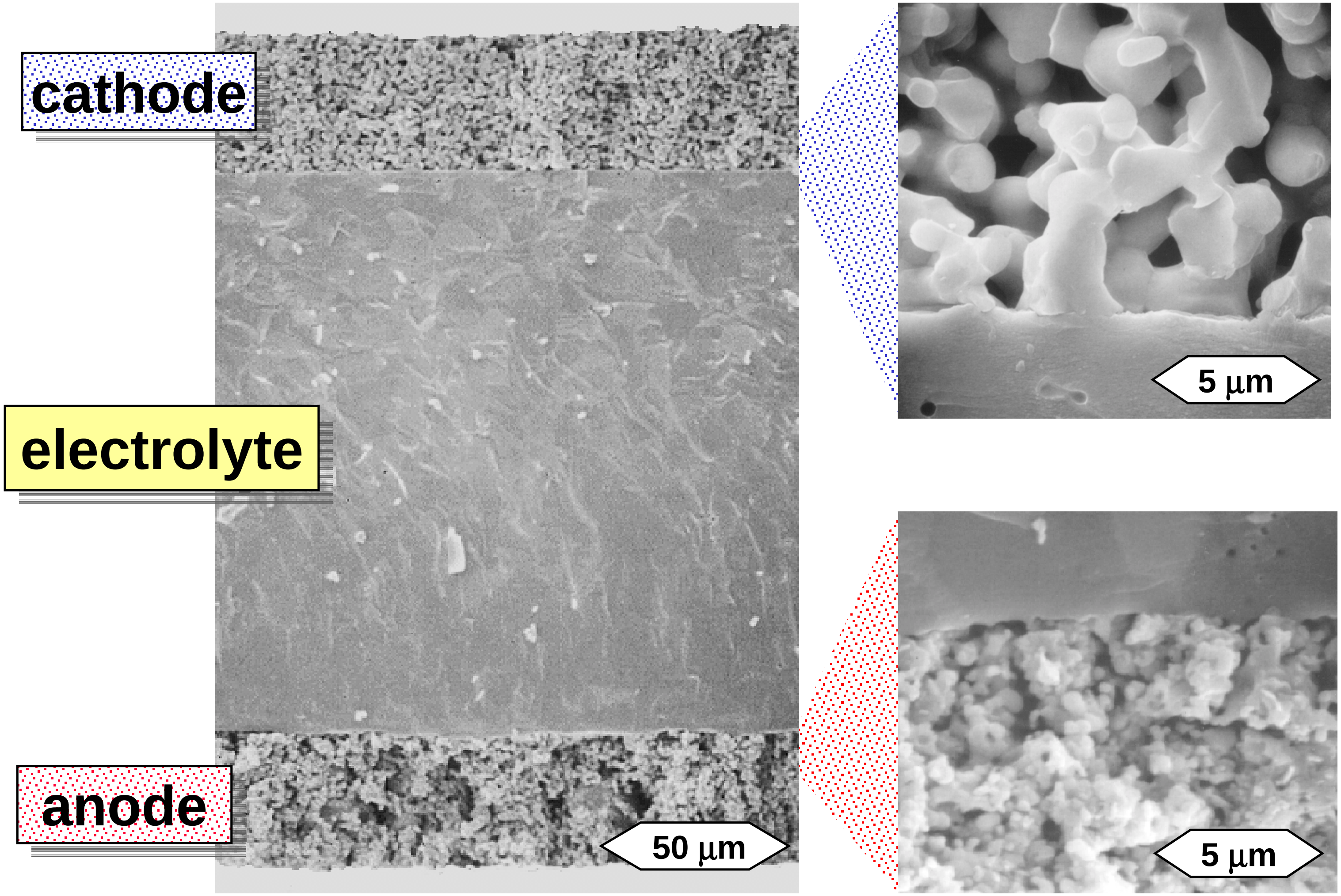
- **porosity**
- **expansion-coefficient**
- **adhesion**
- **gas proof steadiness**
- **adhesion**
- **expansion-coefficient**
- **porosity**



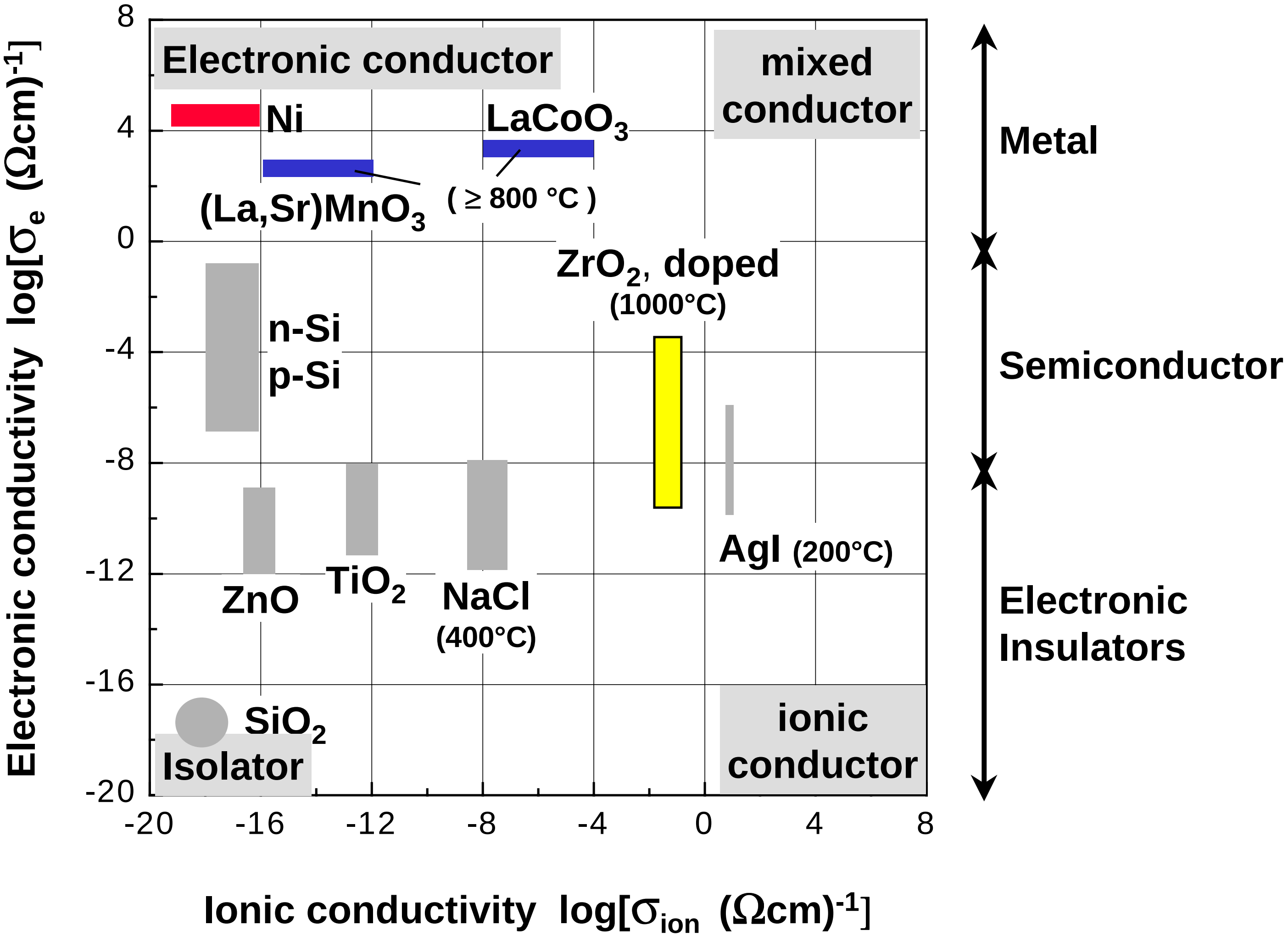
Electrical Characteristics

- **el. conductivity** $(\sigma_{el} + \sigma_{ion})$
- **catalytic activity**
- **Ionic conductivity** $\sigma_{ion} >> \sigma_{el}$
- **catalytic activity**
- **el. conductivity** $(\sigma_{el} + \sigma_{ion})$

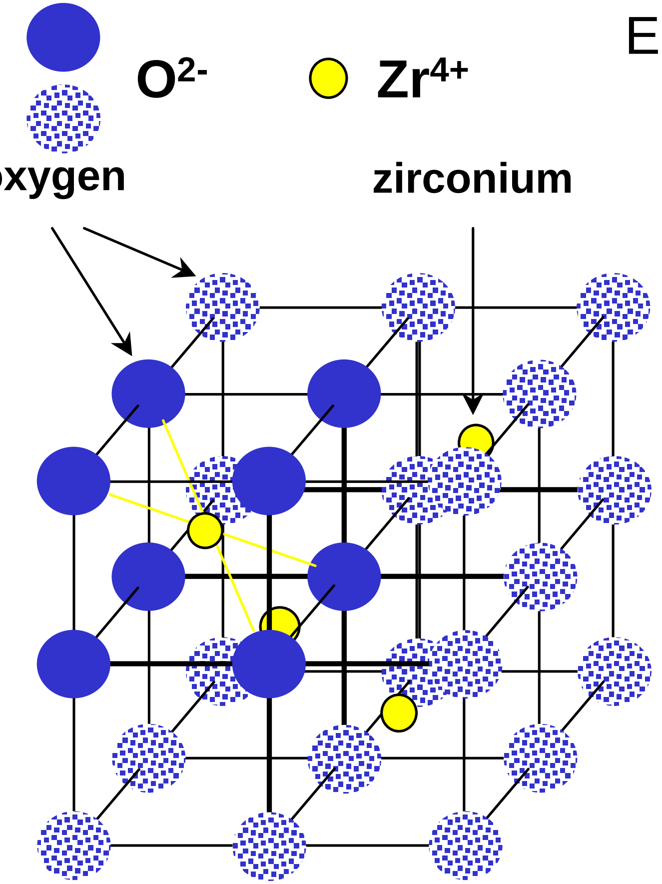
SOFC
Cross section of a single cell (SEM-image)



Electrical Conduction in Ionic Solids and Polymers
Ionic and electronic conduction of different materials



Electrical Conduction in Ionic Solids and Polymers
Yttrium Doping in the Solid Electrolyte Zircon Oxide (ZrO_2)



crystal lattice of the zircon oxide

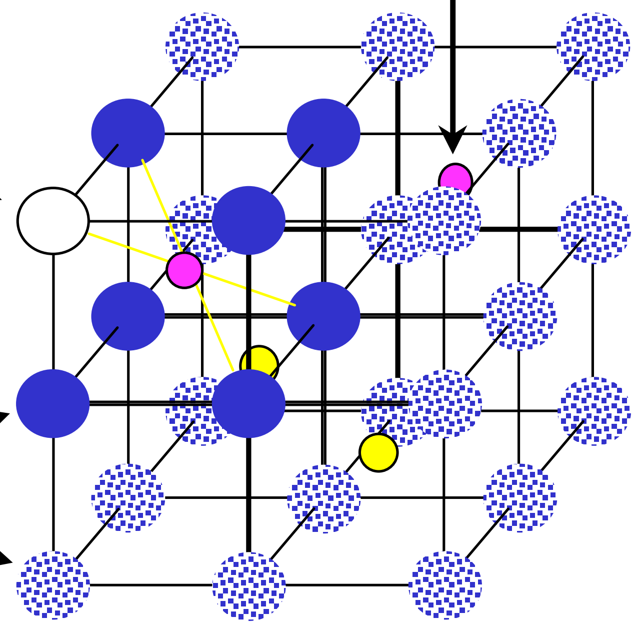
Equation for yttrium oxide (Y_2O_3) doping into the lattice of zircon oxide (ZrO_2)

$$Y_2O_3 \rightarrow 2Y'_{Zr} + 3O_O^X + V_O^{\bullet\bullet}$$

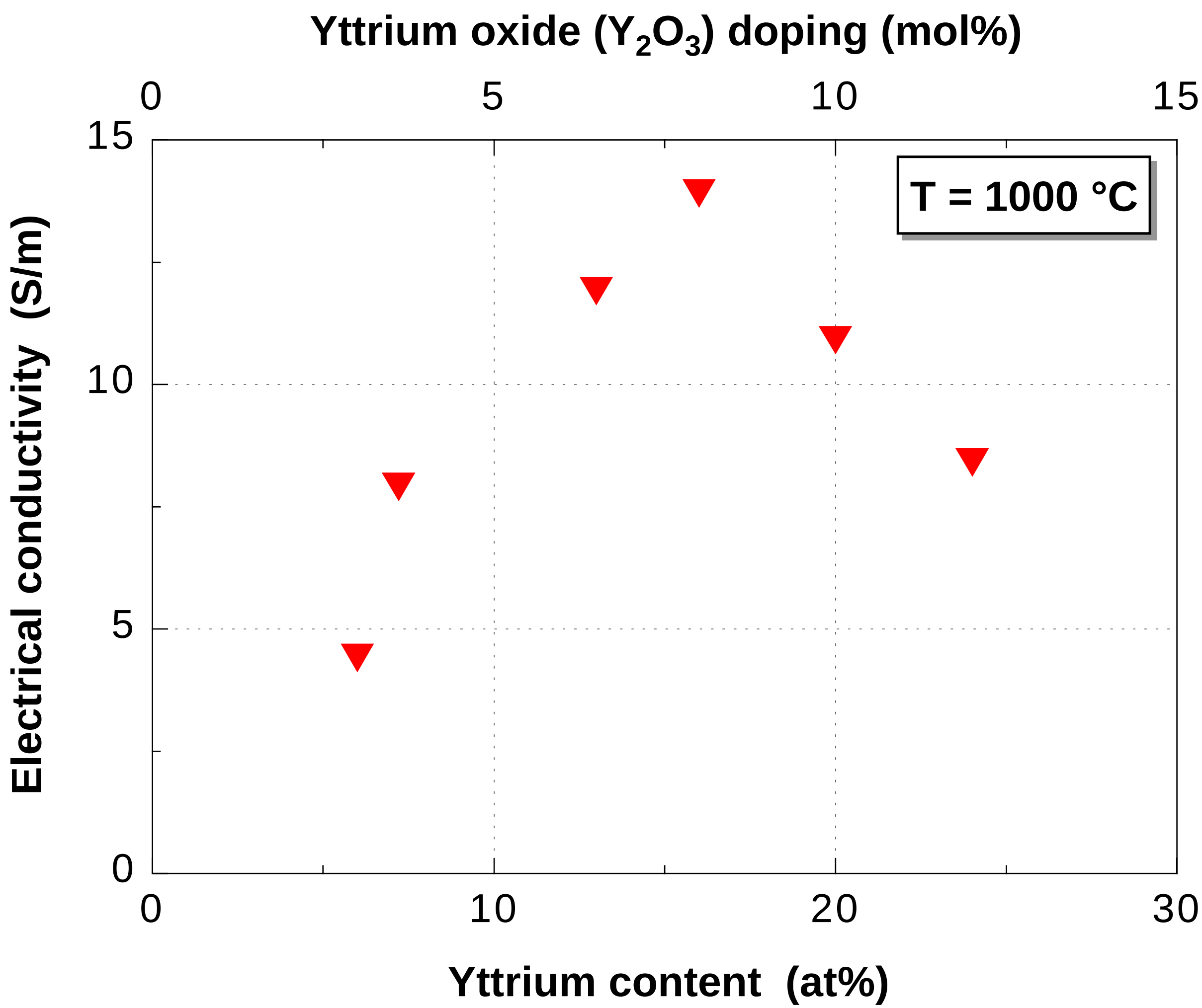
Yttrium on the site of Zirconium
Y^{3+} is negative in comparison with Zr^{4+}

Oxygen vacancy induces 2 positive valence compared with O^{2-}

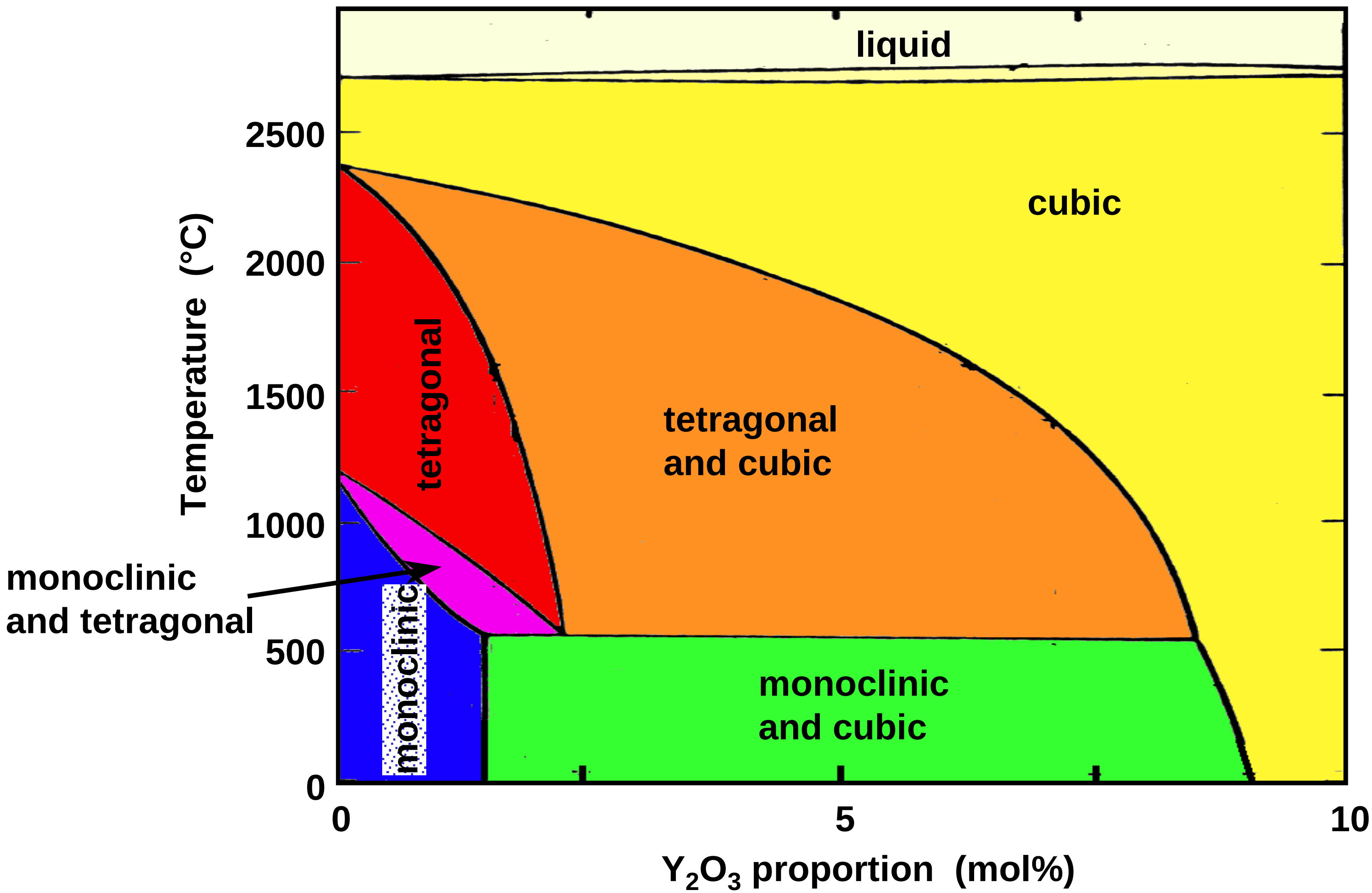
3 oxygen atoms on oxygen site



Electrical Conduction in Ionic Solids and Polymers
Yttrium-doped zircon oxide: conductivity as a function of the doping

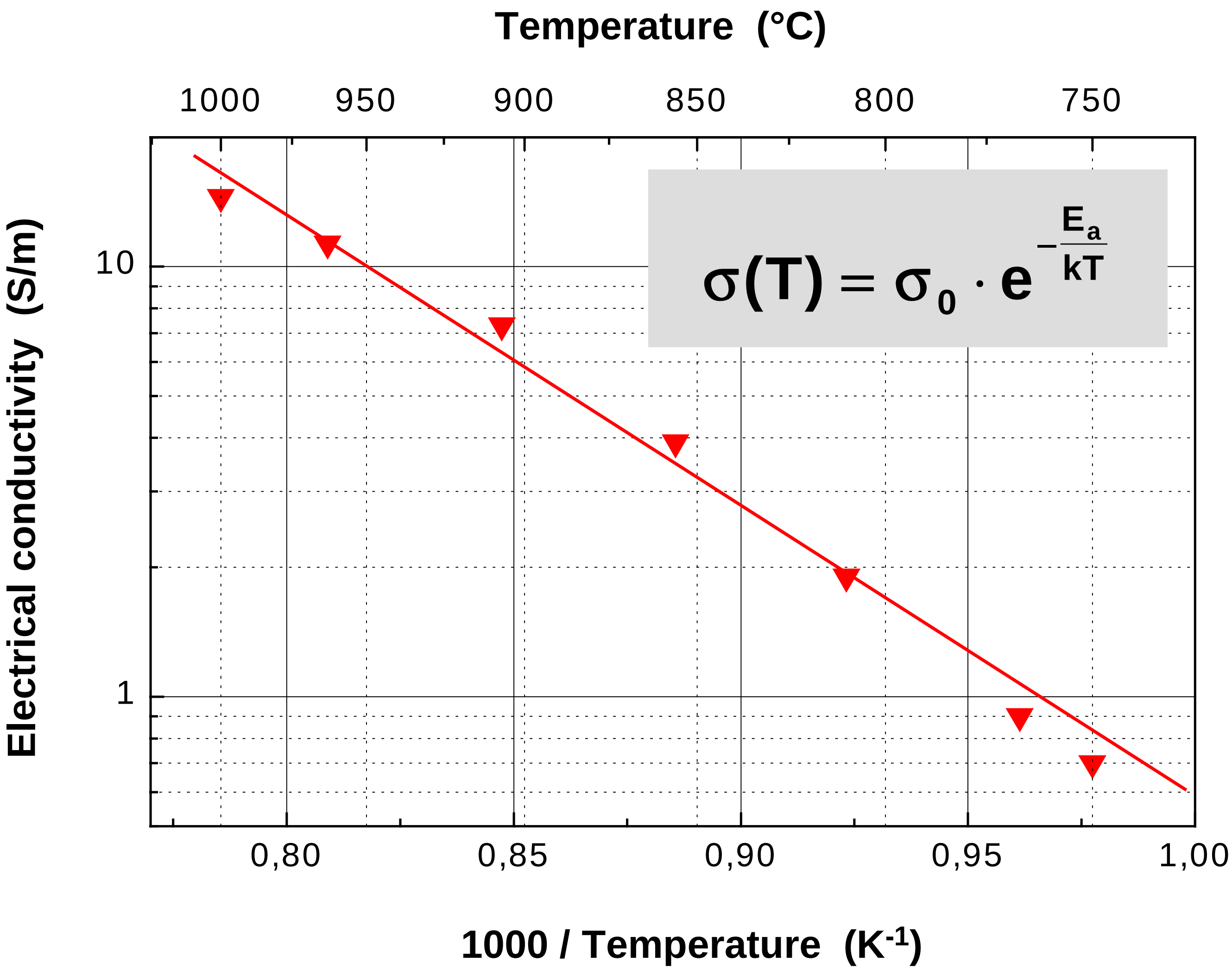


Electrical Conduction in Ionic Solids and Polymers
Phase diagram: Yttrium oxide (Y_2O_3) - Zircon oxide (ZrO_2)



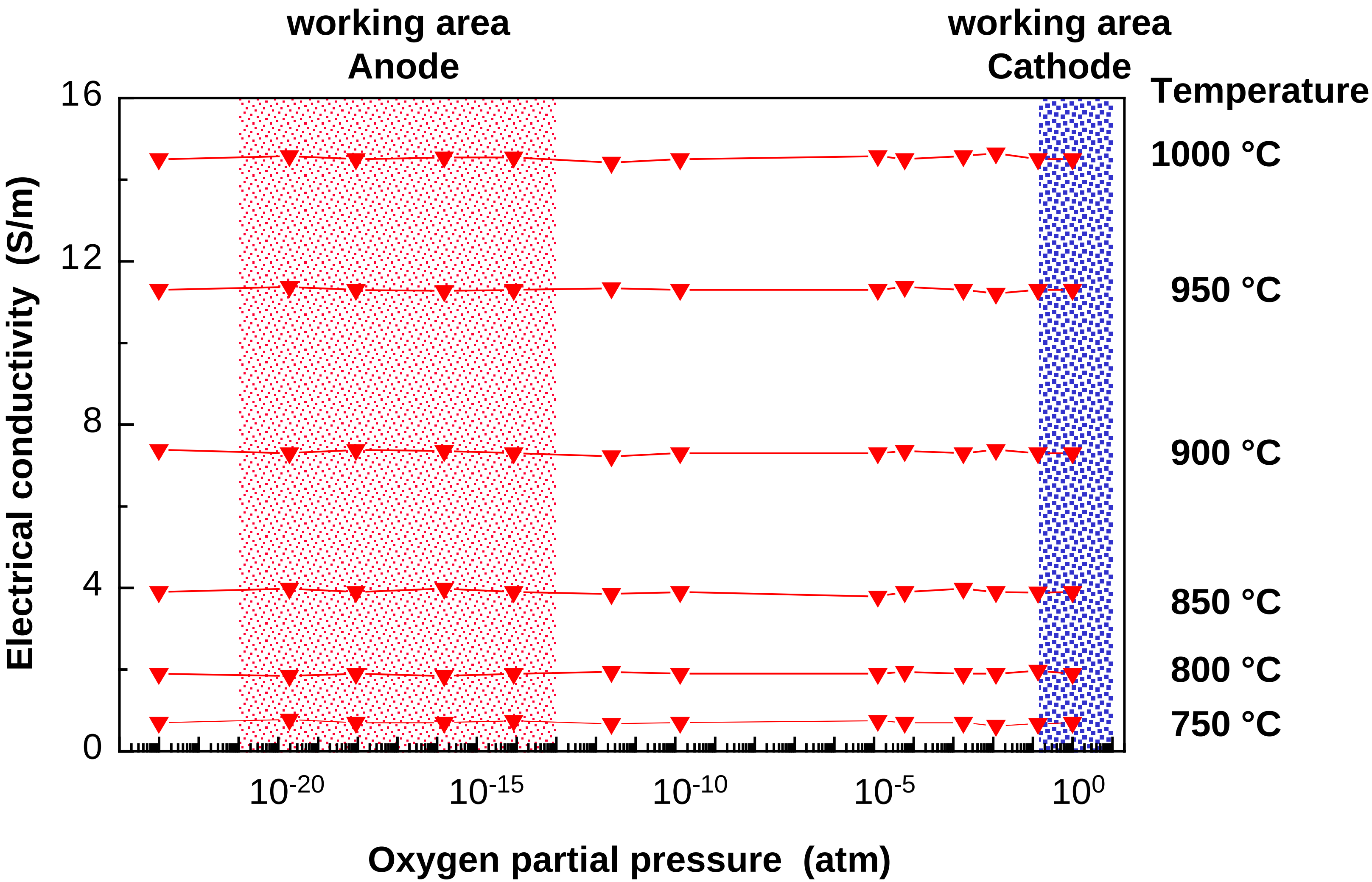
Electrical Conduction in Ionic Solids and Polymers

Y-doped ZrO_2: conductivity as a function of temperature

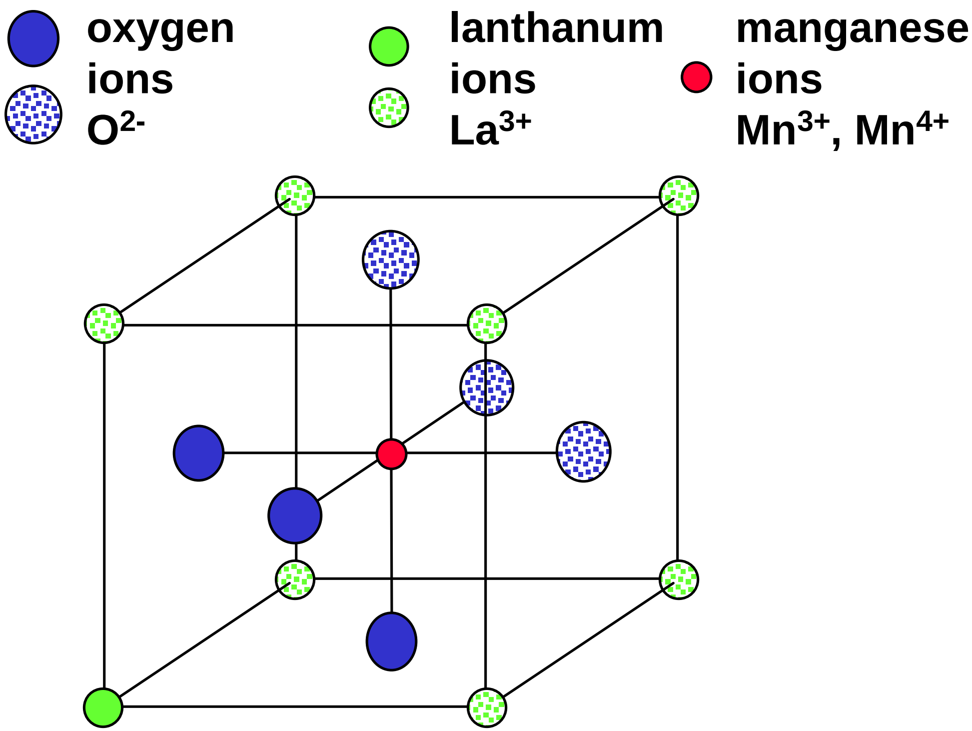


$$\sigma(T) = \sigma_0 \cdot e^{-\frac{E_a}{kT}}$$

Electrical Conduction in Ionic Solids and Polymers
Y-doped ZrO_2: conductivity as a function of oxygen partial pressure



Cathode Side (SOFC): Conduction Mechanism
Hopping Conduction with Example of $LaMnO_3$



e^- $\curvearrowright$ e^- $\curvearrowright$

$$-Mn^{3+}-Mn^{4+}-Mn^{3+}-Mn^{3+}-Mn^{4+}-$$

charge carrier mobility

$$\mu(T) = \frac{e_0 \cdot a_0^2 \cdot \nu_0}{kT} \cdot e^{-\frac{E_a}{kT}}$$

electrical conductivity

$$\sigma(T) = \frac{n \cdot e_0^2 \cdot a_0^2 \cdot \nu_0}{kT} \cdot e^{-\frac{E_a}{kT}}$$

e_0 elementary charge
a_0 lattice constant
ν_0 hopping frequency
E_a activation energy

Cathode Side (SOFC): Increase of Electrical Conductivity of $LaMnO_3$ by doping with Sr or Co

A- site doping: installation of strontium (Sr) at the site of lanthanium
Sr^{2+} ion in place of La^{3+} ion

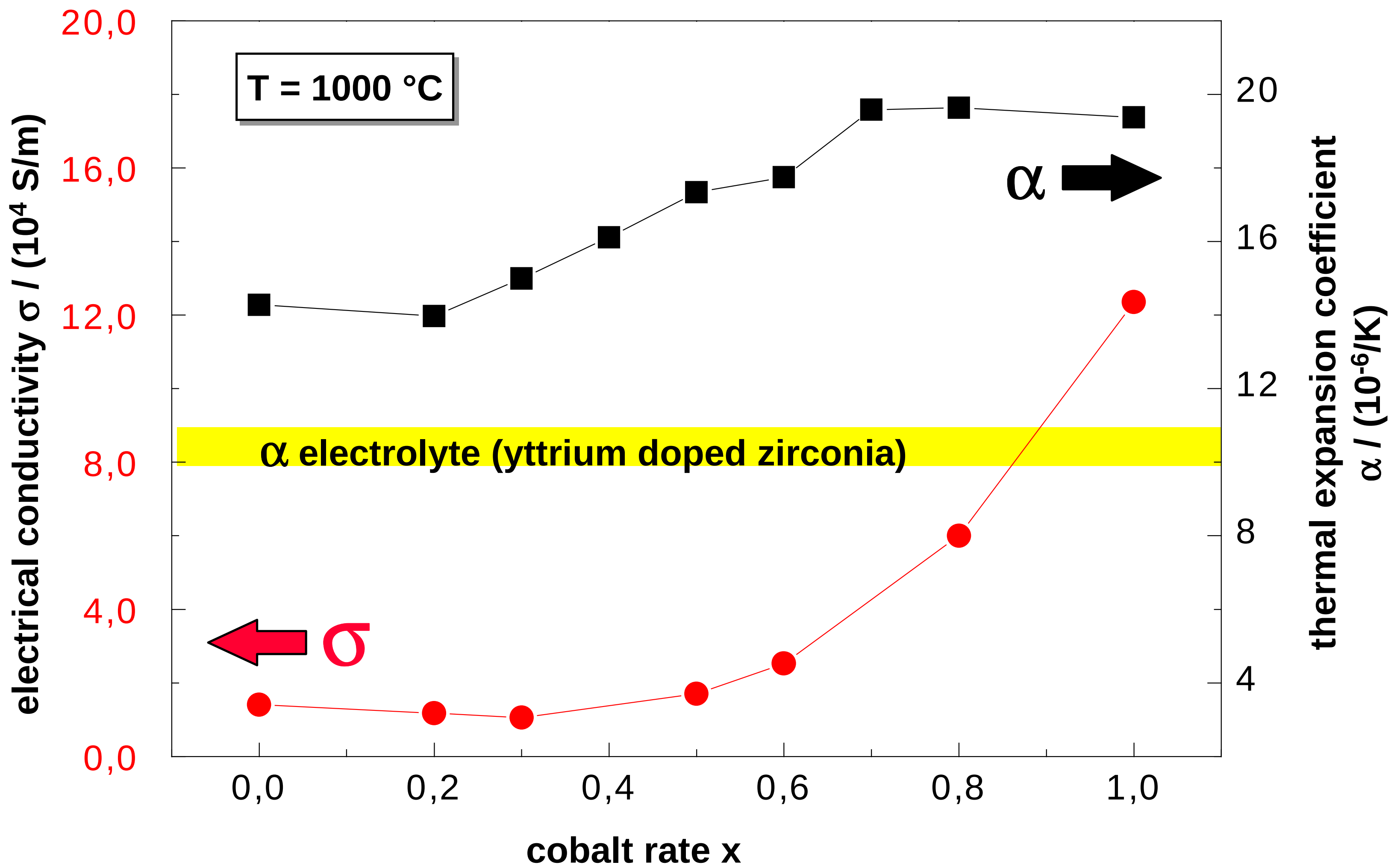
charge compensation: modification of the oxidation valency of magnesium
Mn^{3+} ion becomes Mn^{4+} ion

$$\mathbf{SrO + \frac{1}{2}Mn_2O_3 + \frac{1}{4}O_2 \rightarrow Sr_{La}' + Mn_{Mn}^{\bullet} + 3O_O^X}$$

B- site doping: installation of Cobalt (Co) at the site of magnesium
Co^{2+} ion in place of Mn^{3+} ion

charge compensation: modification of the oxidation valency of magnesium
Mn^{3+} ion becomes Mn^{4+} ion

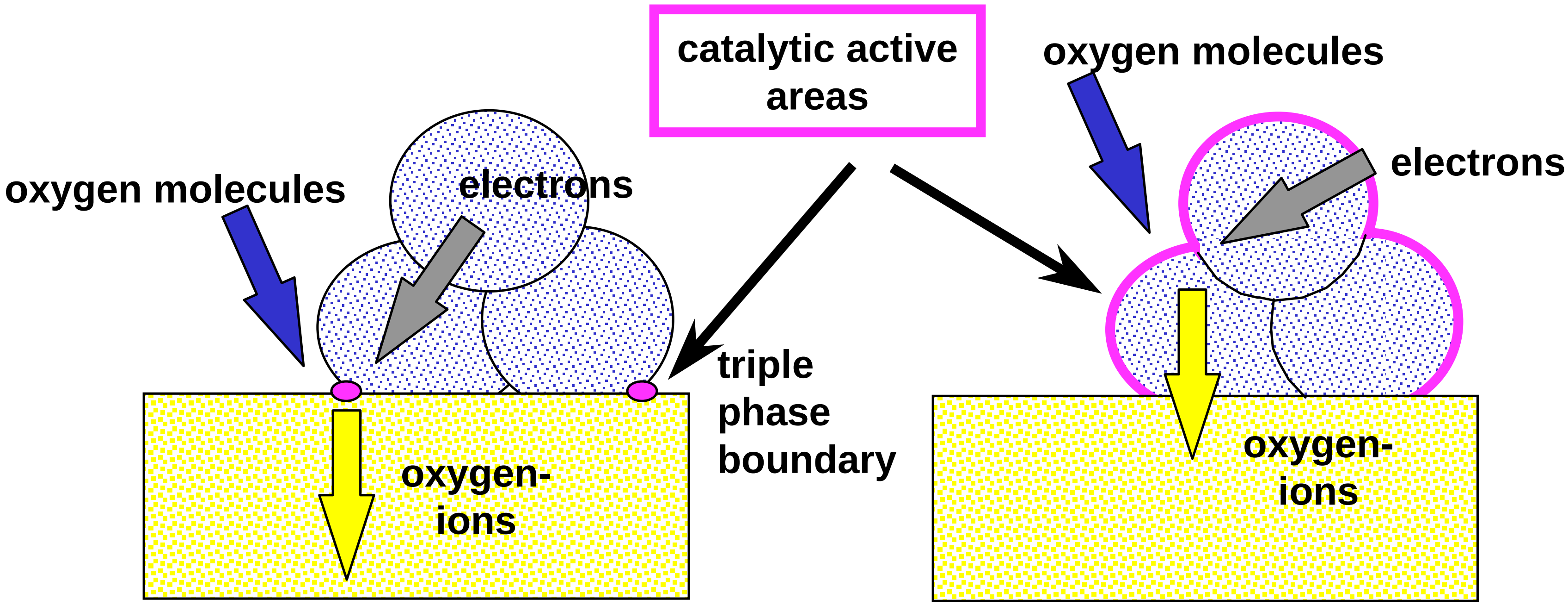
Cathode Side (SOFC): Solid Solution Series of $La_{0.8}Sr_{0.2}Mn_{1-x}Co_xO_3$ Electrical Conductivity and Thermal Expansion Coefficient



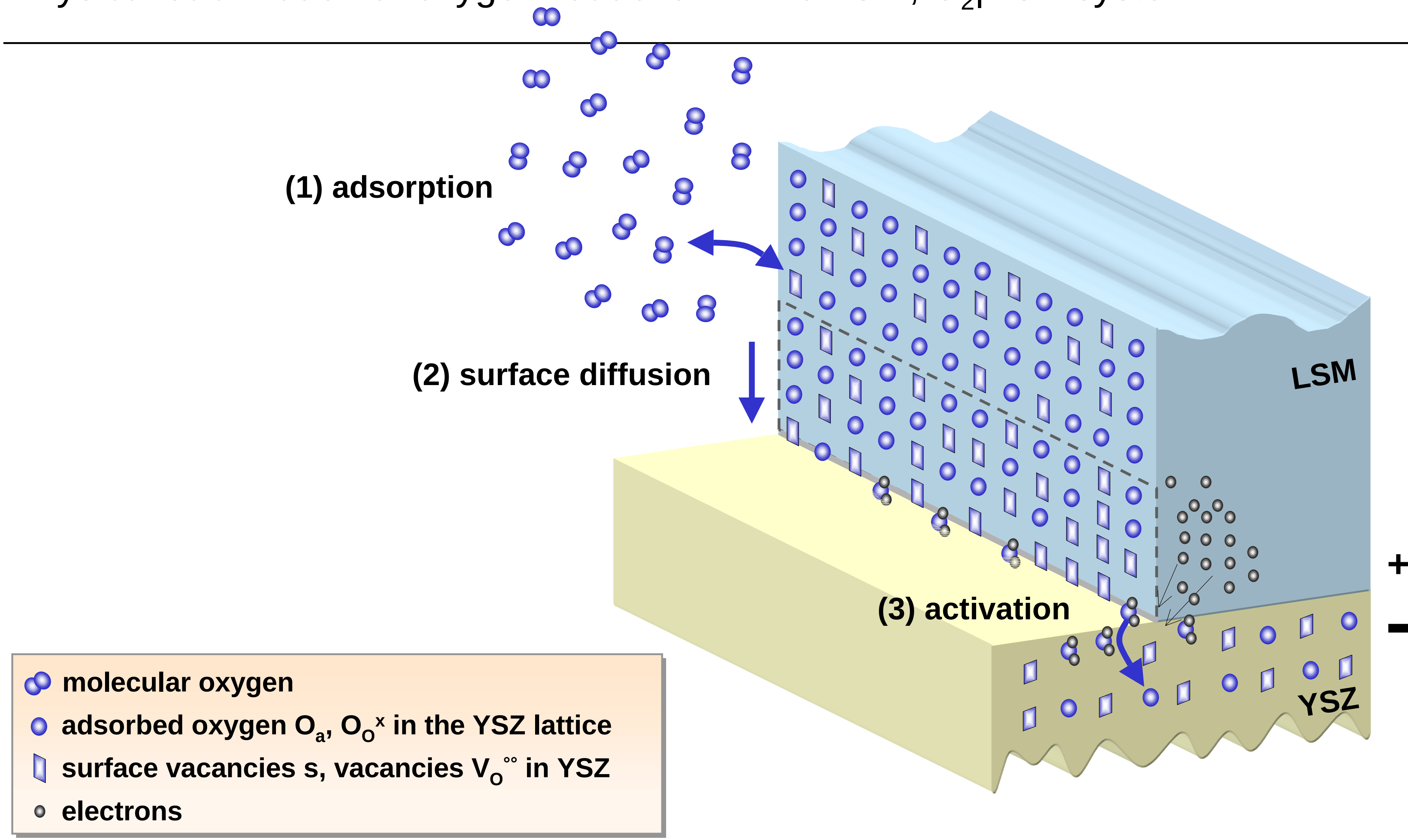
Cathode Side (SOFC): Integration and Transport of Oxygen Ions

electron conducting (σ_{el}) cathode

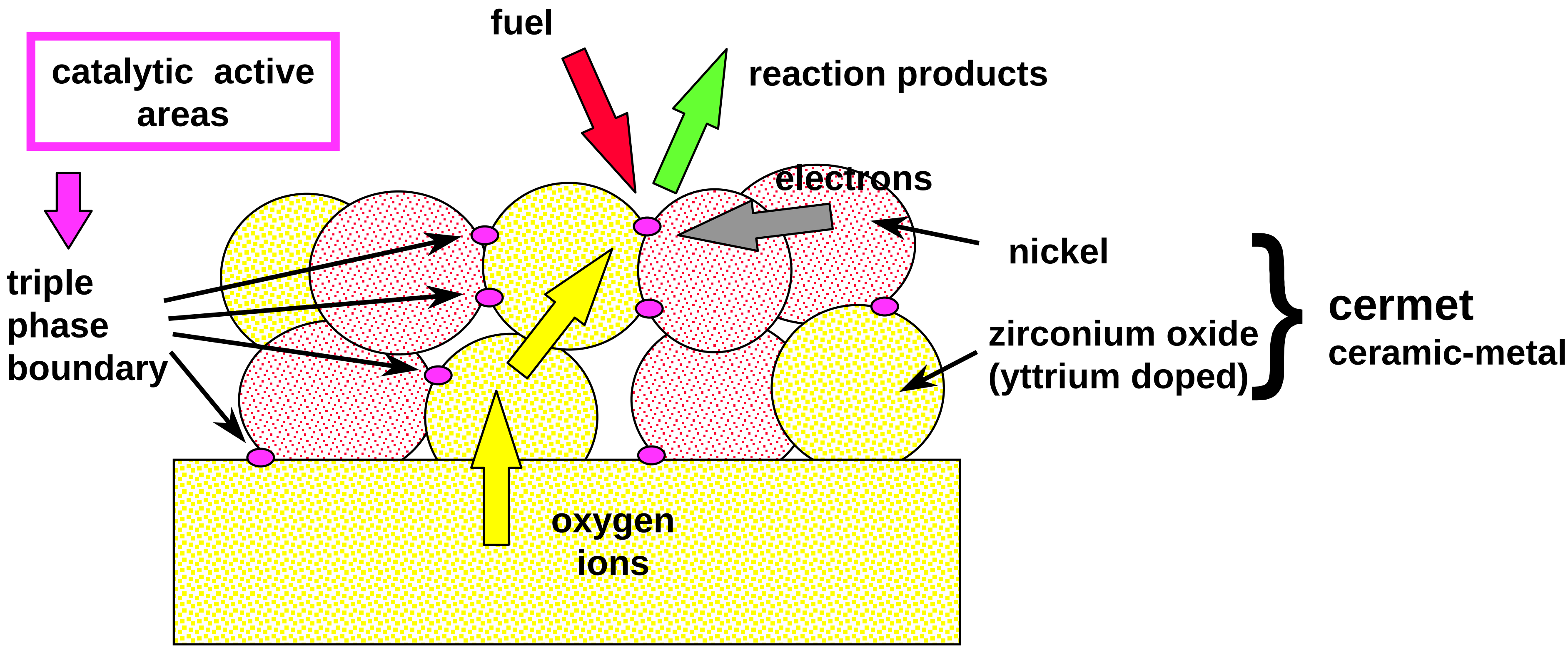
additional reactions at mixed conducting ($\sigma_{el}+\sigma_{ion}$) cathode



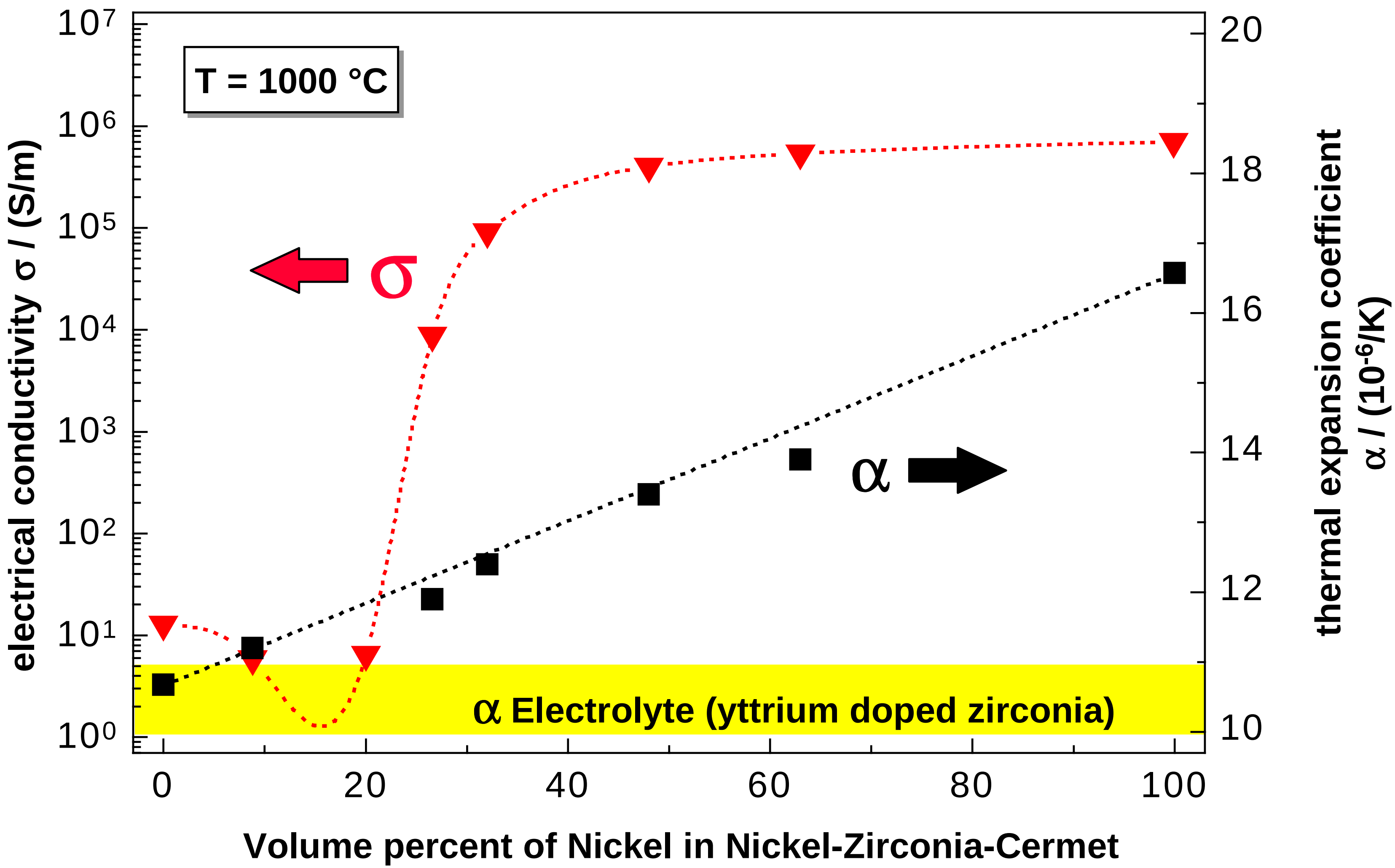
Core Technologies: Modeling and Simulation
Physical sub-model for oxygen reduction in the LSM, O_2|YSZ-system



Anode Side (SOFC): Transport and Removal of Oxygen Ions in a Nickel-Zirconia Cermet Anode

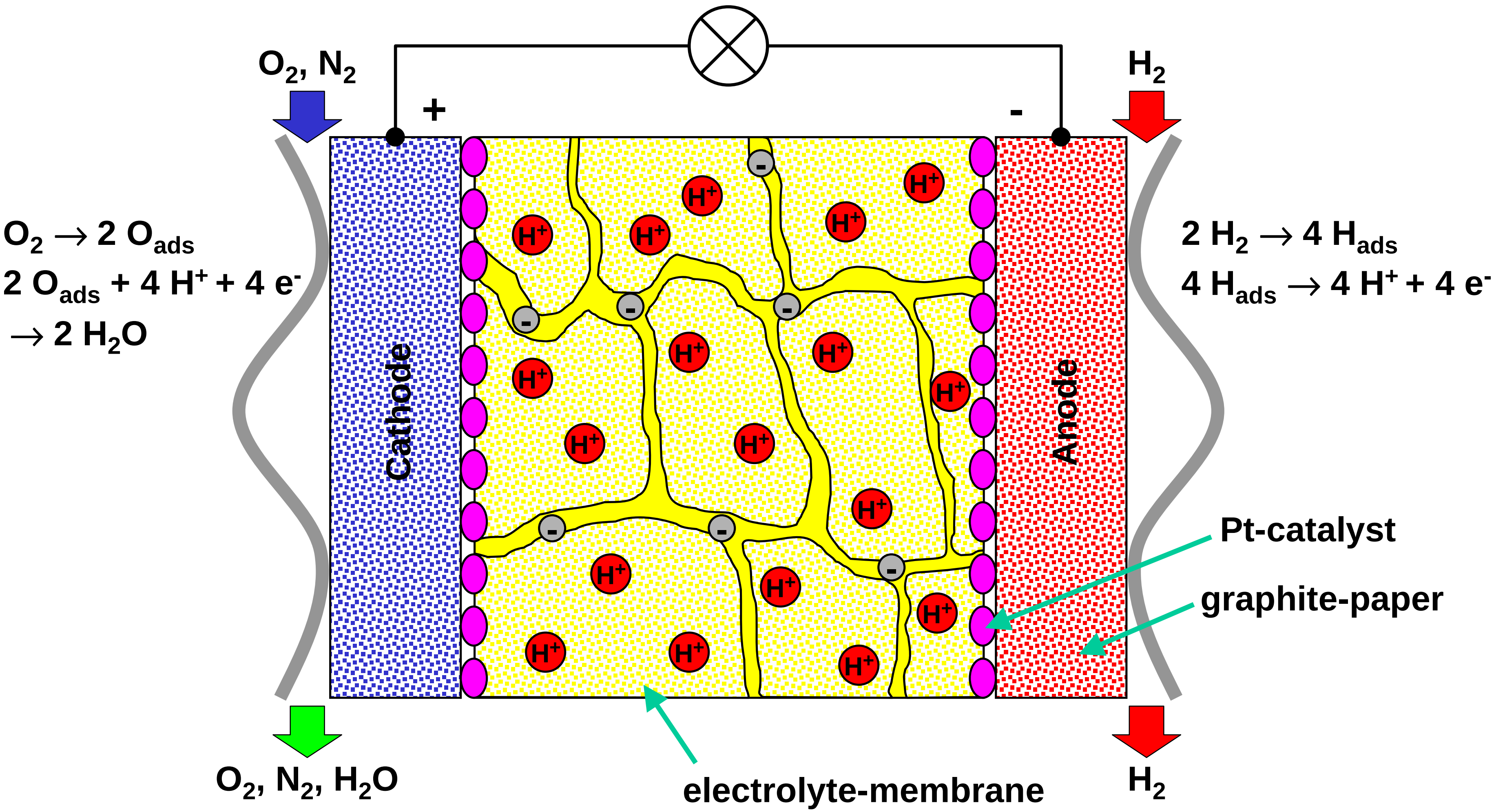


Anode Side (SOFC): Nickel-Zirconia-Cermet
Electrical Conductivity and Thermal expansion Coefficient



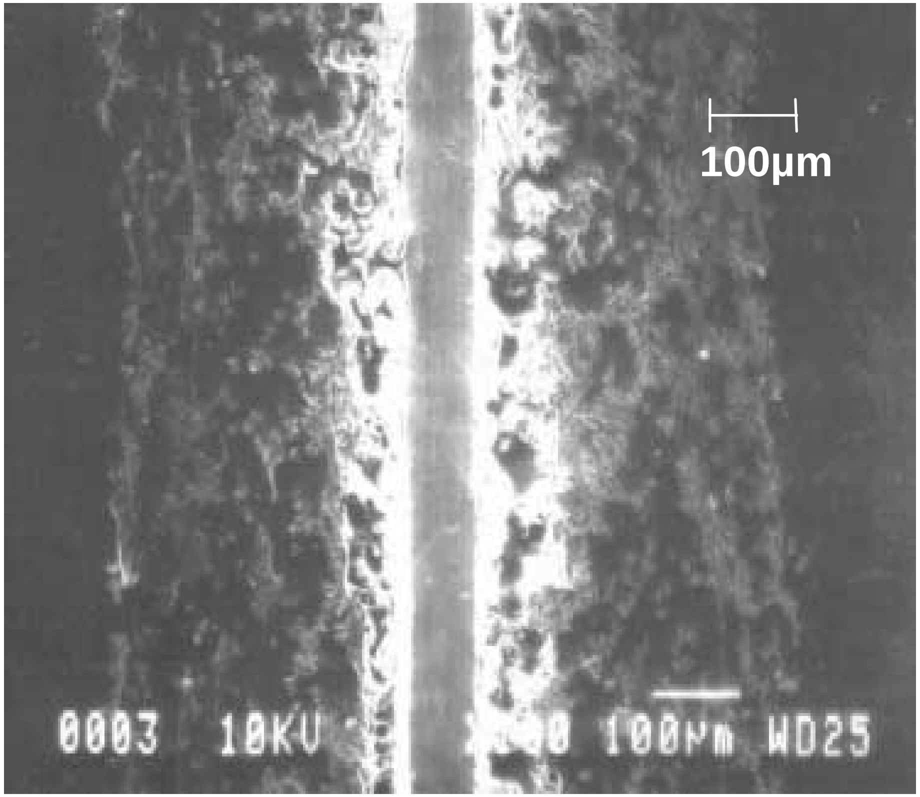
PEMFC
NECAR 3

Principle of a Polymer-Exchange-Membrane Fuel Cell



PEMFC
Microstructure of Electrodes and a Single Cell Element

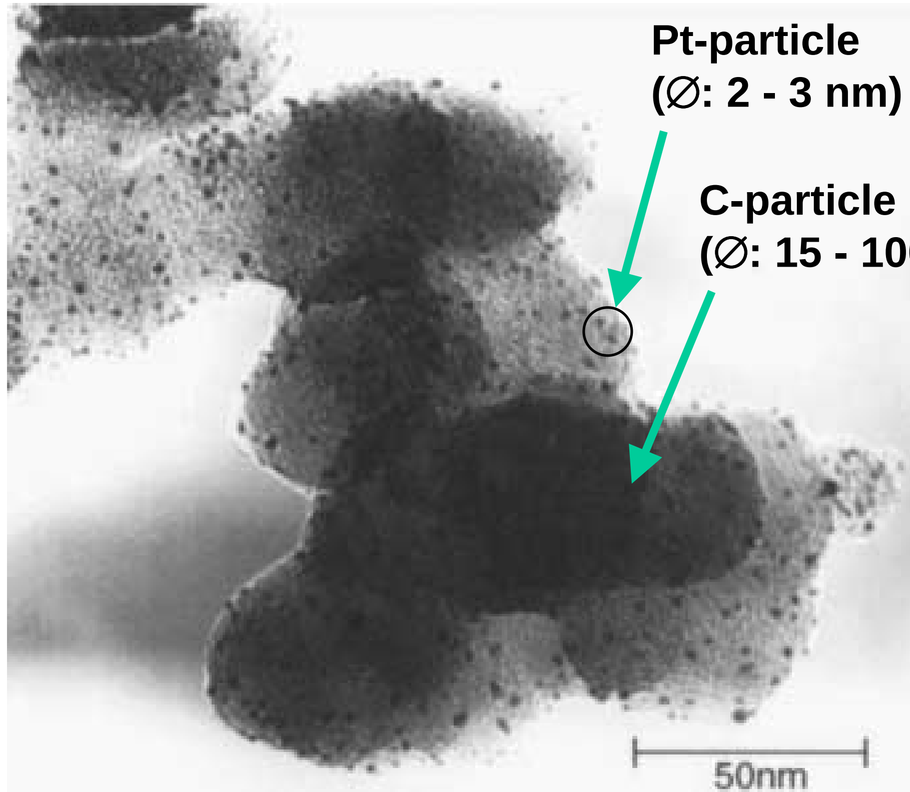
SEM



electrode **electrode**

Pt-catalyst **membrane** **Pt-catalyst**

TEM



Electrical Conduction in Ionic Solids and Polymers
Electrical Properties of Polymers

Conducting polymers

Conductivities as high as 1,5 $\times$ 10^{7} (Ω m)$^{-1}$ have been achieved.
***e.g.* polyacetylene, polyparaphenylene, polypyrrole, and polyaniline doped with appropriate impurities.**

Structure of the *polymer electrolytes*

fluoridated, sulfonated polymers

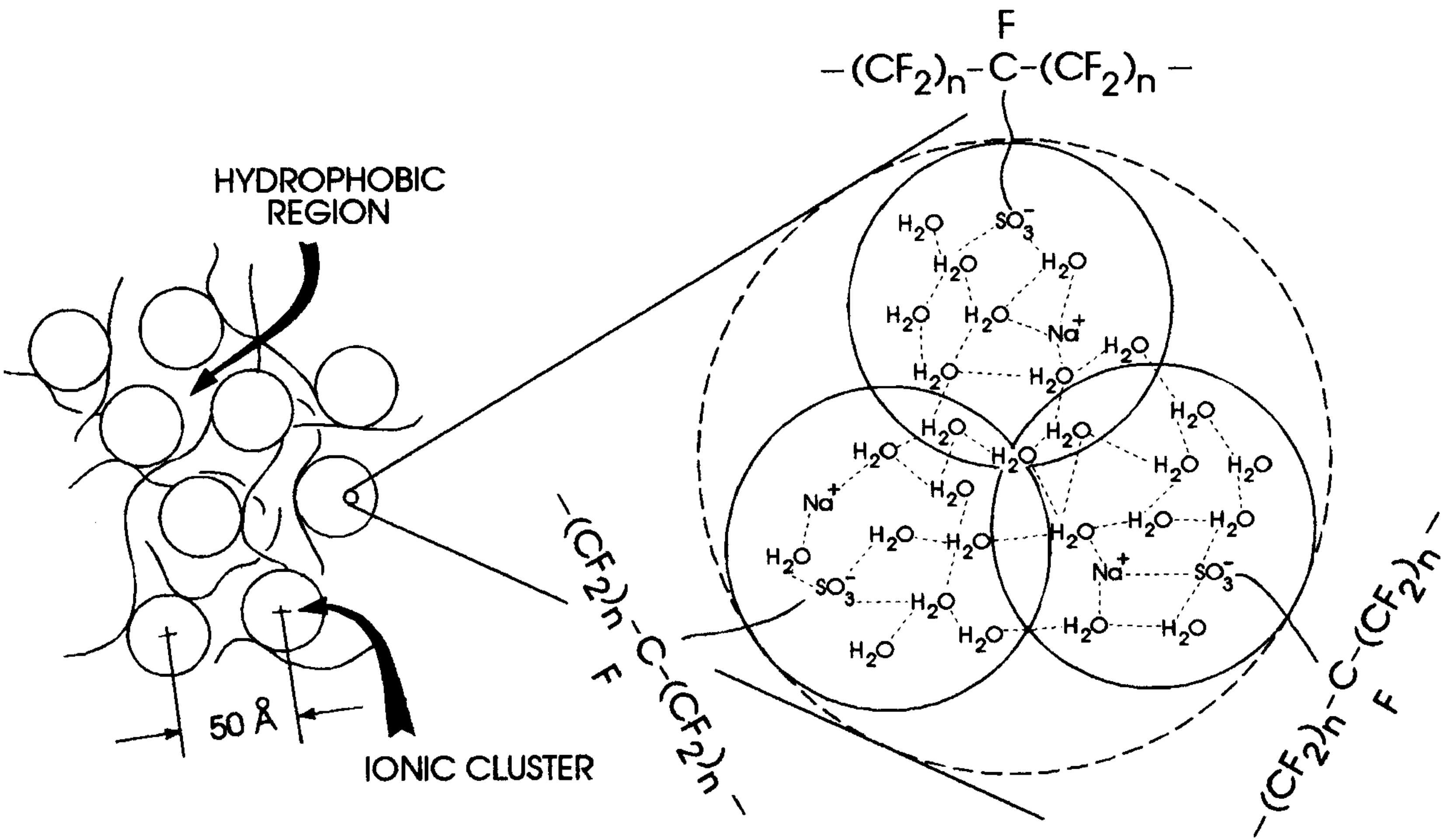
$-[(CF_2\ CF_2)_m\ CF\ CF_2]_n-$
|
O
|
CF_2
|
$CF\ CF_3$
|
O
|
$CF_2\ CF_2\ SO_3$**H**

Nafion (Du Pont)
$\sigma(H^+)$ = 0,059 S/cm (80 °C)

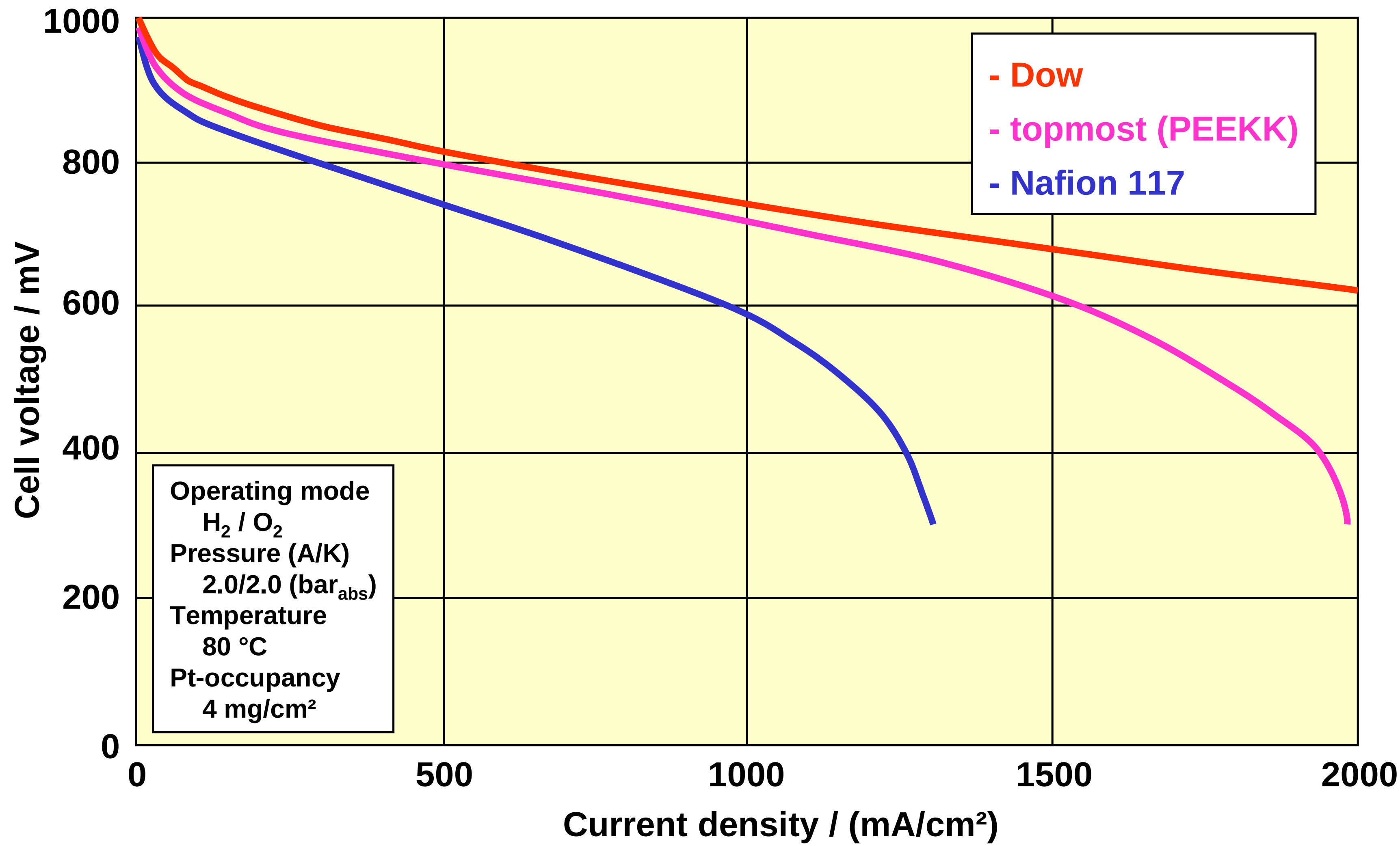
$-[(CF_2\ CF_2)_m\ CF\ CF_2]_n-$
|
O
|
$CF_2\ CF_2\ SO_3$**H**

Dow (Dow Chemicals)
$\sigma(H^+)$ = 0,114 S/cm (80 °C)

PEMFC
Proton Conductivity of the Exchange Membrane

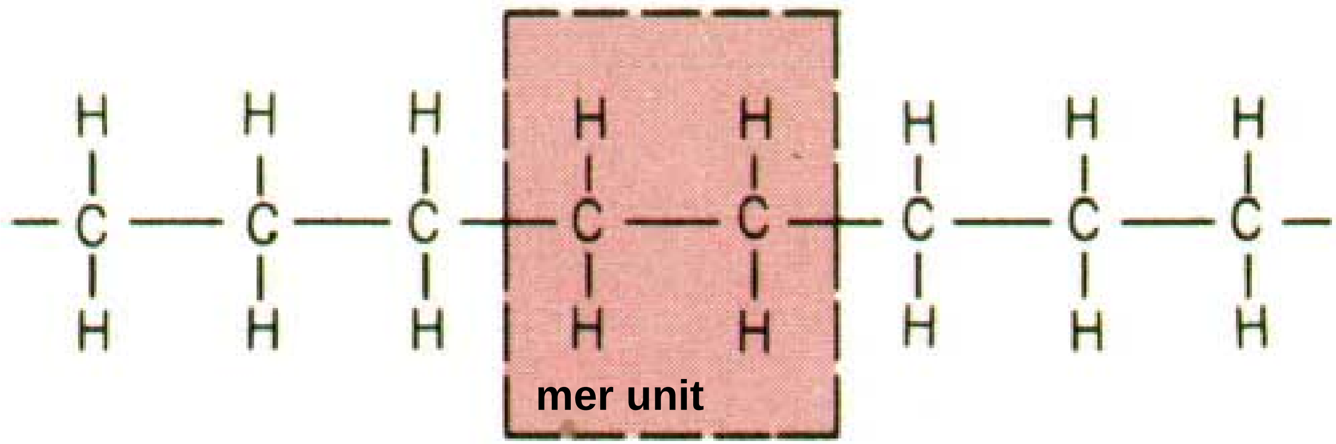


PEMFC
U/I-curve with different Polymer-Electrolyte-Membrane

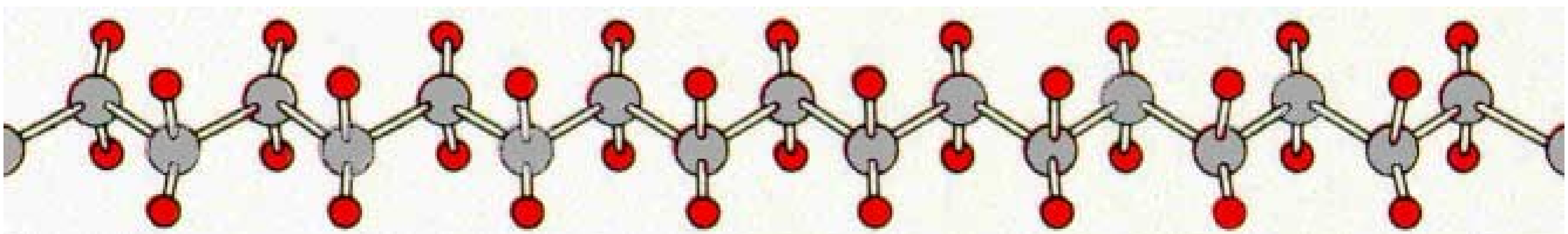


Amorphous Solids (Polymers)
Polyethylene (PE)

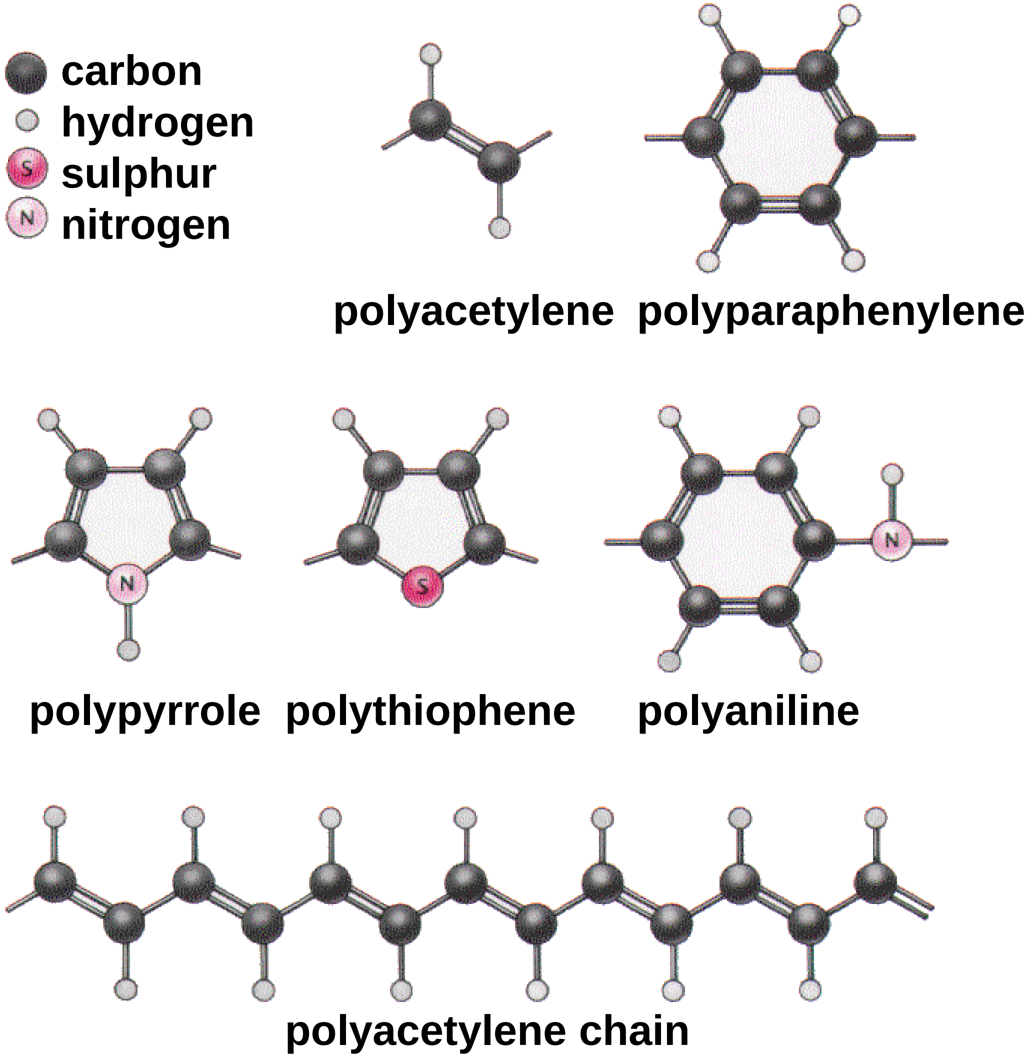
schematic sketch of the mer and chain structures



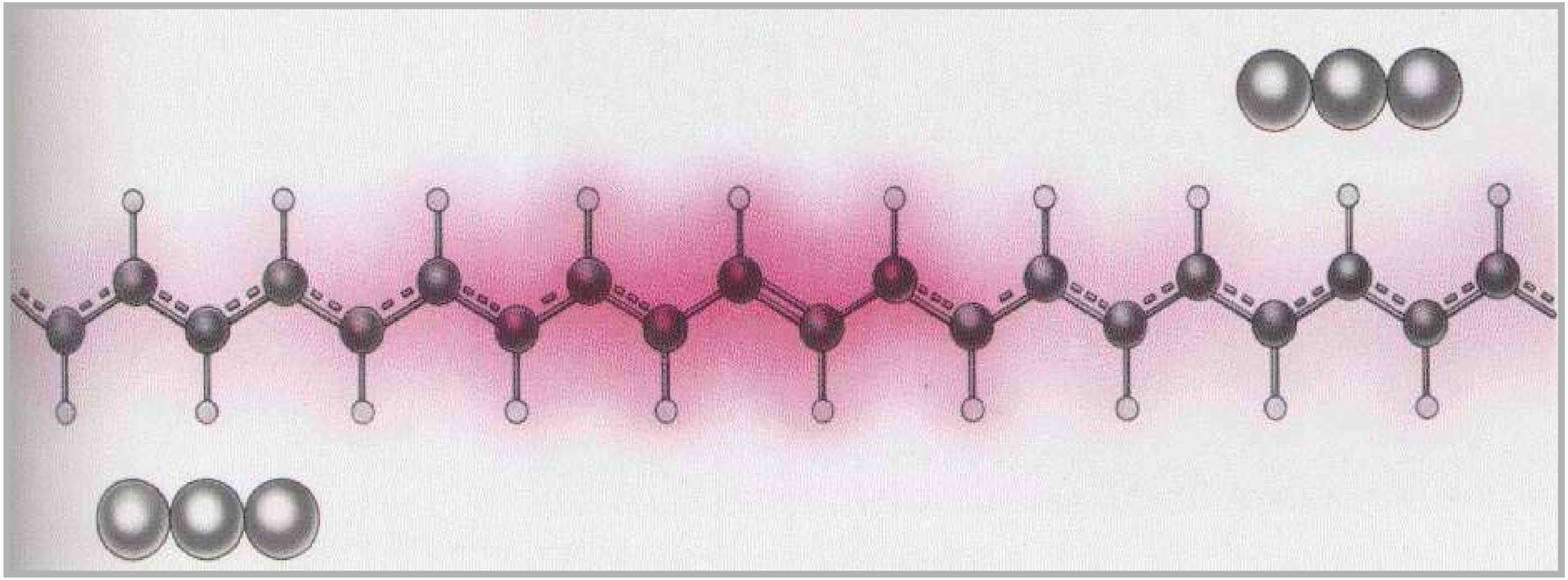
perspective of the molecule



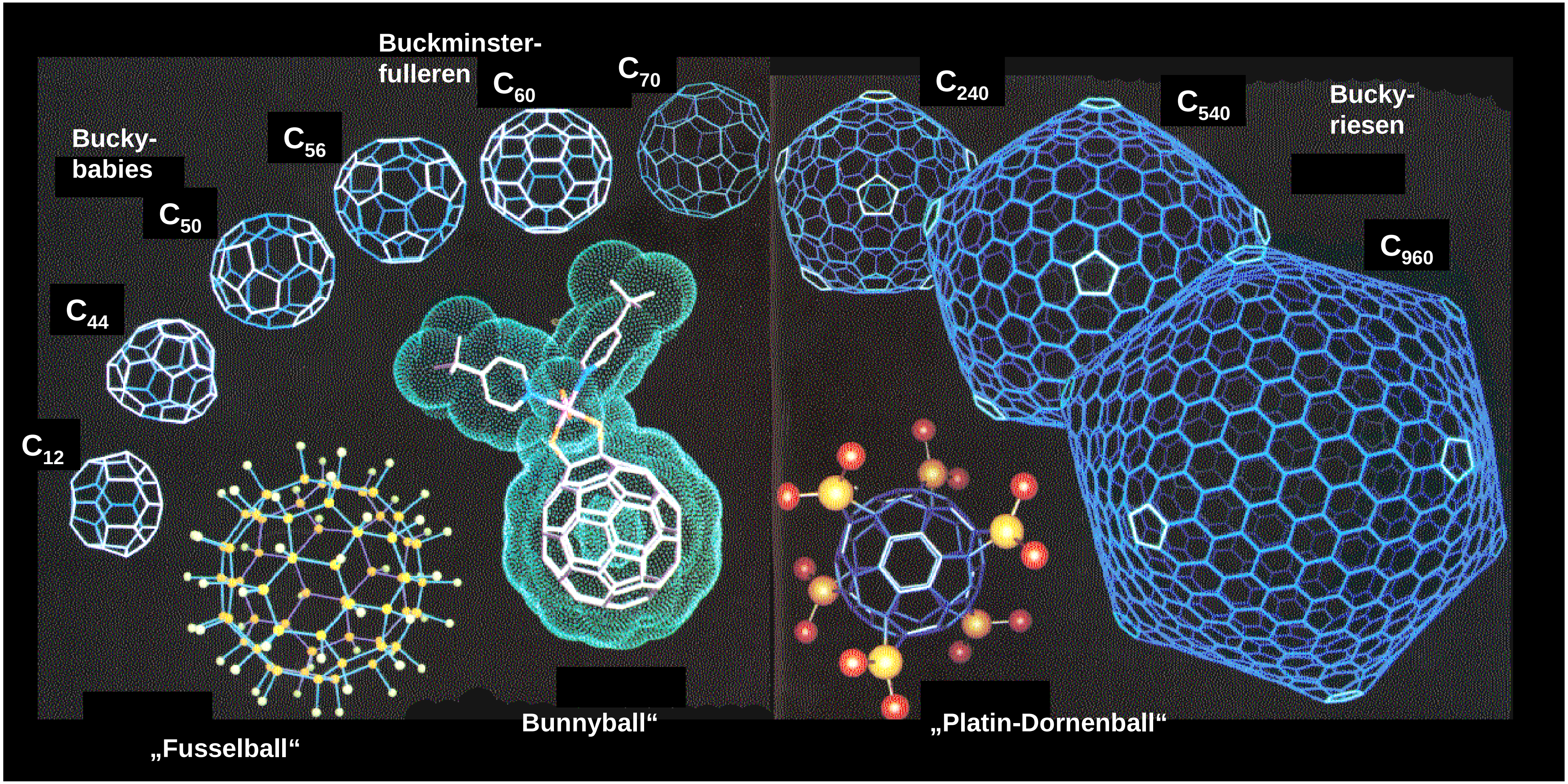
Polymers
Monomer Components of Conductive Polymers



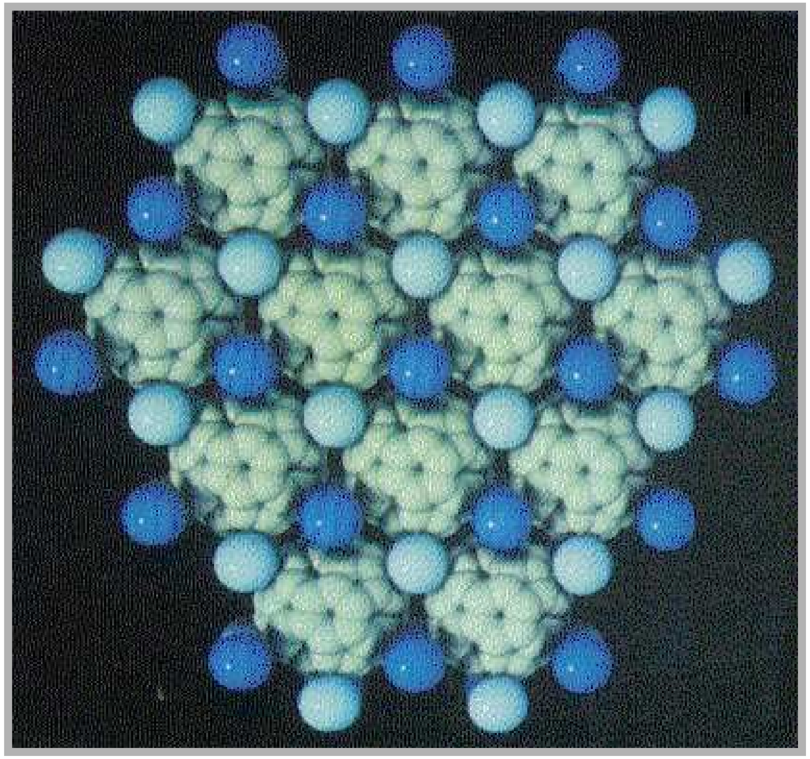
Polymers
p-doped Polyacetylene with delocalized Electrons



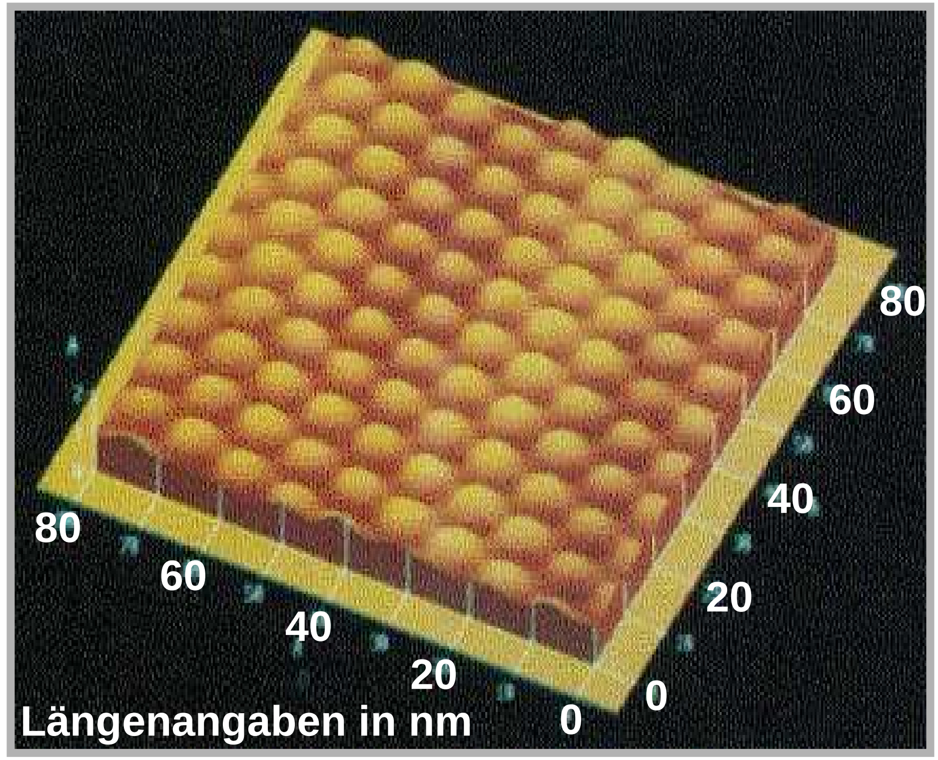
Polymers
Fullerene from C_{32} to C_{960}



Polymers
Electronics with Fullerene



K-doped, superconducting
Buckminsterfullerit K_3C_{60}



K_3C_{60}-layer on GaAs substrate