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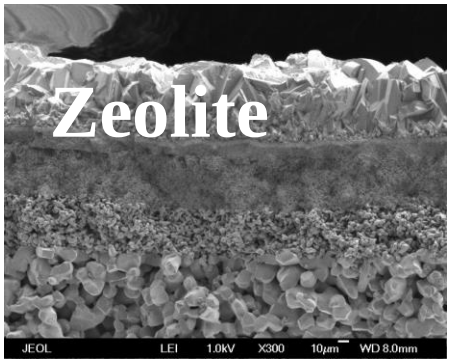
Pre-School
Diffusion Fundamentals VI

Spreading in Nature, *TECHNOLOGY* and Science

Transport-controlled devices: Adsorbents, membranes, catalysts, fuel cells, solar cells, Li^+ batteries…

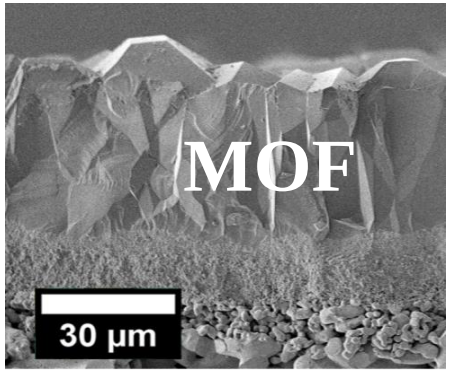
Caro's Background : Inorganic membranes

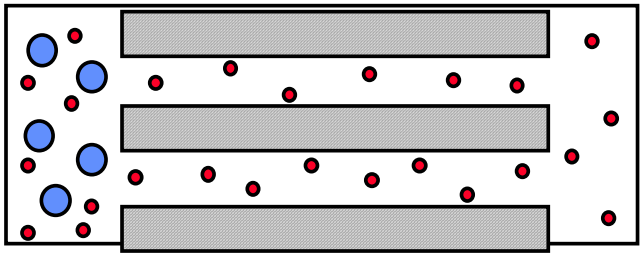


Supported molecular sieve membranes:

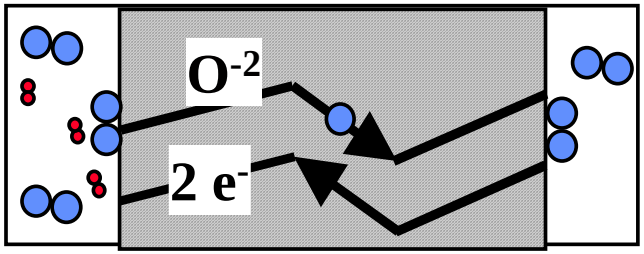
← Zeolite ZSM-5

MOF ZIF-8 →

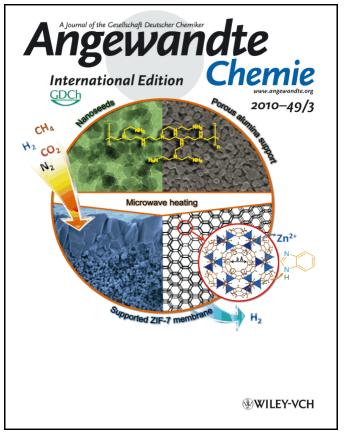




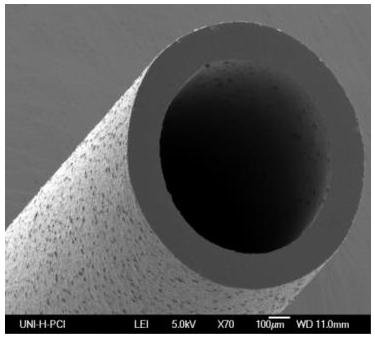
Molecular sieving: zeolite, MOFs, carbons, X-ray amorphous SiO_2

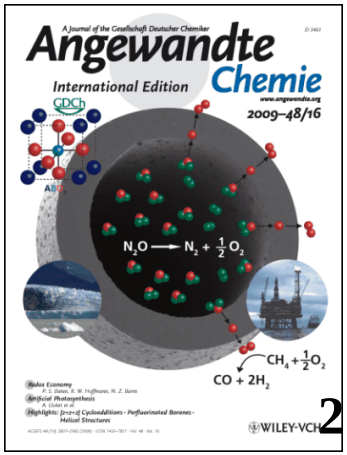


Ionic transport (solid electrolyte):O^{2-}, H^{+} in perovskite, Nafion, ionic liquid, metals



$Ba(Co_{0.4}Fe_{0.4}Zr_{0.2}O_{3-\delta}$
Hollow fiber membrane →





Following Caro‘s expertise on transport in porous and dense media:

Molecular Diffusion in porous functional materials:

→ Adsorbents, catalysts, membranes

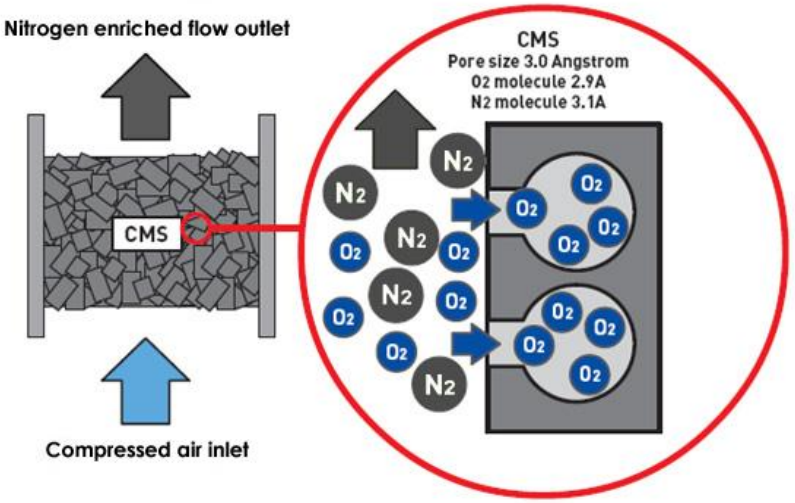
Diffusion of ions and electrons in dense functional materials:

→ Fuel cell, solar cell, Li^+-storage battery

Adsorption and catalysis – adsorbents and catalysts as transport-optimized materials


Linde PSA unit in Leuna

EUROSIDER SAS DI MILLI OTTAVIO & C.



Air separation on carbon molecular sieve (CMS)

Diffusion effect: The slightly smaller oxygen (3.46Å) can easily pass the CMS pores, nitrogen (3.64Å) not

How to reduce cycle time in pressure swing adsorption (PSA) – say from 3 min to 1 min?

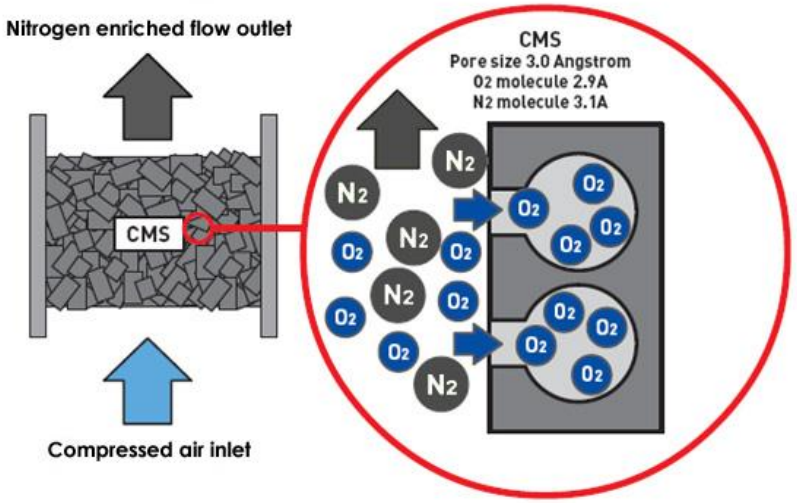
→ We need transport-optimized adsorbents

Do you know a system with gas in – gas out?

Adsorption and catalysis – adsorbents and catalysts as transport-optimized materials

Linde PSA unit in Leuna

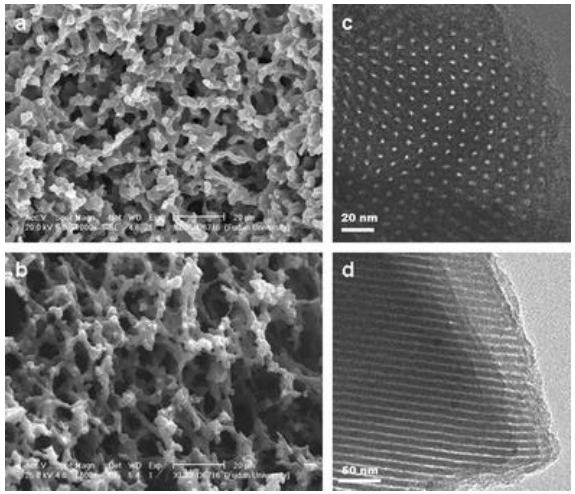
EUROSIDER SAS DI MILLI OTTAVIO & C.

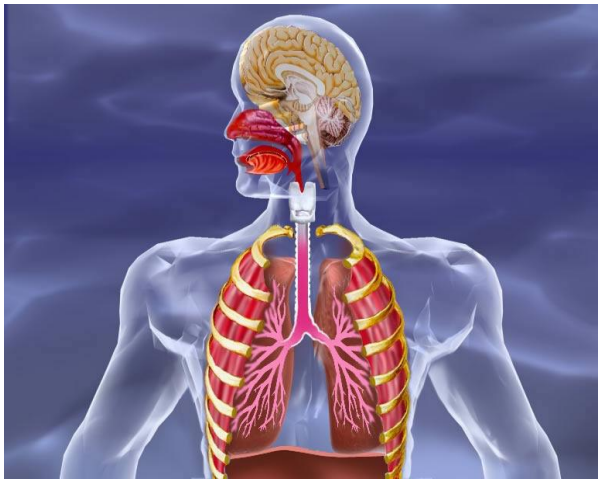


Y. Huang et al.

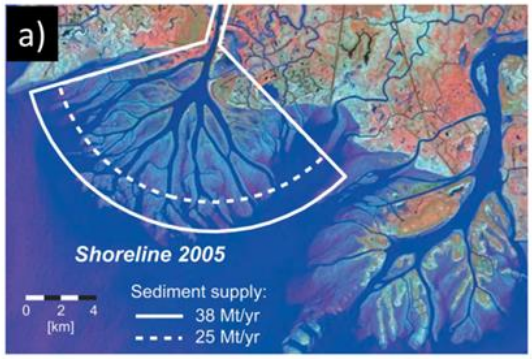
… mesostructures carbonaceous monoliths with hierarchical porosities

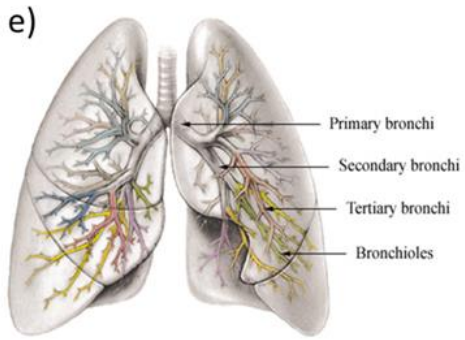
Chem. Commun. 2008, 2641

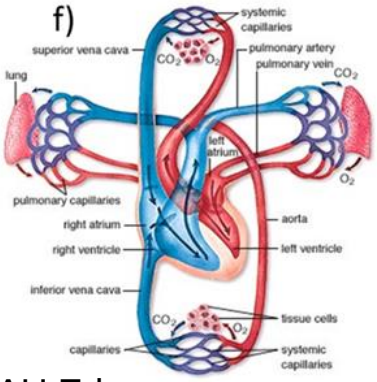


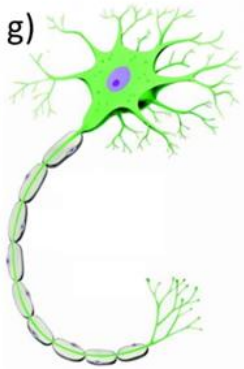


Transport-optimized systems with hierarchical structure









a) river delta
b) lightning

c) roots of a tree
d) leaf

e) lung
f) blood circuit
g) nerves

Courtesy of Prof. W. Schwieger, FAU Erlangen

Experiment in thoughts: Two cases

Case a)

Extremely active catalyst – lousy diffusion in the pellet

The pellet must be small, otherwise ther interior of the pellet is not used and Expen-sive noble metal is wasted

→ Make the pellet small

→ Improve transport

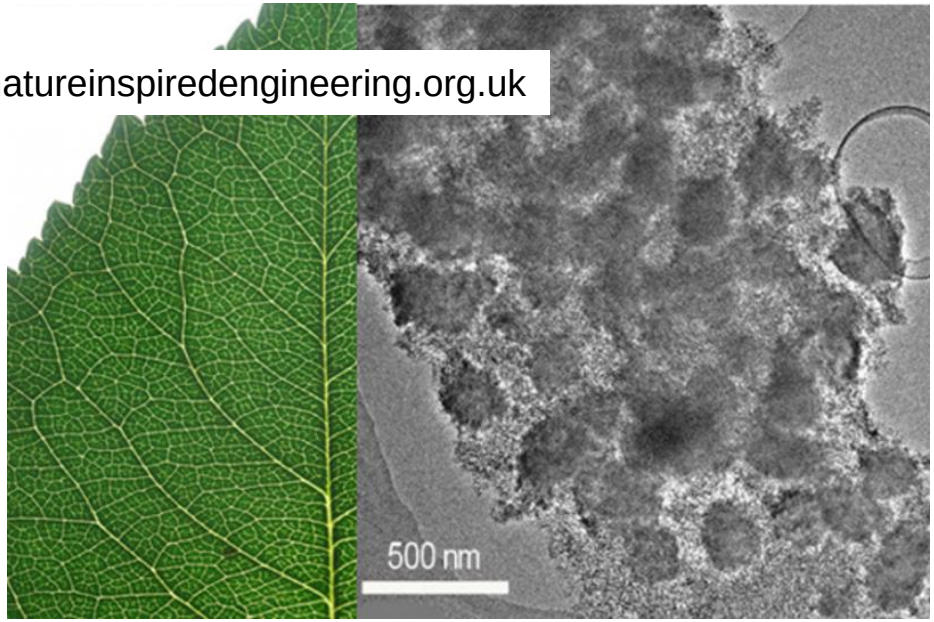
Case b)

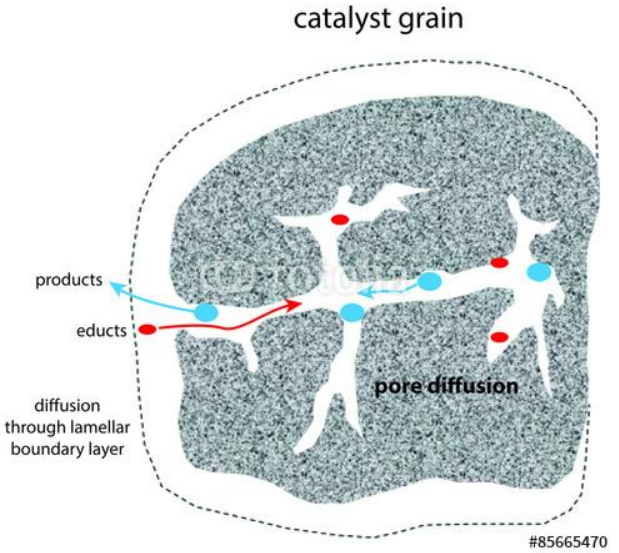
Low-active catalyst – fast diffusion in pellet

The whole pellet is catalytically used

→ Make the catalyst more active

→ Size of pellet can be enlarged





transport in a catalyst grain
fotolia.com

There is mathematics behind it: Effectiveness factor η of a pellet:

Two extreme cases:

a) Highly active catalyst – lousy diffusion in the pellet

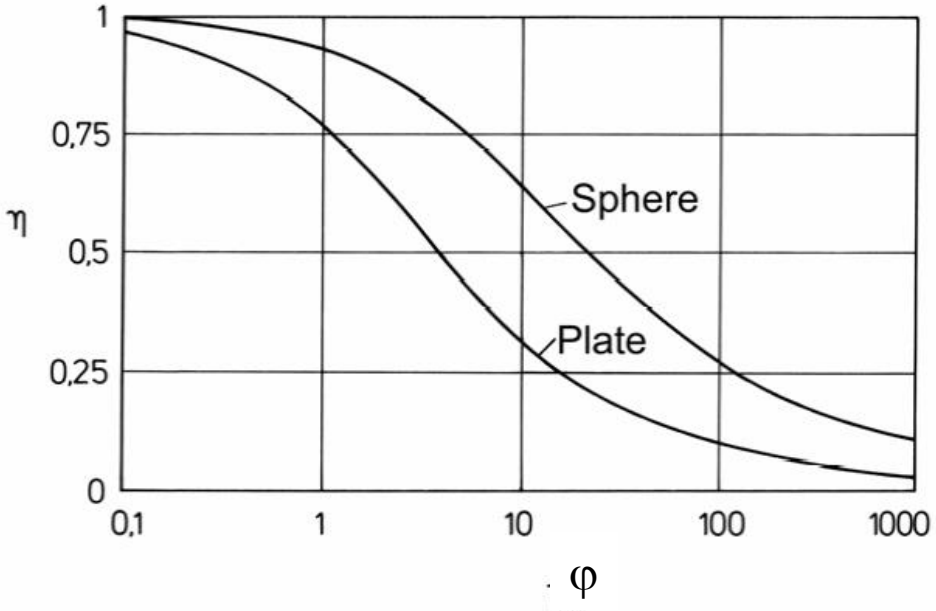
b) Low-active catalyst – fast diffusion in pellet of size L

We form a dimension-less parameter ϕ describing the ratio of

- Catalytic reaction rate proportional $k \cdot c^{n-1}$
- Diffusive transport in pellet proportional D/L^2

$$\varphi^2 = \frac{k \cdot c^{n-1} L^2}{D} \rightarrow \varphi = L\sqrt{\frac{k \cdot c^{n-1}}{D}}$$

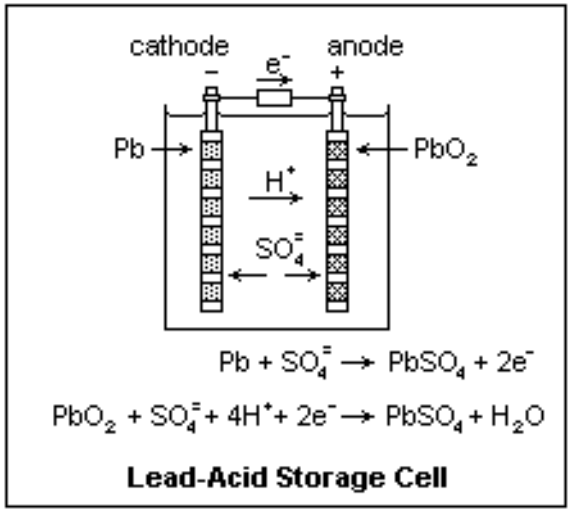
If reaction rate k >> Diffusion rate D/L^2
→ φ is large and η is low

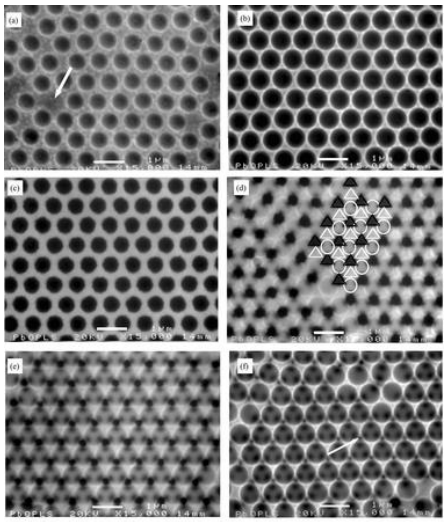


Which battery is Working Horse und Cash Cow?

Is it Li^+? No, → Lead starter battery in cars

http://mysite.du.edu/
~jcalvert/phys/lead.htm





P.N. Bartlett…
Templated PbO_2…
J. Mater. Chem.
12 (2002) 3130

Negative pole:
$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Positive pole:
$PbO_2 + SO_4^{2-} + 4\ H_3O^+ + 2e^- \rightarrow PbSO_4 + 6\ H_2O$

De-charging/de-loading: H_2SO_4 is consumed and H_2O is formed
Charging/loading: opposite, water is consumed, H_2SO_4 is released

$Pb + PbO_2 + 2\ H_2SO_4 \leftrightarrows PbSO_4 + 2\ H_2O$ + electricity

Transport problem like in heterogeneous catalysis:
During entering a porous medium, one component is consumed,
a product leaves by **counter diffusion**: Transport-optimized Pb/PbO_2 layers

Gas transport through a porous membrane

Perfect molecular sieving is the exception
→ usually we have an interplay of adsorption and diffusion

Membrane selectivity = Adsorption selectivity x Diffusion selectivity

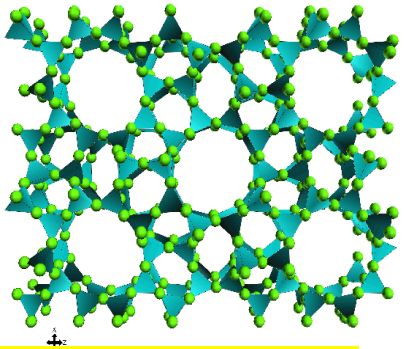
Mixture A/B equimolar 50%/50%	**Ratio of the amounts adsorbed, c_A and c_B in the membrane:** **Mixed gas isotherm!**	**Ratio of the diffusion coefficients D_A and D_B in the membrane:** **Mixed gas diffusion!**

Two innovative methods to determine the mixed gas data:
- IR –microscopy (see Kärger lecture)
- in silicio = molecular dynamics

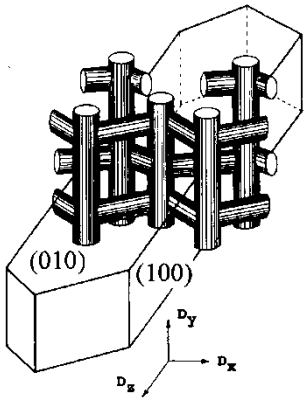
R. Krishna
J. Phys. Chem. C 113 (2009) 19756
R. Krishna , J.M. van Baten,
J. Phys. Chem. 116 (2012) 23556

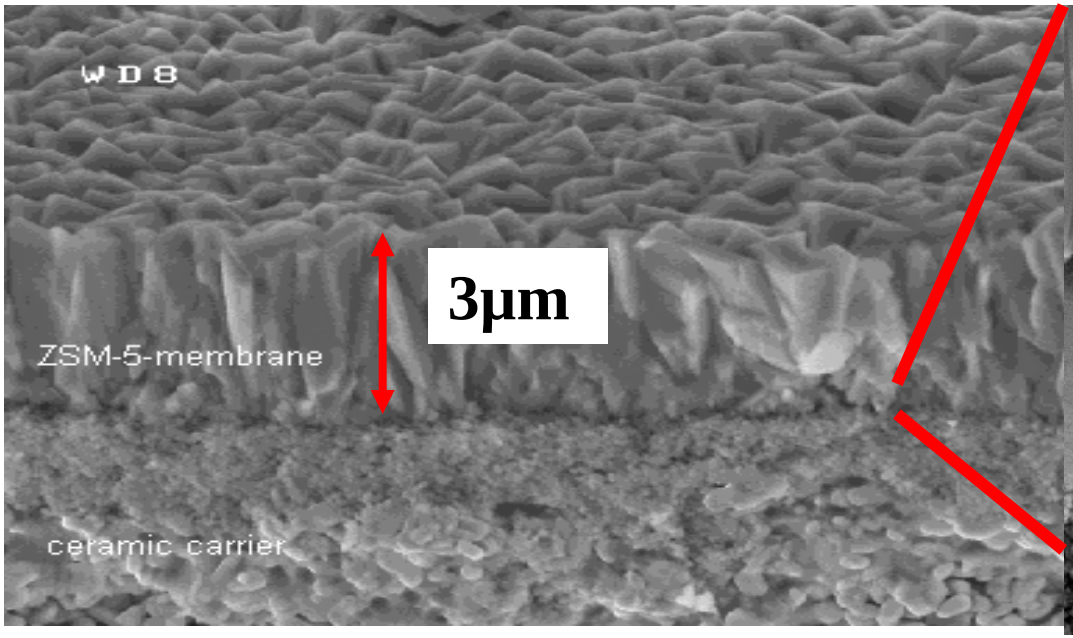
Zeolite membrane: Supported silicalite I membrane in the separation of 1-butene/i-butene

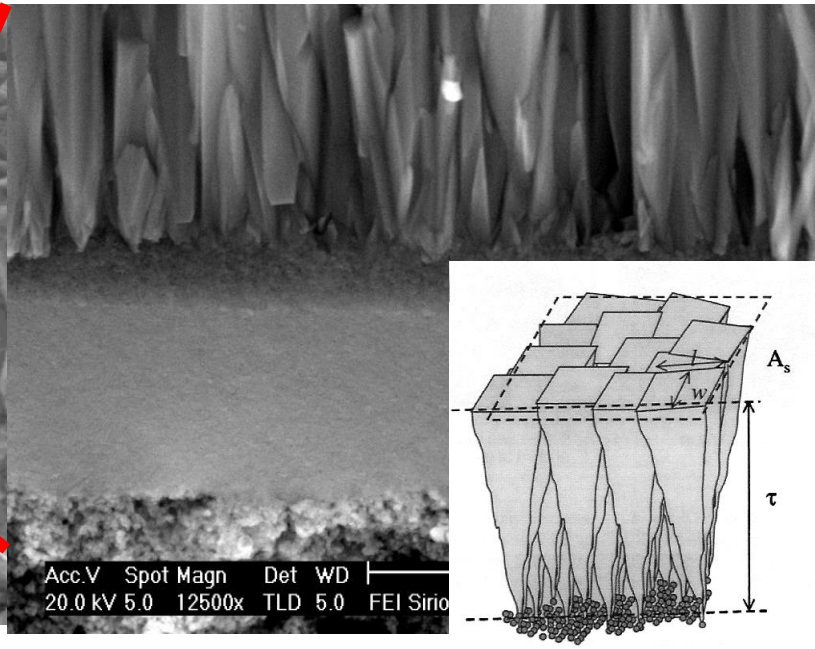
∅ **i-butene = 5.3 Å**
∅ **1-butene = 4.7 Å**



Pore size ≈ 5 Å





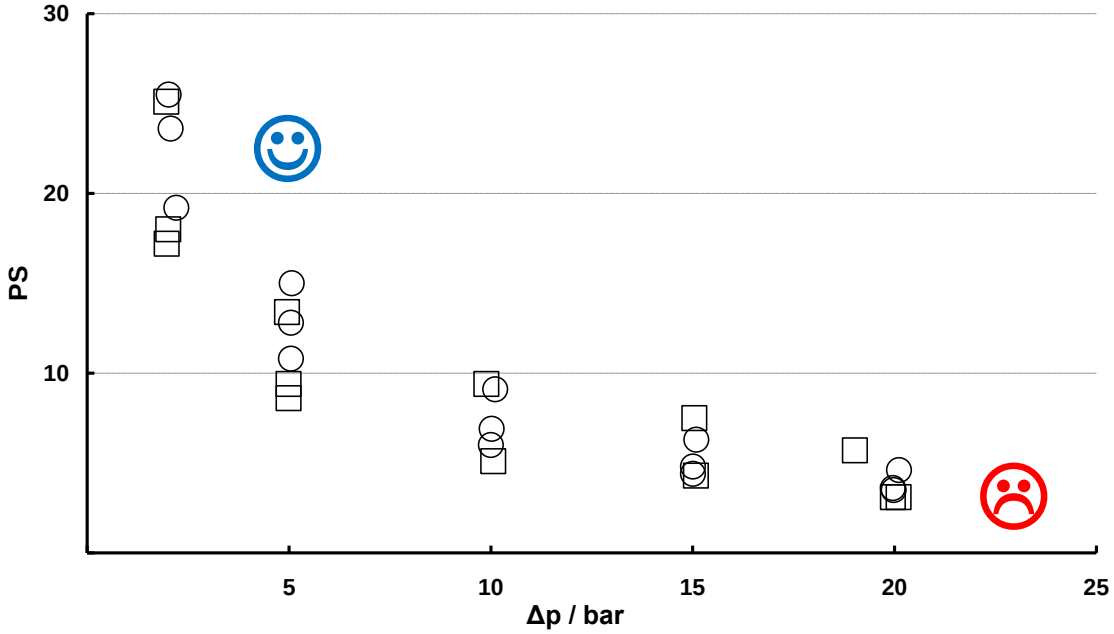


Supported silicalite I membrane in the separation of 1-butene/i-butene

Separation factor 1-butene/i-butene at 130 °C and 1 bar: 20 ☺

But: 1-butene/i-butene selectivity decreases with increasing pressure ☹

Why?



Permselectivity

$$PS = \frac{flux_{1\text{-butene}}}{flux_{i\text{-butene}}}$$

Flux of 1-butene drops
Who is guilty?

Flux

$$J_{1\text{-butene}} \approx -D_{1\text{-butene}} gradc_{1\text{-butene}}$$

H. Voß…J. Caro
J. Membr. Sci. 329 (2009)11

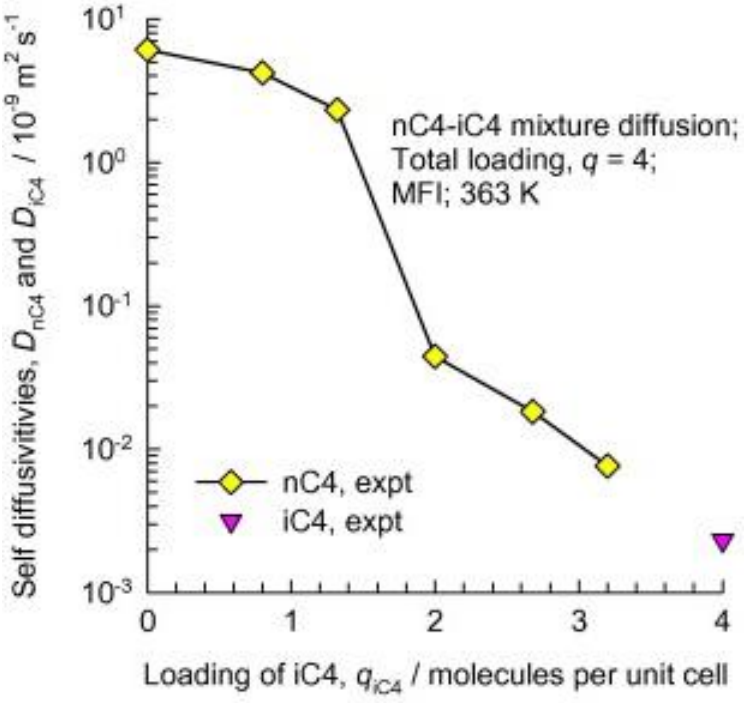
What happens at increasing pressure?

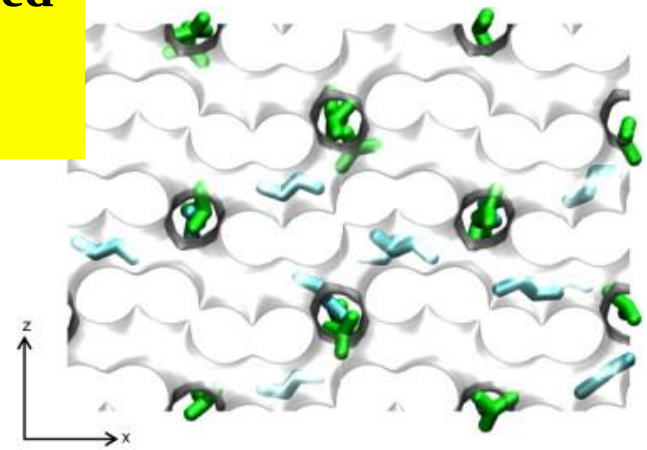
Location of a species in a pore system controls the diffusion of another co-adsorbed mobile component

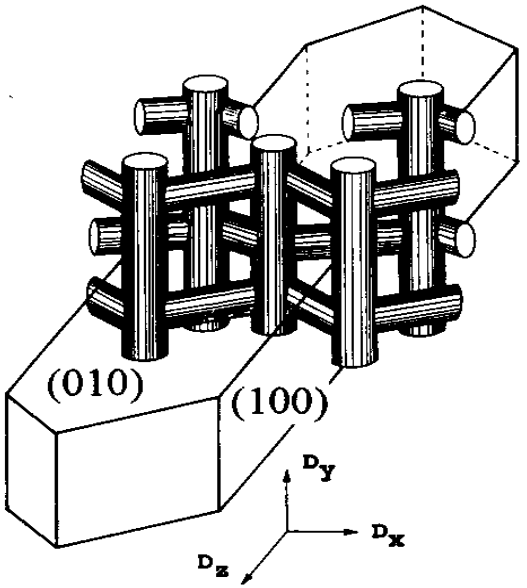
Pinien-Prozessionsspinner
Pine processionary
Thaumetopoea pityocampa;
Syn.: Traumatocampa pityocampa

Immobile i-butene in the channel crossings blocks the diffusion of the mobile 1-butene

With increasing pressure: i-butene becomes adsorbed
Adsorption site: Channel crossings
→ i-butene blocks diffusion of 1-butene







M. Fernandez, J. Kärger, D. Freude et al.
Micropor. Mesopor. Mater. 105 (2007) 124.

Molecular Diffusion in porous functional materials:

→ Adsorbents, catalysts, membranes

Diffusion of ions and electrons in dense functional materials:

→ Fuel cell, solar cell, Li^+-storage battery

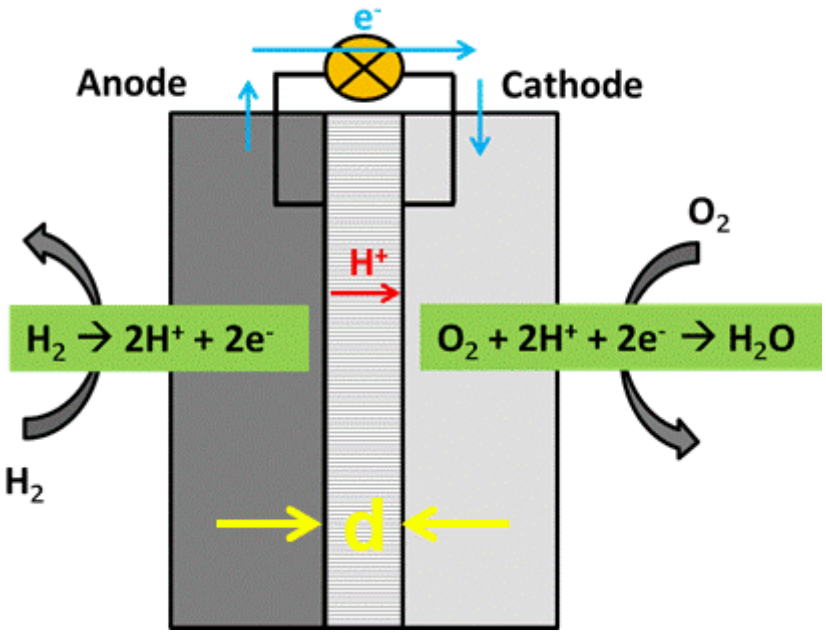
Diffusion effects in proton exchange membrane (PEM) fuel cells

1. Hydrogen is split into protons and electrons at anode side
2. Protons diffuse through Nafion, electrons go around and do work
3. Protons, electrons and oxygen from air form water at cathode side

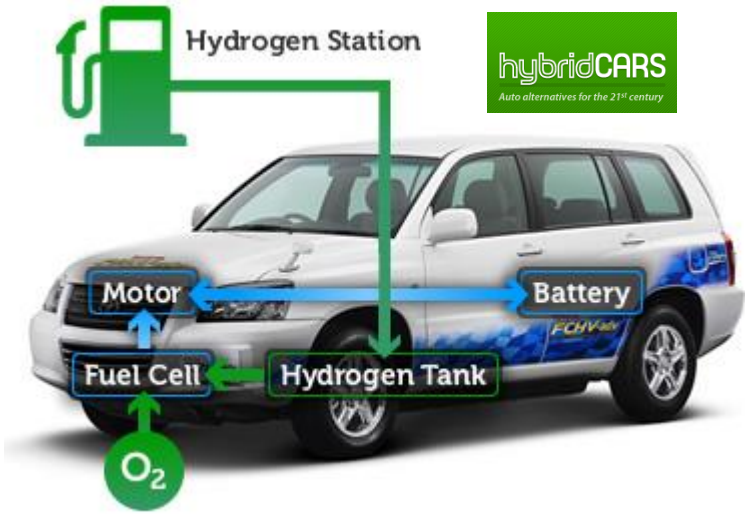
Which process is limiting the electrical current?

→ Proton diffusion through the Nafion

You can simply find out by playing with membrane thickness d



$H_2 + ½\ O_2 \rightarrow H_2O$



Diffusion effects in proton exchange membrane (PEM) fuel cells

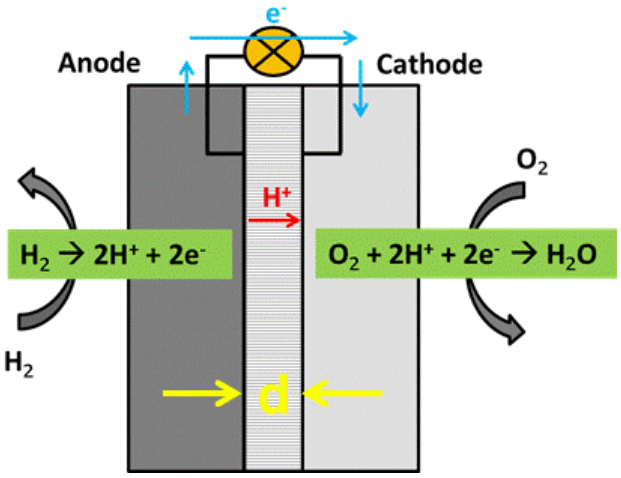
Which process is limiting the electrical current? →Proton diffusion through Nafion

It is known that the proton H^+ is attached to water H_2O giving H_3O^+

If we know the diffusion coefficient D of water in Nafion, we can estimate an upper limit if the current

Self-diffusion coefficient D* of water in Nafion can be measured (e.g. by PFG NMR Kaerger Lecture)

$$J_{H^+} \approx -D_{H^+}\,\mathrm{grad}\,c_{H^+} \approx -D^*_{H_2O}\frac{\Delta c_{H_2O}}{d} \approx -D^*_{H_2O}\frac{c_{H_2O\ \mathrm{Nafion/cathode}}}{d}$$



Surprise!

The current is much higher than predicted!

Why?

There must be an additional transport mechanism:

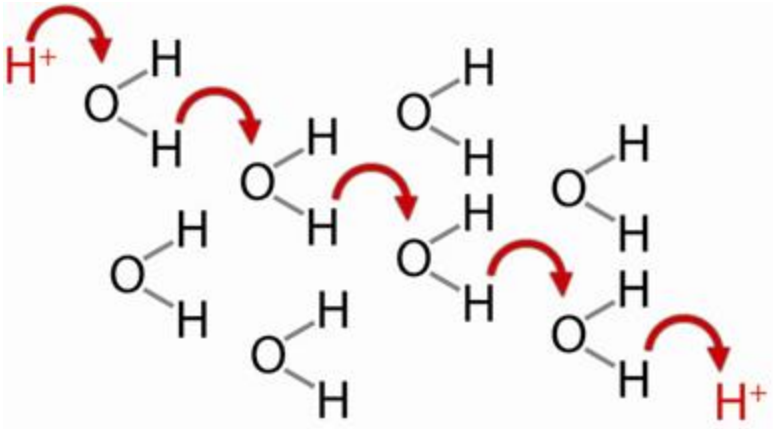
→ Grotthus Mechanism

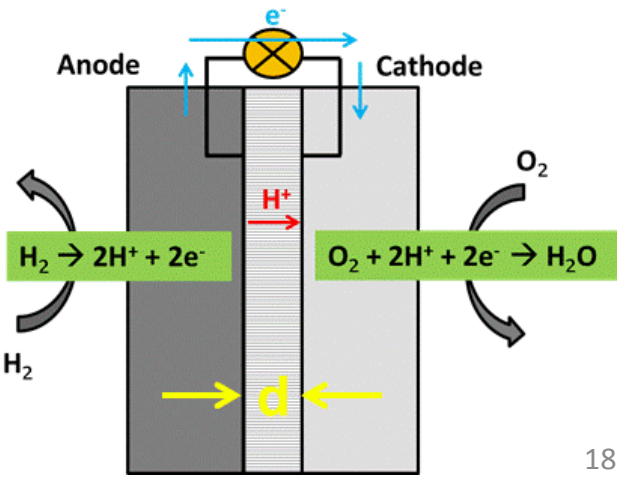
Diffusion effects in proton exchange membrane (PEM) fuel cells

Proton transport by two mechanisms

Water as vehicel for protons:
Can be aproximated by diffusion coefficient of H_3O^+ in Nafion

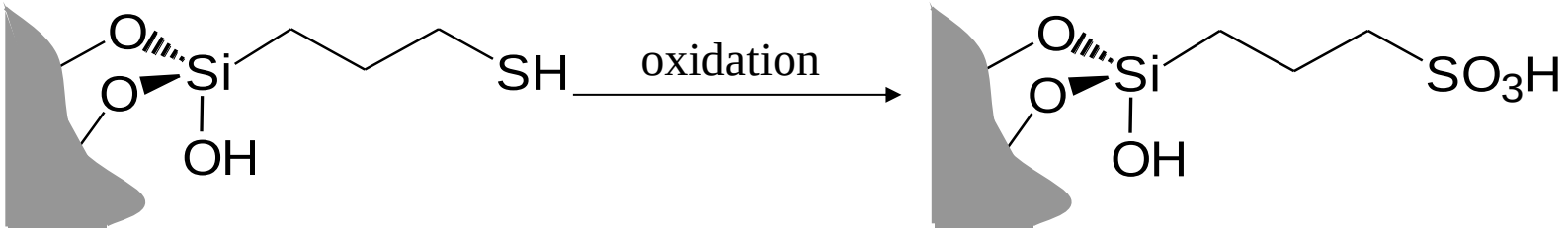
Plus Grotthus mechanism:
Hopping of protons from water to water in H-bridged water structure





J. Caro,
Diffusion in porous functional materials: Zeolite gas separation membranes, proton exchange membrane fuel cell, dye sensitized solar cells
Micropor. Mesopor. Mater. 125 (2009) 79.

New materials for proton exchange membrane (PEM) fuel cells: Substitution of the expensive Nafion by inorganic porous materials



Oxidation of the thiol group to the sulfuric acid group

Proton transport in sulfonated porous materials

$$J_{H^+} = -D_{H^+} \, \mathrm{grdc}_{H^+}$$

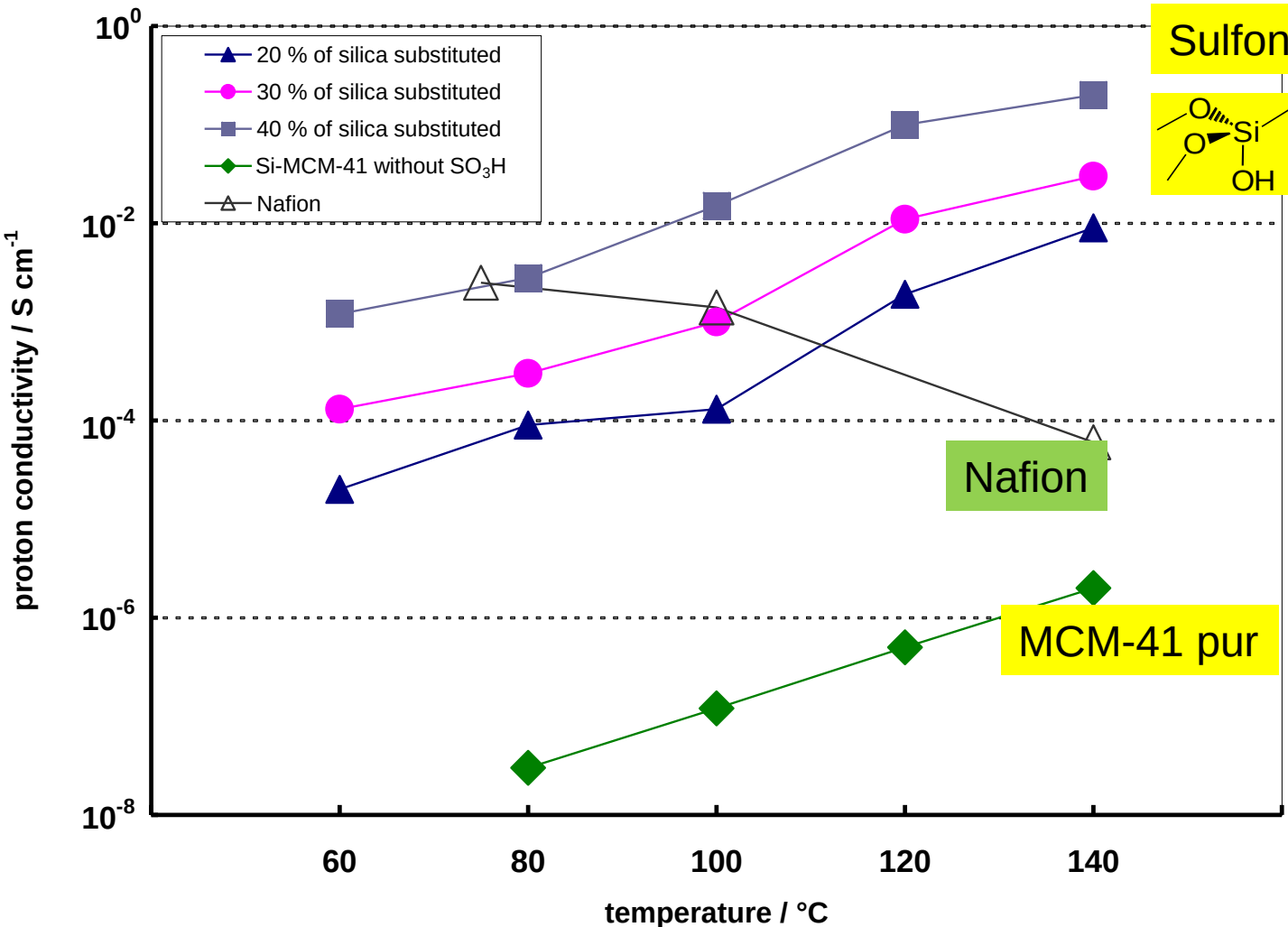
R. Marschall … J. Caro
Proton conductivity of sulfonic acid functionalised mesoporous materials
Micropor. Mesopor. Mater. 99 (2007) 190

$$D_{\mathrm{Self}\ H_2O} + \mathrm{Grotthus}$$

New materials for proton exchange membrane (PEM) fuel cells
Substitution of the expensive Nafion by inorganic porous materials
Sulfonated MCM-41 improves protoc conductivity

R. Marschall … J. Caro
Micropor. Mesopor. Mater. 99 (2007) 190

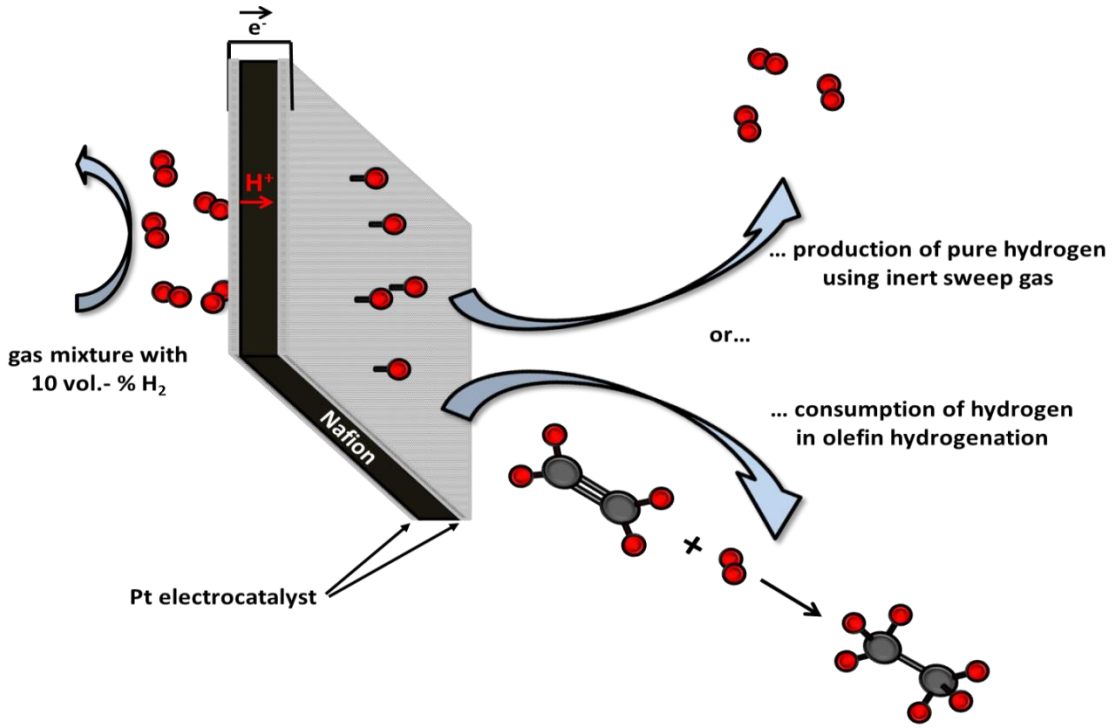
Proton flux = Conductivity x Electric Field Strength

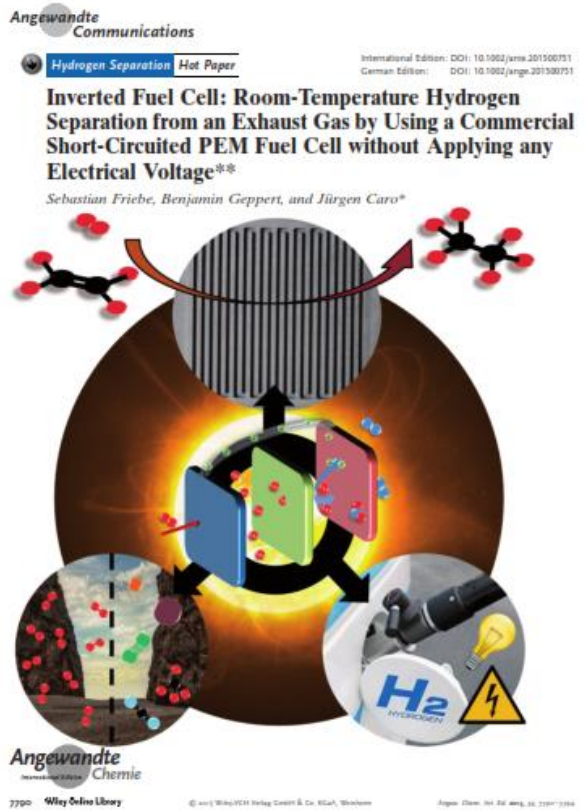


Fuel cell turned on the head: Use of a commercial PEM Fuel Cell for hydrogen separation at room temperature

Short-cut of the two Pt electro-catalyst layer by a cable

S. Friebe … J. Caro
Angew. Chem. Int. Ed. 54 (2015) 7790

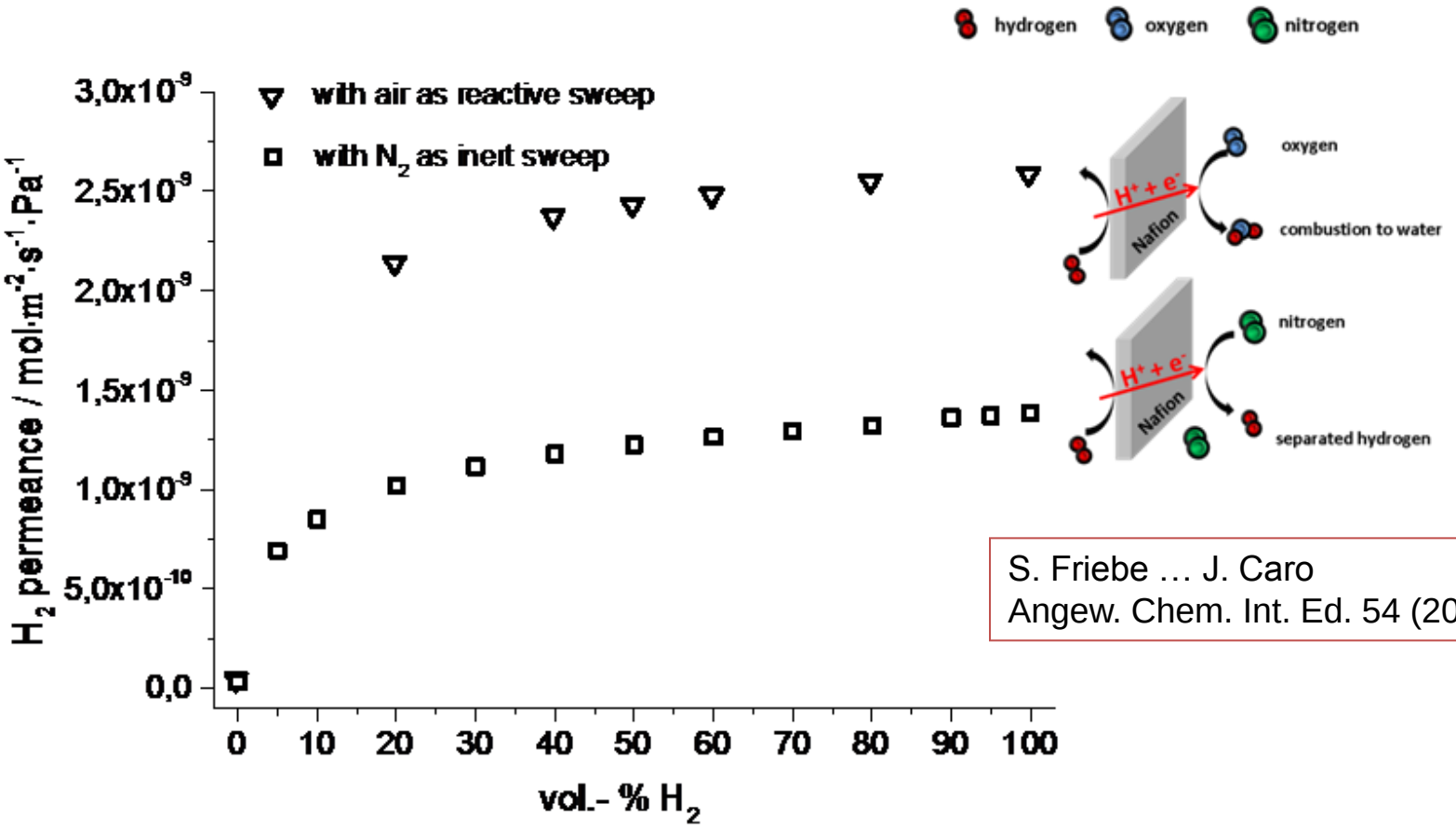




- **Hydrogen can be separated from waste gases as long as the hydrogen partial pressure over the membrane is different**

- **PEM Fuel Cell can be oparated as catalytic membrane reactor in olefin hydrogenation**

Hydrogen separation from a simulated waste gas stream



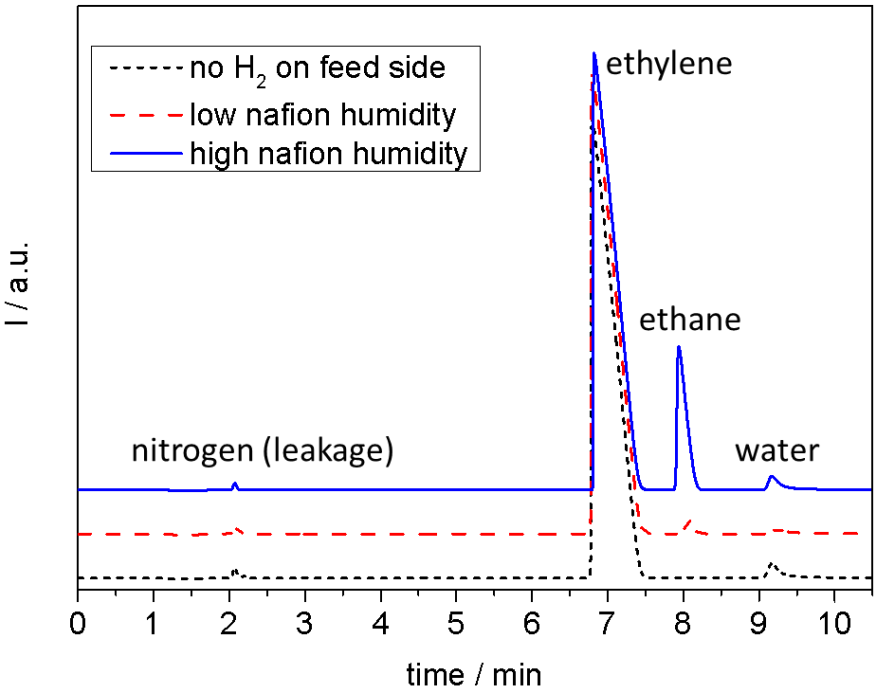
S. Friebe … J. Caro
Angew. Chem. Int. Ed. 54 (2015) 7790

Why is hydrogen flux through the membrane higher if oxygen is used as sweep gas?
→ since hydrogen combustion reduces the hydrogen partial pressure more effectively

$$J_{H^+} \approx -D_{H^+}\,\mathrm{gradc}_{H^+} \approx -D_{H^+}\frac{\Delta c_{H^+}}{d}$$

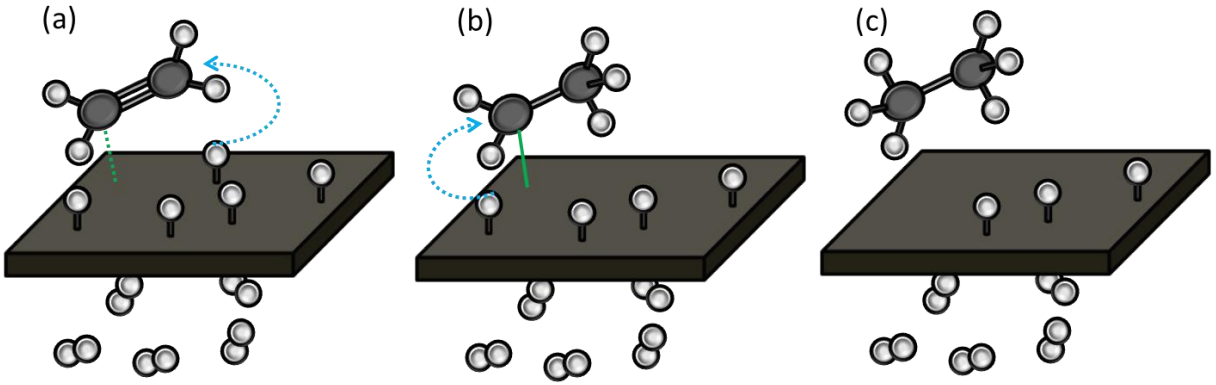
Hydrogen separation from a simulated waste gas stream

Ethane formation as example for catalytic olefin hydration

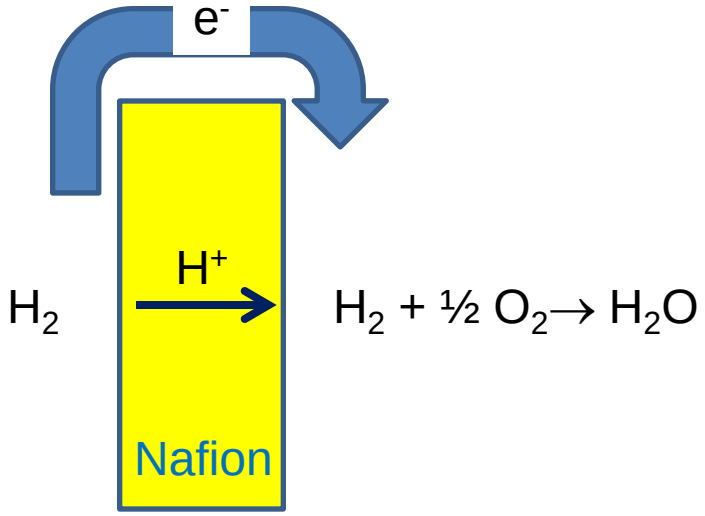


Consumption of H_2 by olefin hydrogenation
Ethene + $H_2 \rightarrow$ ethane

$$J_{H^+} \approx -D_{H^+} \, \mathrm{grad} c_{H^+} \approx -D_{H^+} \frac{\Delta c_{H^+}}{d}$$

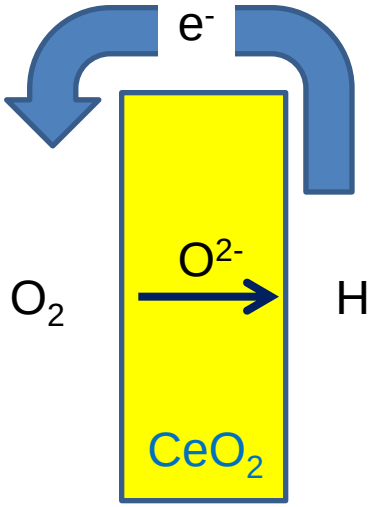


Proton Exchange Membrane (PEM) Fuel Cell



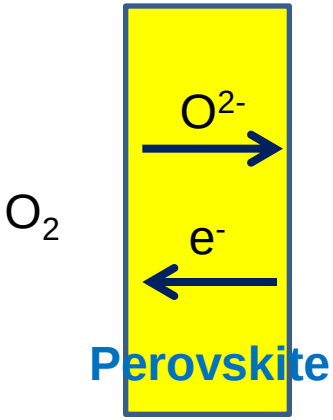
$H_2 + ½ O_2 \rightarrow H_2O$

Solid Oxide Fuel Cell (SOFC)



$H_2 + ½ O_2 \rightarrow H_2O$

Mixed Oxygen Ion – Electron Conductor



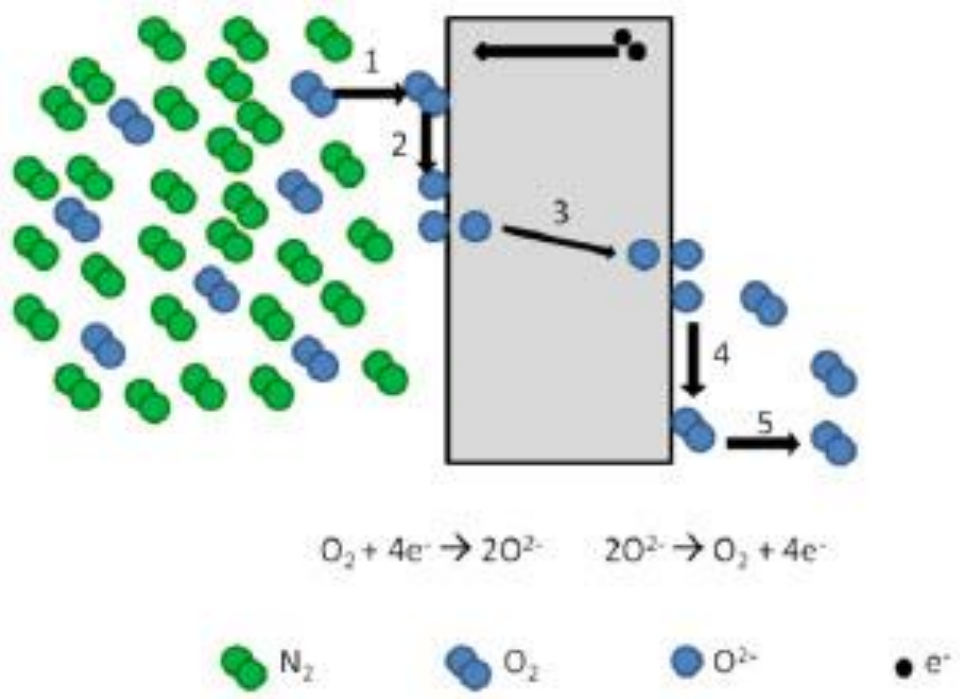
$H_2 + ½ O_2 \rightarrow H_2O$

Oxygen flux through perovskite membranes: 2 surface reactions and bulk transport by diffusion What is rate limiting? Surface reaction contra diffusion

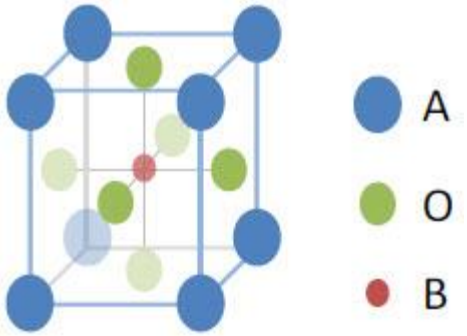
1 +2: The surface process oxygen insertion $O_2 \rightarrow 2O$ and $O + 2e^- \rightarrow O^{2-}$

3: The bulk diffusion of oxygen ions (since $D_{electrons} >> D_{oxygen\ ions}$)

4 +5: The surface reaction oxygen release: $O^{2-} \rightarrow O + 2e^-$ and $2O \rightarrow O_2$



$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)

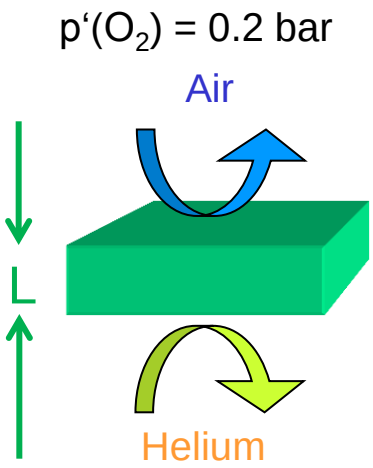


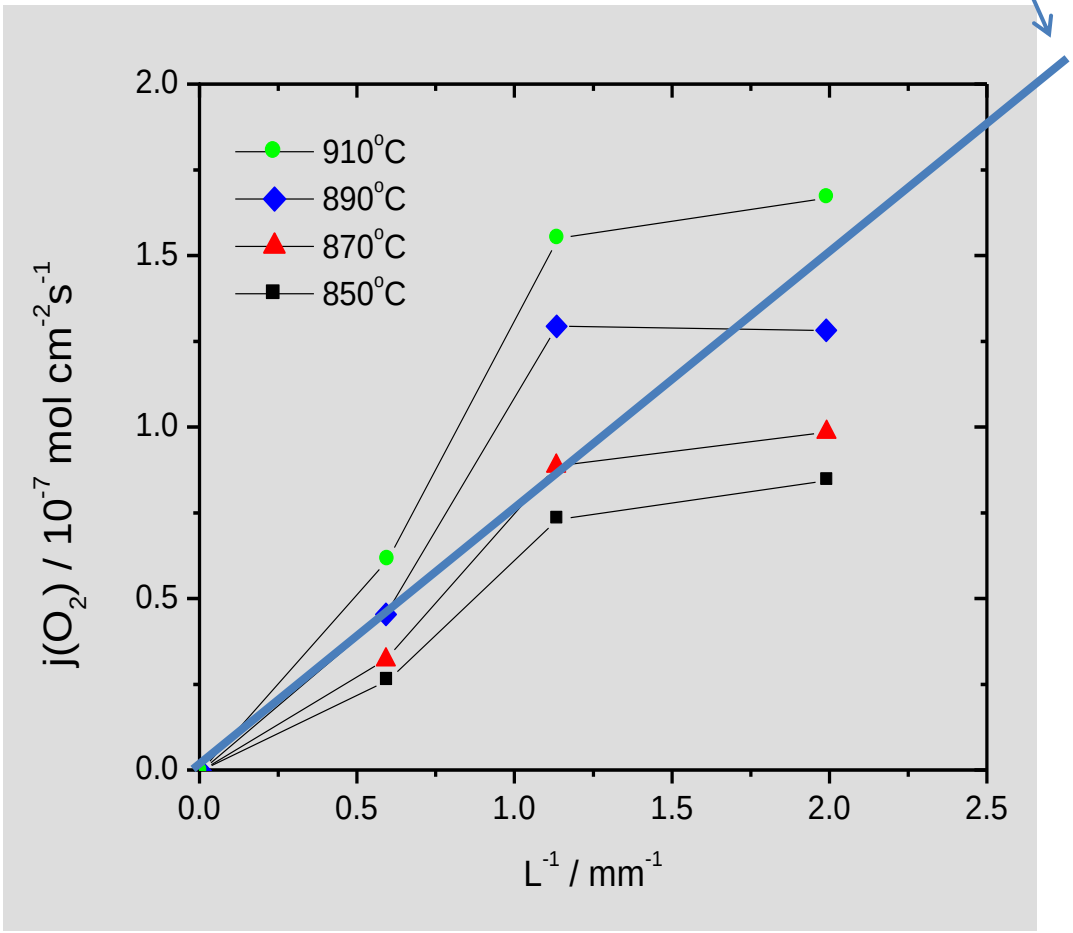
Oxygen(ion) transport 800 – 900°C

Oxygen flux through 3 perovskite membranes of different thickness

$$j_{O_2} \approx -D_{O_2}\,\mathrm{grad}c_{O_2} \approx -D_{O_2}\frac{\Delta c_{O_2}}{L} \quad \Rightarrow$$

Expected: $J(O_2)$ proportional L^{-1} at constant driving force $grdc_{O2}$

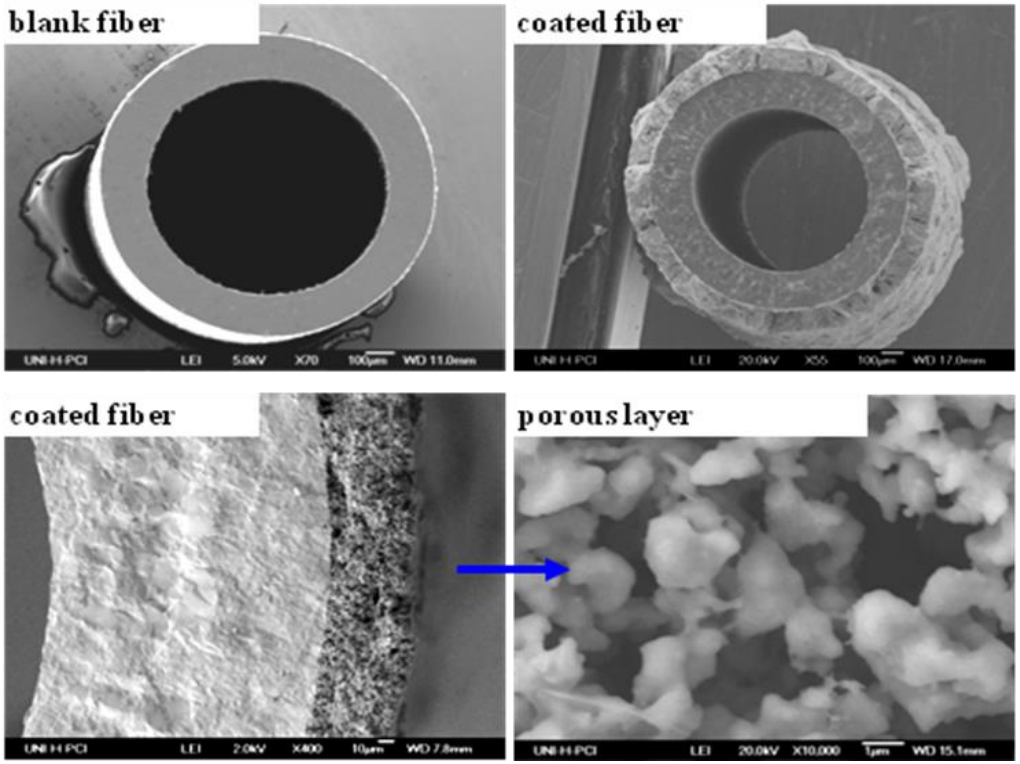


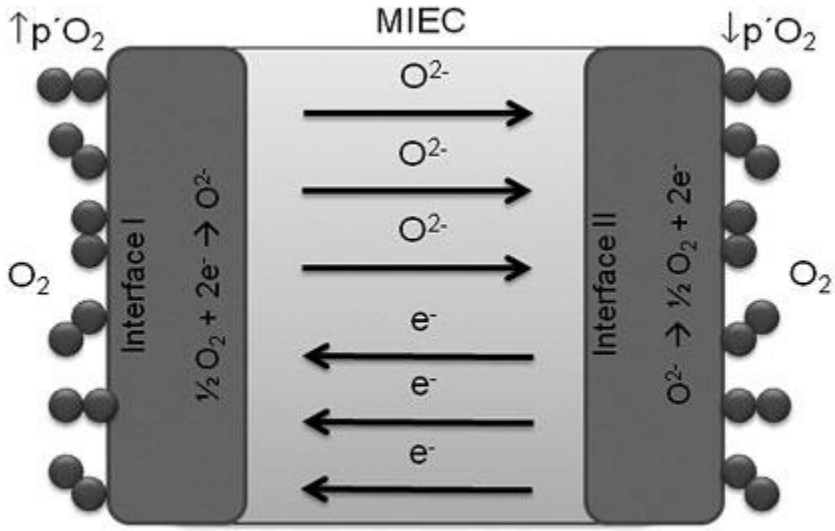


Courtesy of Dr. M. Schroeder, RWTH Aachen

Deviation from linearity: Oxygen transport is not controlled by oxygen ion bulk diffusion

Can we accelerate the surface reaction?
Yes, porous coating enlarges the surface area and facilitates surface reaction! But...





$$j_{O_2} \approx -D_{O_2}\,\mathrm{grad}c_{O_2} \approx -D_{O_2}\frac{\Delta c_{O_2}}{L}$$

Negative effect if the porous coating is on

→ Air side, since enrichment of N_2 and depletion of O_2 in the porous layer

→ Oxygen side, since there is residual O_2 in the porous coating

We spoil $\mathrm{grad}c_{O2}$

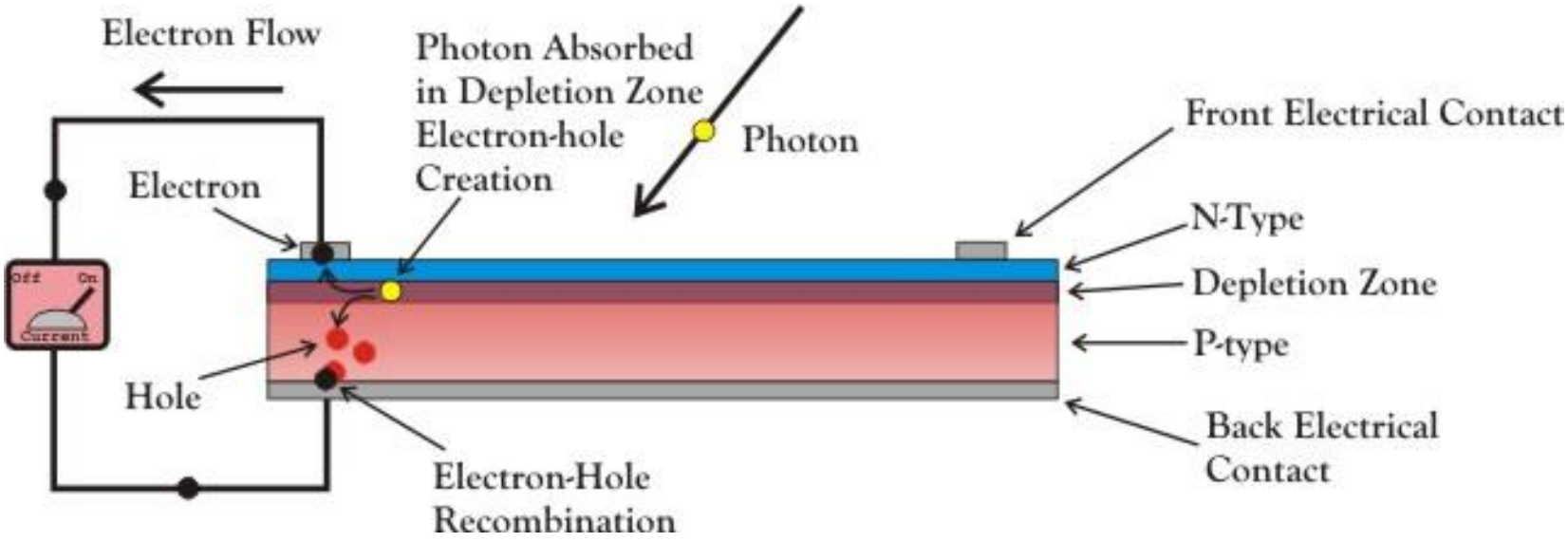
Molecular Diffusion in porous functional materials:

→ Adsorbents, catalysts, membranes

Diffusion of ions and electrons in dense functional materials:

→ Fuel cell, solar cells, Li^+-storage battery

Classical Silicium solar cell

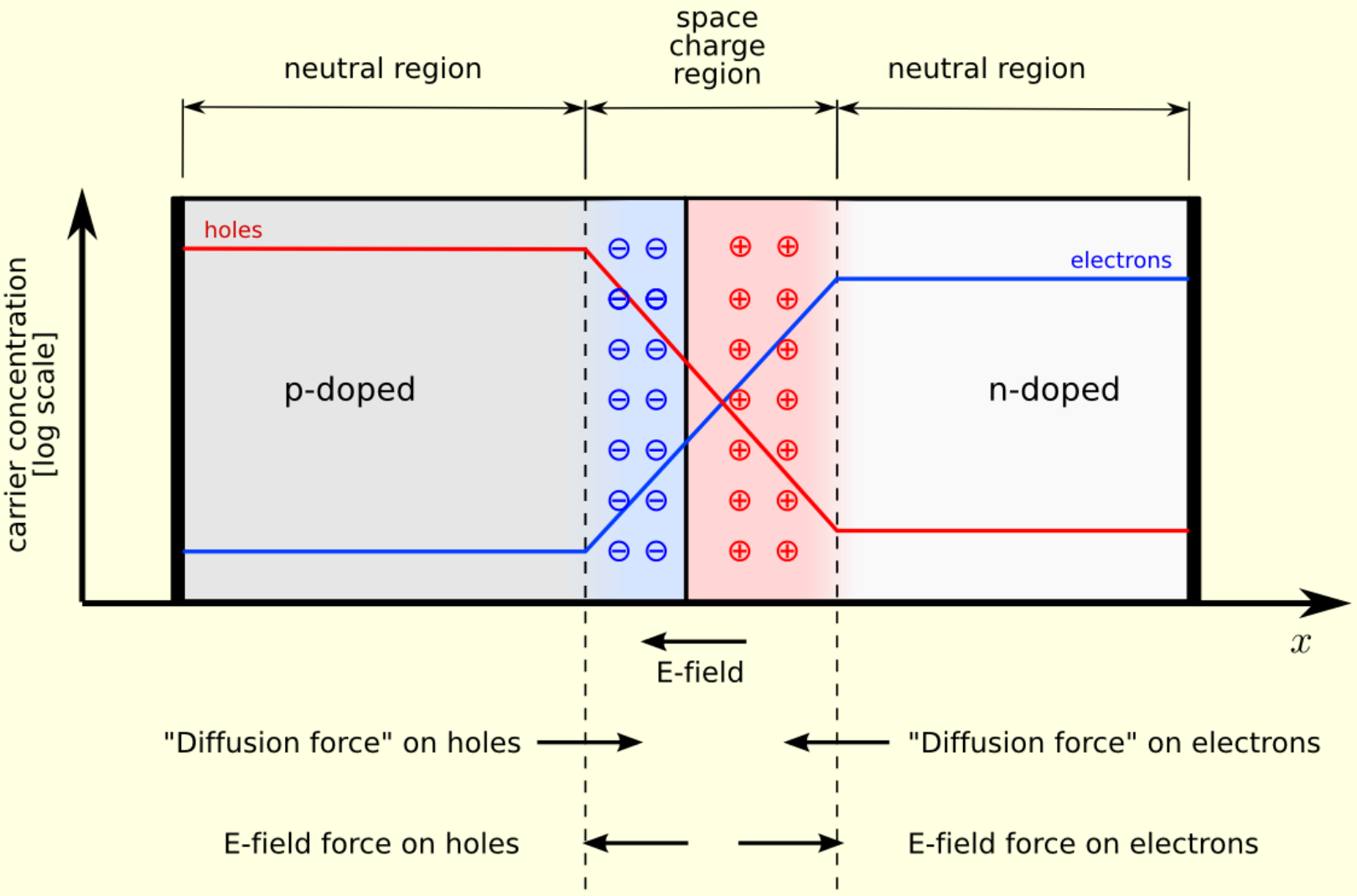


The operation of a photovoltaic (PV) cell requires 3 basic attributes:

- The absorption of light, generating either electron-hole pairs or excitons.
- The separation of charge carriers of opposite types.
- The separate extraction of those carriers to an external circuit.

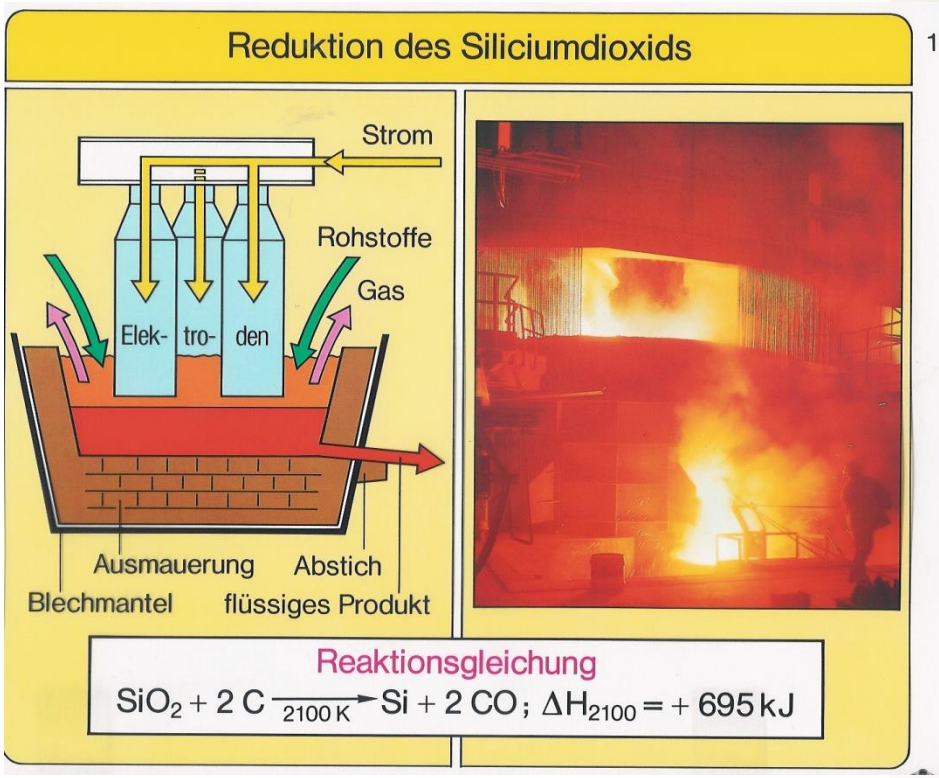
http://tatoobild.com/solar/solar-pv-cells-free-electricity-from-the-sun.html

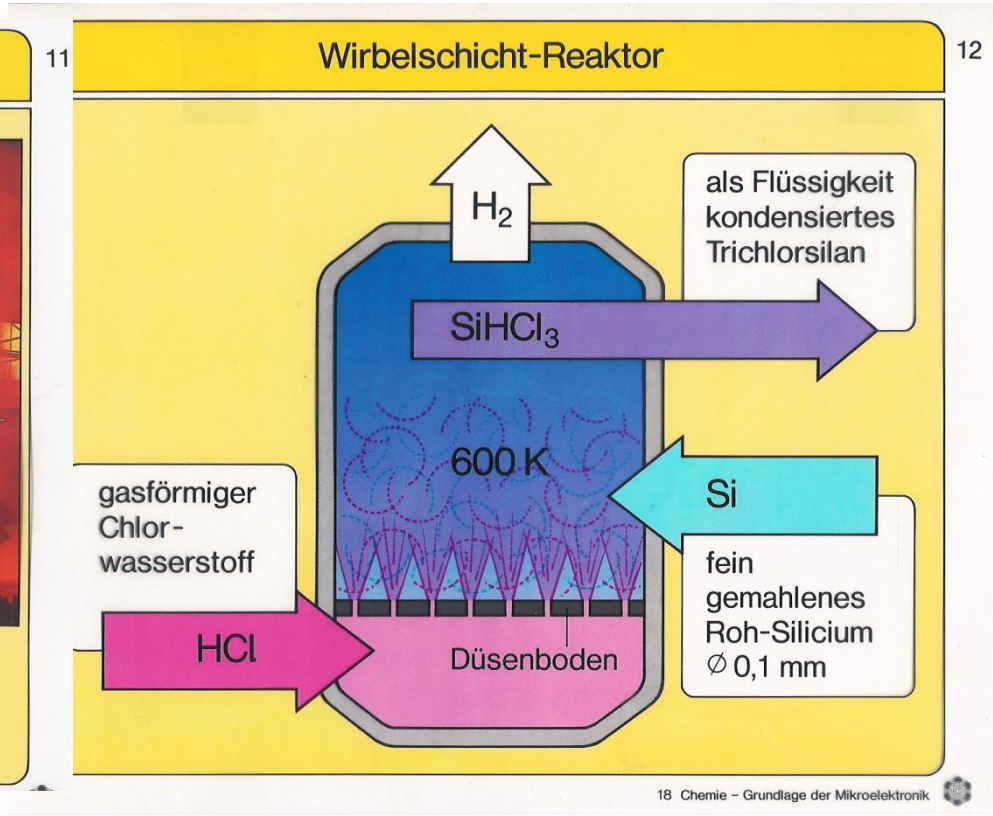
Diffusion of holes and electrons: Space charge region



Production of solar silicium is dirty high-temperature chemistry

In Germany, a Si cell needs about 1.5 years to „earn“ the energy used for its production





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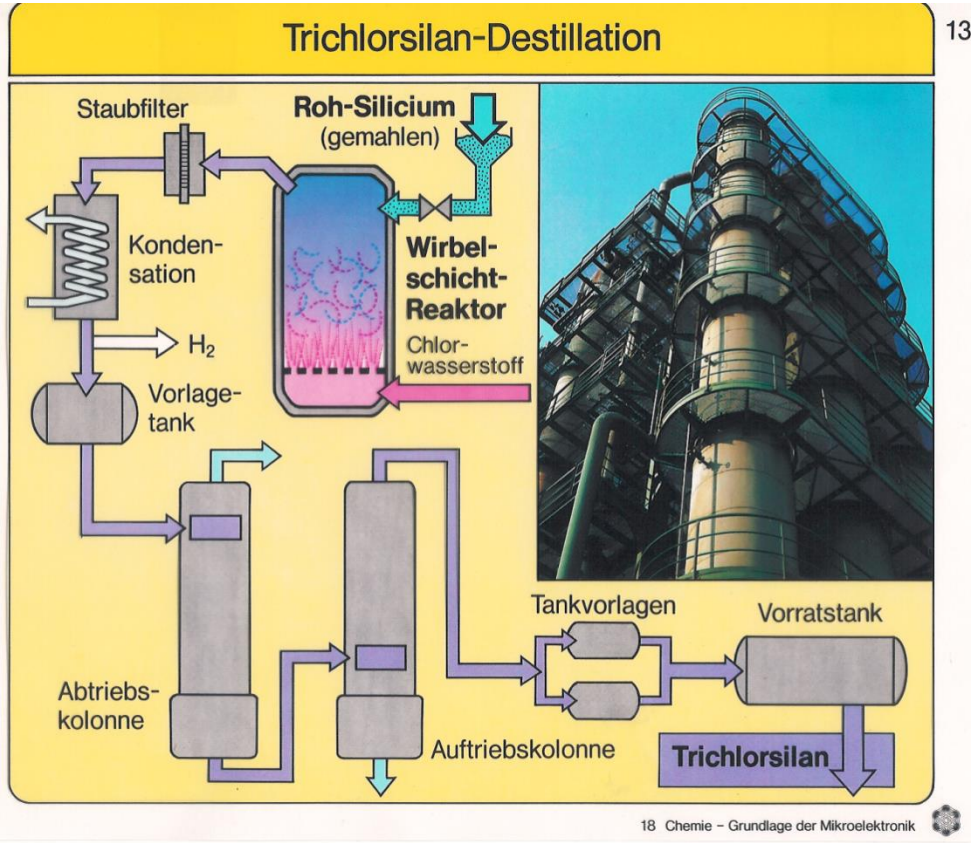

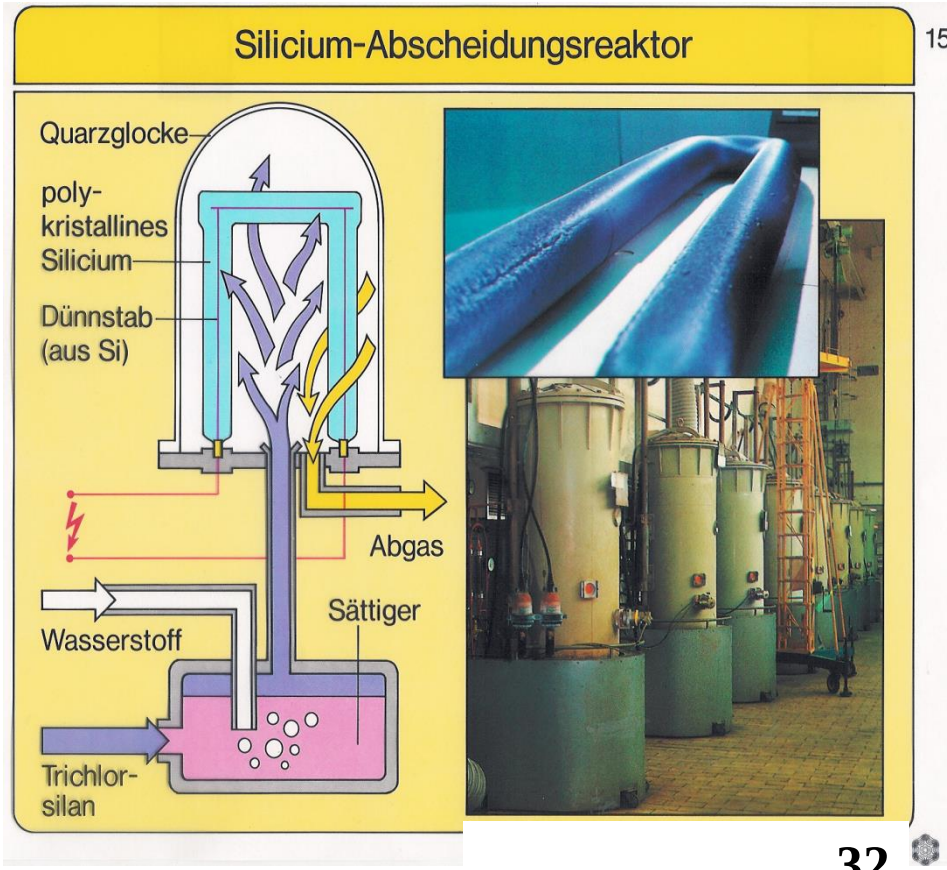

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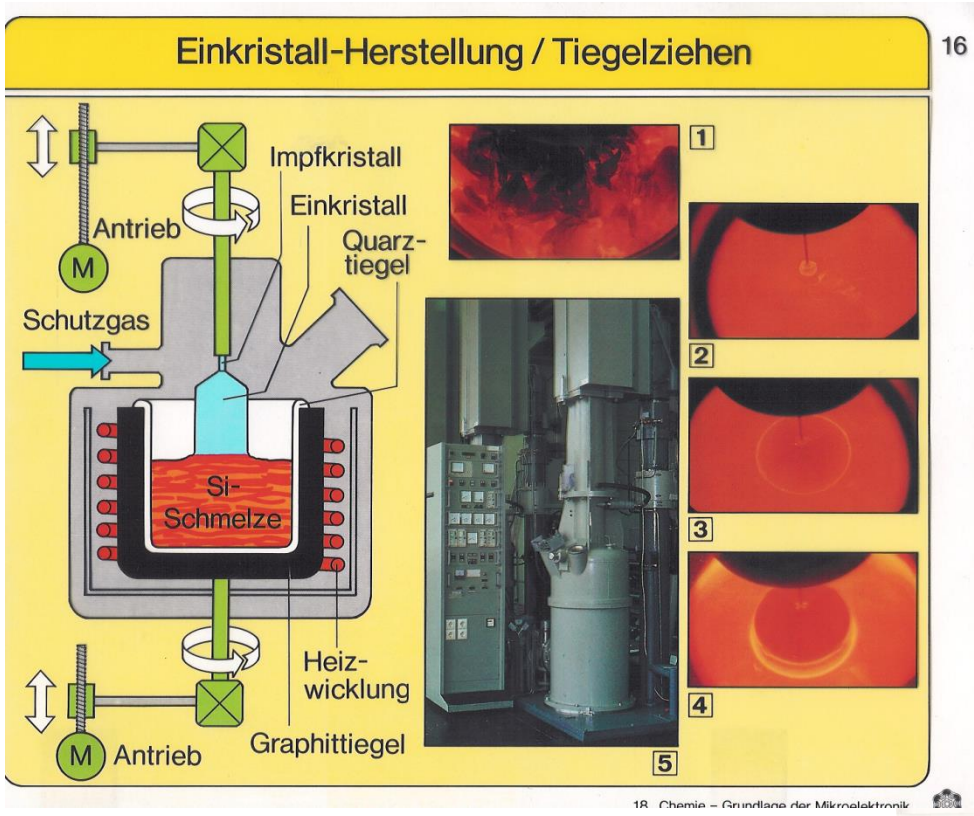
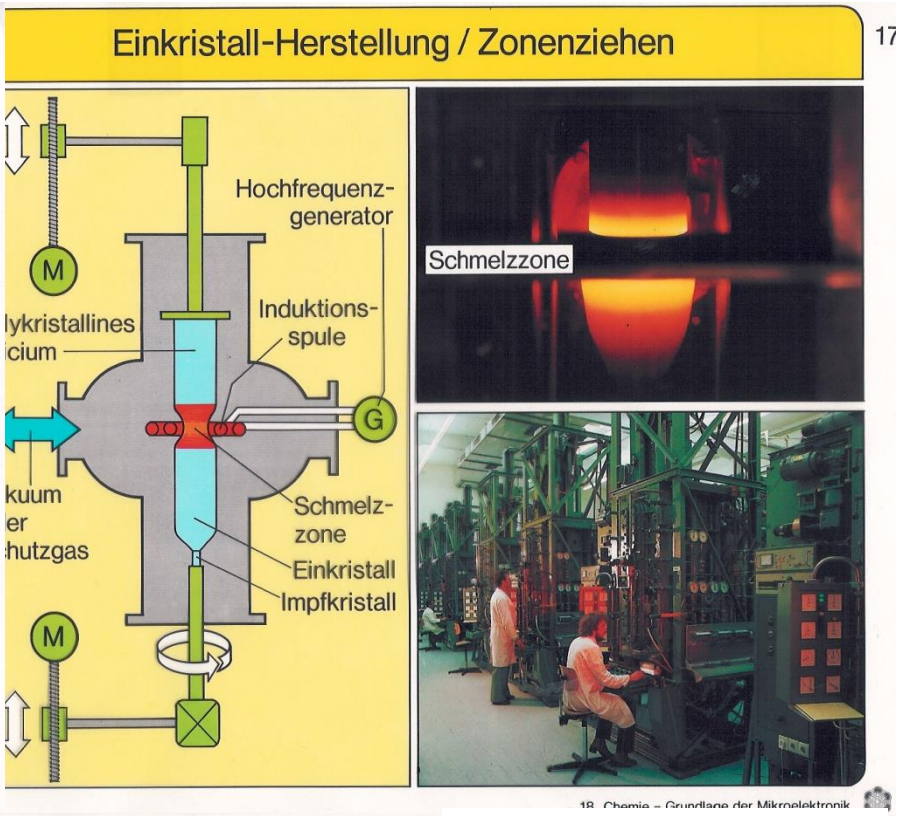
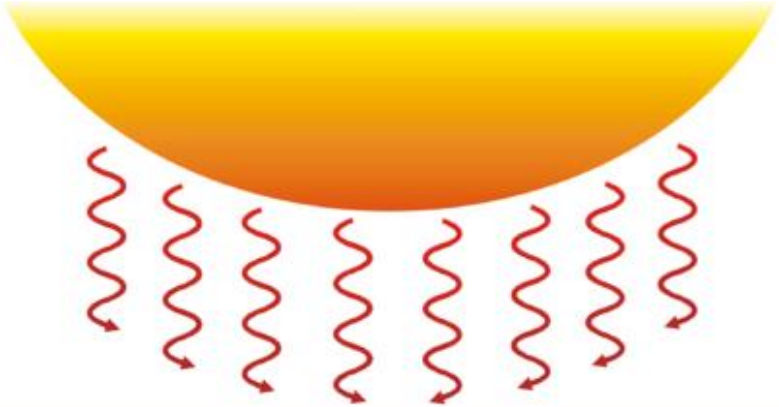
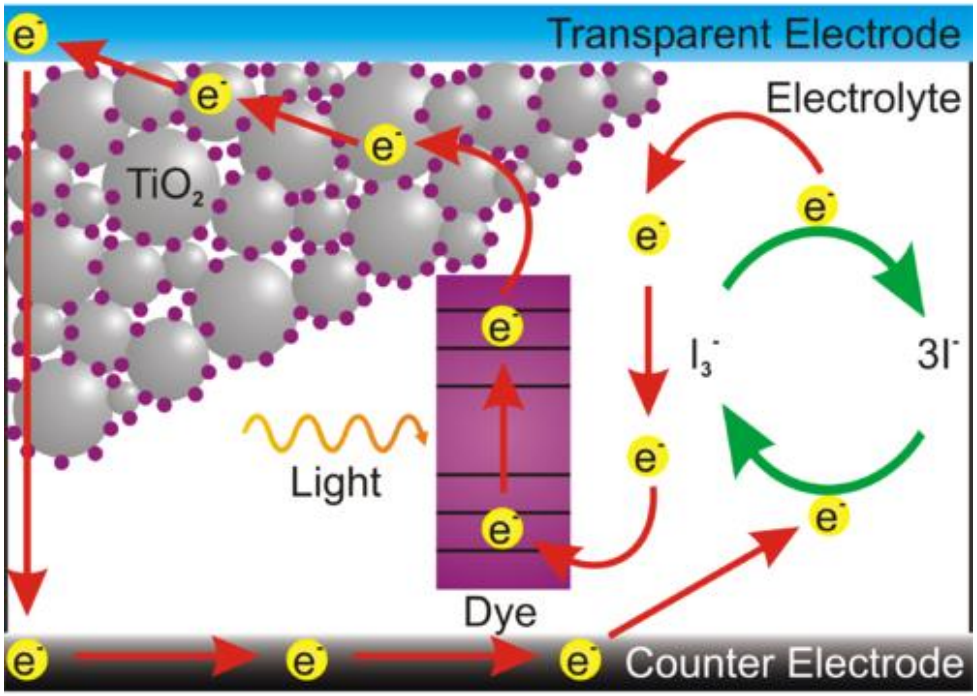




Next generation solar cell is not Si-based: Electron diffusion in dye-sensitized solar cells after Grätzel

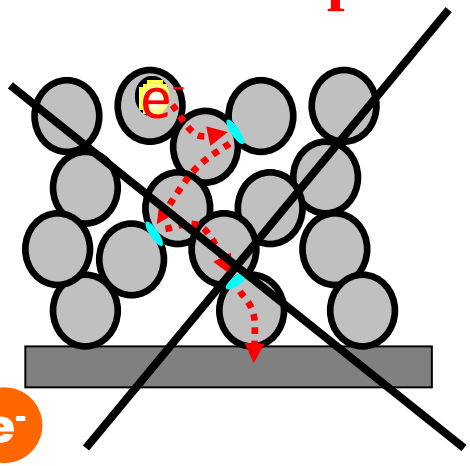


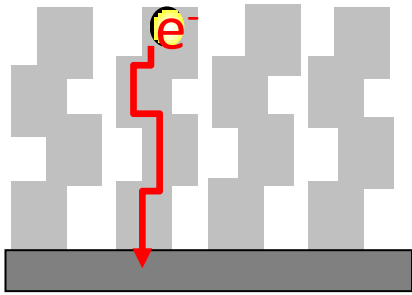


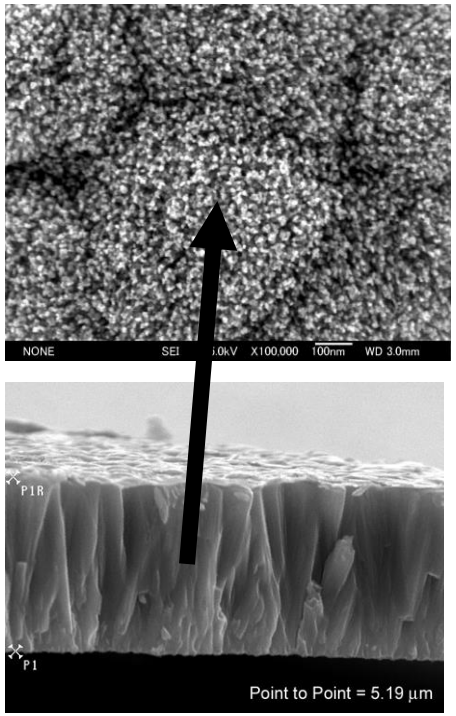
Diffusion of the photo-generated electrons can limit the current

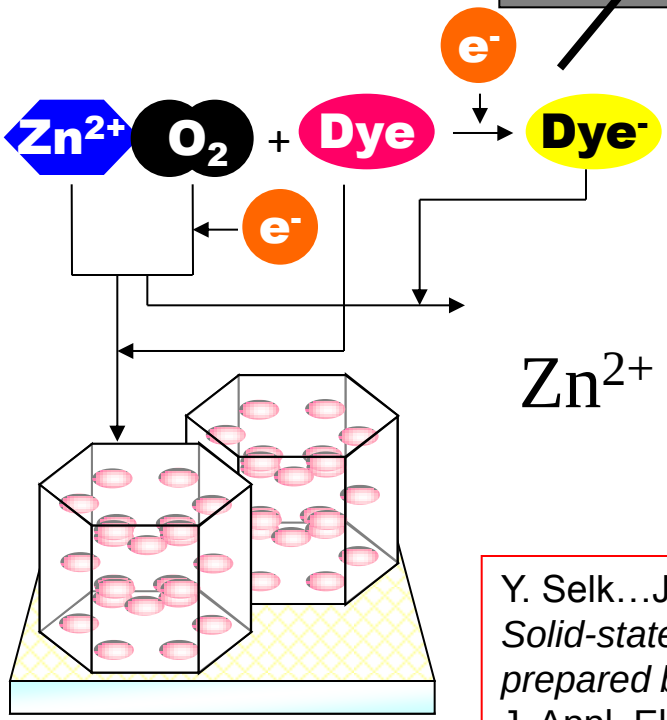
New way: Electrochemical preparation of a dye sensitized solar cell with better electron transport

ZnO or TiO_2 semiconductor layer is directly deposited on the cathode from salt solution at room temperature, dye is co-precipitated and incorporated





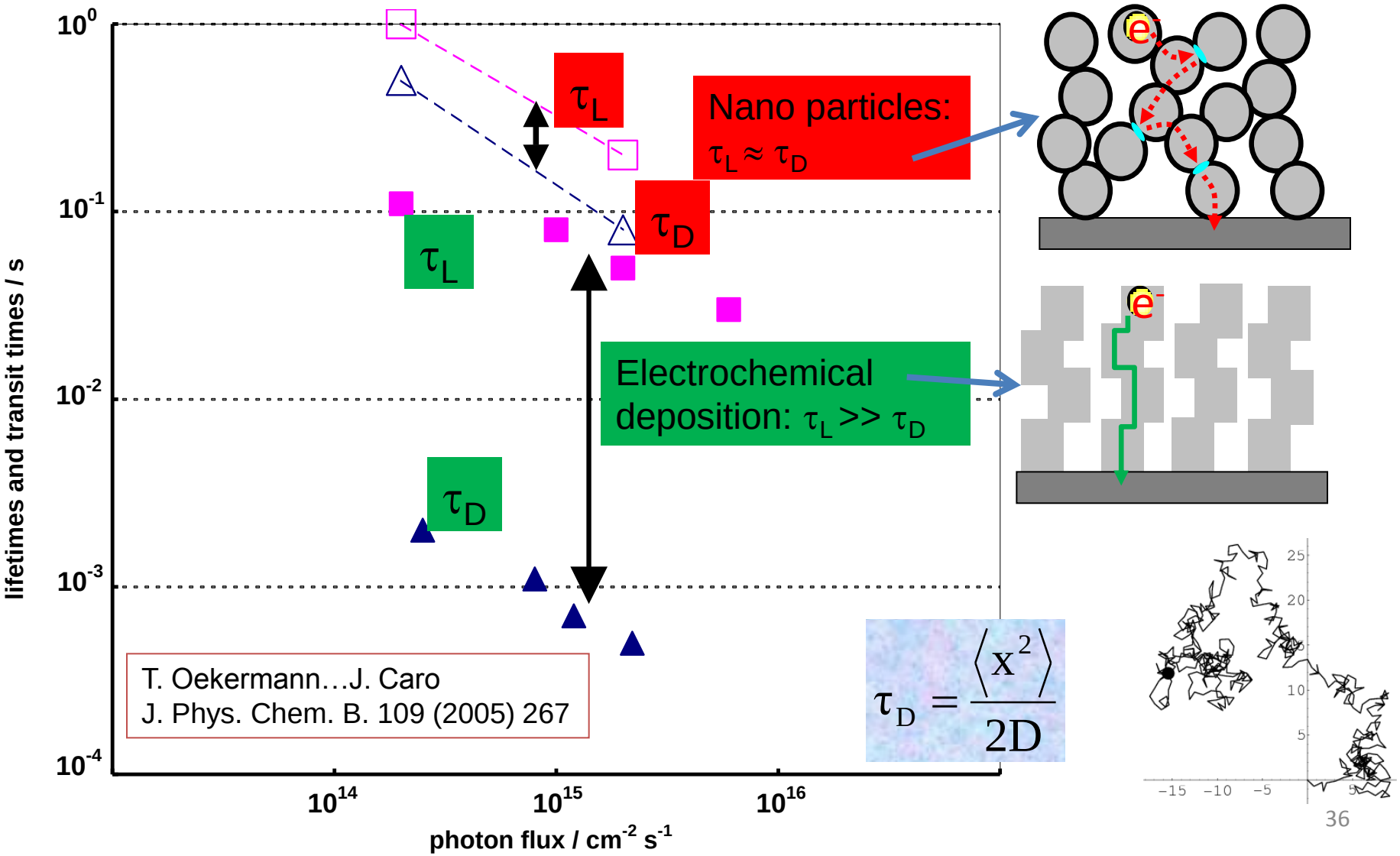




$$Zn^{2+} + \tfrac{1}{2}\, O_2 + 2e^- \rightarrow ZnO \text{ (porous)}$$

Y. Selk…J. Caro,
Solid-state dye-sensitized ZnO solar cells prepared by low-temperature methods,
J. Appl. Electrochem. 41 (2011) 445.

For the construction of dye-sensitized solar cells: Short electron diffusion time τ_D from the TiO_2 layer to the electrode and long life time τ_L in the TiO_2 layer



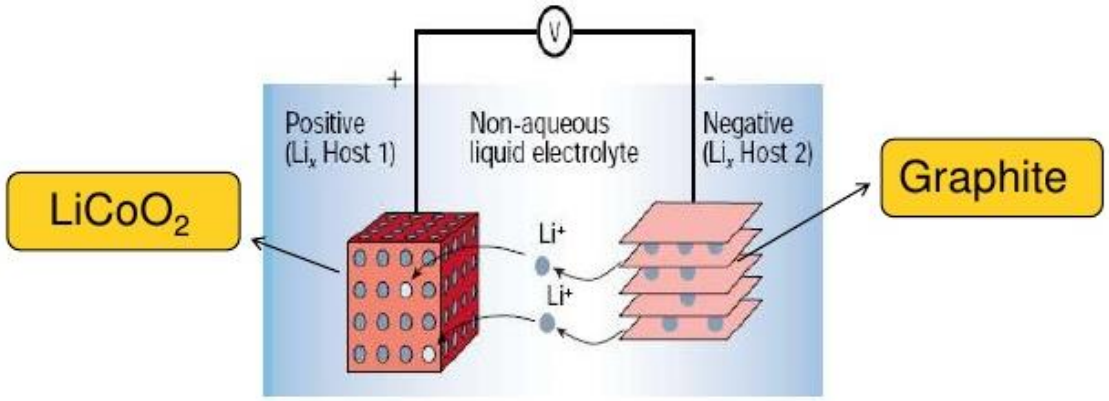
Molecular diffusion in porous functional materials:

→ Adsorbents, catalysts, membranes

Diffusion of ions and electrons in dense functional materials:

→ Fuel cell, solar cell, Li^+-storage battery

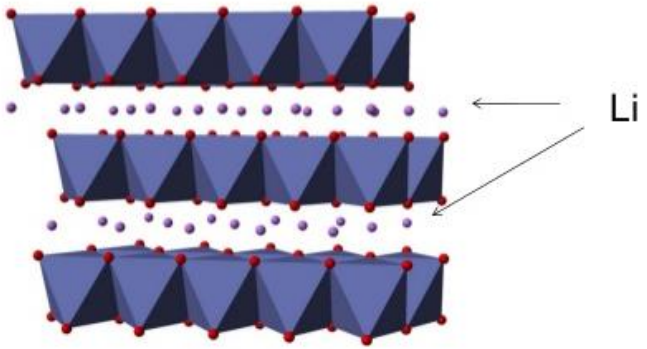
Li^+ Ion rechargeable Batteries: Graphite – CoO_2



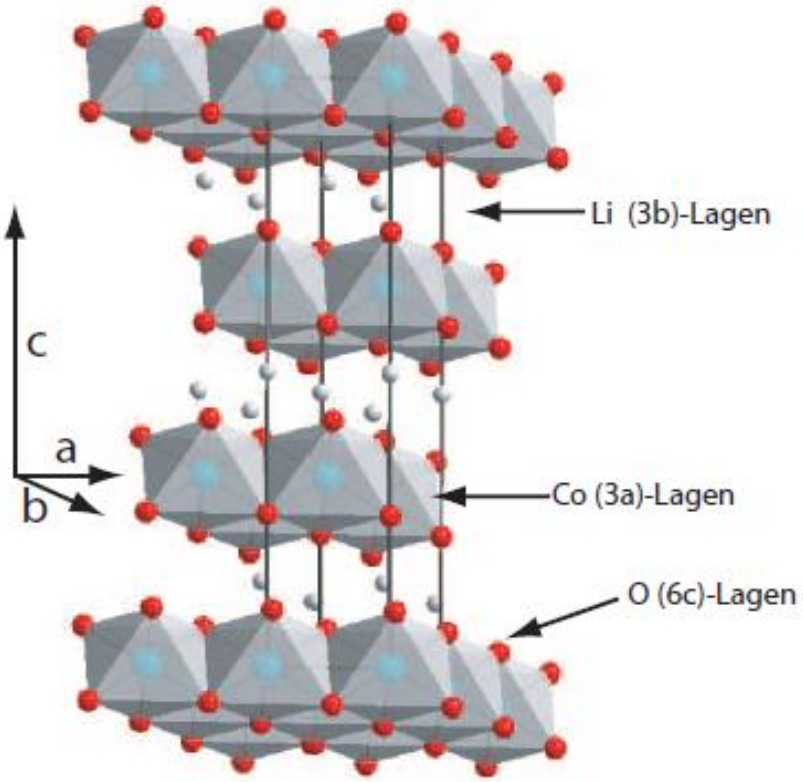
Negative Electrode (Dis-charging):
Li in $C_6 \rightarrow C_6 + Li^+ + e^-$
Intercalation of Li^+ between the graphite layers, e^- interacts with π-elektrons system
1 graphite ring hosts 1 Li^+ + 1 e^- auf

Positive Electrode (Dis-charging):
$Li^+ + e^- + Co^{iv} O_2 \rightarrow LiCo^{iii}O_2$

- $LiCoO_2$
- Li moves into CoO_2 octahedra slabs
- How fast can the LI get in there?



Anisotropy of diffusion – diffusion coefficient of Li^+ ions becomes a tensor



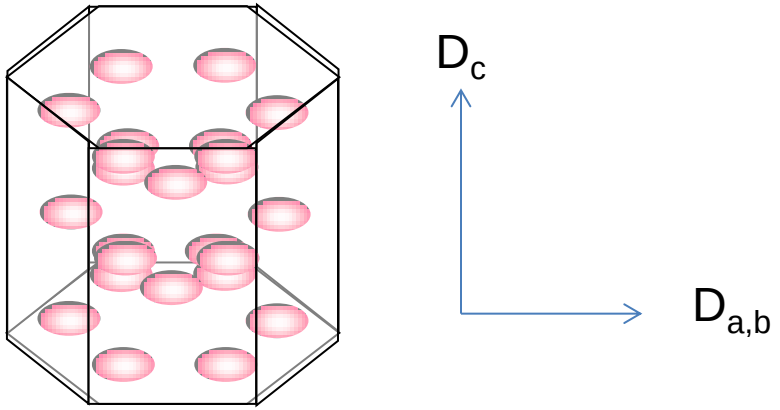
Hexagonal layered structure of $LiCoO_2$

For isotropic diffusion systems

$$D = \frac{< x^2 > + < y^2 > + < z^2 >}{6\tau} = \frac{< x^2 >}{2\tau} = D_X = D_y = D_z$$

For hexagonal systems, $< x^2 > = < y^2 >$

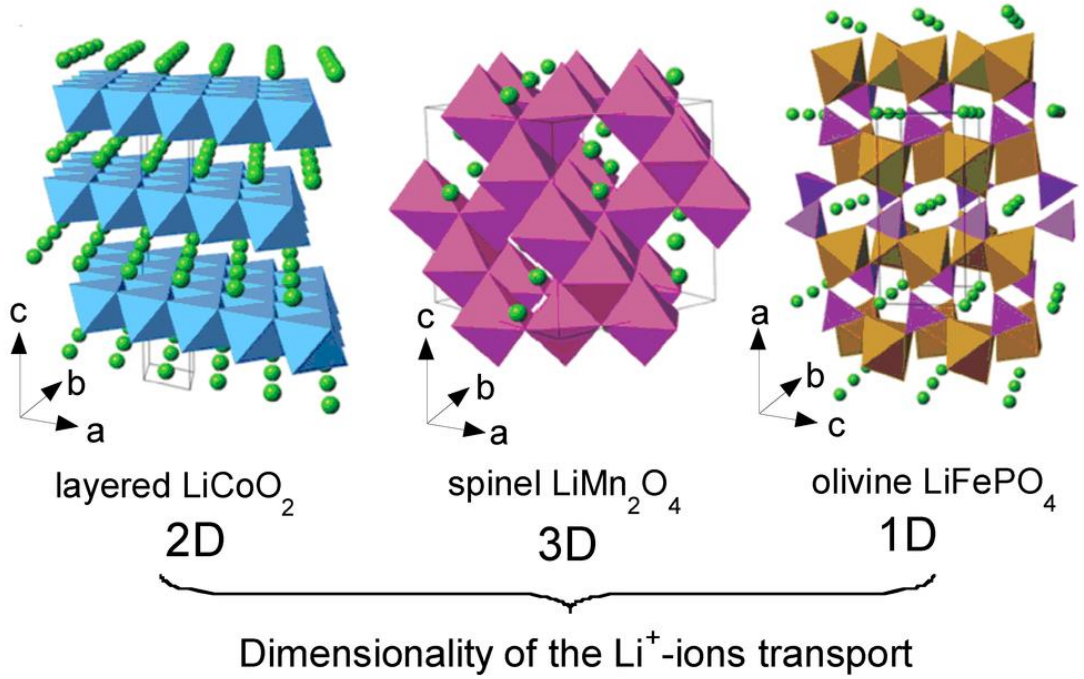
$$\overline{D} = \frac{2}{3} D_{a,b} + \frac{1}{3} D_c$$

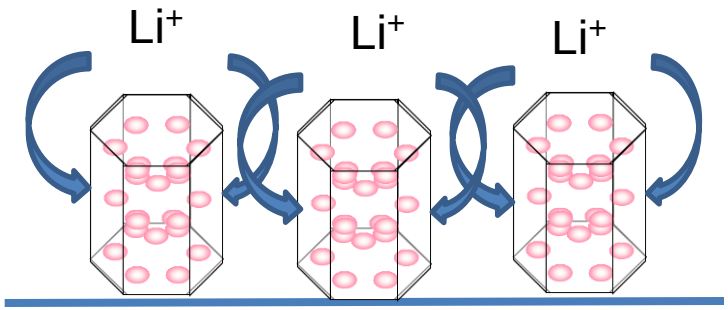


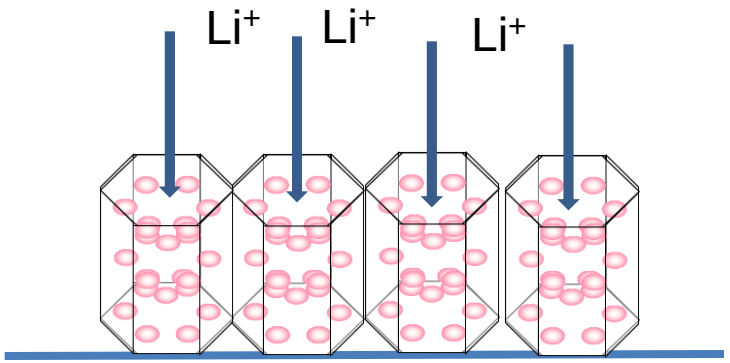
We know from single crystal studies that for Li ions $D_c << D_{a,b}$

From atomic understanding of Li^+ ions transport to construction of Li^+ batteries

C.M. Julien et al.
Inorganics 2014, 2(1), 132-154







Diffusion tensor describes direction-dependent diffusion: Anisotropic pore structures, anisotropic crystal structures

Assumption: **Also the concentration gradients in y- or z-direction influence diffusive transport in x-direction**

$$\begin{pmatrix} j_x \\ j_y \\ j_z \end{pmatrix} = -\begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix} \cdot \begin{pmatrix} grdc_x \\ grdc_y \\ grdc_z \end{pmatrix}$$

$D_{x,y}$ = proportionality factor between flux in x-direction and concentration gradient in y-direction, often small or zero

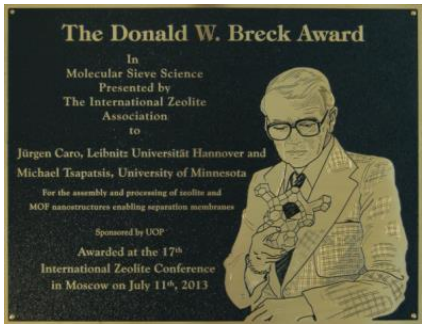
$$\vec{j}_x = -D_{xx}grdc_x - D_{xy}grdc_y - D_{xz}grdc_z$$

Often: After Onsager reciprocal relations: $D_{xy} = D_{yx}$

Optimization of diffusive transport can be decisive for function of

- Catalysts, Adsorbents

Hierarchical structure like lung. In catalysis, the ratio of reaction and transport in a porous catalyst grain determines its size and shape



- Pore Membranes (zeolite, MOF)

Membrane selectivity = adsorption x diffusion selectivity

- PEM fuel cells

Proton diffusion in the PEM can control cell performance,
$D(H^+) \approx D(H_3O^+)$ + Grotthus, also hydrogen recovery possible

- Si and Grätzel - Solar cells

Electrochemical ZnO layer deposition decreases the ratio electron diffusion time (short) to electron life time (long)

Thank you

- Pb and Li-Batteries

Hierarchical structure allowing counter diffusion, anisotropy of Li^+ diffusion in non-cubic hosts