UiO : Department of Chemistry
University of Oslo

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Space Charge Layers and Their Role in Properties of Interfaces in Solid State Ionics

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with good help from Dr. Jonathan M. Polfus, SINTEF; graphics, computations…

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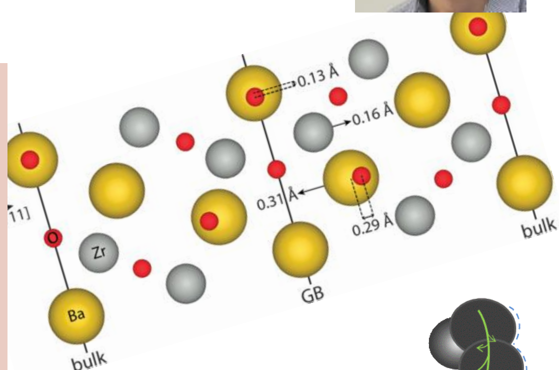
Outline
- Intro & overview
- Grain boundaries
- Surfaces
- Electrodes

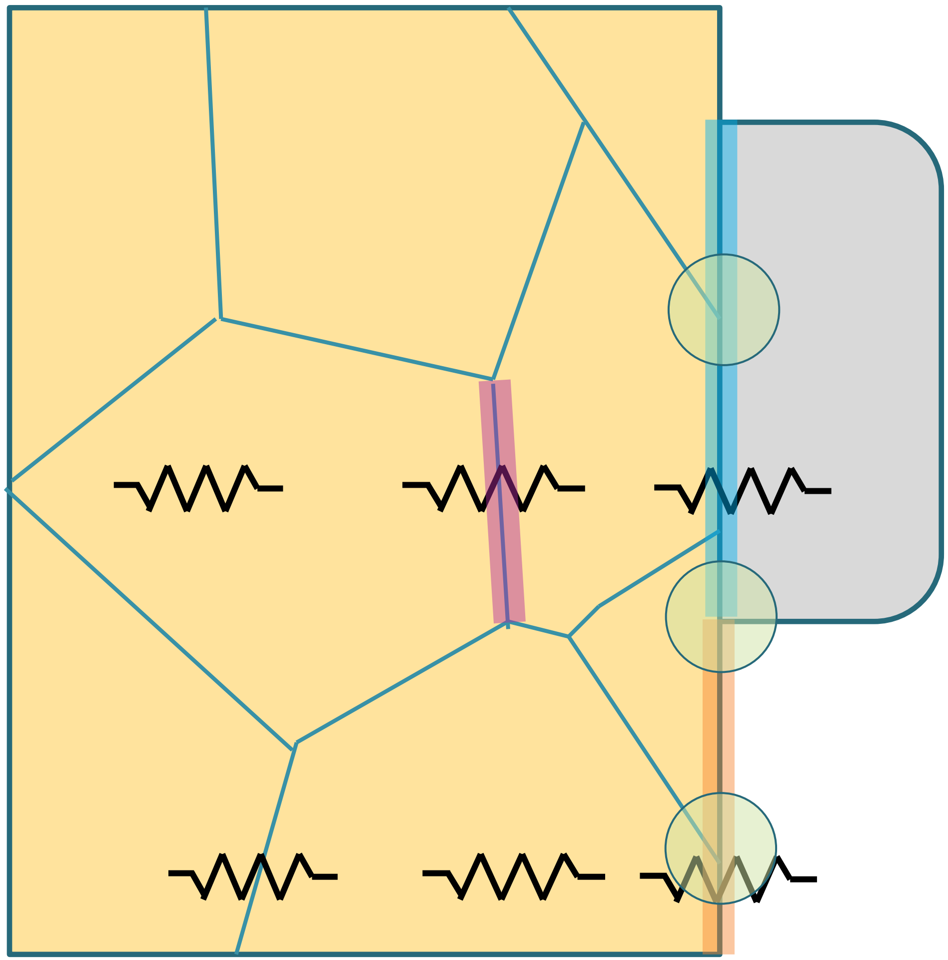
Concluding remarks

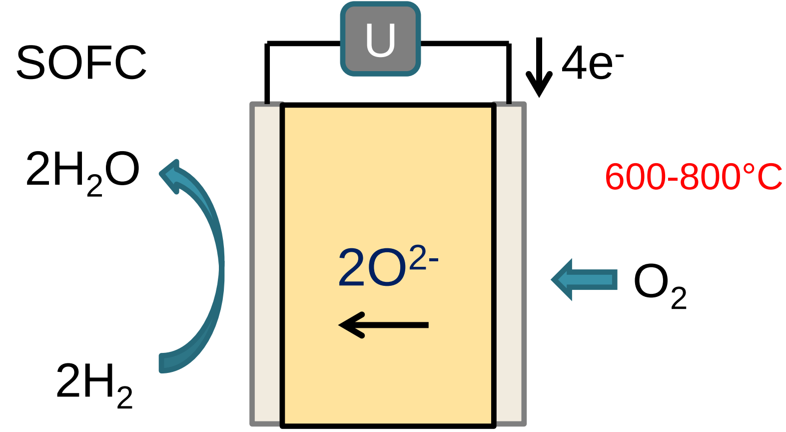


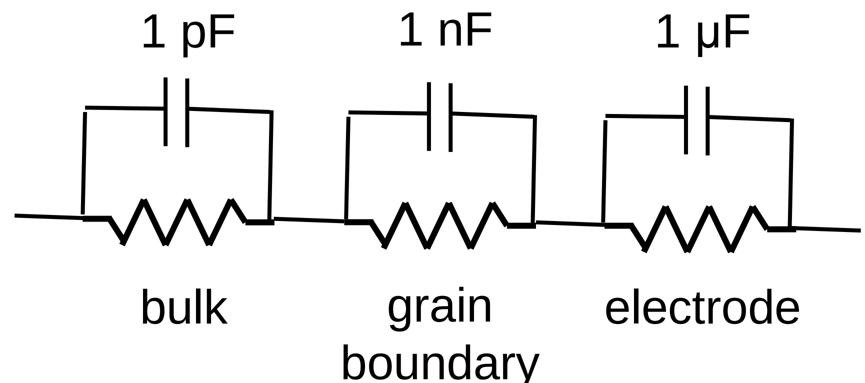
FOXCET

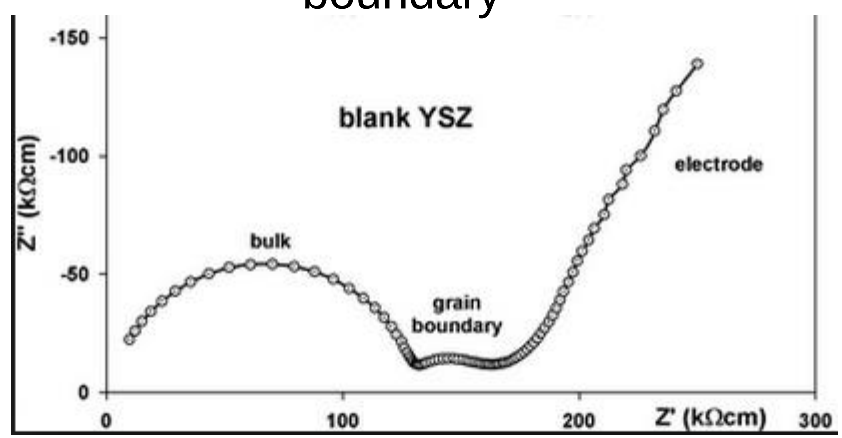
Solid state ionics

- Bulk
- Grain boundaries
- Surfaces, electrodes

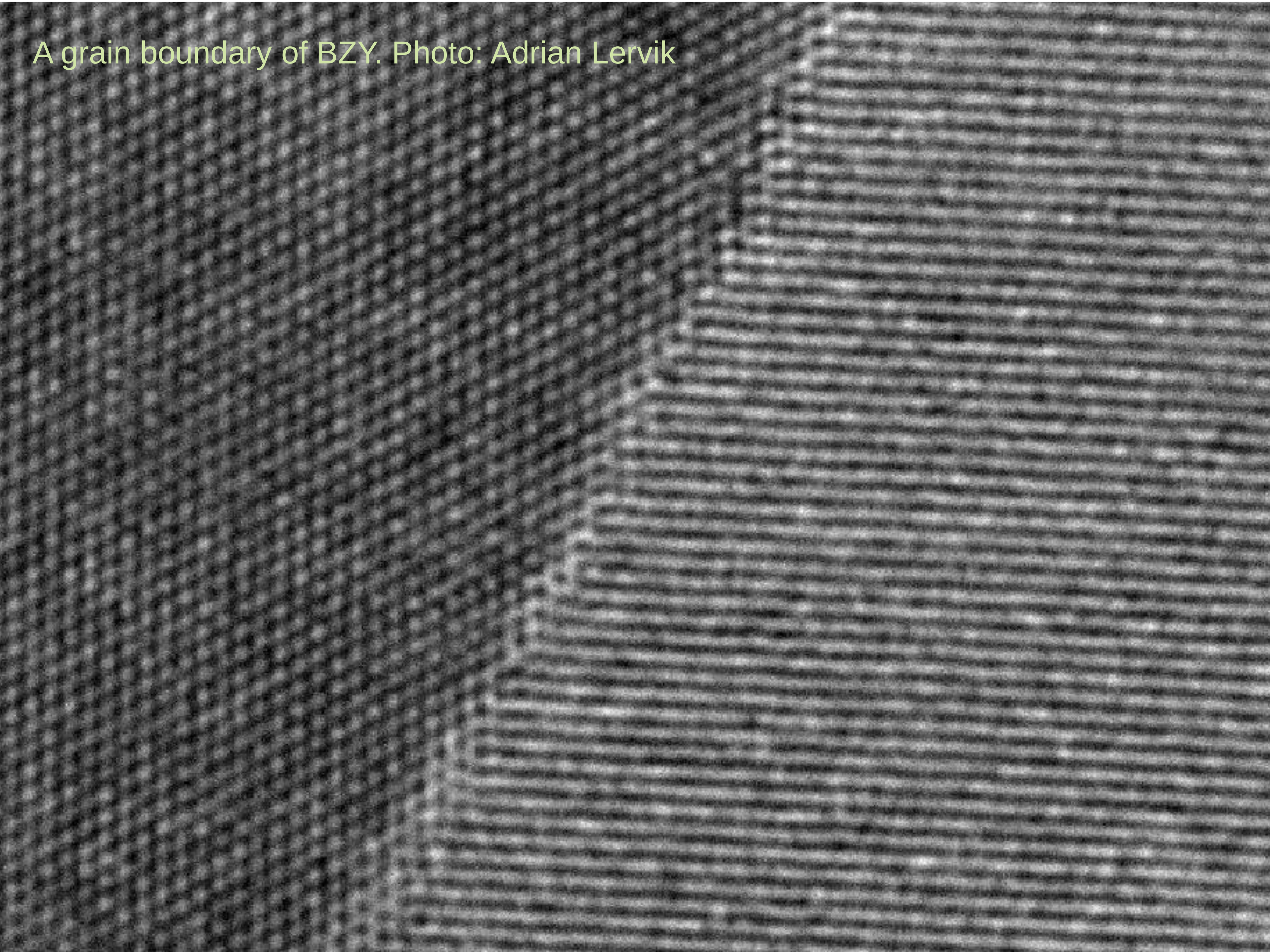




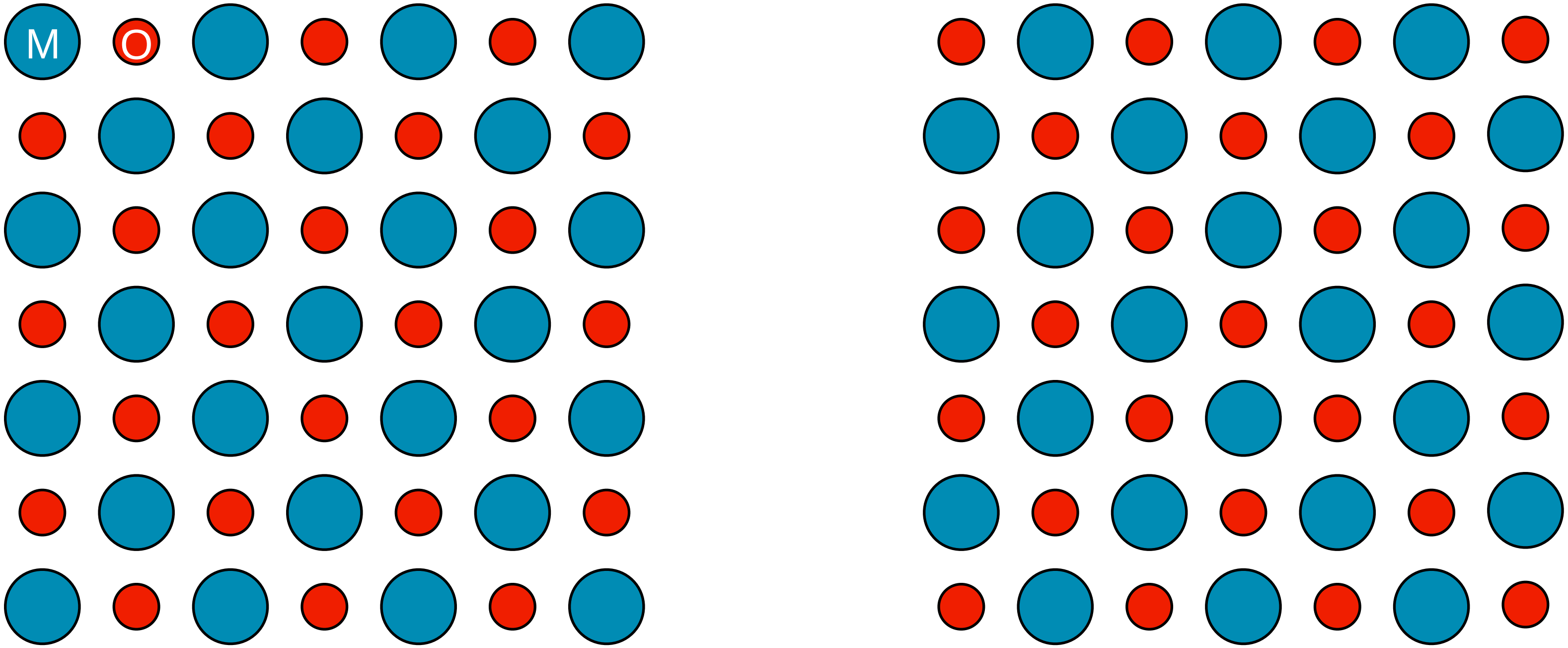




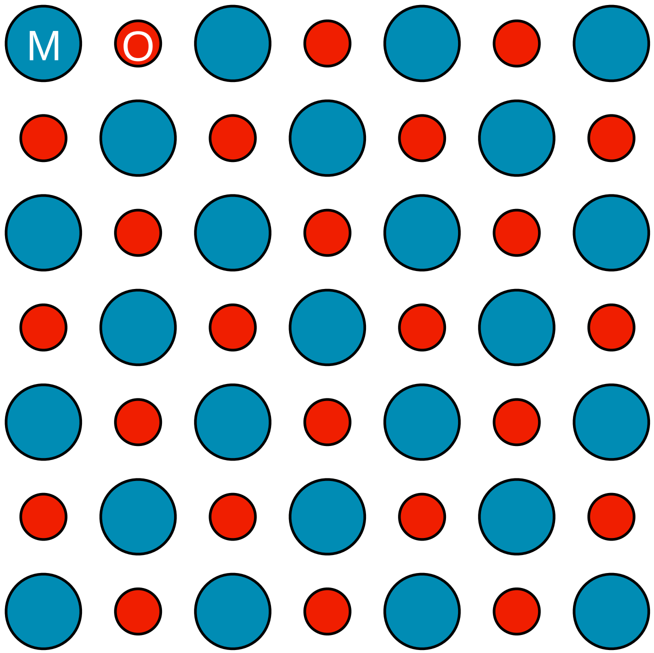
Ruiz-Morales *et al.*, *J. Mater. Chem.*, 2008

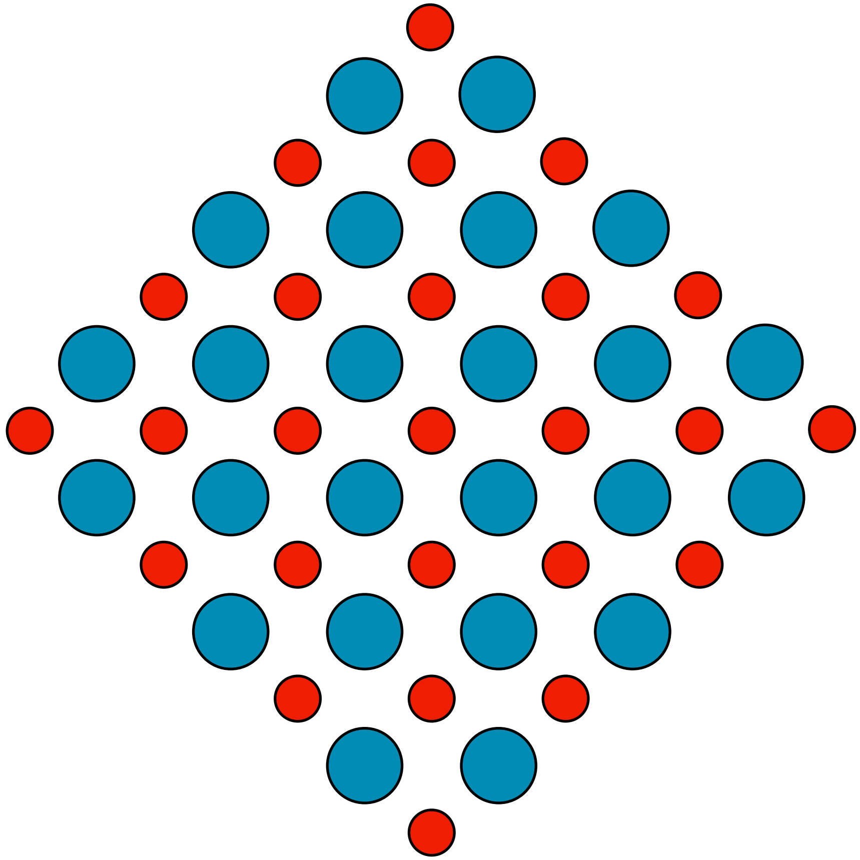

A grain boundary of BZY. Photo: Adrian Lervik

Two grains of metal oxide

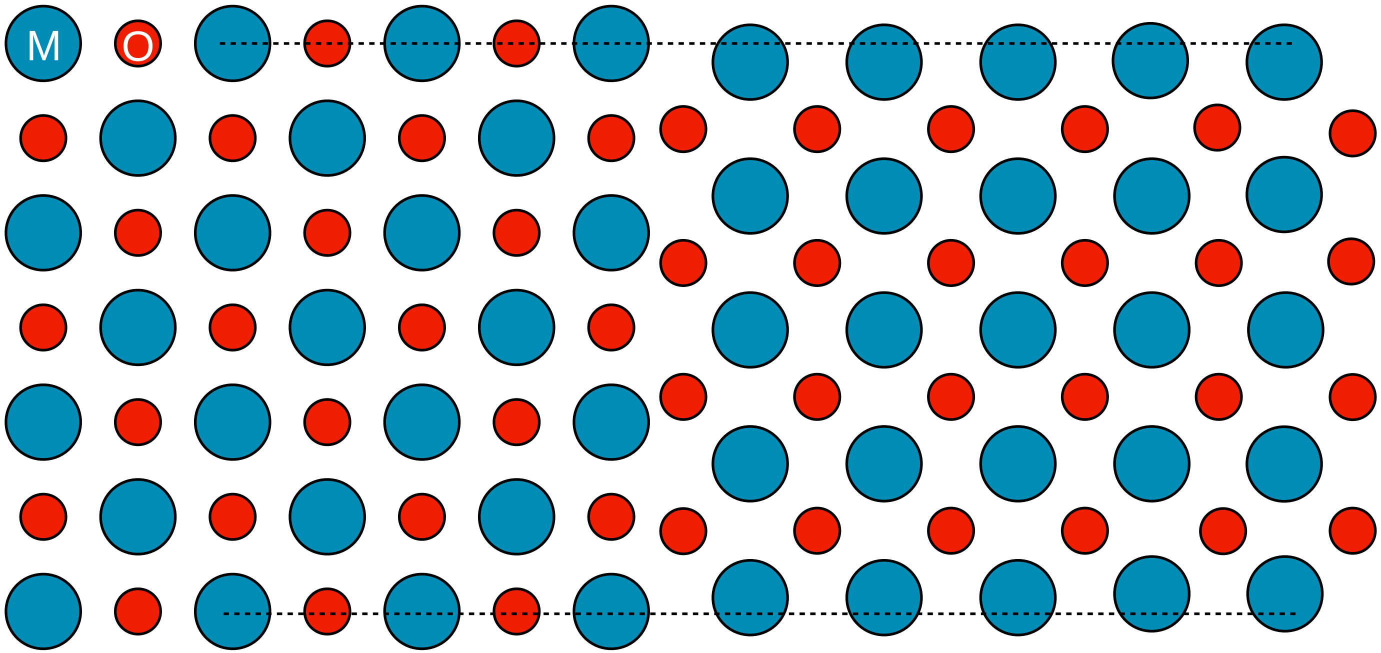


Misalign

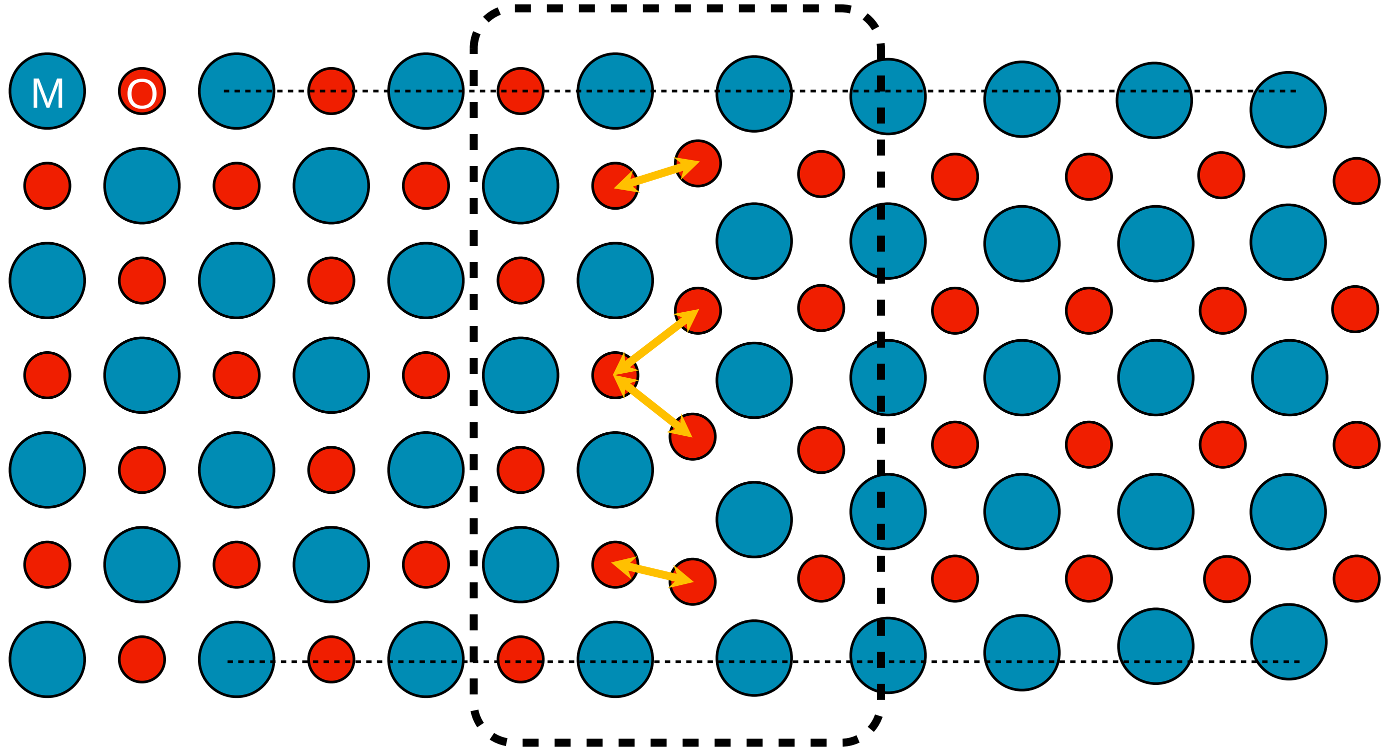




Make a grain boundary

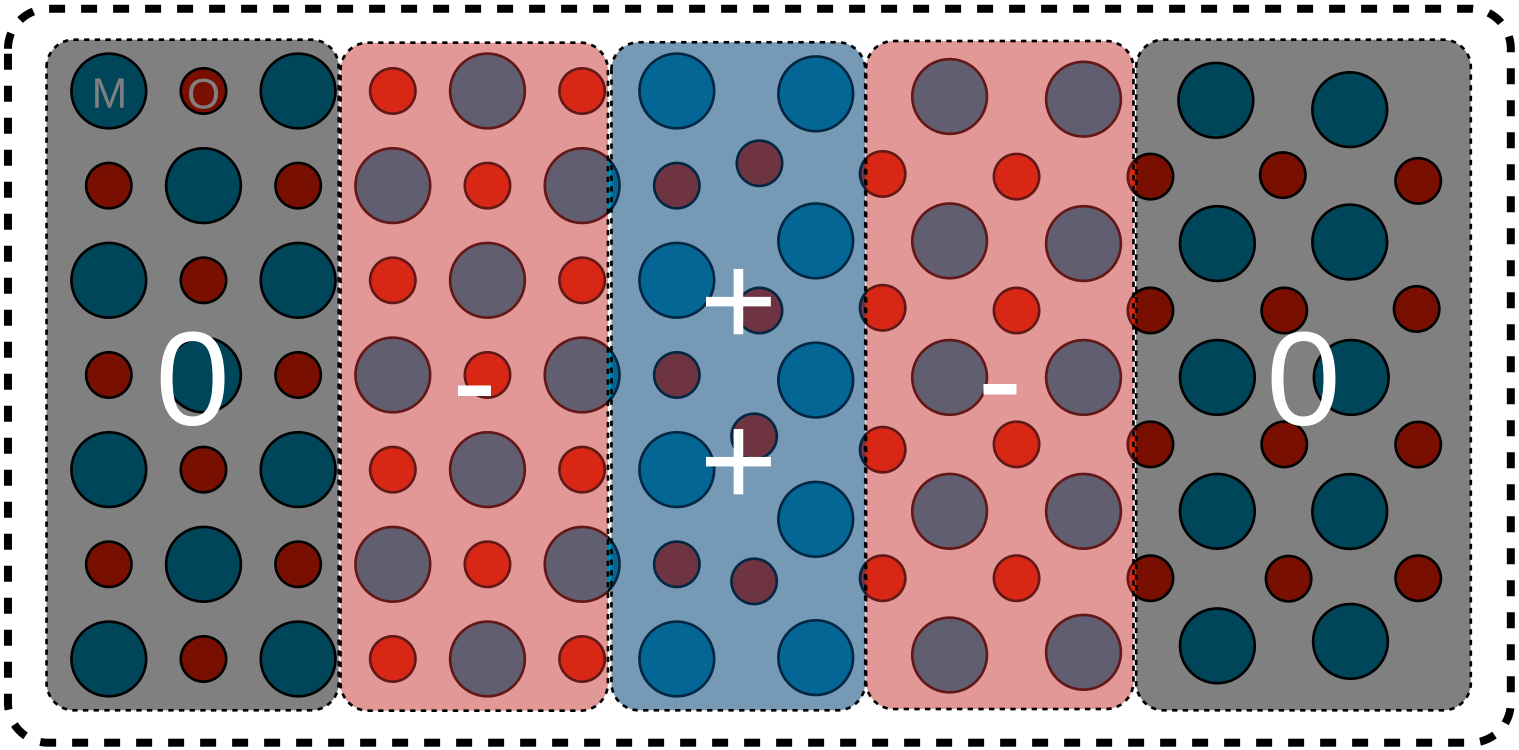


Relax



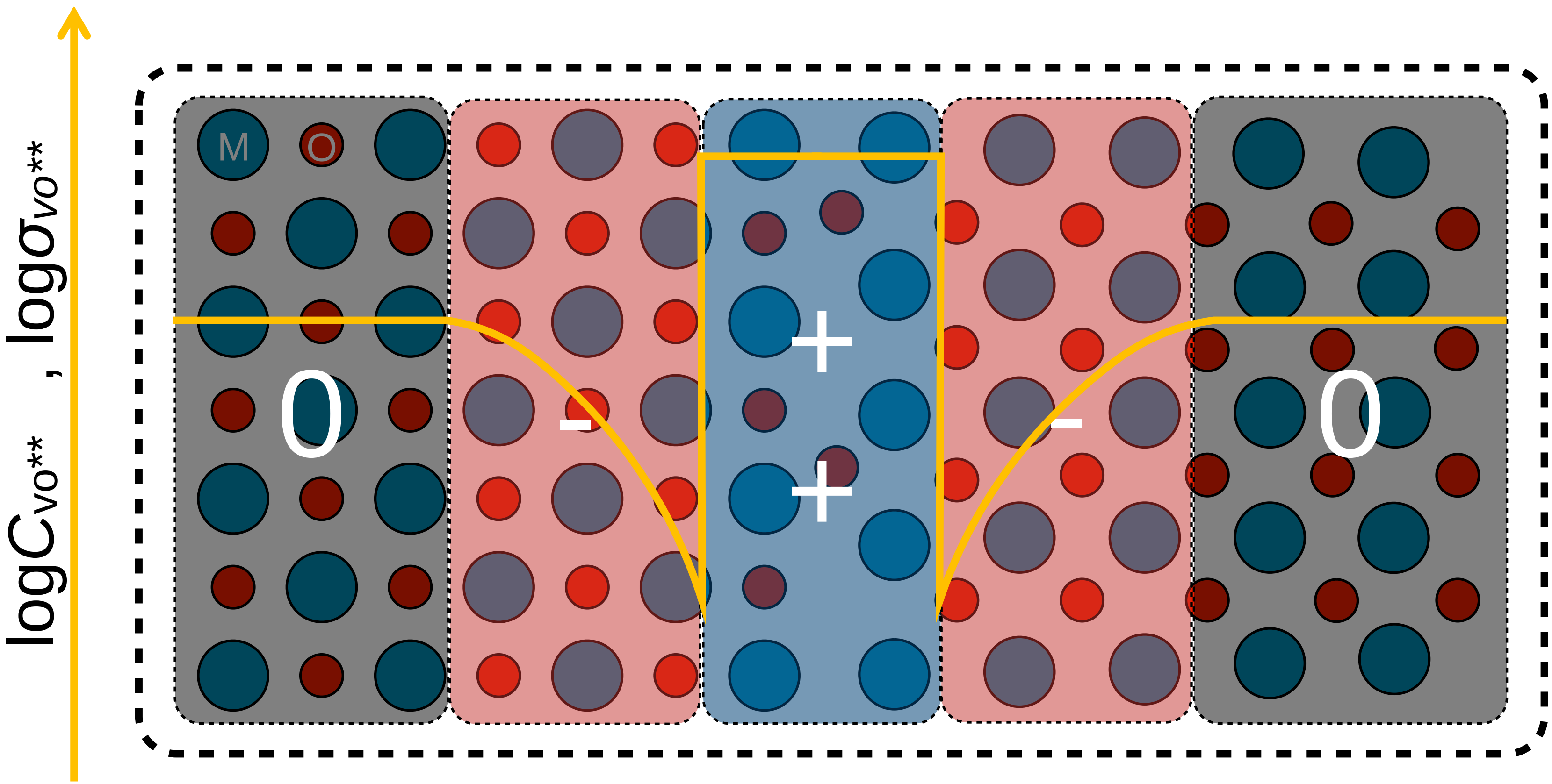
- Mismatch; higher energy
  - Electrostatic
  - Steric

Relaxation by excess of a preferred defect



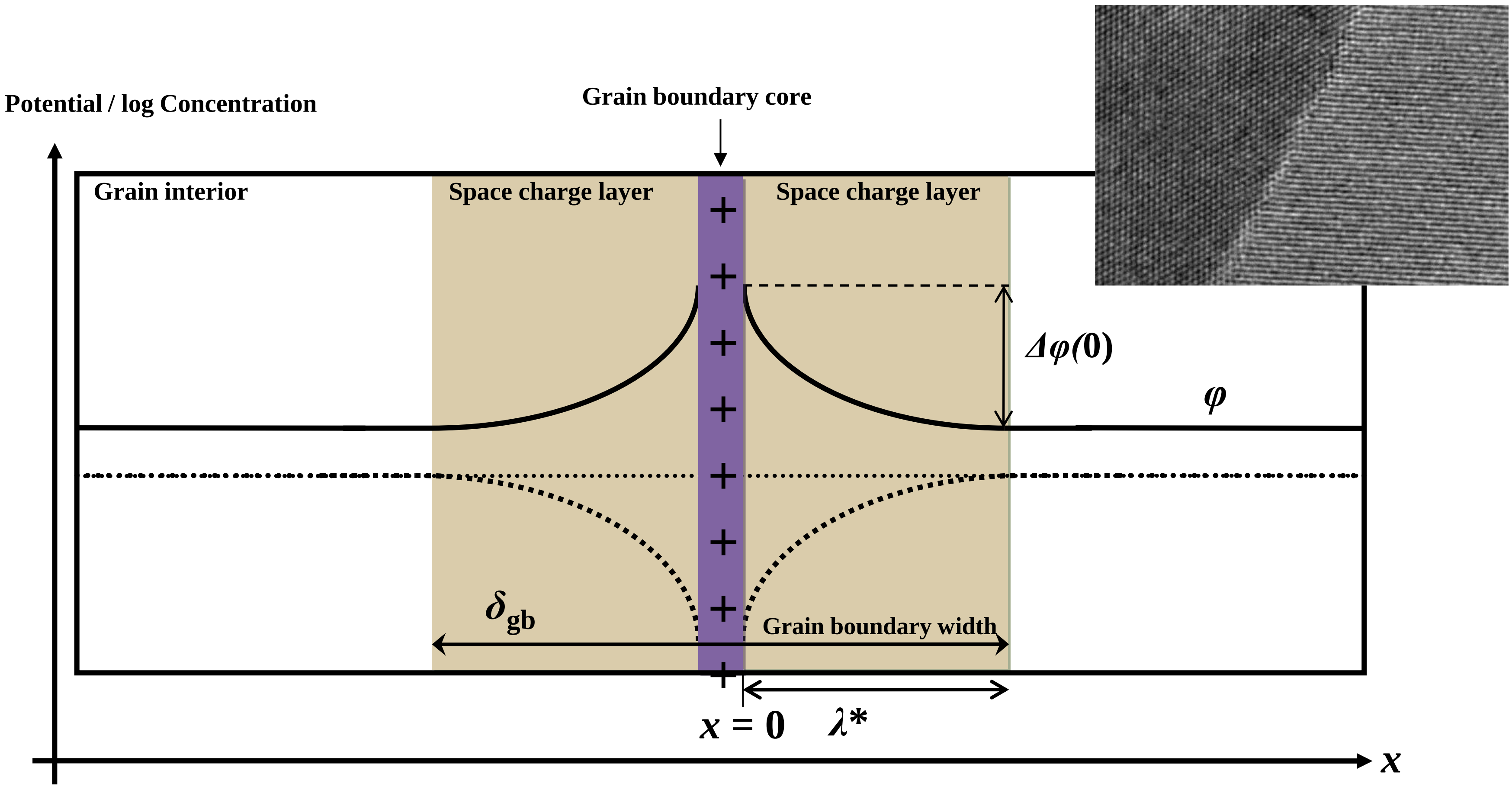
- Charge separation

Resulting electrical potential and effects on defect concentrations



- Electrical potential; Positive core and space charge layer
- Space charge layer
  - Concentration of charged defects affected dramatically
  - Conductivity changed dramatically

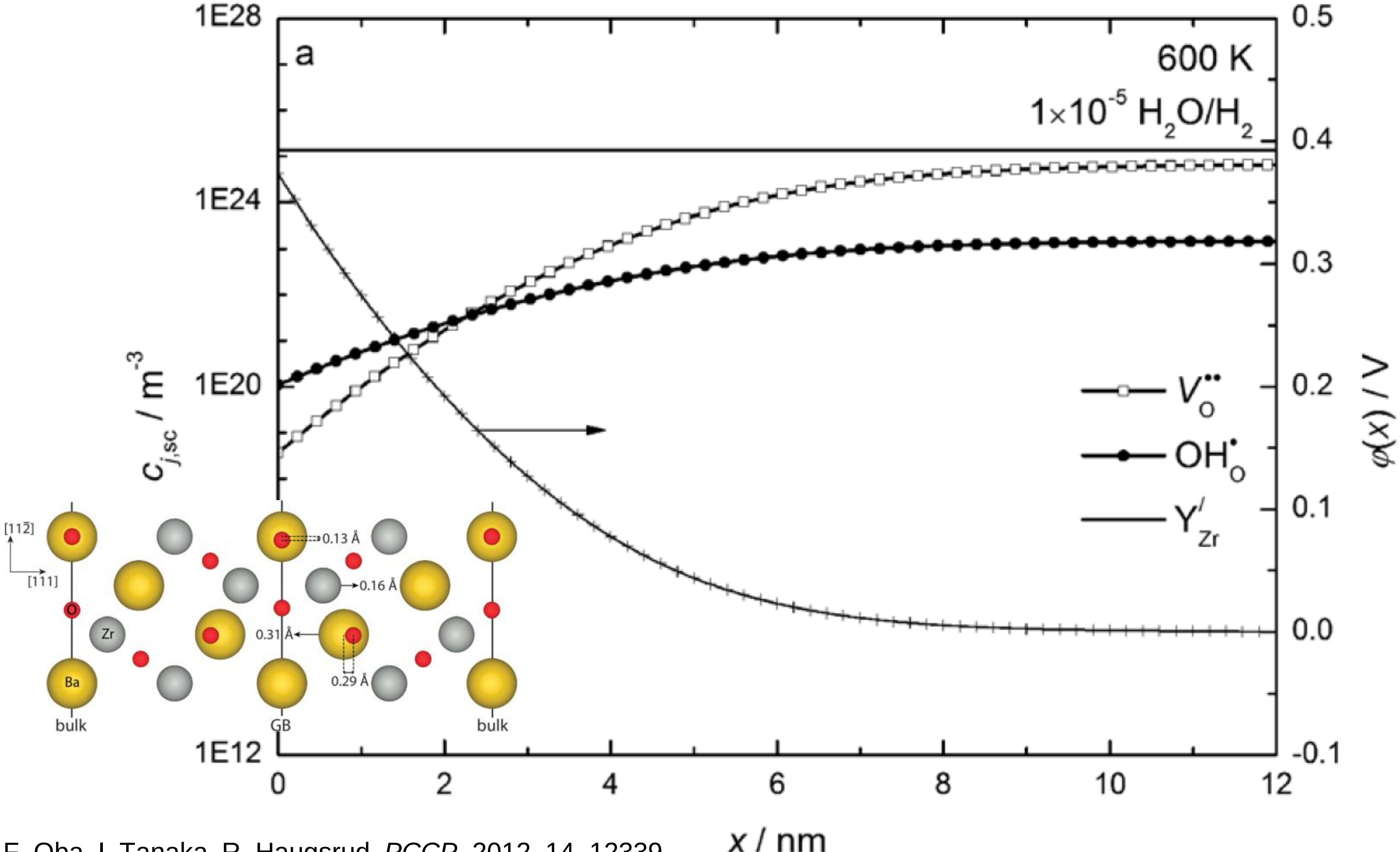
Schematic overview of a charged grain boundary



Kjølseth, C.; Fjeld, H.; Prytz, Ø.; Dahl, P. I.; Estournès, C.; Haugsrud, R.; Norby, T. *Solid State Ionics* 2010, 181, 268–275.

DFT; defect energies in core vs bulk + electrochemical equilibrium

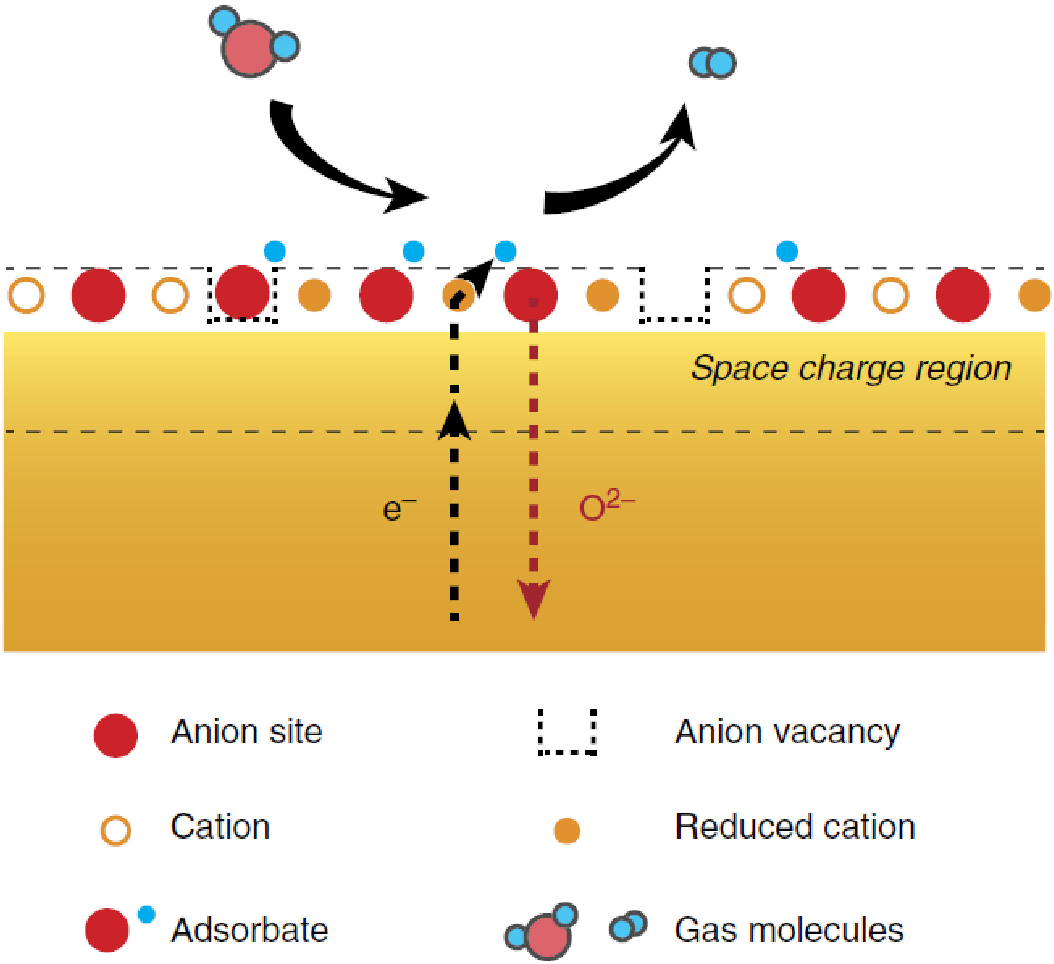
Yields potential and concentration profile in space-charge region
Example: $BaZrO_3$ Σ3 (111)



J. M. Polfus, K. Toyoura, F. Oba, I. Tanaka, R. Haugsrud, *PCCP*,.2012, 14, 12339.

Space charge layer (SCL) in surface region often overlooked

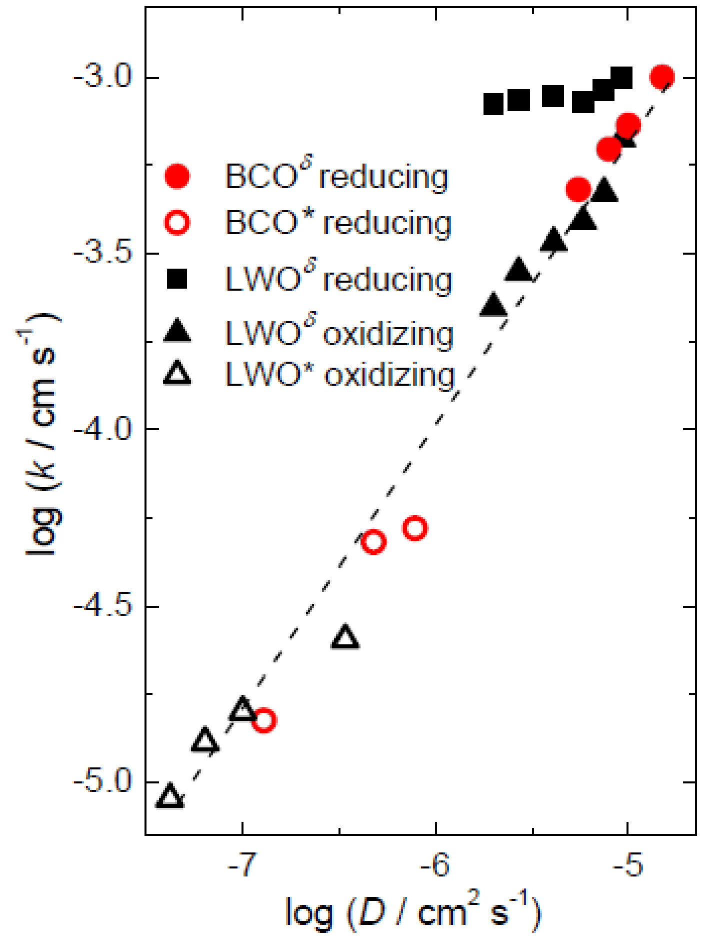
- Two immediate effects of SCLs
  - «Bulk-like» diffusion in SCL with depleted defect concentrations
  - Surface active species affected by interaction with SCL thermodynamics
- How can we distinguish them from «normal» molecular surface kinetics models?



Z.A. Feng, *et al.*, *Nature Comm.* 5 (2014) 5374

Surface kinetics and bulk transport

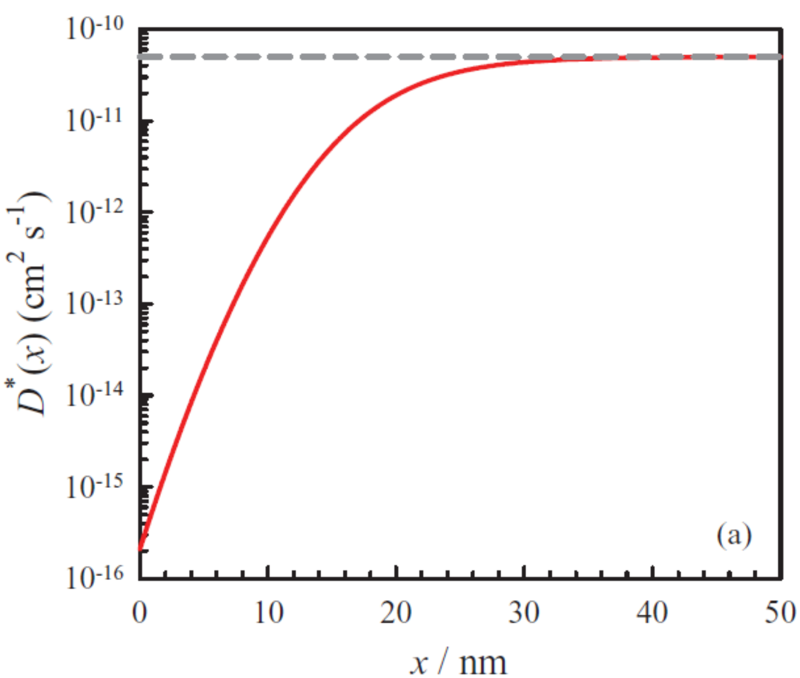
- Observation that they are often correlated
- …which makes sense if it is the SCL that determines what we interpret as surface kinetics…
- The same defects that rule bulk transport also rules transport in the SCL



R. Hancke, Ph.D thesis, UiO, (2013)

Diffusion profile can be predicted from SCL theory

- D and k evaluated numerically



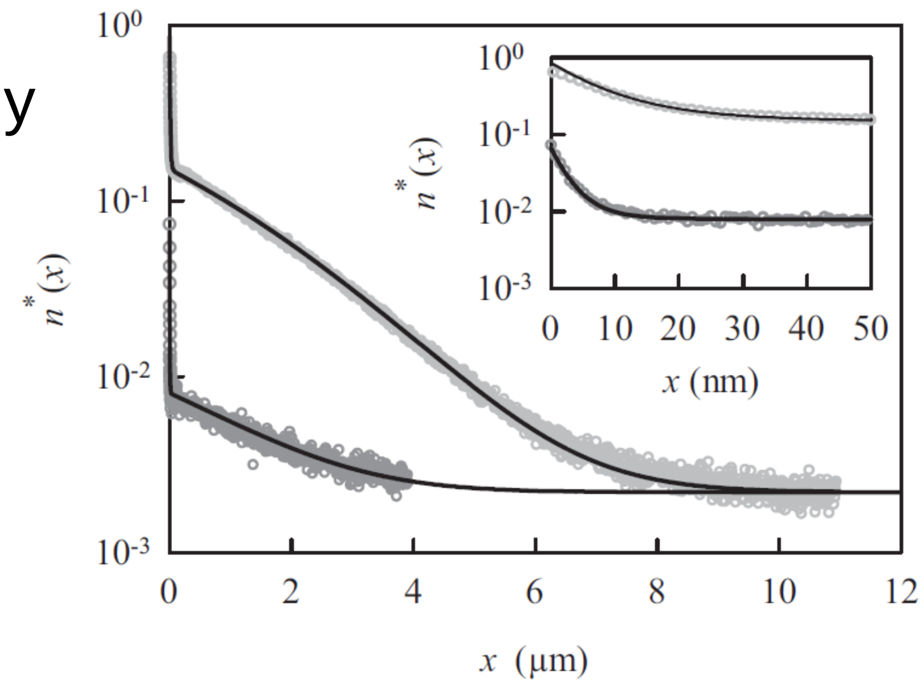


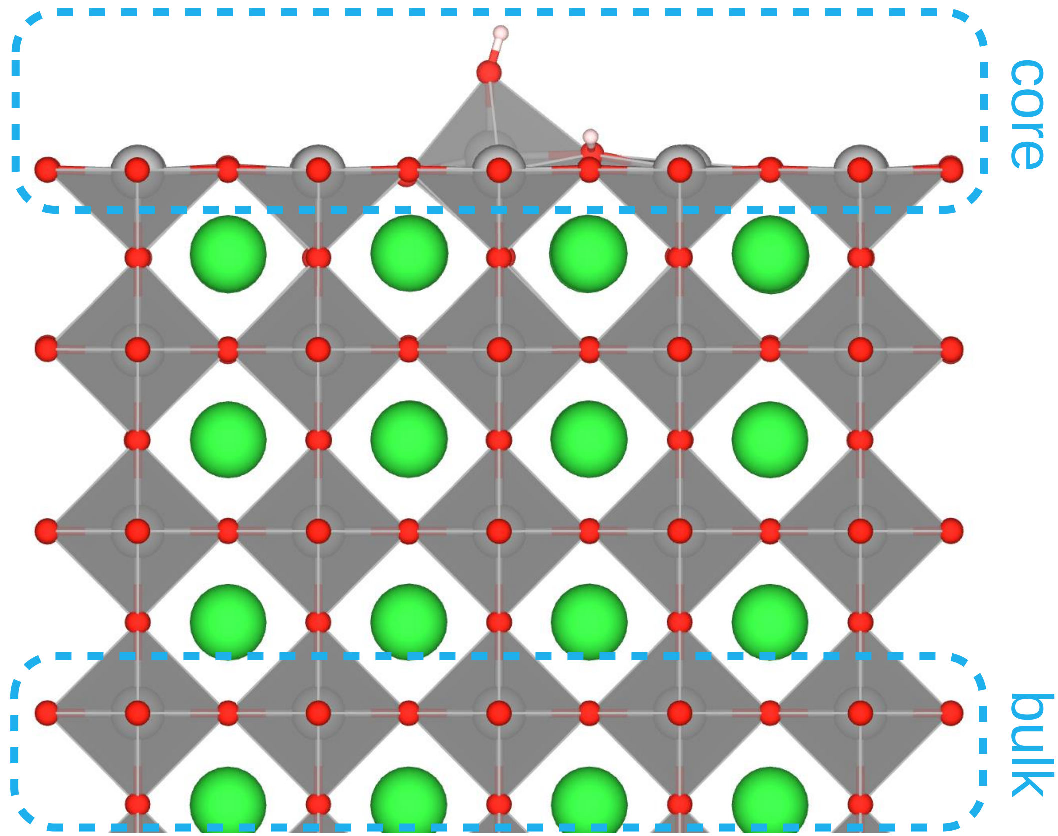
FIG. 5. Comparison of oxygen isotope diffusion profiles measured for $SrTiO_3$ single-crystal samples treated in buffered HF (light grey symbols) and not treated in buffered HF (dark grey symbols). Calculated solutions are shown as solid black lines. The inset shows the additional profile due to the space-charge layer. Both samples were exposed to ^{18}O-enriched gas at the same temperature (T = 1123 K) and oxygen activity ($aO_2 = 0.50$) for the same period of time ($t = 1.85 \times 10^3$ s).

R. De Souza *et al.*, *Phys. Rev. B,* 85 (2012) 174109

Surface space-charge model

$O_{ad}^{//}$ $OH_{ad}^{/}$

$OH_O^{\bullet}$ $v_O^{\bullet\bullet}$ $Y_{Zr}^{/}$

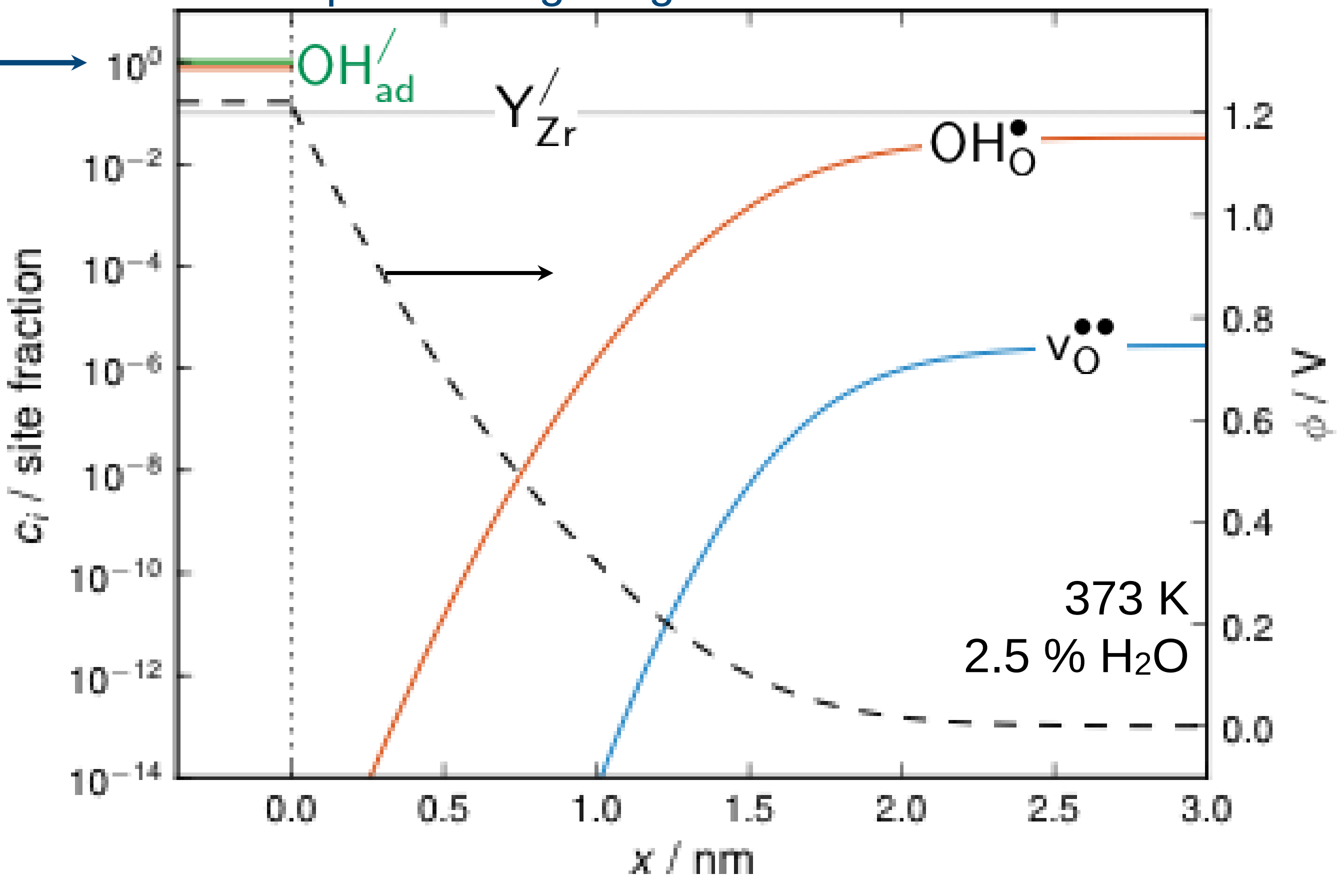


$OH_O^{\bullet}$ $v_O^{\bullet\bullet}$ $Y_{Zr}^{/}$

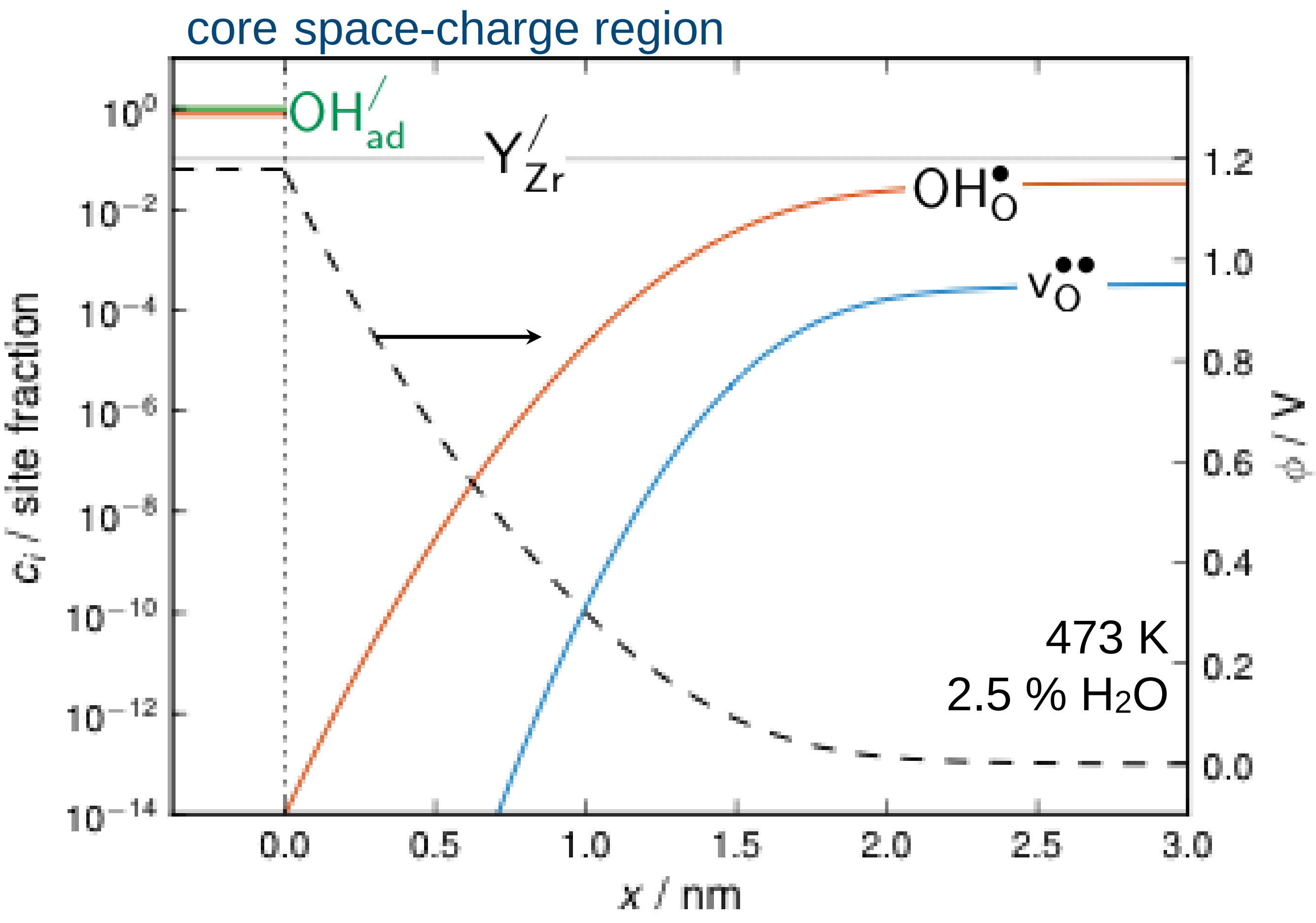
Potential and concentration profile: 373 K

core space-charge region

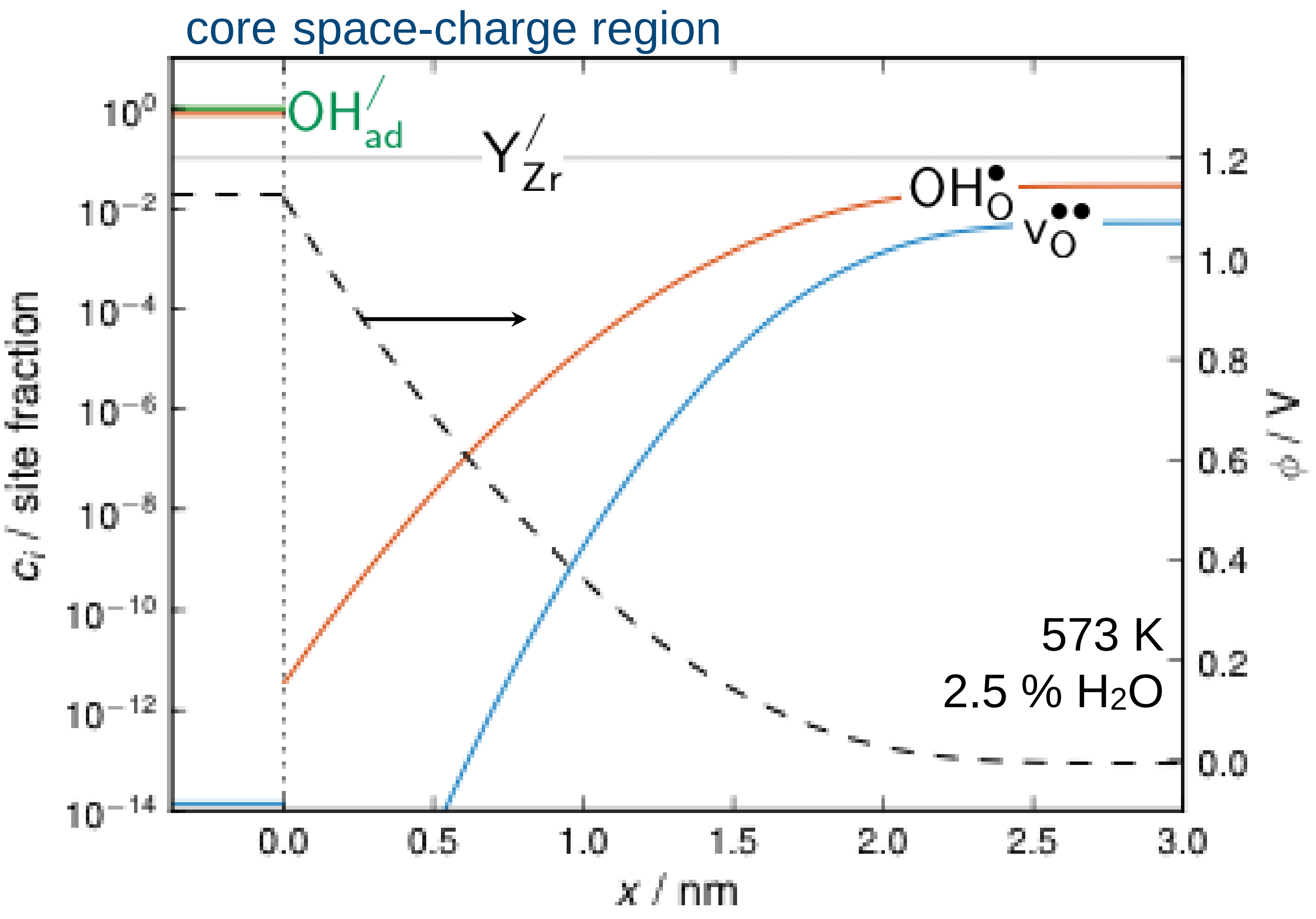
$N_{s,O} = 2N_{s,Zr}$



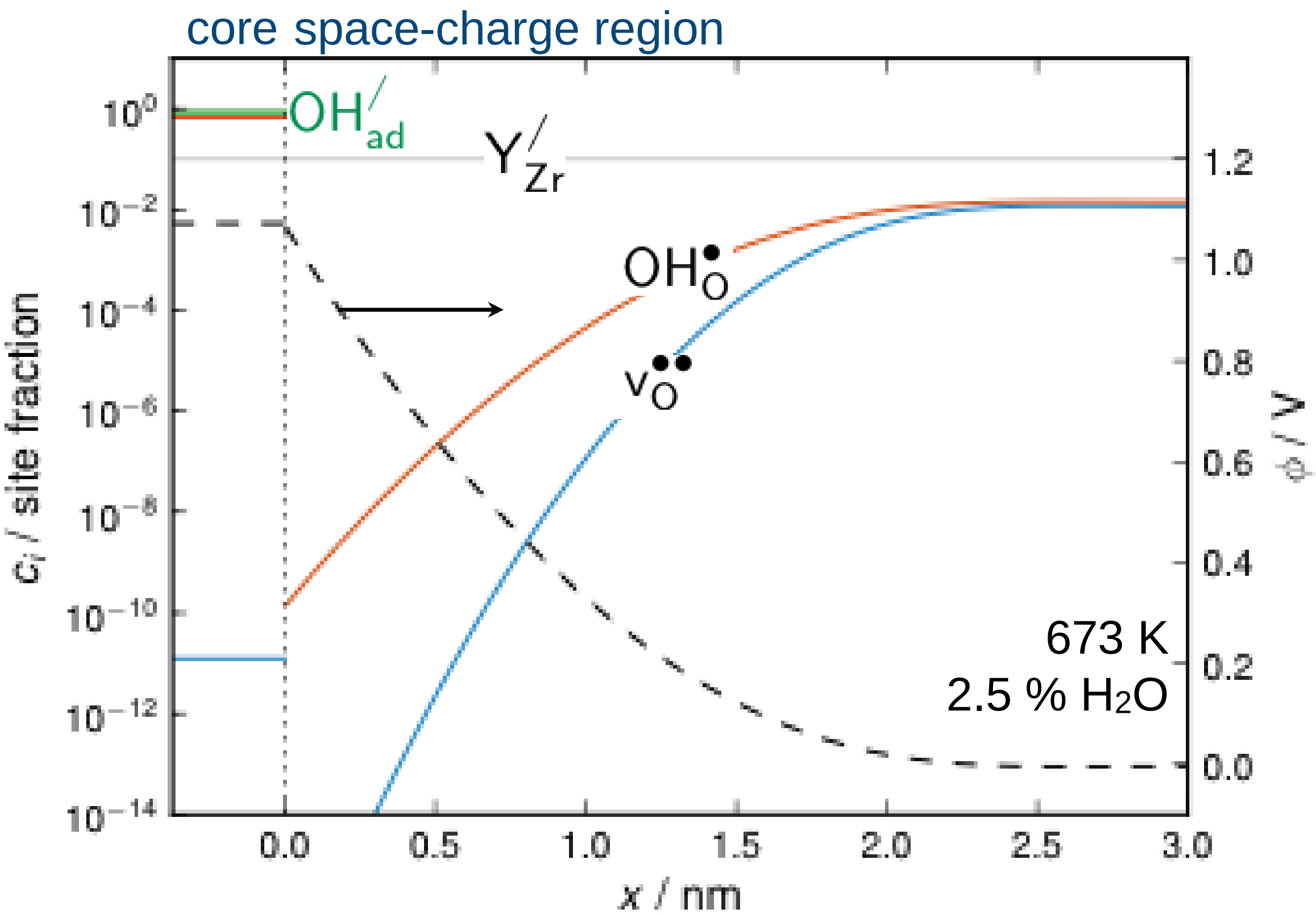
Potential and concentration profile: 473 K



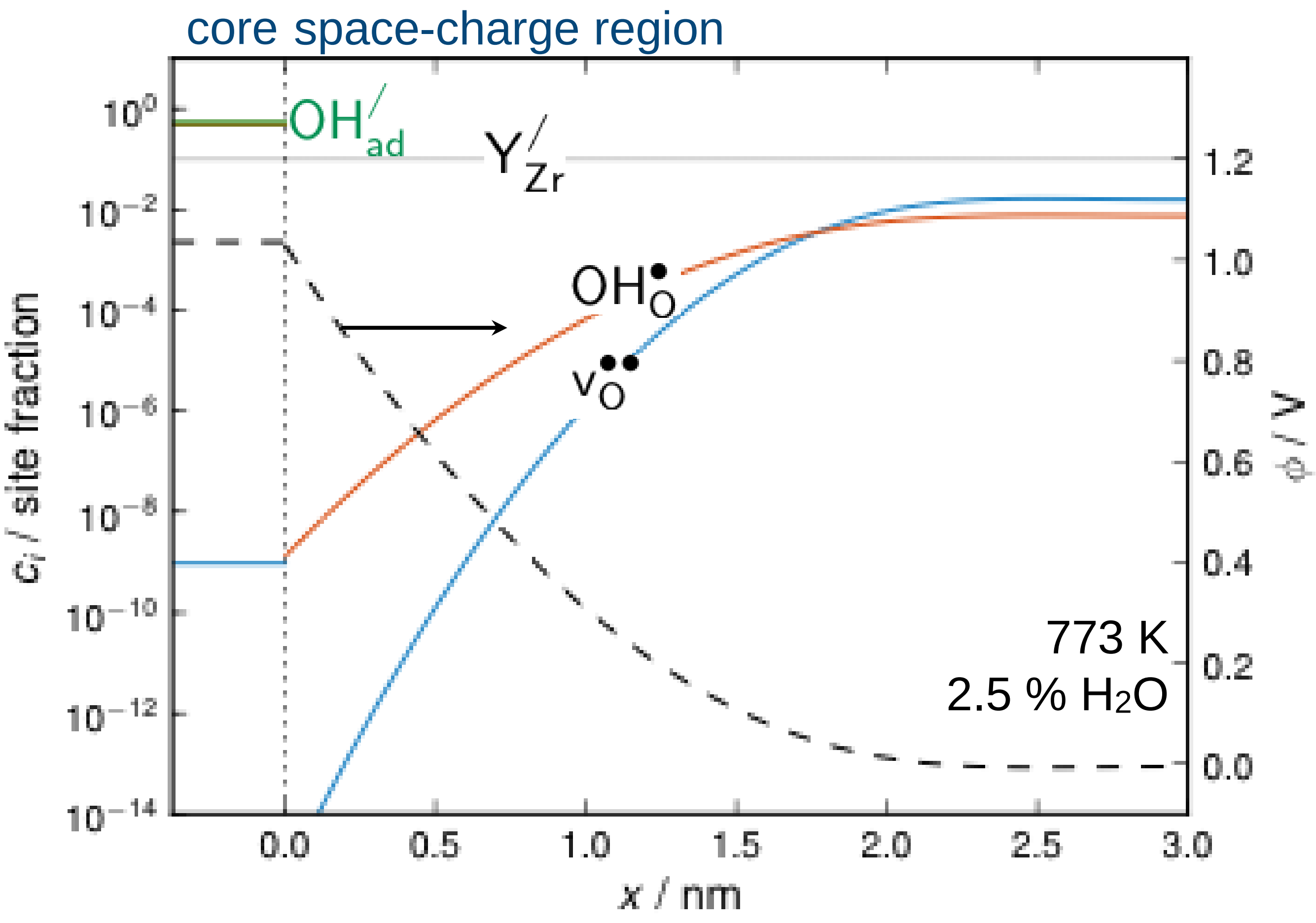
Potential and concentration profile: 573 K



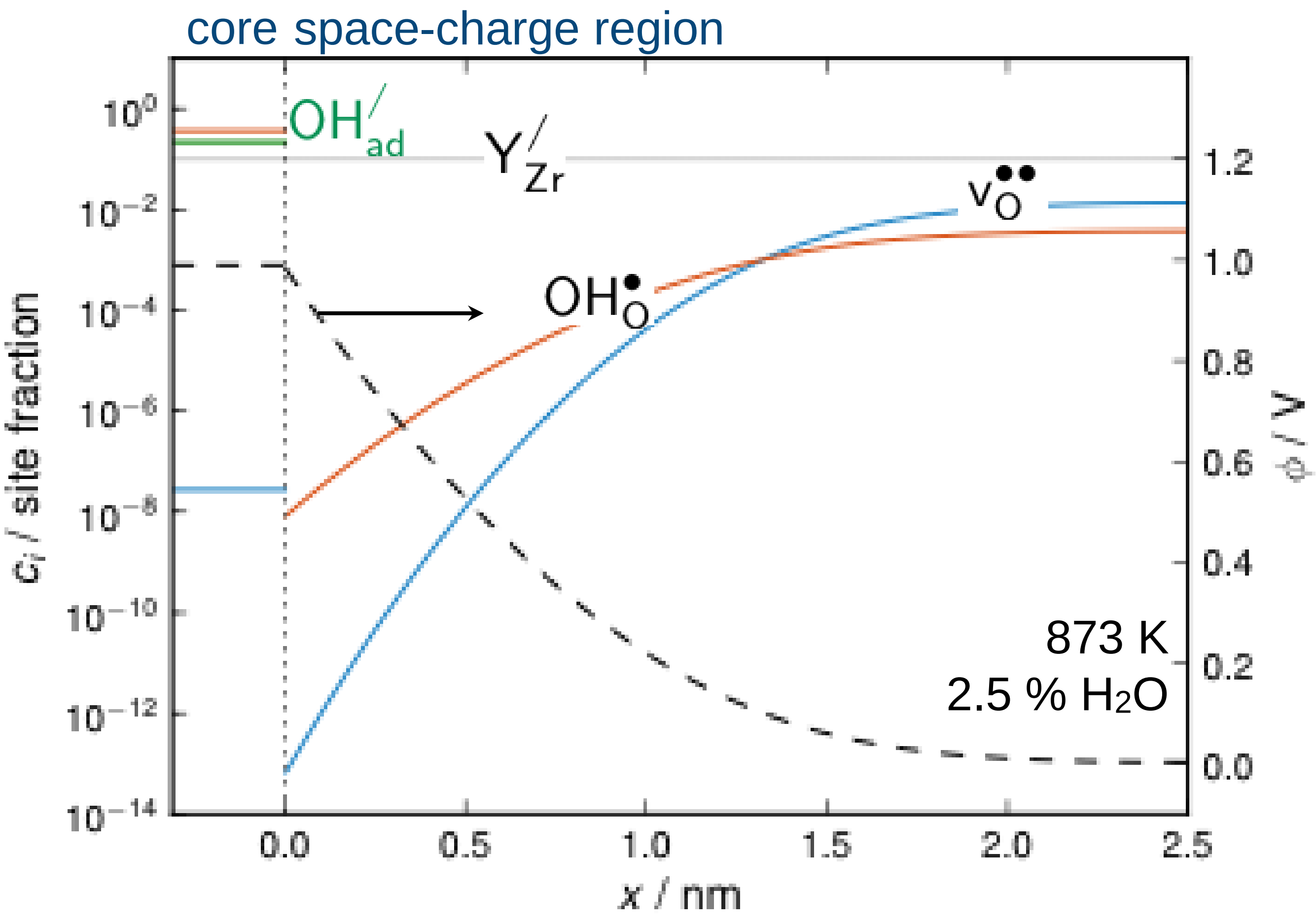
Potential and concentration profile: 673 K



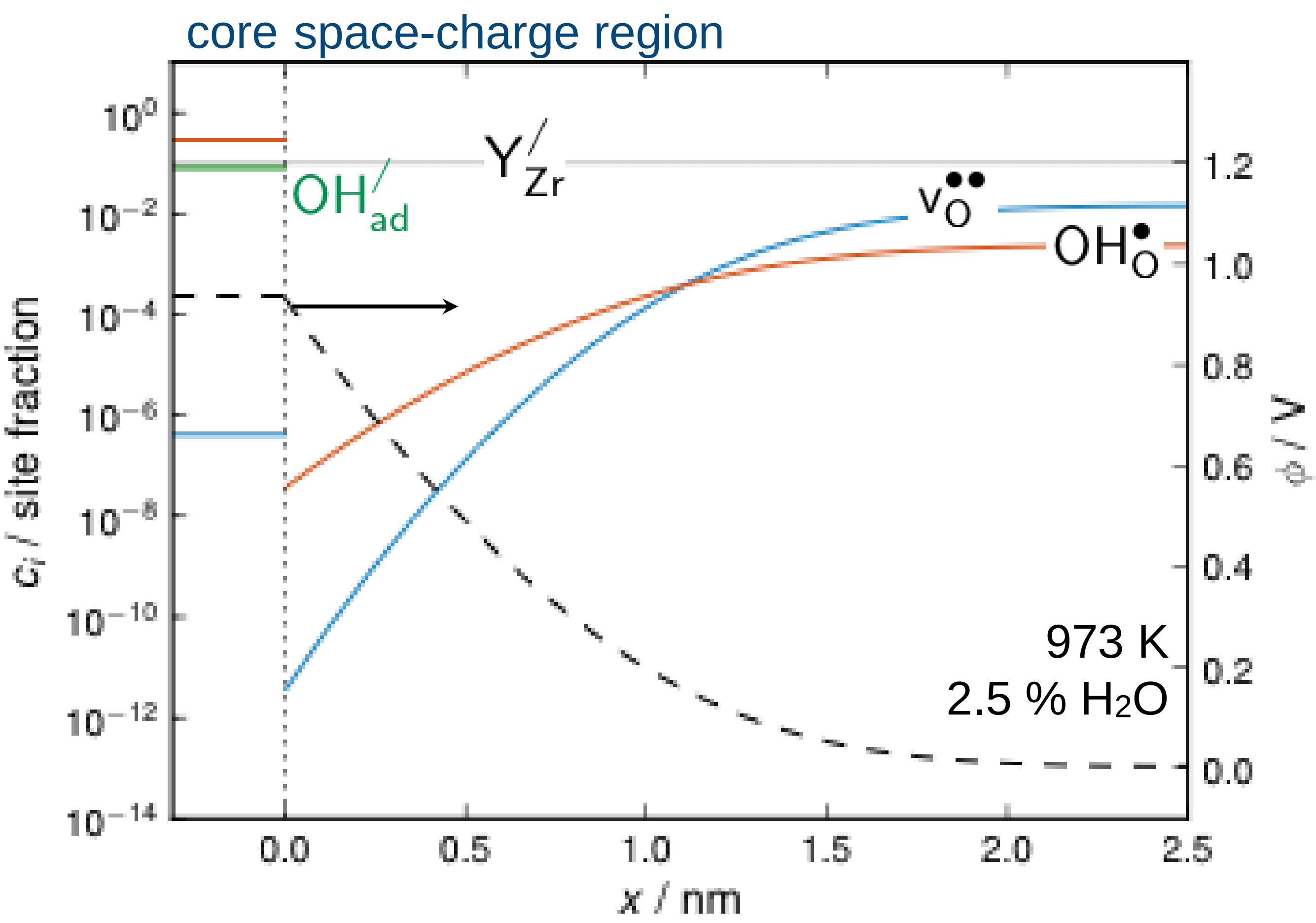
Potential and concentration profile: 773 K



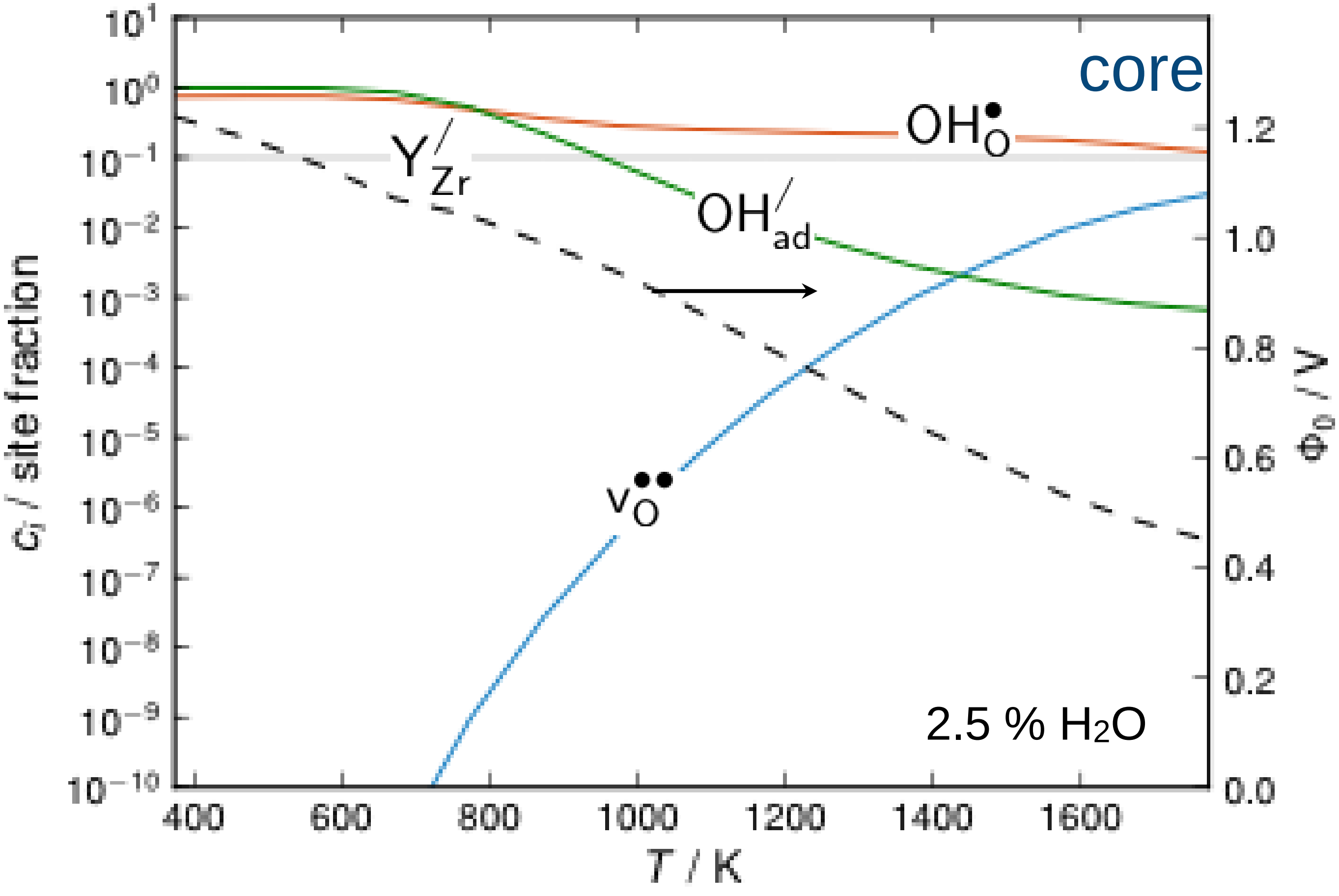
Potential and concentration profile: 873 K



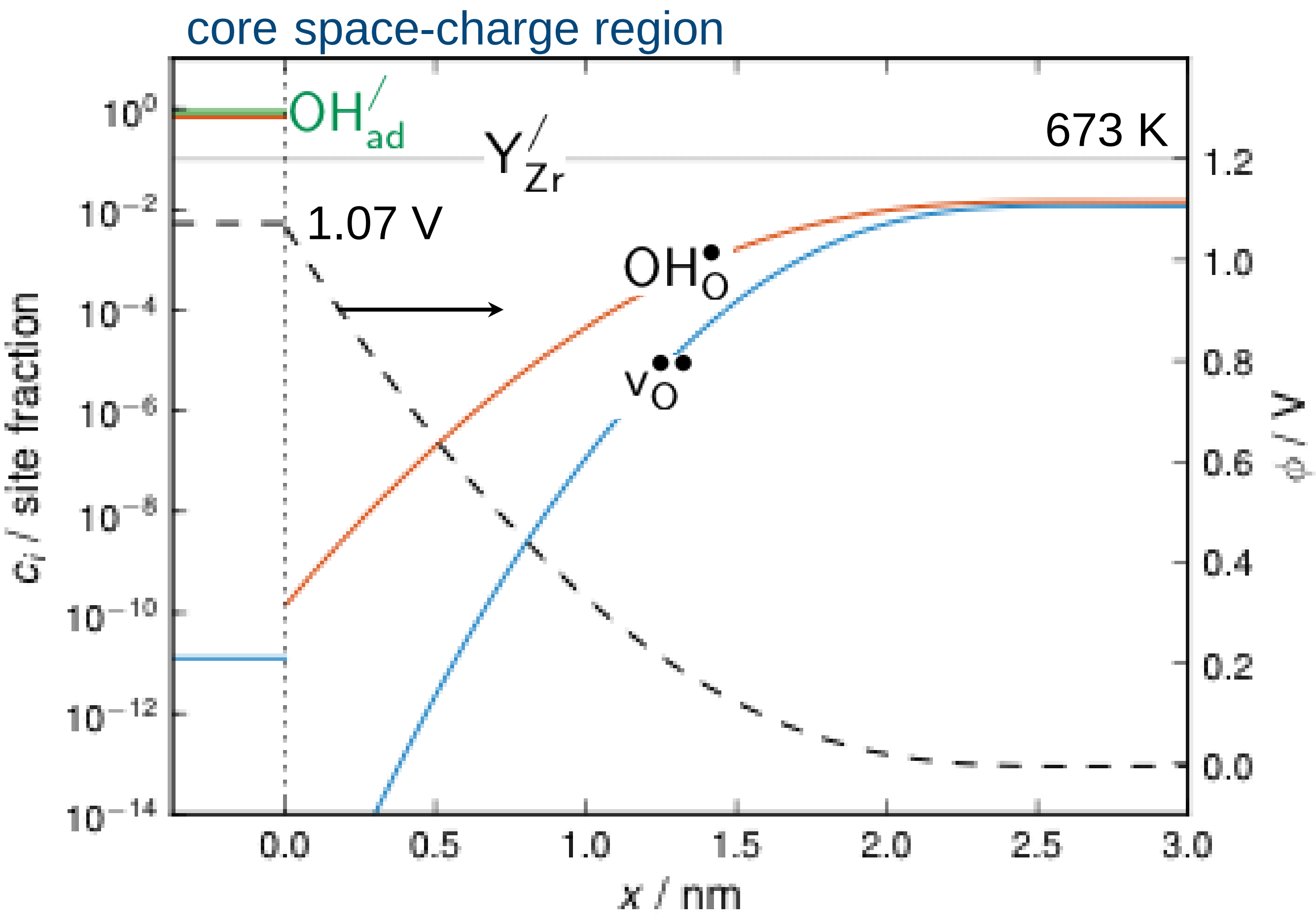
Potential and concentration profile: 973 K



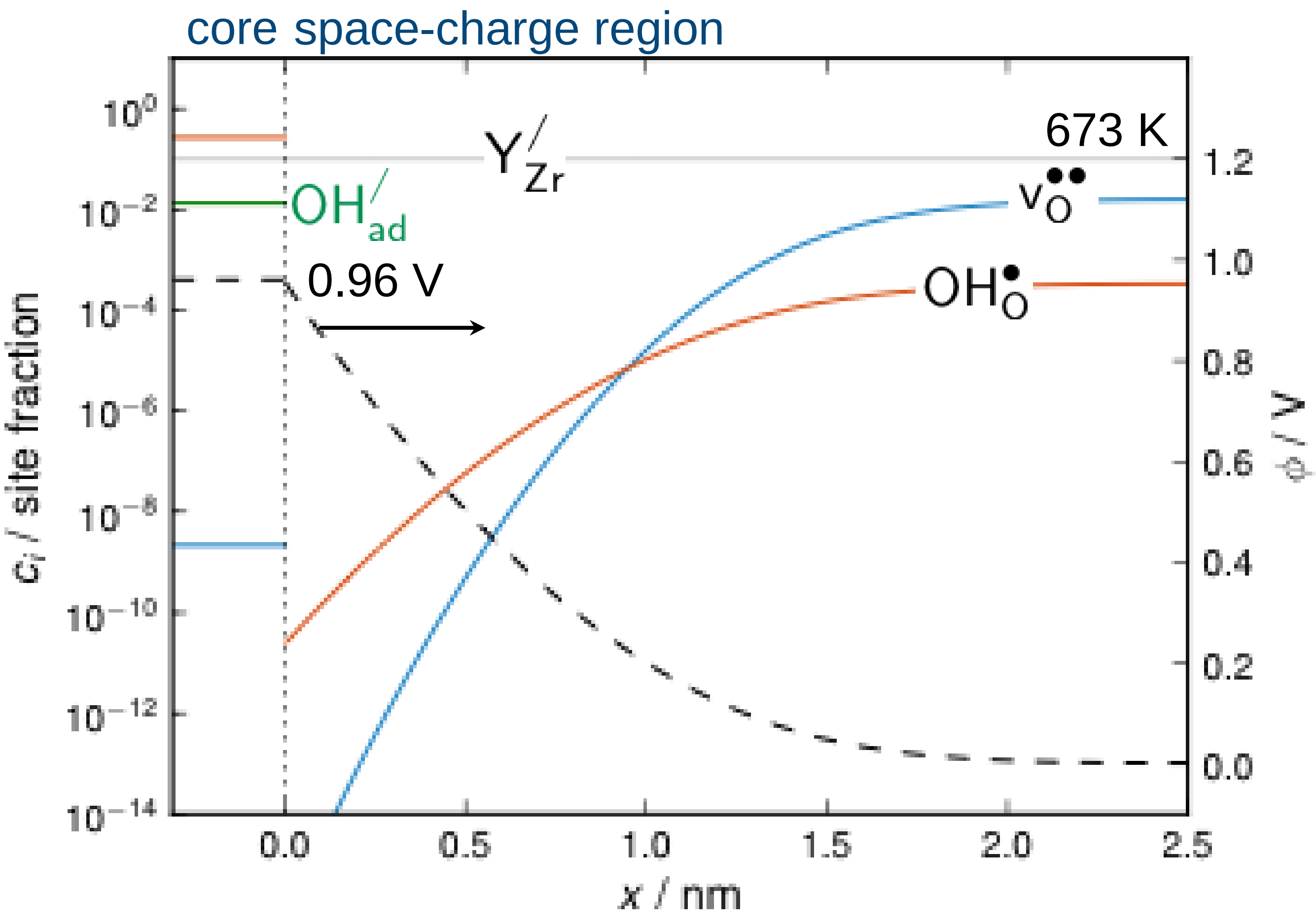
Surface concentrations: *T*



Surface concentrations: $p(H_2O)$=0.025 bar



Surface concentrations: $p(H_2O)$=1E-5 bar



…not entirely new…

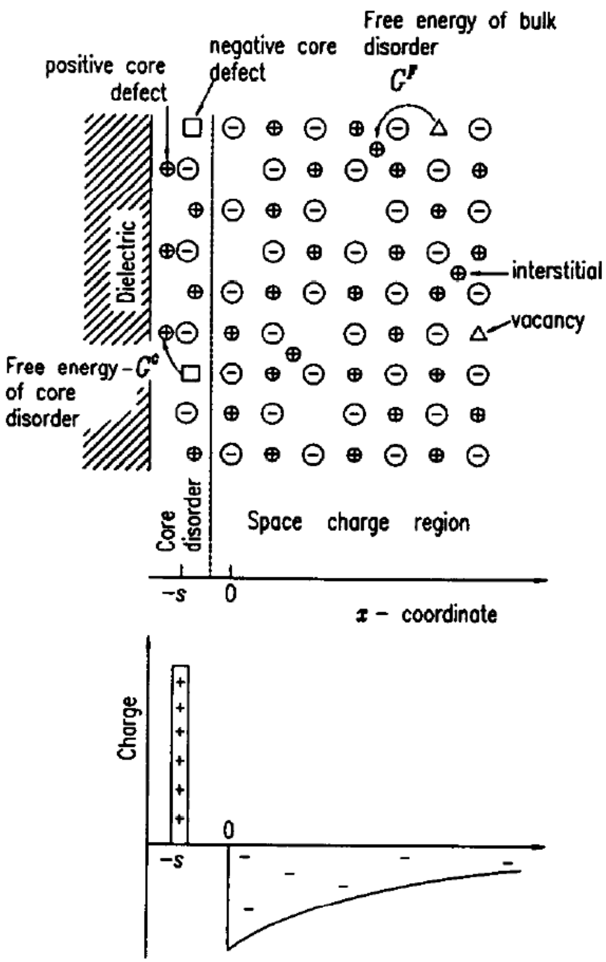


Fig. 1. Schematic picture of the A/MX interface describing the core and the space charge region.

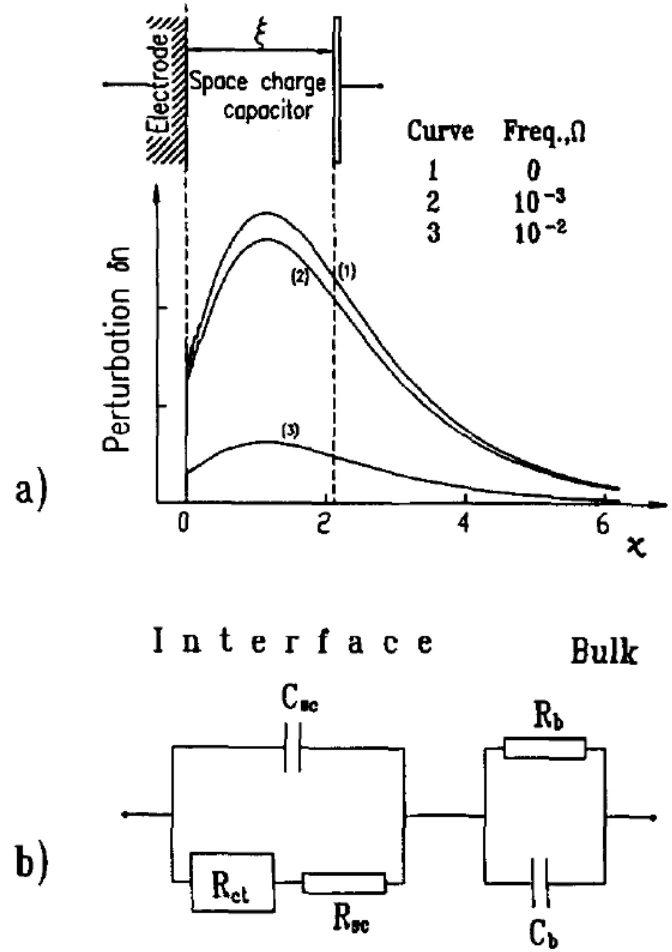
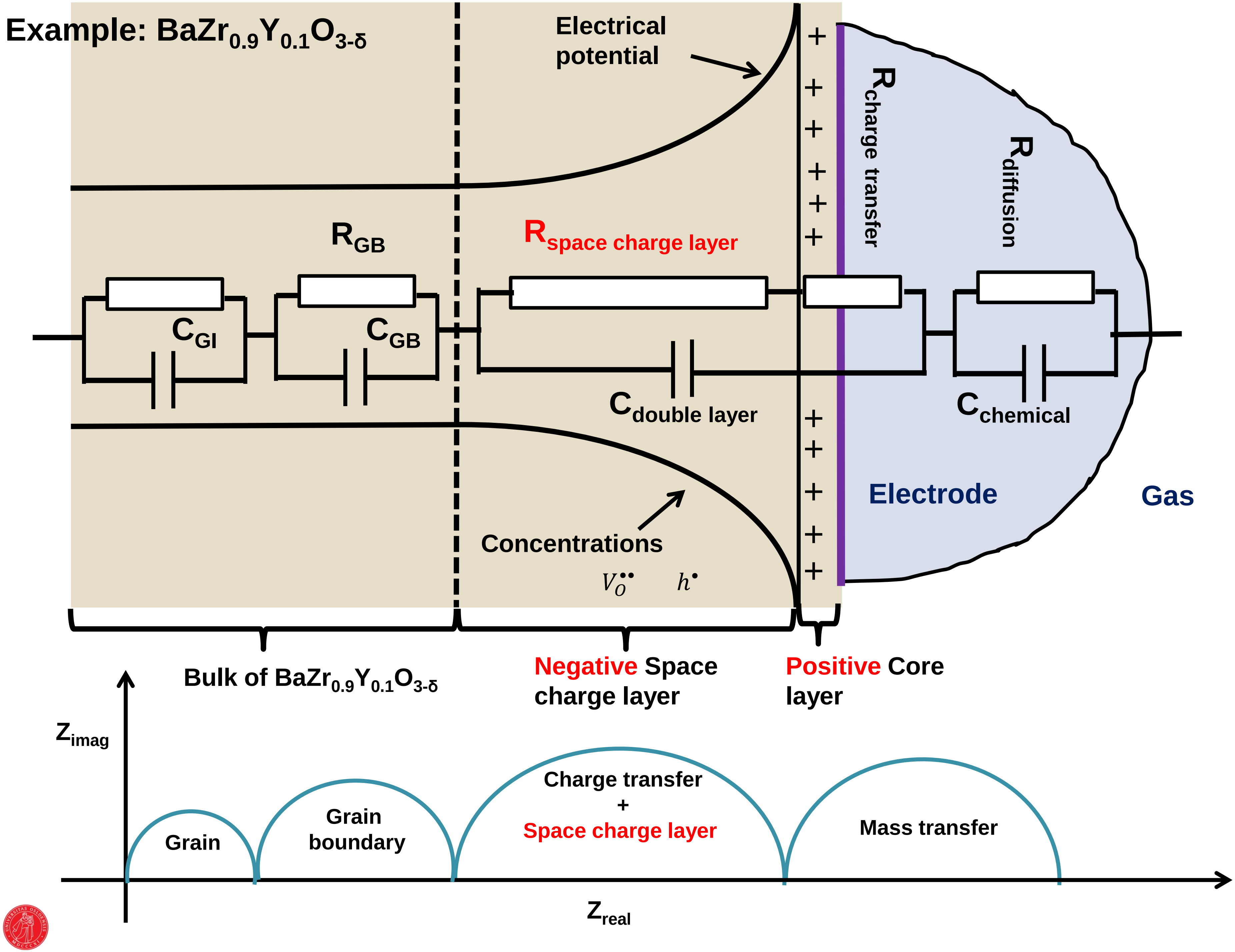
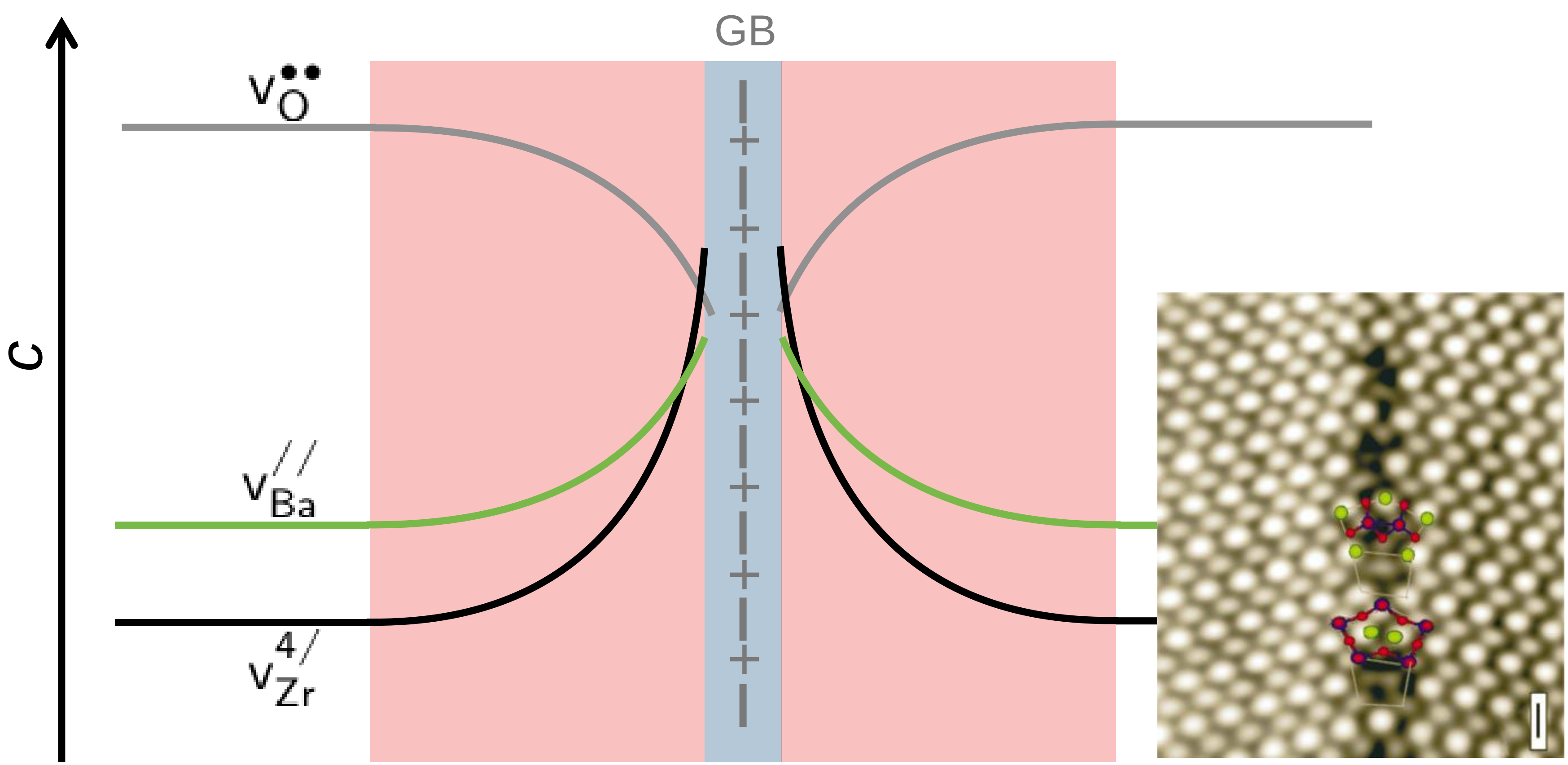


Fig. 3. (a) Perturbation of the mobile charge carrier density calculated for different frequencies of the excitation signal. (b) Equivalent circuit approximation of the calculated frequency response. The parameters are discussed in details in Ref. [23].

J. Jamnik, J. Maier, S. Pejovnik, *Solid State Ionics* 75 (1995) 51-58


Example: $BaZr_{0.9}Y_{0.1}O_{3-\delta}$
Electrical potential
$R_{charge\ transfer}$
$R_{diffusion}$
R_{GB}
$R_{space\ charge\ layer}$
C_{GI}
C_{GB}
$C_{double\ layer}$
$C_{chemical}$
Electrode
Gas
Concentrations
$V_O^{\bullet\bullet}$ $h^{\bullet}$
Bulk of $BaZr_{0.9}Y_{0.1}O_{3-\delta}$
Negative Space charge layer
Positive Core layer
Z_{imag}
Z_{real}
Grain
Grain boundary
Charge transfer + Space charge layer
Mass transfer

Enhanced transport *along* grain boundaries



Concluding remarks

- Core of 2D interfaces have different defect formation energies than bulk
  - Relief of mismatch
    - Grain boundaries
    - Heterophase boundaries
    - Electrode interfaces
    - Surfaces
    - (Dislocations, clusters…)
- Gives variations in charge, electrical potential, and defect concentrations
- Region in bulk where these variations are significant is called the space charge layer (SCL)
  - Symmetric or asymmetric
- SCLs may give enhanced (parallel) or impeded (series) transport
- Modelled through DFT and numerical electrochemical equilibration
- Relatively well developed for grain boundaries
- Applicable also to surfaces and electrodes