UiO : Department of Chemistry
University of Oslo

EERA European Energy Research Alliance

AMPEA Advanced Materials and Processes for Energy Applications

EERA/AMPEA workshop,
Oslo, 7-8 February 2017

Fundamentals of materials for high temperature fuel cells, electrolysers, and gas separation membranes

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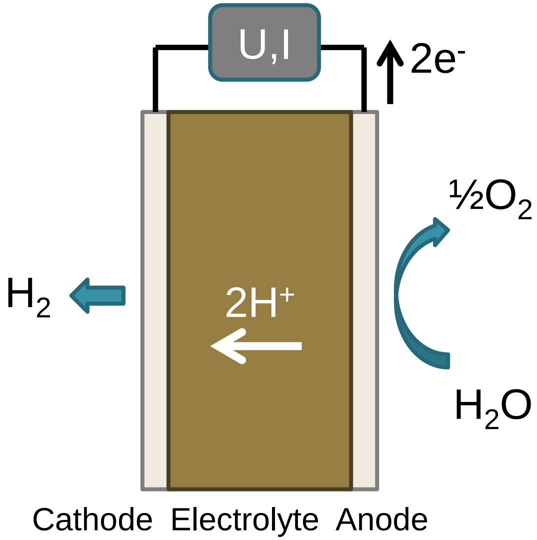
Thanks to students and scientists at UiO, CoorsTek MS AS, ITQ Valencia, NTNU, and SINTEF and for project funding from RCN (FOXCET, ROMA, NaProCs, PROTON, METALLICA) and EU FCH (ELECTRA)

FOXCET FCH Electra

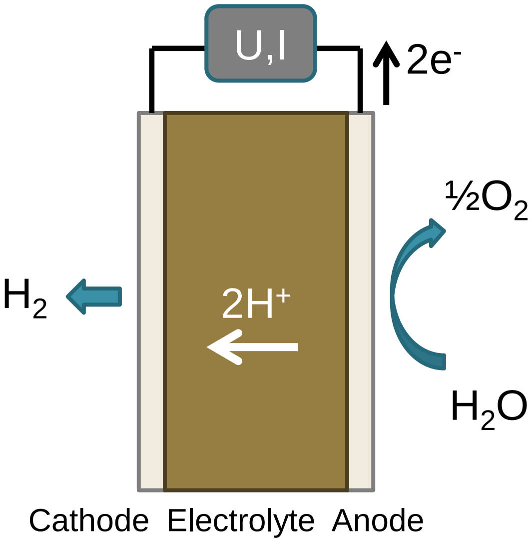


Outline

- Solid HT vs liquid LT
- Solid ion conductors
    - Charge carriers
    - Mobility
    - Trapping
    - Space charge
- Electrodes & surfaces
- Solid HT vs liquid LT

The membrane

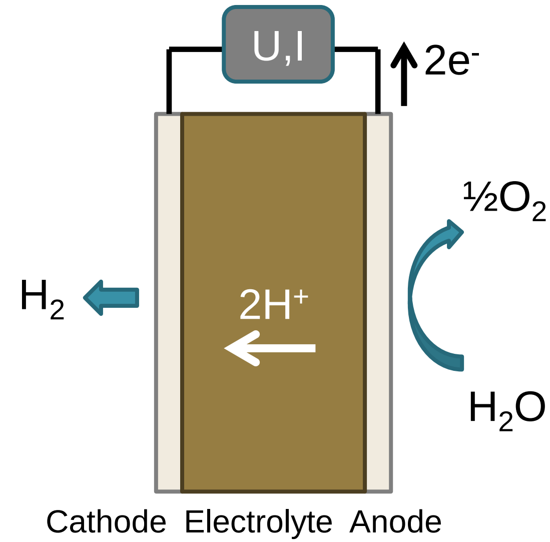
$$\sigma_i = z_i e c_i u_i = z_i F C_i u_i$$



Solids vs liquids HT vs LT

- Solid electrolytes: Ionic compounds
- Liquid electrolytes: Covalent liquids (or ionic liquids)

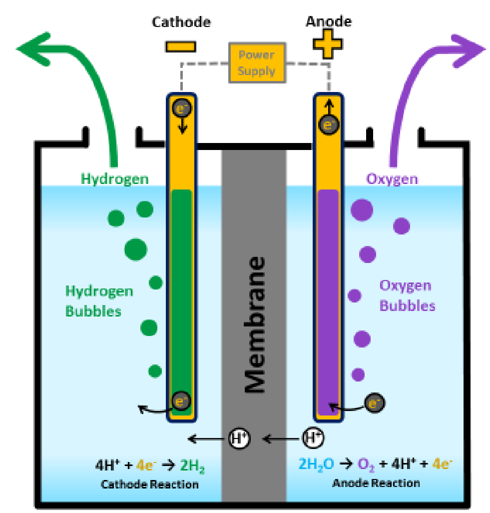
- $BaZrO_3$ $E_g \approx 3.2$ eV
- $H_2O(l)$ $E_g \approx 7$ eV *
- * C. Fang, Wun-Fan Li, R.S. Koster, J. Klimeš, A. van Blaaderen, M.A. van Huis, «The accurate calculation of the band gap of liquid water by means of GW corrections applied to plane-wave density functional theory molecular dynamics simulations«, *PCCP.*, 2015,**17**, 365-375.



- Which has the higher mobility of ionic charge carriers?
- Which has the higher mobility of electronic charge carriers?

- Which has stronger trapping?
- Which has more charge separation and space charge effects?

- Which has better electrode kinetics?
- Which has better thermal management and integration?



Solids vs liquids HT vs LT

- H_2 fuel cells «easy»; Liquid LT or solid-state HT
- C-containing fuels: HT solid-state or ionic liquids

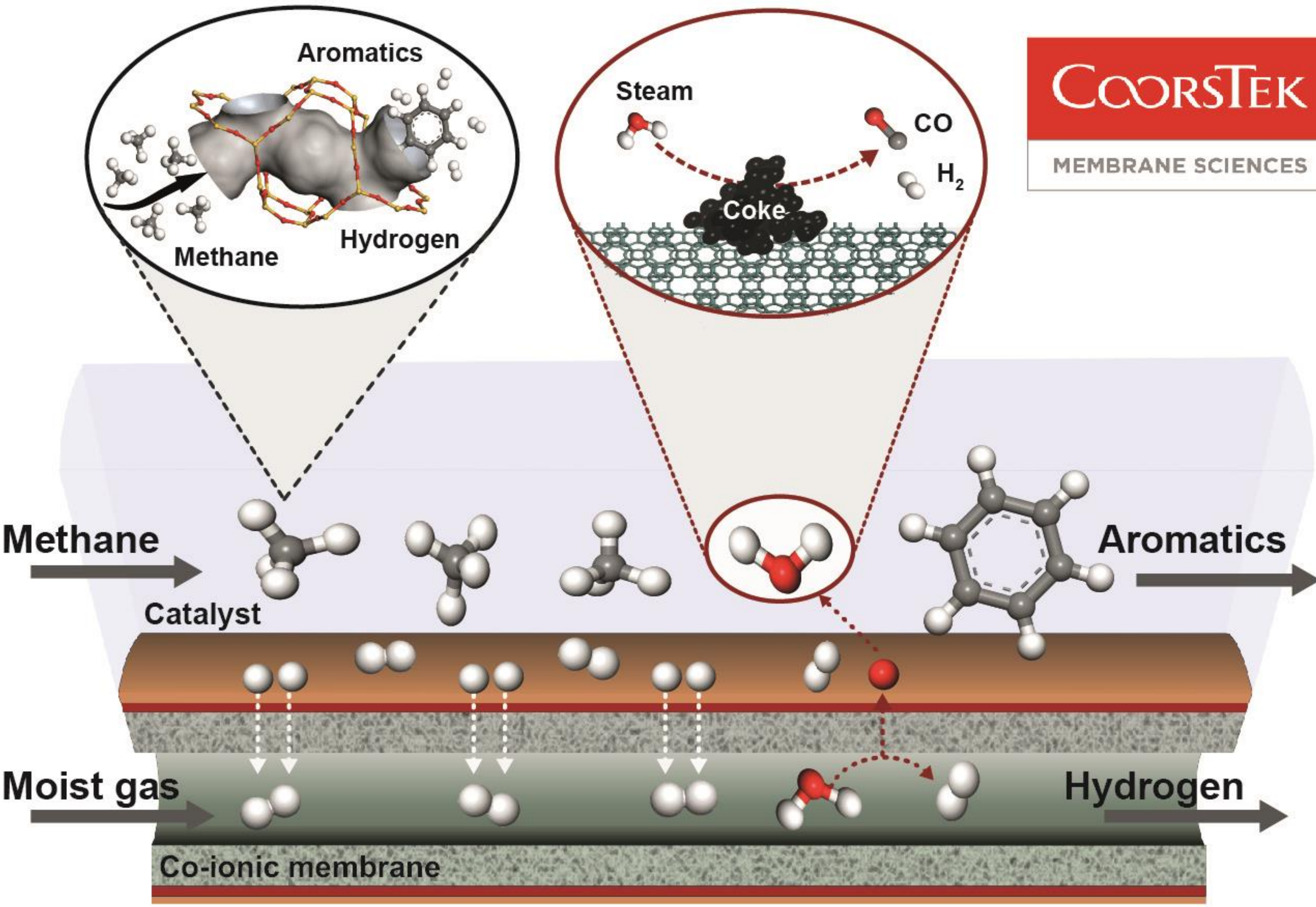
- $H_2O \rightarrow H_2$ electrolysers: Liquid LT, solid-state HT.
  - Faradayic vs thermal efficiency

- Electrochemical and catalytic reactors and pumps: HT

- Mixed conducting gas separation membranes: HT
  - Solid-state. Can ionic liquids be used?

- Li ion batteries?

Catalytic dehydrogenation of natural gas using proton and co-ionic ceramics



CoorsTek
MEMBRANE SCIENCES

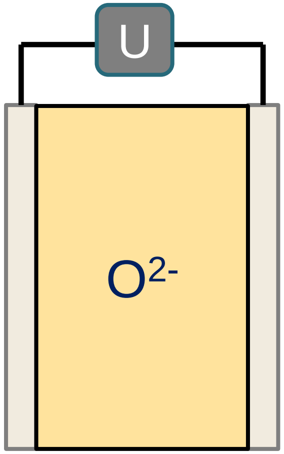
S.H. Morejudo, R. Zanón, S. Escolástico, I. Yuste-Tirados, H. Malerød-Fjeld, P.K. Vestre, W.G. Coors, A. Martínez, T. Norby, J.M. Serra, C. Kjølseth, **"Direct conversion of methane to aromatics in a catalytic co-ionic membrane reactor"**, *Science*, **353** [6299] (2016) 563-566.

Solid-state ionic conductors

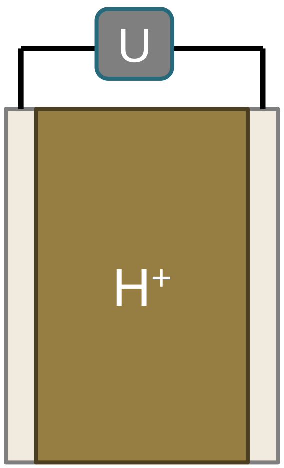
- O^{2-}
  - Acceptor-doped, vacancy mechanism
    - $Y:ZrO_2$, $Gd:CeO_2$, $Sr,Mg:LaGaO_3$
  - Inherently disordered
    - $\delta\text{-}Bi_2O_3$, $La_2Mo_2O_9$, $La_{10}O_{3+\delta}(SiO_4)_6$, $Ca_{12}Al_{14}O_{33}$,

- H^+
  - Acceptor-doped, hydratable (protonatable)
    - $Y:BaZrO_2$, $Sr:LaNbO_4$
  - Inherently disordered, hydratable (protonatable)
    - $La_{28}W_7O_{54}$, $Ca_{12}Al_{14}O_{33}$
  - Solid acids, inherently disordered
    - CsH_2PO_4, $CsHSO_4$

- H_3O^+, Li^+, Na^+
  - $\beta\text{-}Al_2O_3$
  - $La_{2/3-x}Li_{3x}V_{1/3-2x}TiO_3$



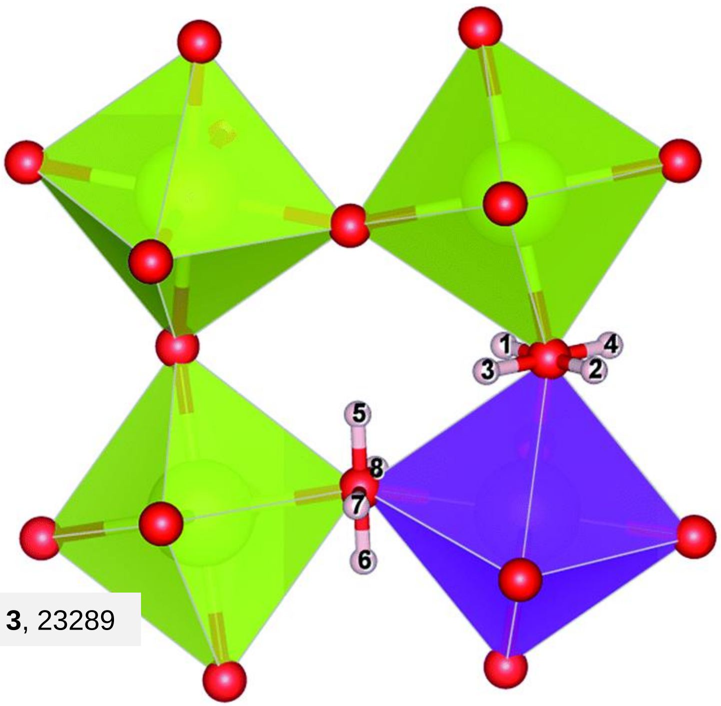
600-800°C



200-600°C

Charge carrier trapping

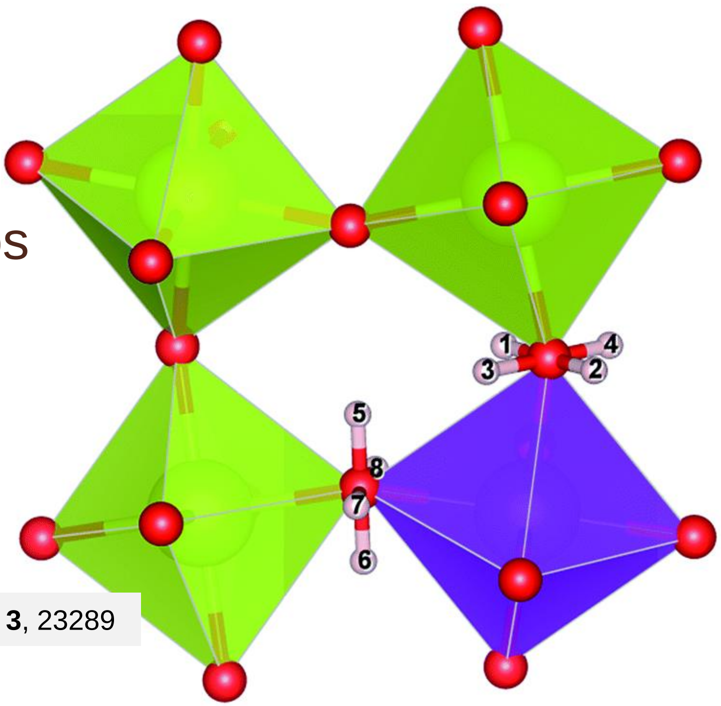
- Charge carriers charge compensated by
  - Dopants
    - Attracted to and associates with (trapped at) immobile dopant
    - Dissociation energy adds to enthalpy of mobility
  - Similar to aqueous acids
    - Dissociation (protolysis)
  - Inherent disorder
    - No trapping



A. Løken *et al.*, *J. Mater. Chem. A*, 2015, **3**, 23289

Charge carrier trapping

- Percolation thresholds
  - Effect of trapping varies with dopant level in a complex manner
- Paired dopant traps
  - May reduce the number of effective traps
  - May reduce hydratability



A. Løken *et al.*, *J. Mater. Chem. A*, 2015, **3**, 23289

Interfaces and extended defects

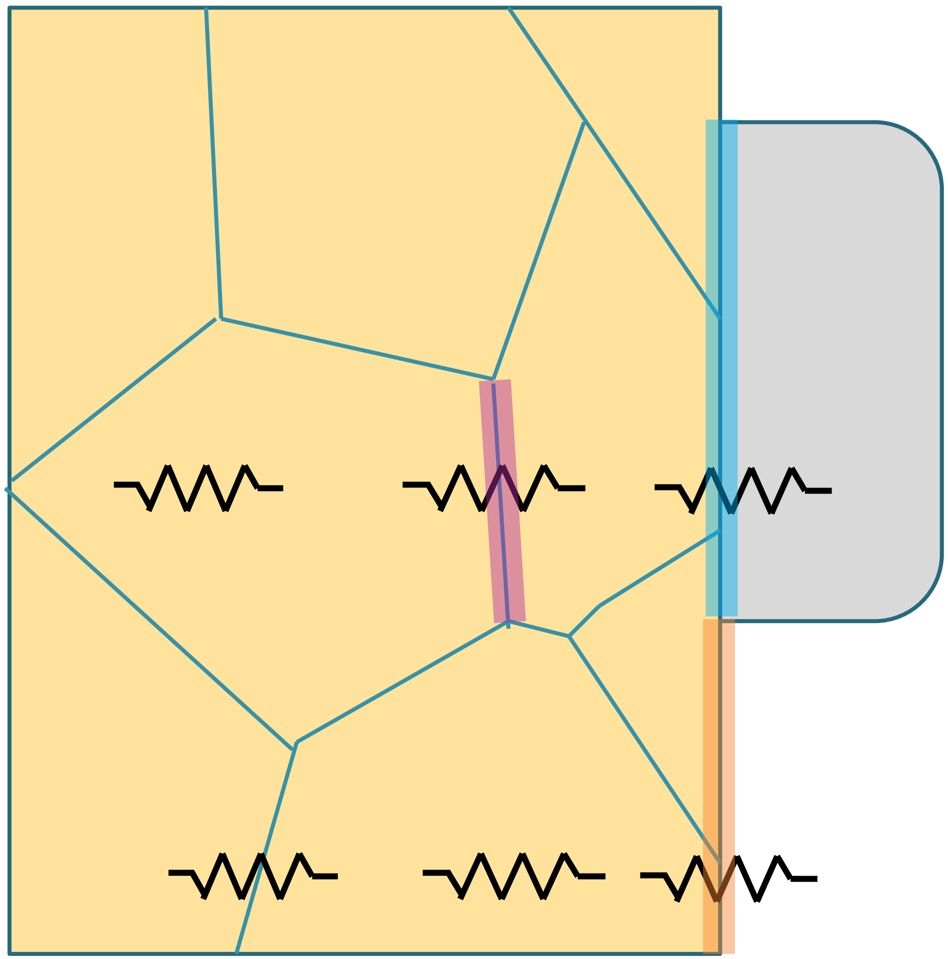
Charge separation

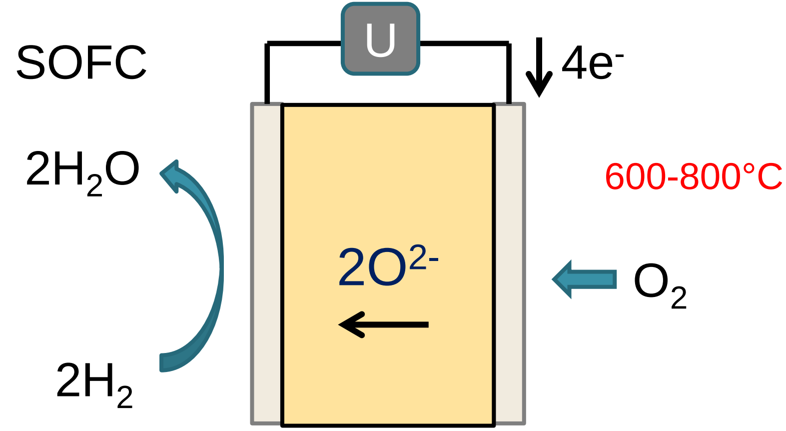
Space charge regions

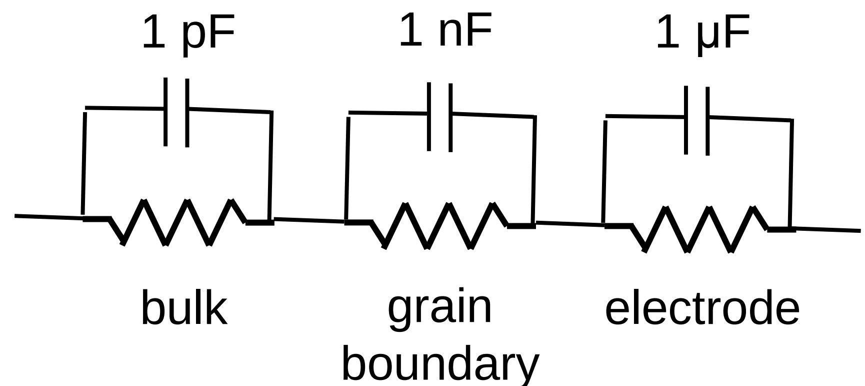
Enrichment or depletion of charge carriers

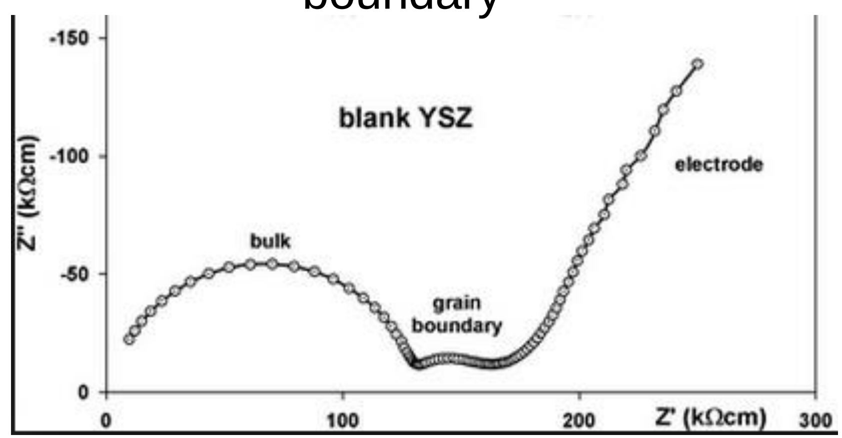
Space charge

- Bulk
- Grain boundaries
- Surfaces, electrodes





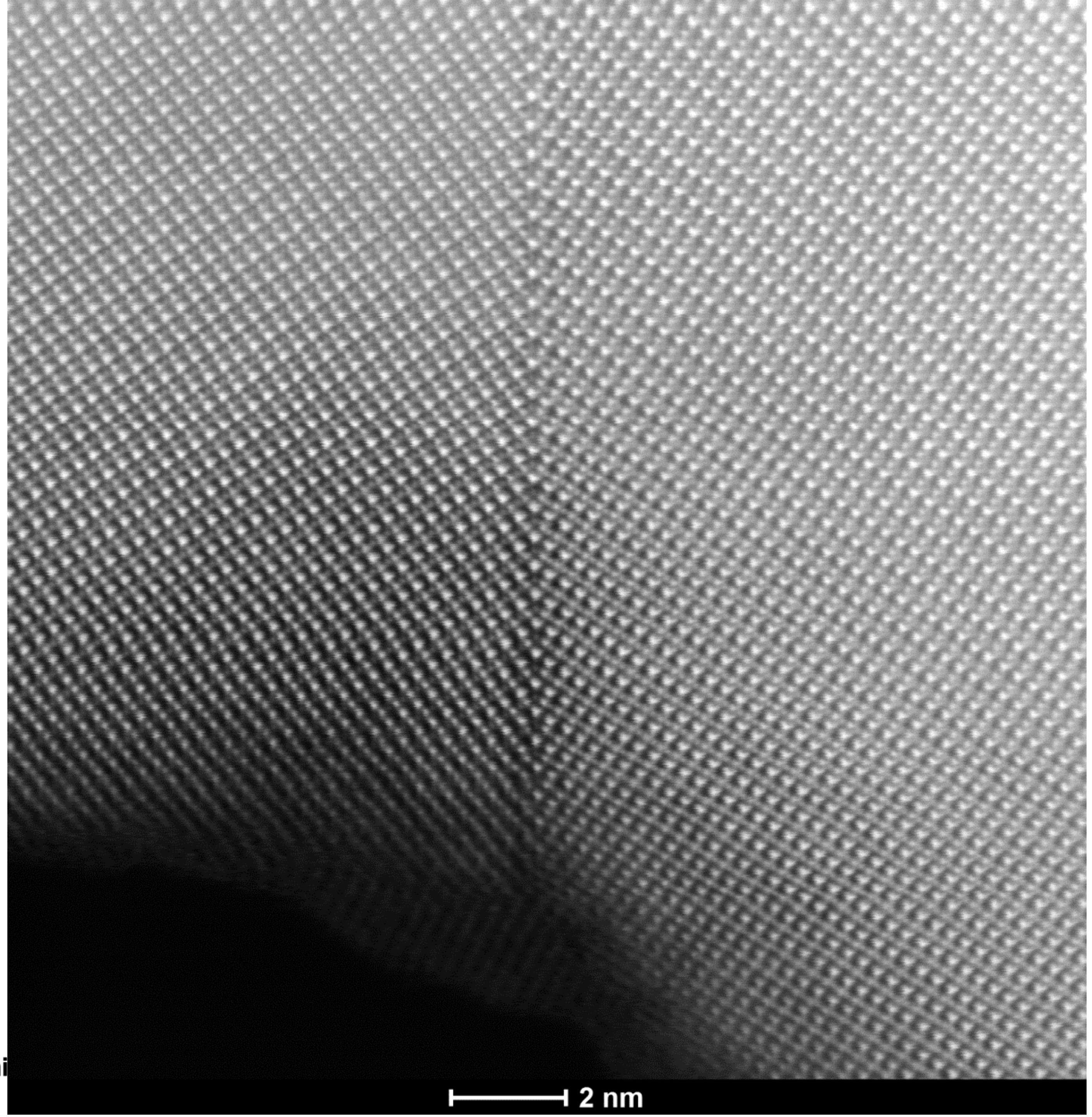




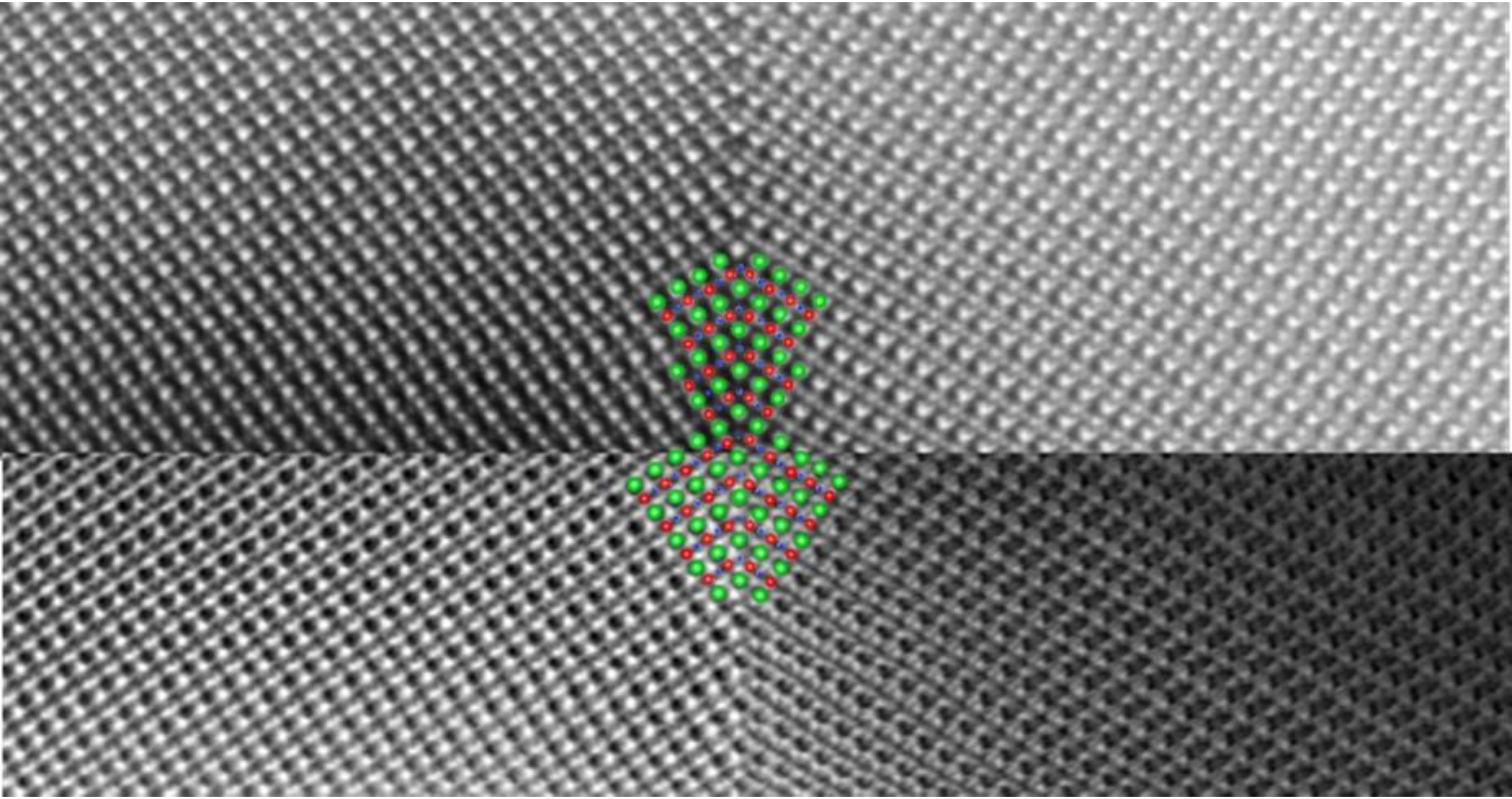
Ruiz-Morales *et al.*, *J. Mater. Chem.*, 2008

Grain boundary in 10%Y-doped $BaZrO_3$

Sample/photo: Adrian Lervik / Phuong D. Nguyen



Grain boundaries in 10%Y-doped $BaZrO_3$
Sample/photo: Adrian Lervik/Phuong D. Nguyen



TEM electron holography

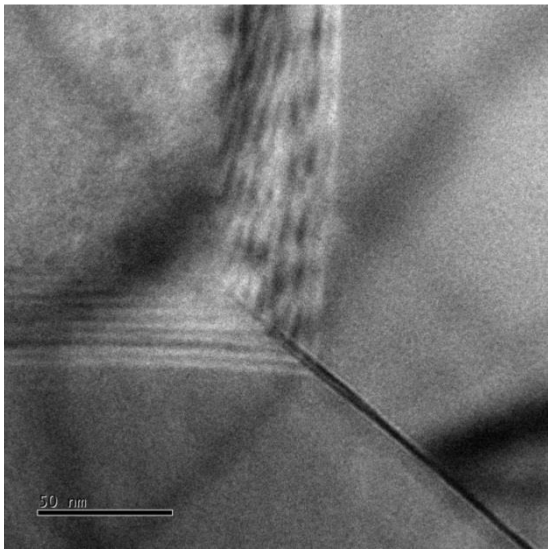
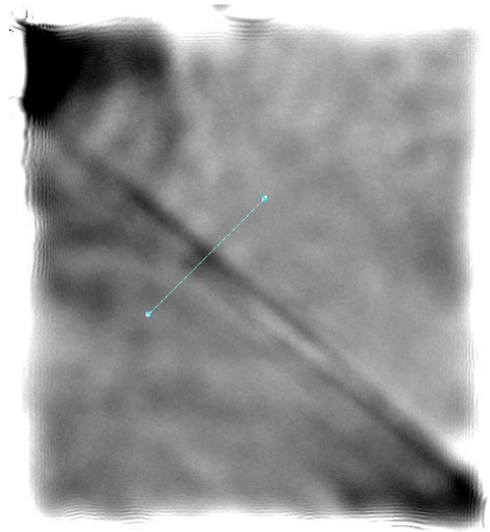
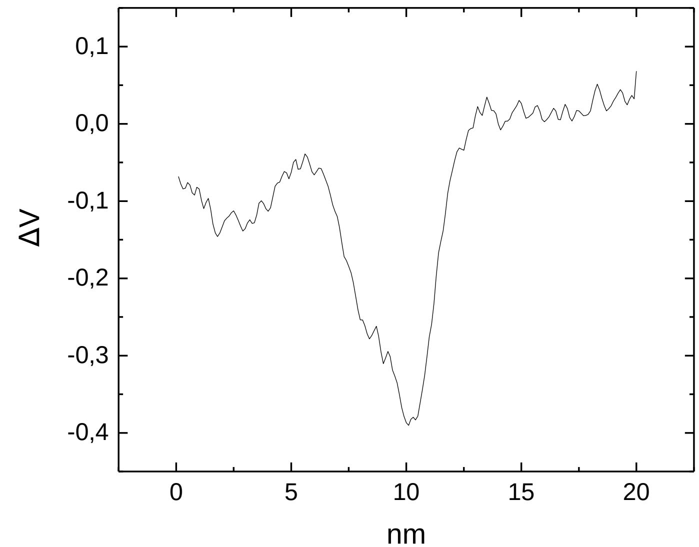


Image of grain boundary



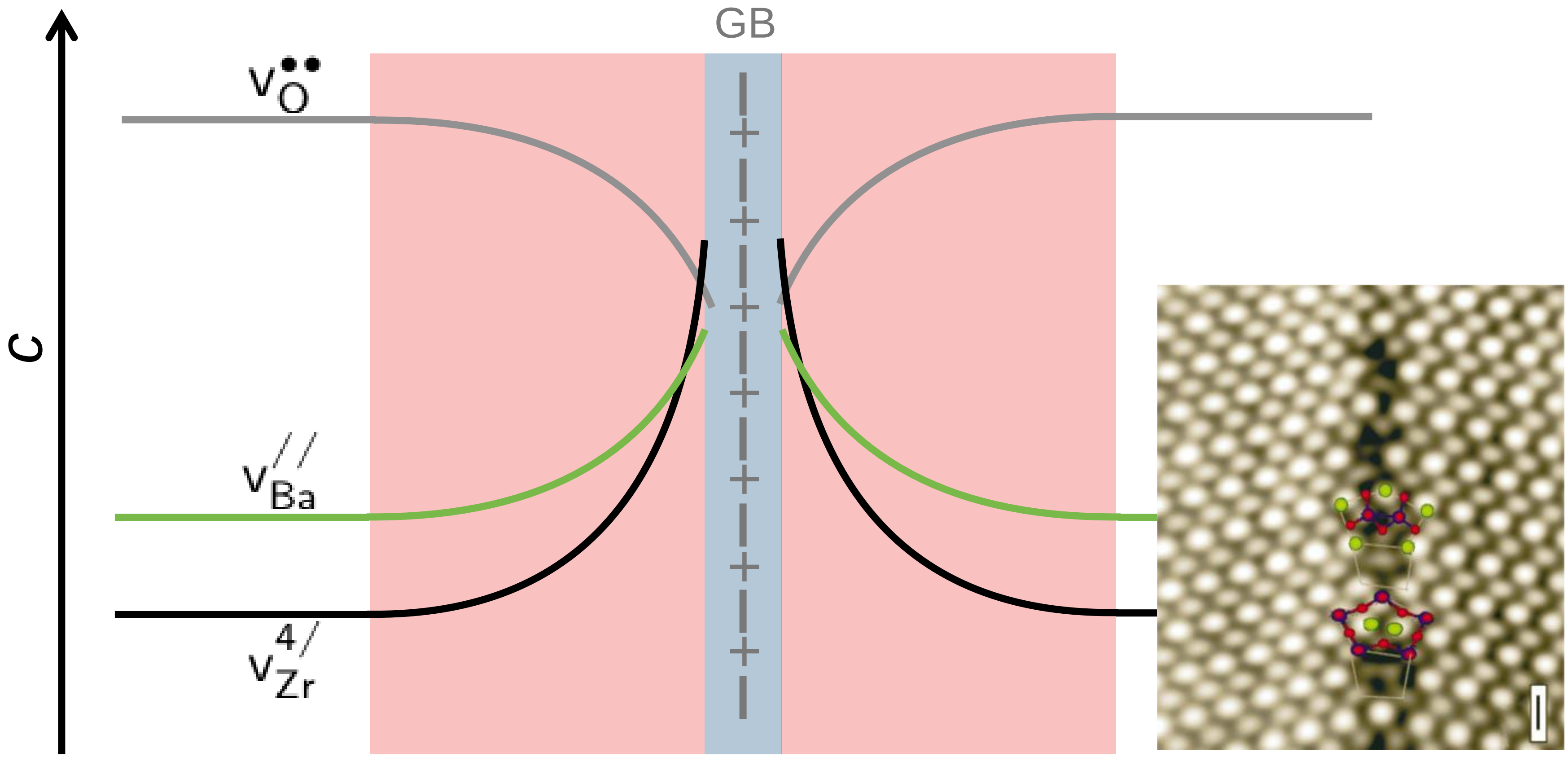
Reconstructed phase map



Potential profile from line scan. Tentatively, the grain boundary core is negative, not positive as expected.

Results by Tarjei Bondevik, PhD fellow in the FOXCET project

Enhanced transport *along* grain boundaries



$SrTiO_3/BaZrO_3/MgO$

600 ℃

Film (multi layers,
layer thickness 8~11 nm)

position1

$BaZrO_3/SrTiO_3$ interface

$BaZrO_3$ [100] (001)/$SrTiO_3$ [100] (001)

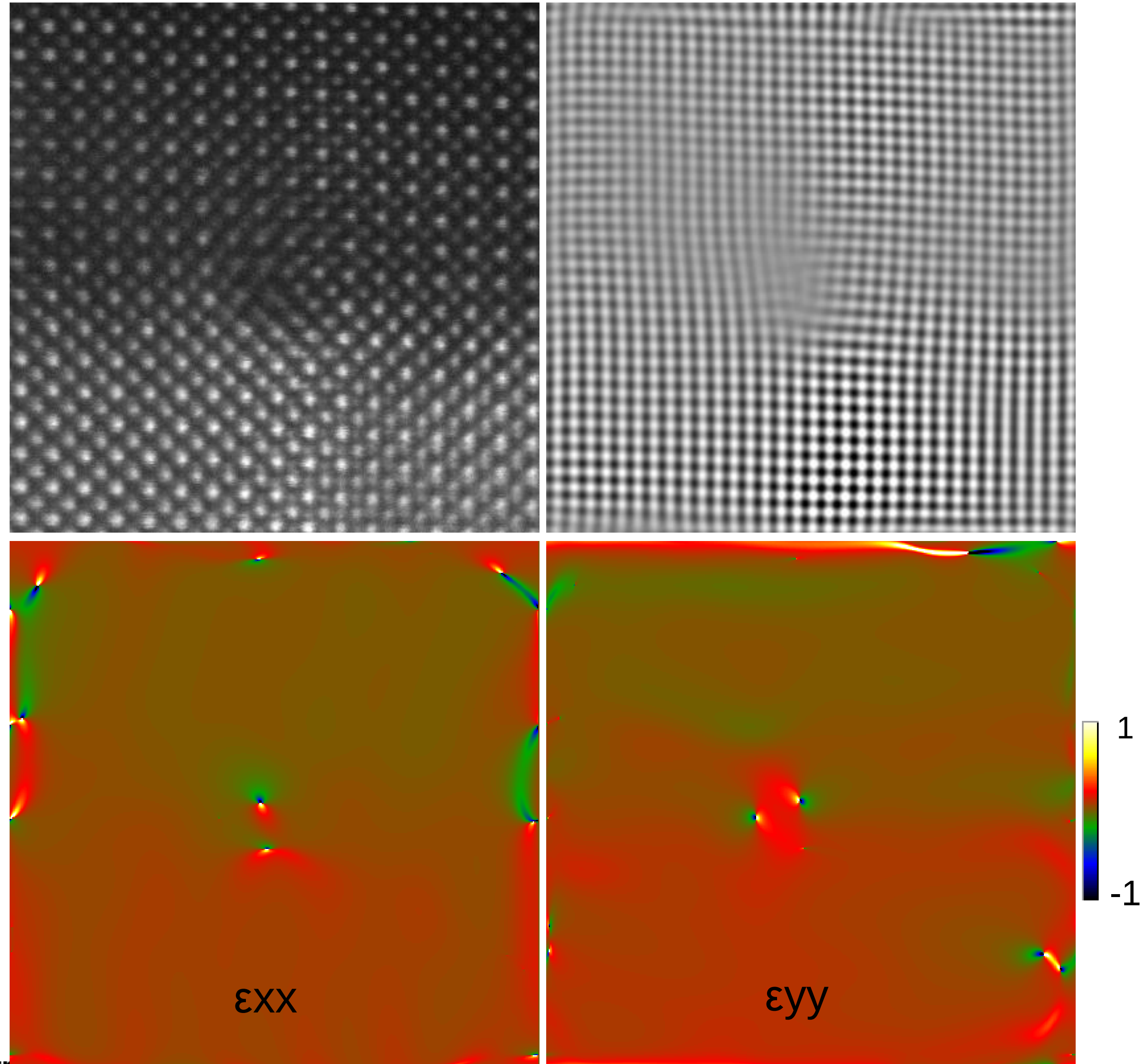
There is dislocation (εxx and εyy) at the interface (flat).

Geometric phase analysis (GPA)

Sample by PLD: Sarmad Saeed
STEM imaging and analysis: Wei Zhan

HAADF-STEM

Fourier filtered



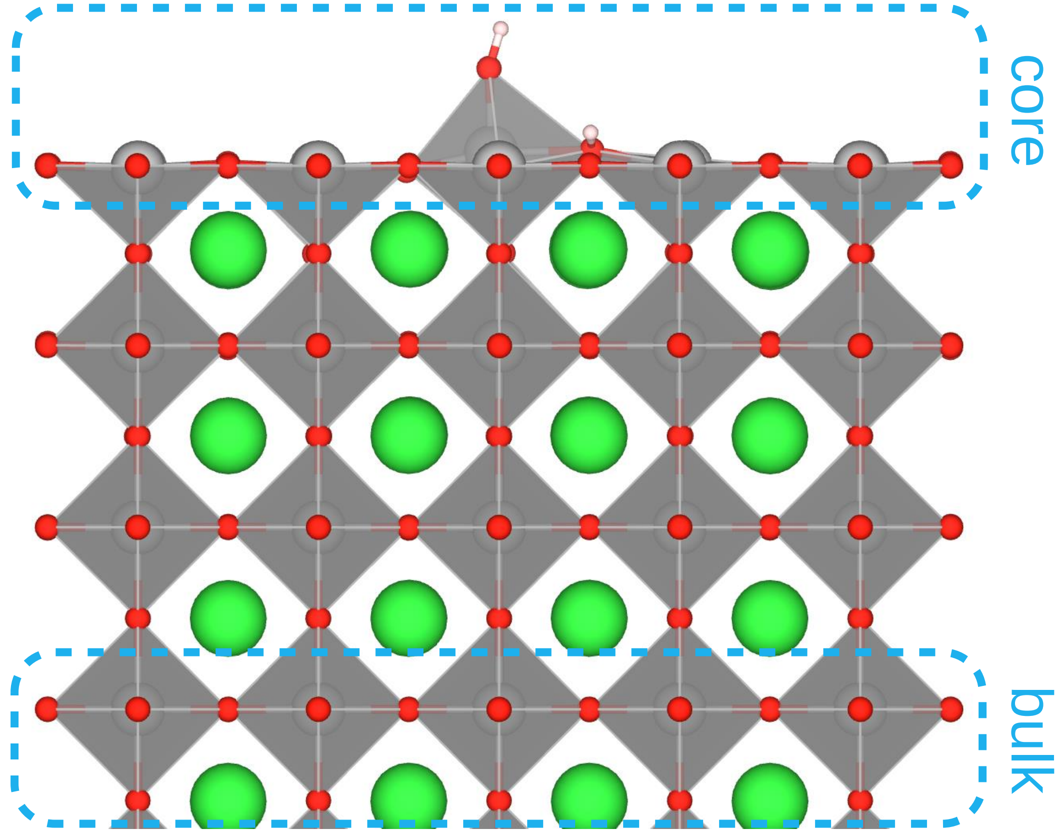
Jonathan Polfus, SINTEF; DFT modelling of interfaces Surface space-charge model

J.M. Polfus, T.S. Bjørheim, T. Norby, R. Bredesen, **“Surface Defect Chemistry of Y-substituted and hydrated $BaZrO_3$ with Subsurface Space-Charge Regions”**, *J. Materials Chemistry A*, **4** [19] (2016) 7437-7444.

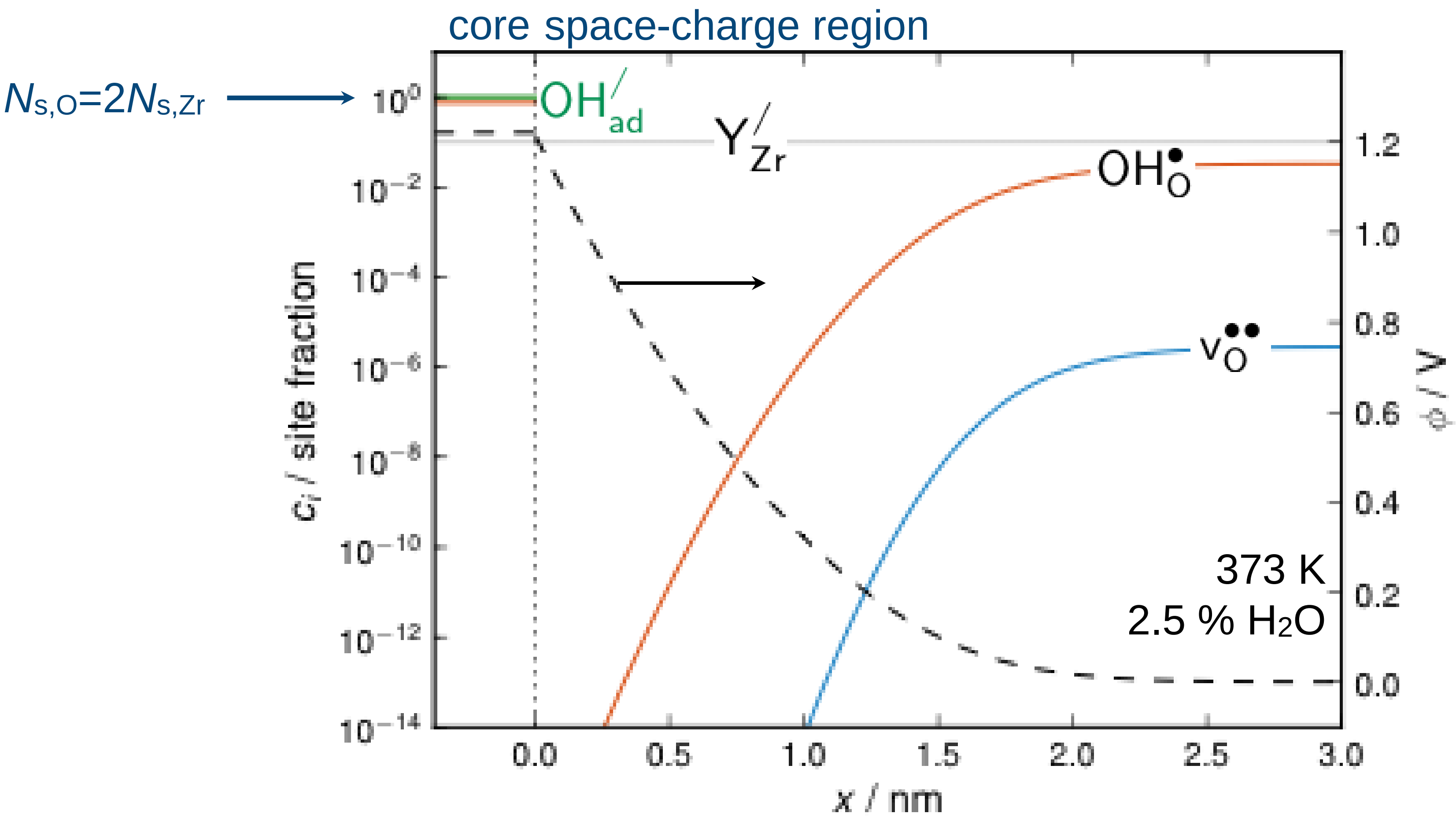
$O_{ad}^{//}$ $OH_{ad}^{/}$

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

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



Potential and concentration profile: 373 K

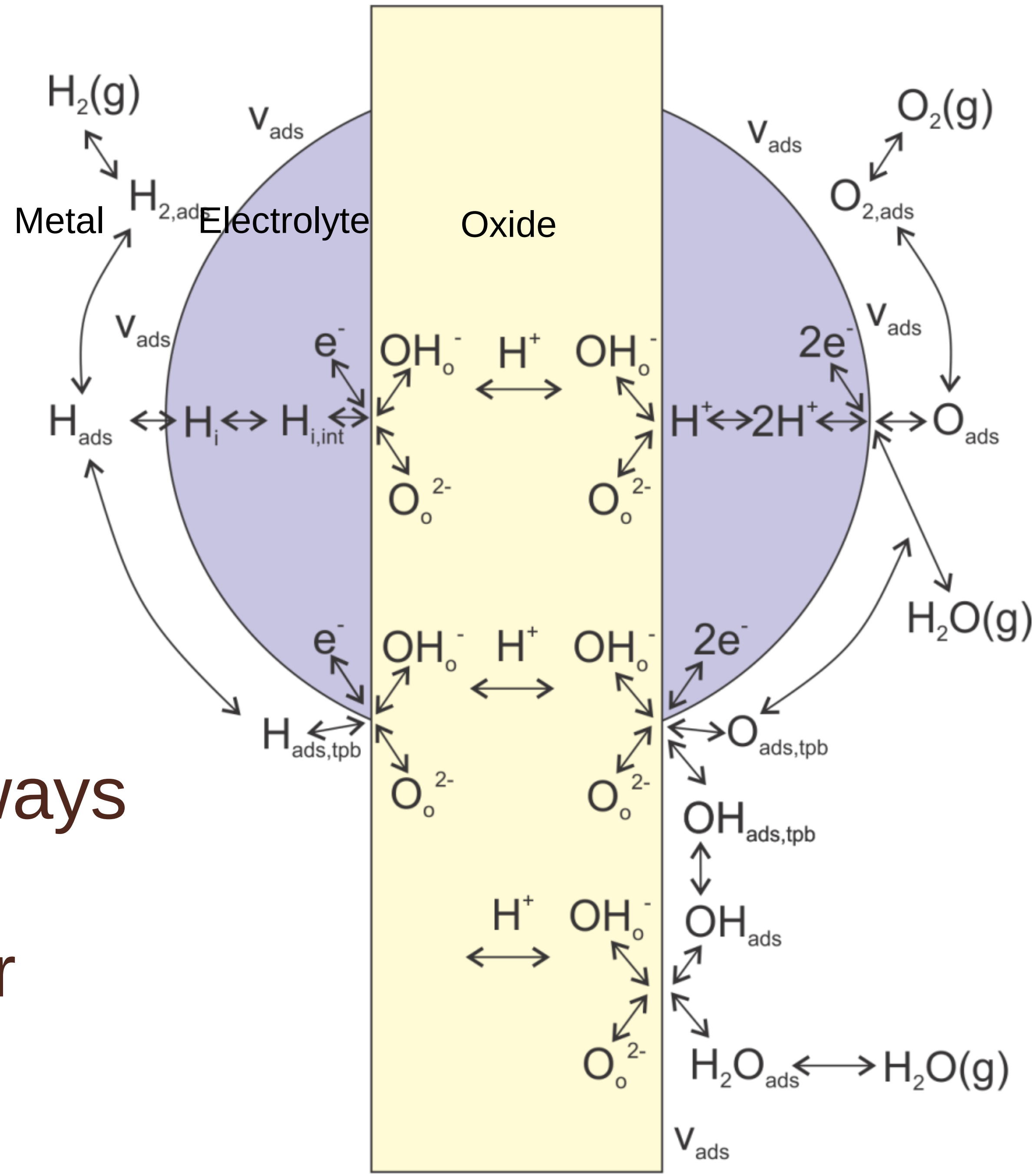


Electrodics

Electrodes

Reaction pathways

Charge transfer

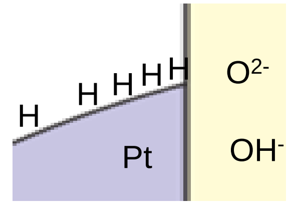


Charge transfer (ct) in H_2+H_2O; Pt, Cu on BZCY

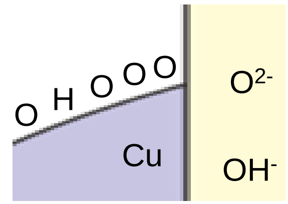
$$\mathrm{H}_{\mathrm{ads,pb}} + \mathrm{O}^{2-}_{\mathrm{O,pb}} \leftrightarrow \mathrm{v}_{\mathrm{ads,pb}} + \mathrm{OH}^{-}_{\mathrm{O,pb}} + \mathrm{e}^{-}$$

$$G^{eq}_{ct,red} = \frac{1}{R^{eq}_{ct,red}} = \frac{n_{red} e i_{0,red}}{kT} = \frac{(n_{red} e)^2}{kT} k^{0}_{ct,red} Q^{\beta_{red}}_{react,red} Q^{1-\beta_{red}}_{prod,red}$$

$$G^{eq}_{ct,Pt/BZCY,red} = \frac{1}{R^{eq}_{ct,Pt/BZCY,red}} = 1000\,\mathrm{S/cm}\exp\left(-\frac{0.93\,\mathrm{eV}}{kT}\right) p_{H_2}^{-1/4}$$



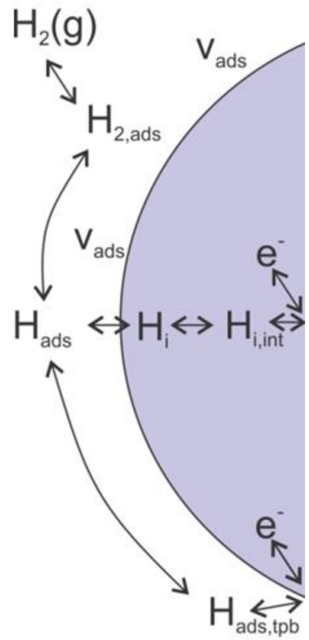
$$G^{eq}_{ct,Cu/BZCY,red} = \frac{1}{R^{eq}_{ct,Cu/BZCY,red}} = 160\,\mathrm{S/cm}\exp\left(-\frac{0.82\,\mathrm{eV}}{kT}\right) p_{H_2}^{+3/4}$$



S.A. Robinson, C. Kjølseth, T. Norby, “Comparison of Cu and Pt point-contact electrodes on proton conducting $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-d}$“, submitted.

Mass transfer (MT) in H_2+H_2O; Pt, Cu on BZCY

- Adsorption
- Dissociation
- Dissolution
- Diffusion



$$G_{mt,Pt/BZCY,red}^{eq} = \frac{1}{R_{mt,Pt/BZCY,red}^{eq}} = 2.6\,\mathrm{S/cm}\exp\left(-\frac{0.73\,\mathrm{eV}}{kT}\right)p_{H_2}^{1/2}$$

Pt mediocre H_2 catalyst

$$G_{mt,Cu/BZCY,red}^{eq} = \frac{1}{R_{mt,Cu/BZCY,red}^{eq}} = 10000\,\mathrm{S/cm}\exp\left(-\frac{1.21\,\mathrm{eV}}{kT}\right)p_{H_2}^{1/2}$$

Cu poor H_2 catalyst. Uses more tpb surface

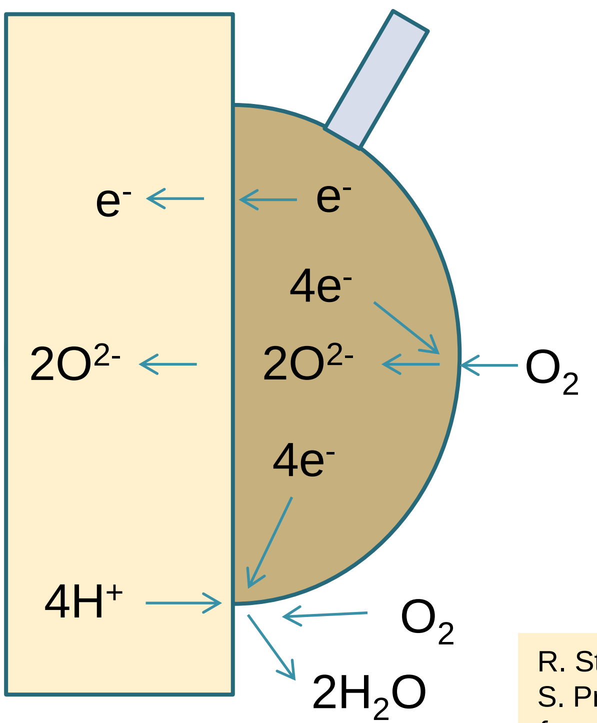
S.A. Robinson, C. Kjølseth, T. Norby, "Comparison of Cu and Pt point-contact electrodes on proton conducting $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-d}$", submitted.

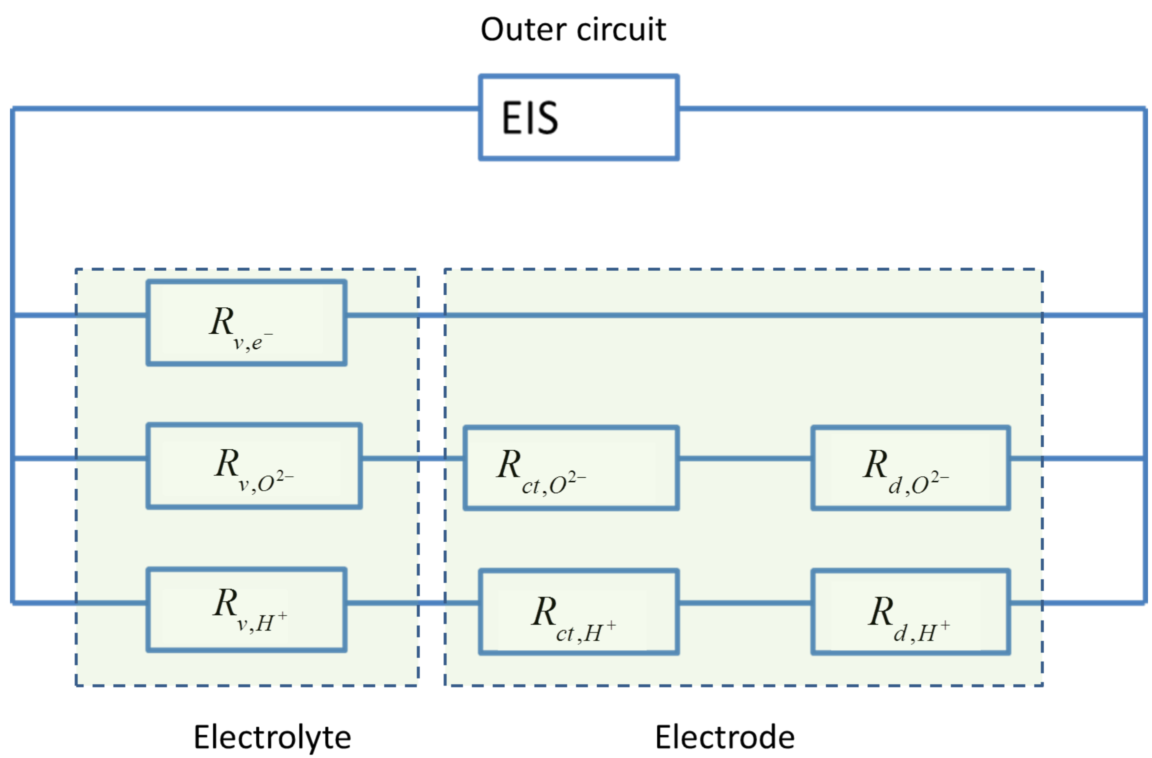
PCFC oxygen electrodes (cathodes)

- Mixed conductivity: protons, oxide ions, electrons (holes)

Typical oxide H^+ conductor

Typical PCFC cathode

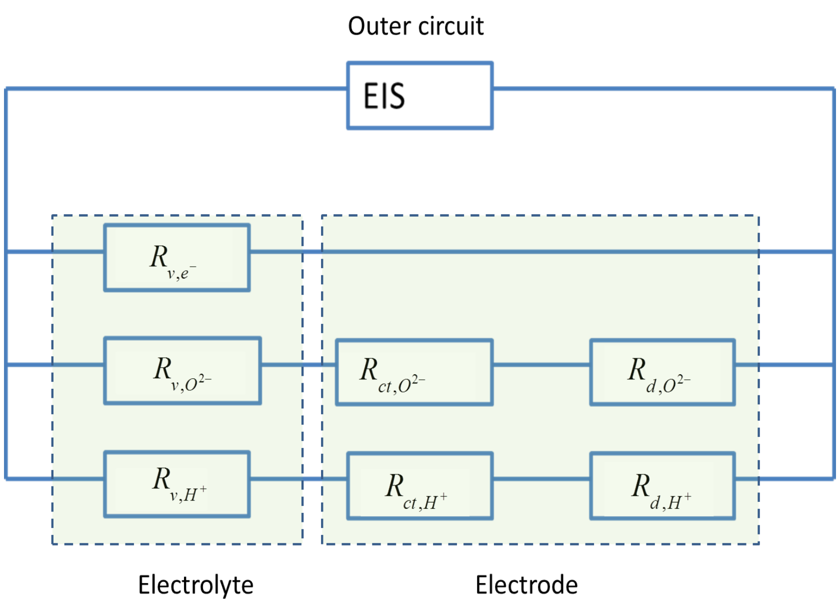


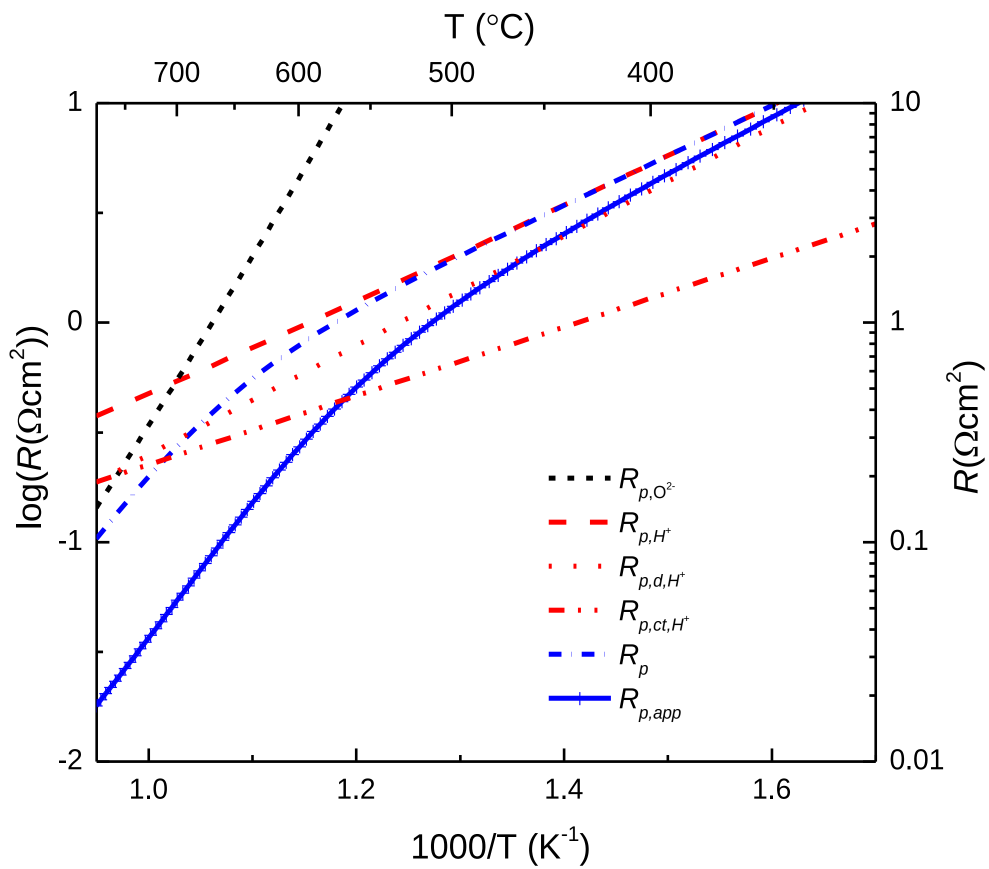


R. Strandbakke, V. Cherepanov, A. Zuev, D.S. Tsvetkov, C. Argirusis, G. Sourkouni-Argirusis, S. Prünte, T. Norby, *"Gd- and Pr-based double perovskite cobaltites as oxygen side electrodes for proton ceramic fuel cells and electrolyser cells", Solid State Ionics*, **278** (2015) 120.

Perovskite electrode on $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ (BZCY)

- Modelling by fitting all data
- Protons vs oxide ions
- Effect of electronic conduction
- CT and MT(d)





Jamnik & Maier 1995; Shouldn't electrodes have space charge layers, too?

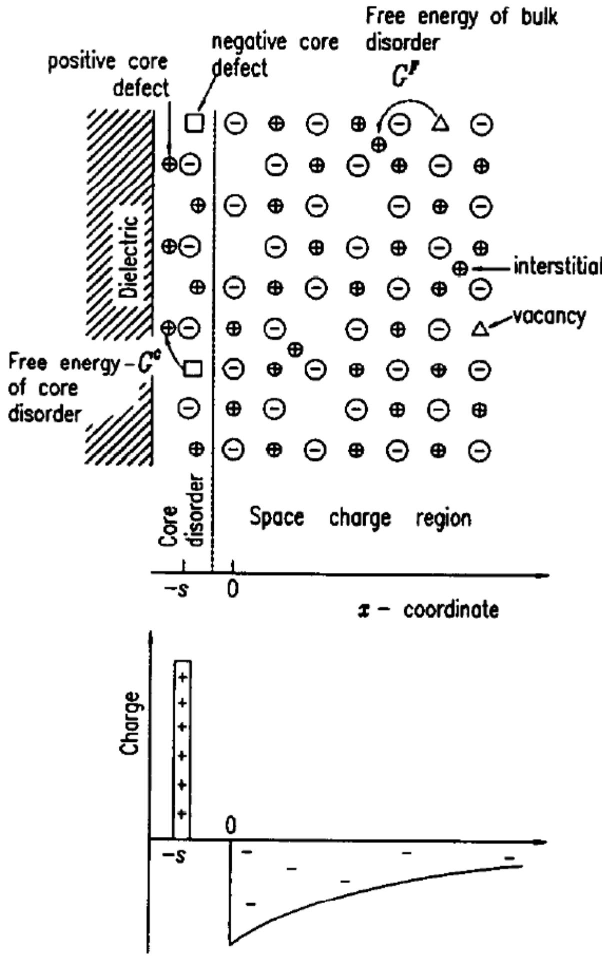


Fig. 1. Schematic picture of the A/MX interface describing the core and the space charge region.

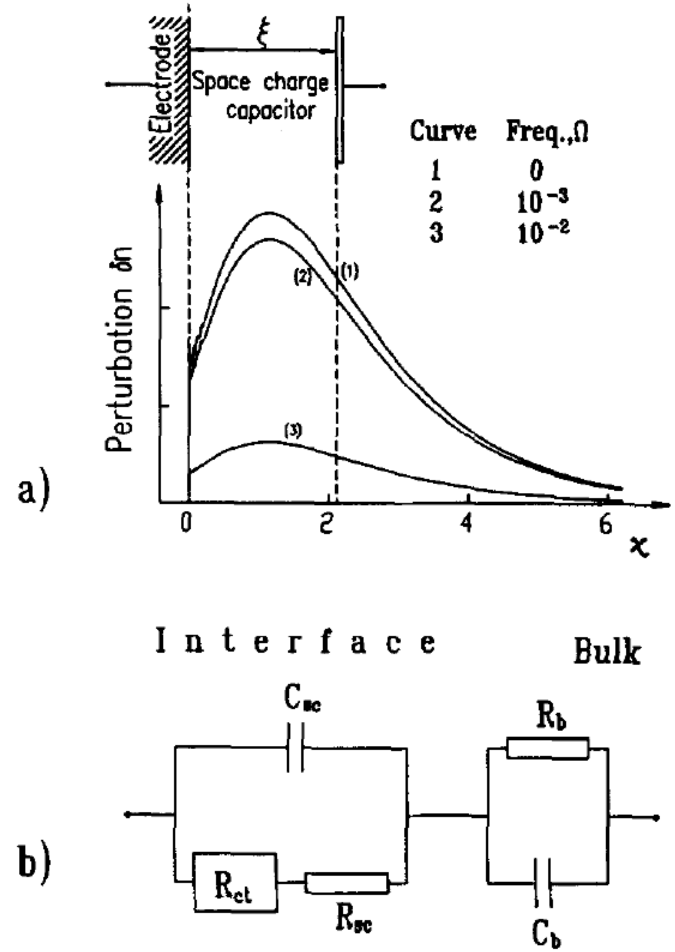
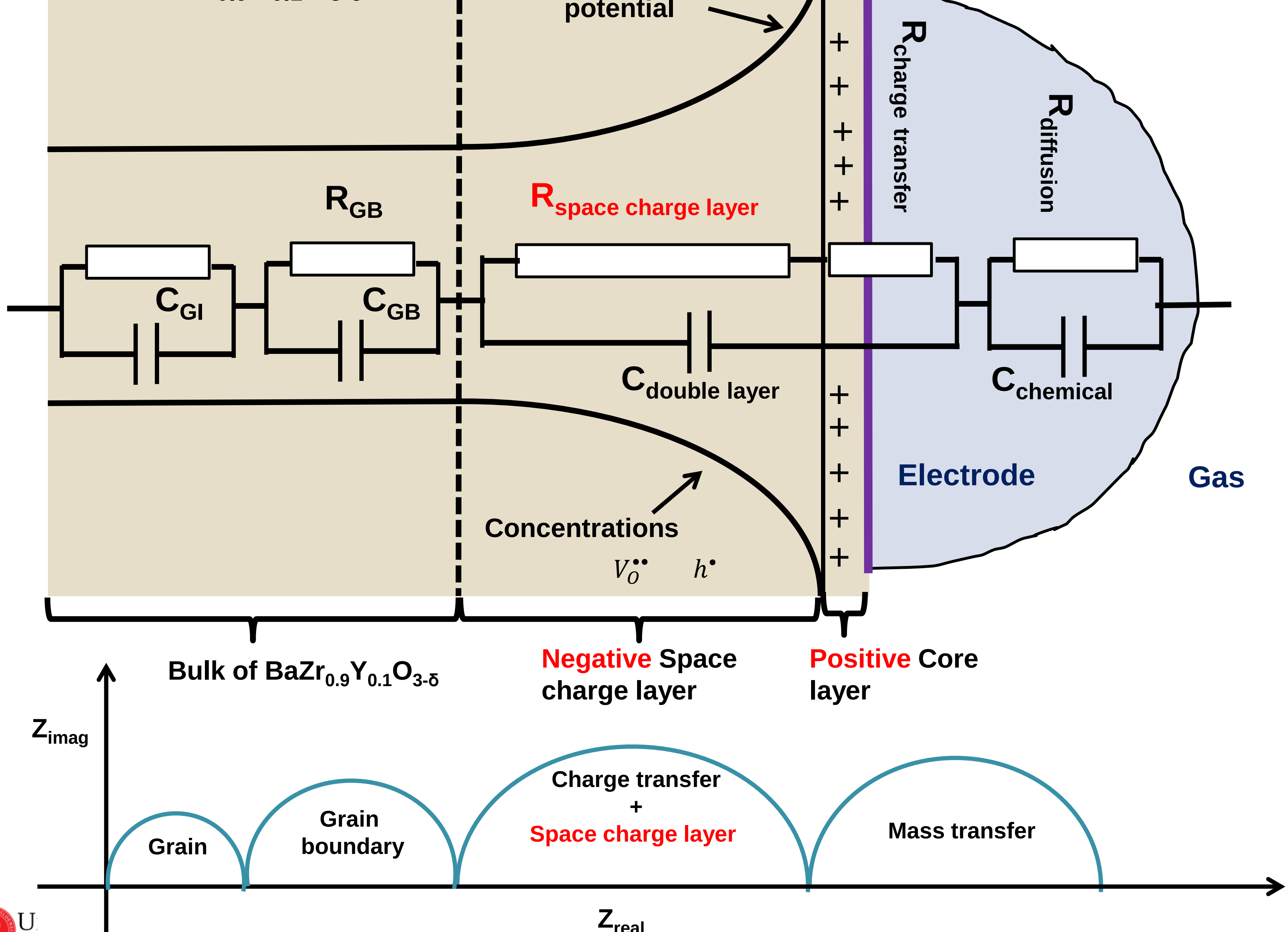


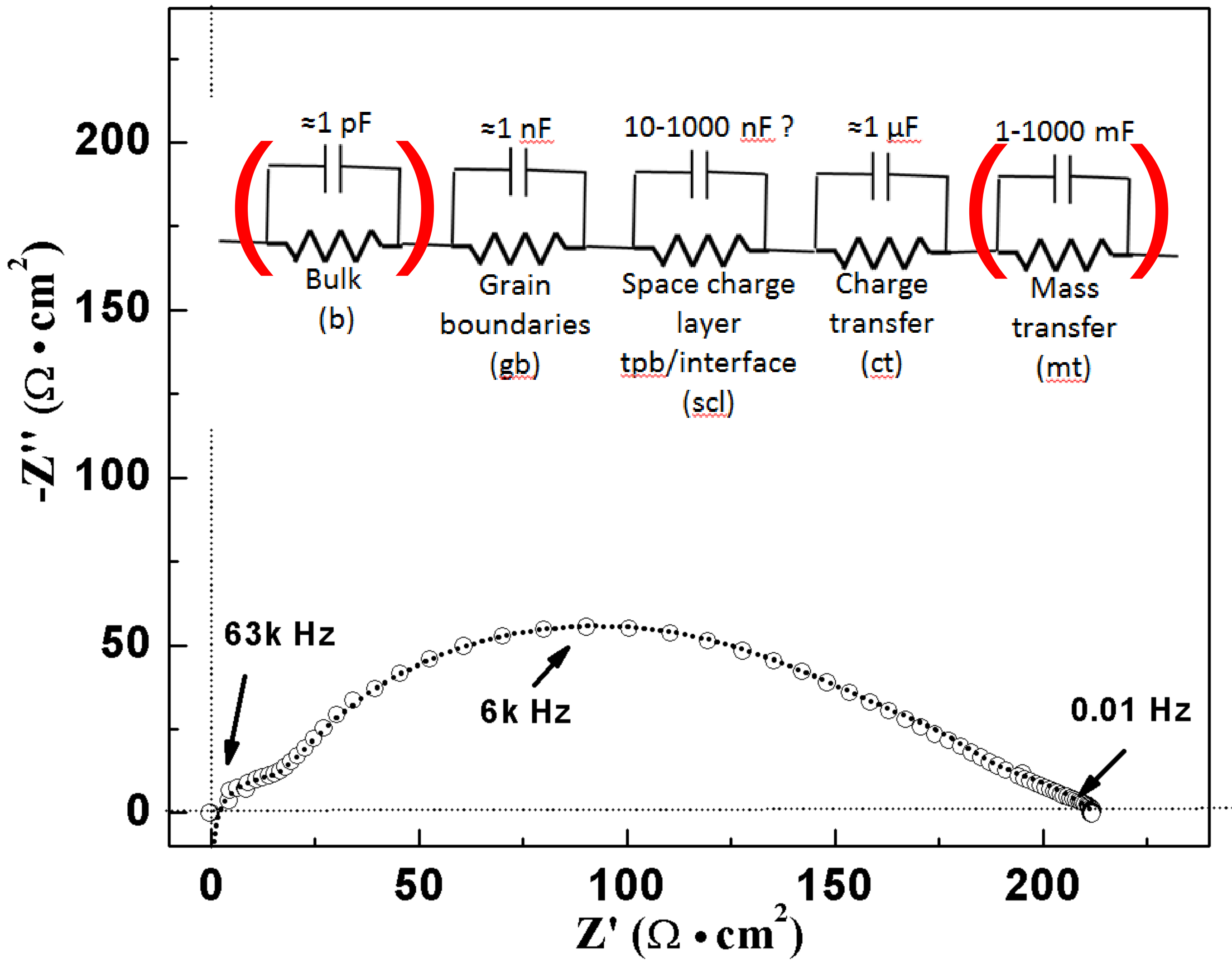
Fig. 3. (a) Perturbation of the mobile charge carrier density calculated for different frequencies of the excitation signal. (b) Equivalent circuit approximation of the calculated frequency response. The parameters are discussed in details in Ref. [23].

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

Example: $BaZr_{0.9}Y_{0.1}O_{3-\delta}$

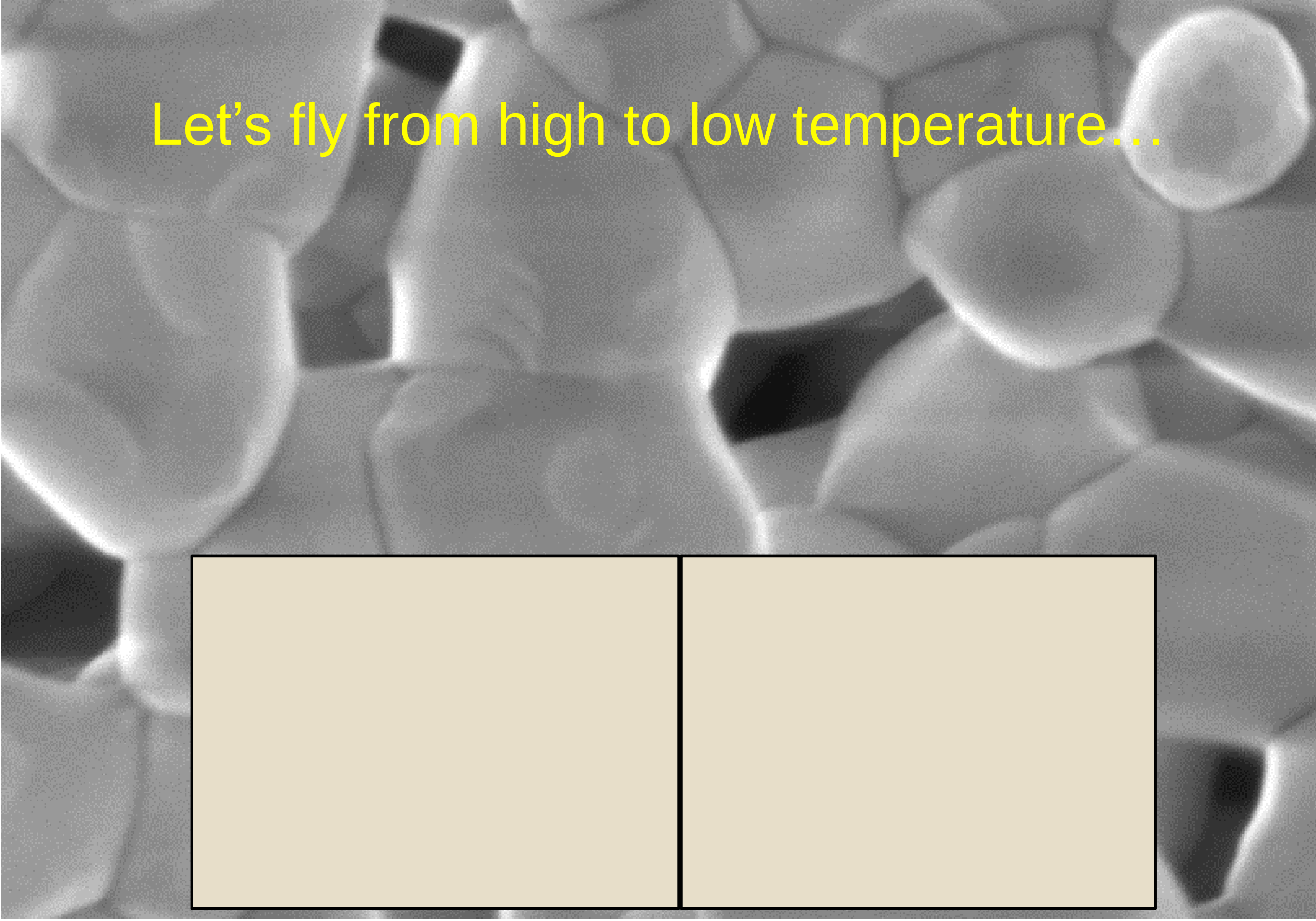


B+GB+SCL+CT for nanograined Ni on BZY in H_2+H_2O



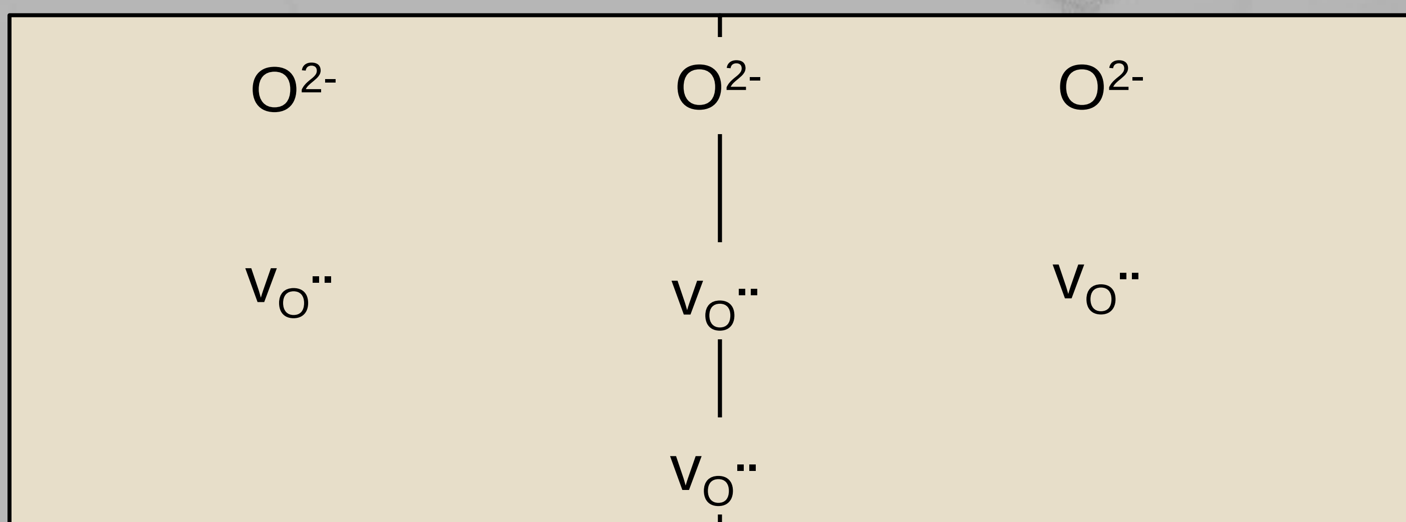
Min Chen, T. Norby, "Space Charge Layer Effect at the Ni/$BaZr_{0.9}Y_{0.1}O_{3-\delta}$ Electrode Interface in Proton Ceramic Electrochemical Cells", under publication

Let’s fly from high to low temperature…



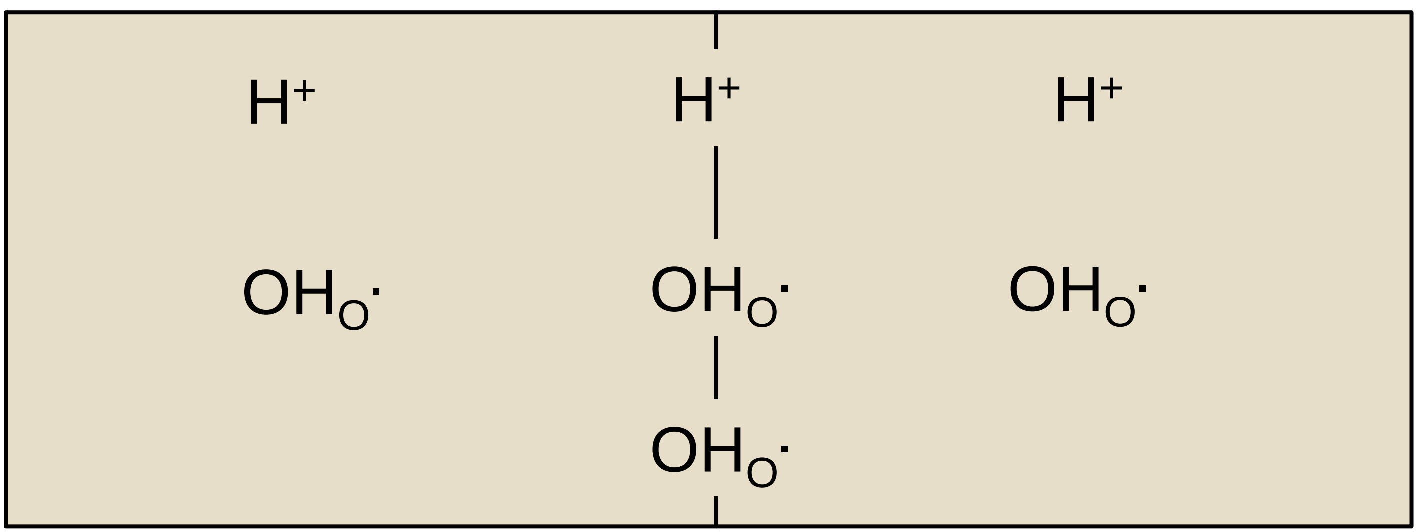
Porous oxide ceramic

- Acceptor doped; oxygen vacancies
- High temperatures – dry atmospheres
- Bulk oxide ion conduction
- Grain boundary resistance



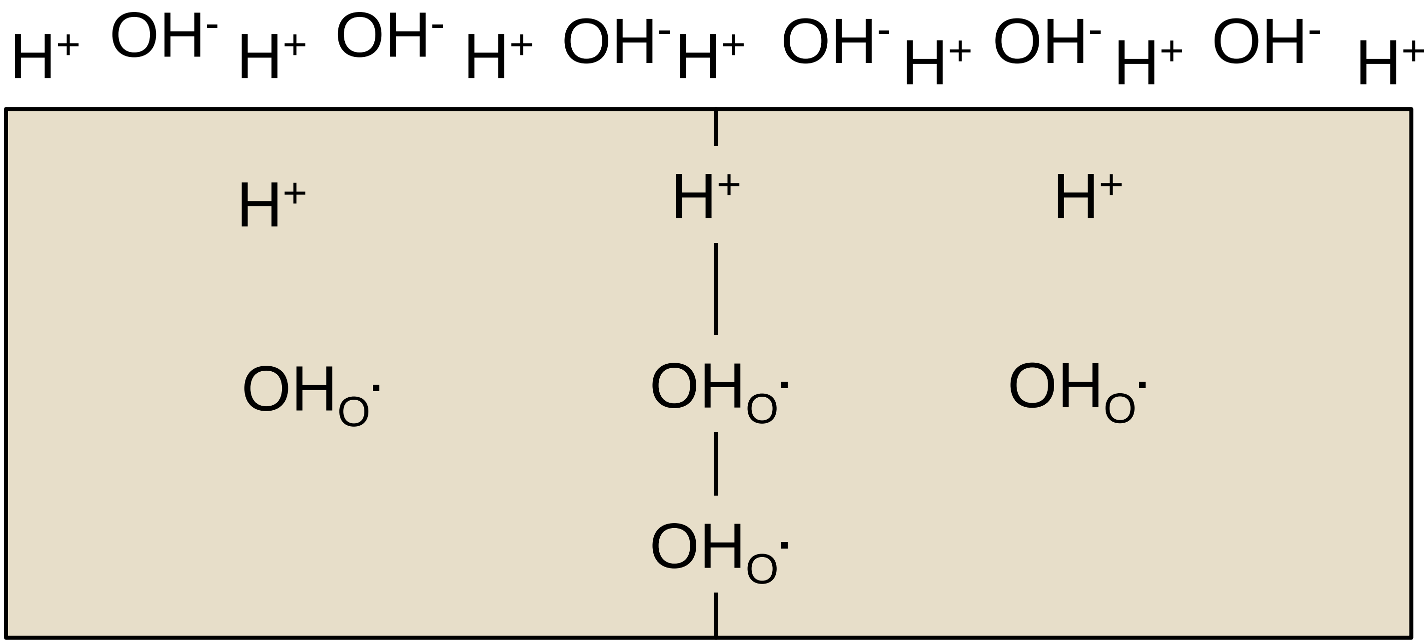
Porous oxide ceramic

- Lower temperatures – wet atmospheres
- Hydrated, protonated
- Bulk proton conduction
- Grain boundary resistance



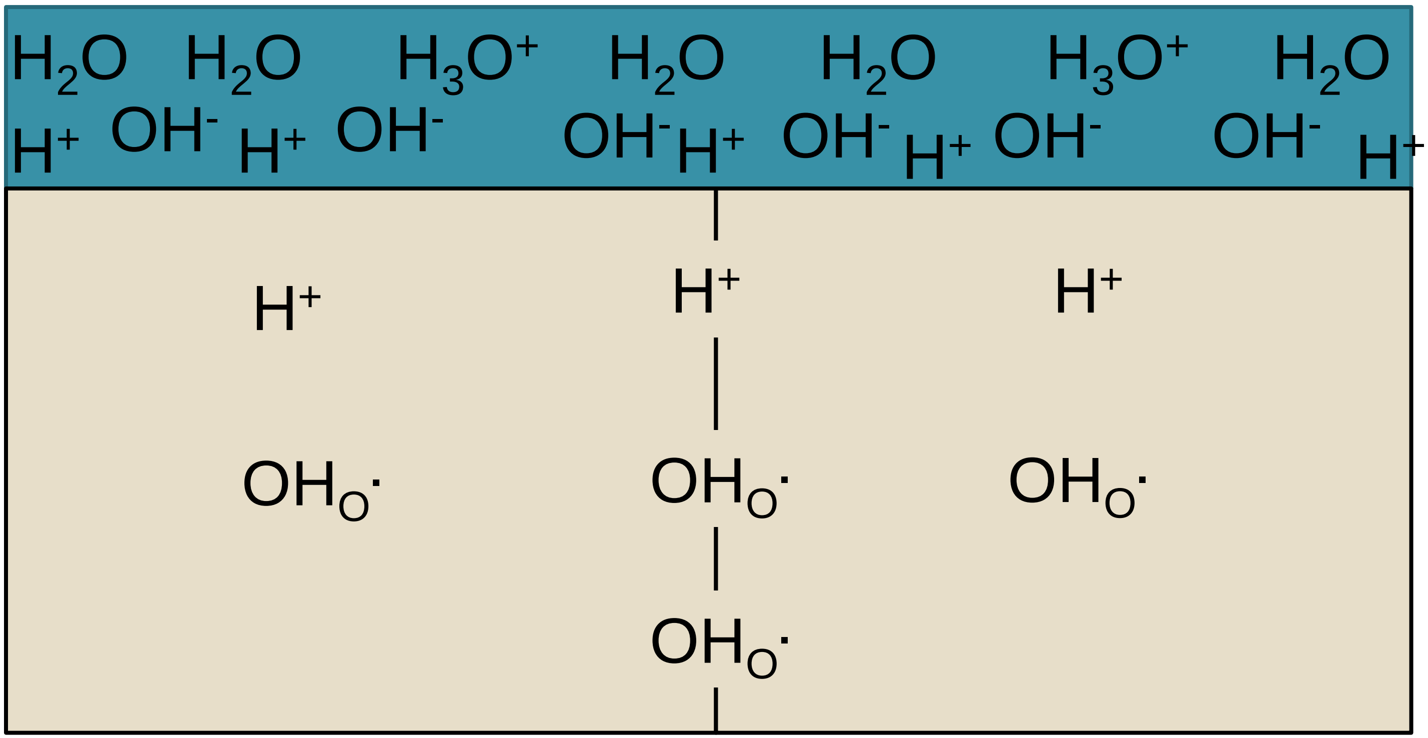
Porous oxide ceramic

- Intermediate temperatures – wet atmospheres
- Surface chemisorbed water
- Surface proton conduction



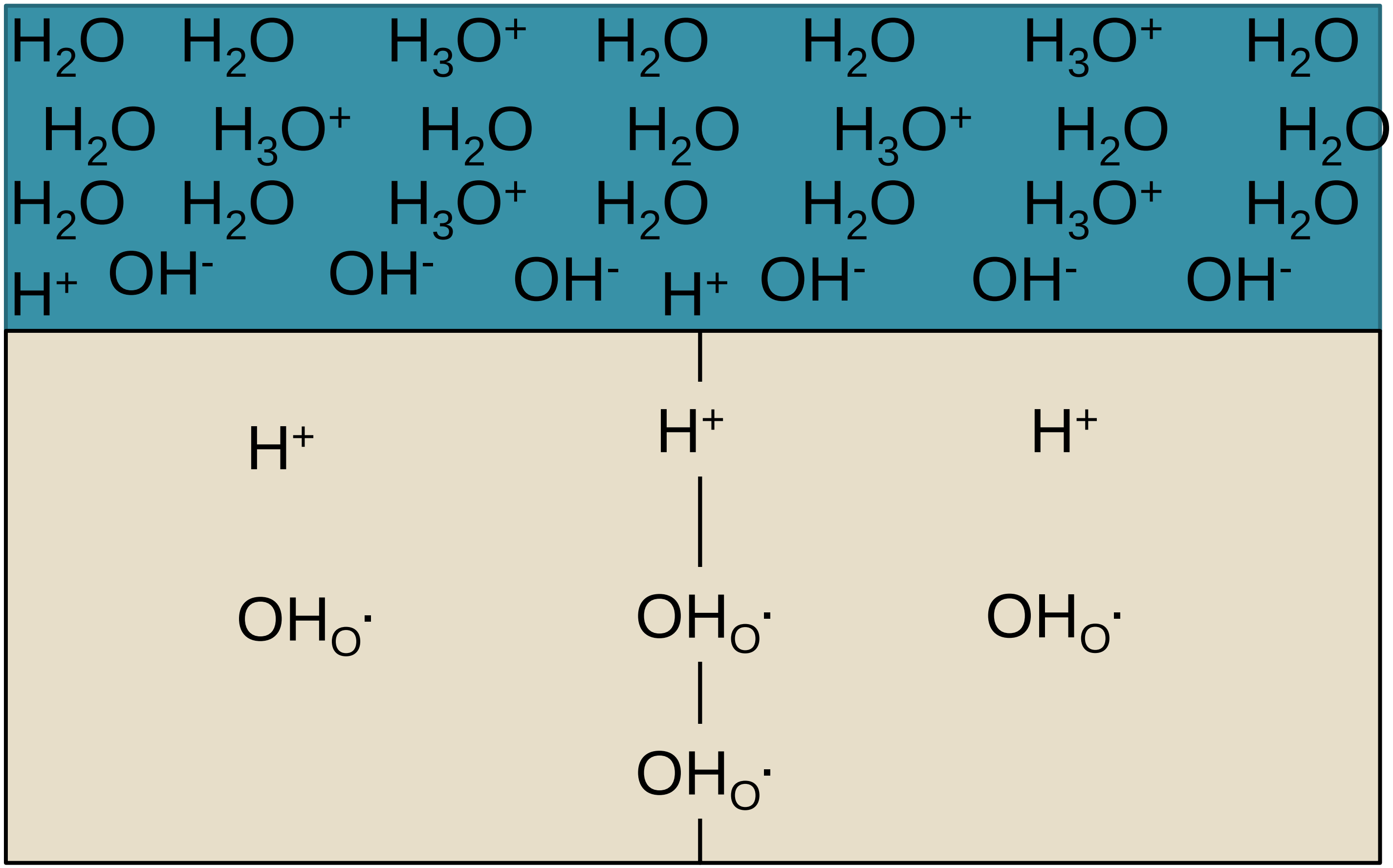
Porous oxide ceramic

- Lower temperatures – wetter atmospheres
- Surface physisorbed water – one layer – «ice-like»



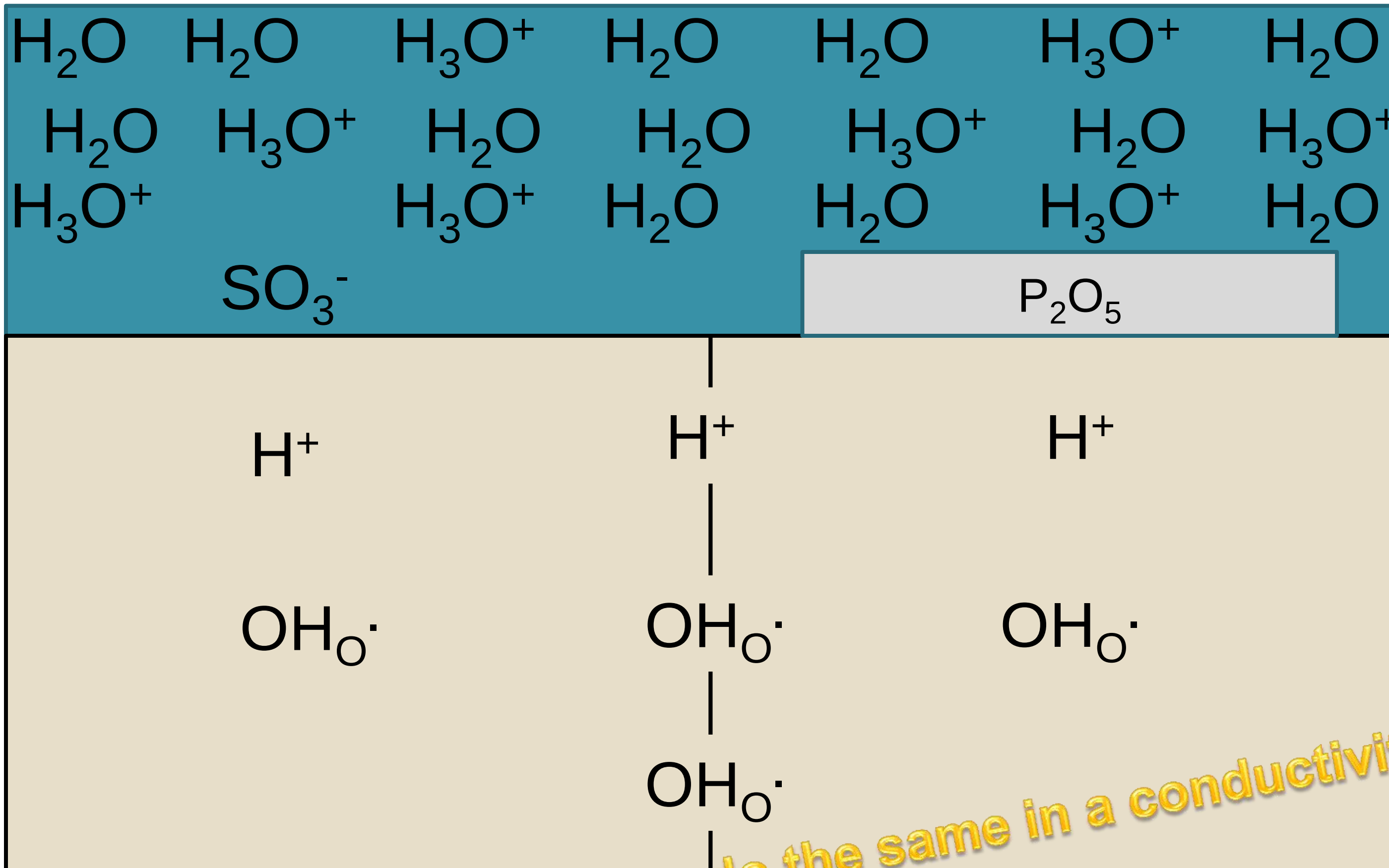
Porous oxide ceramic

- Lower temperatures – wetter atmospheres
- Surface physisorbed water – multilayer – «water-like»

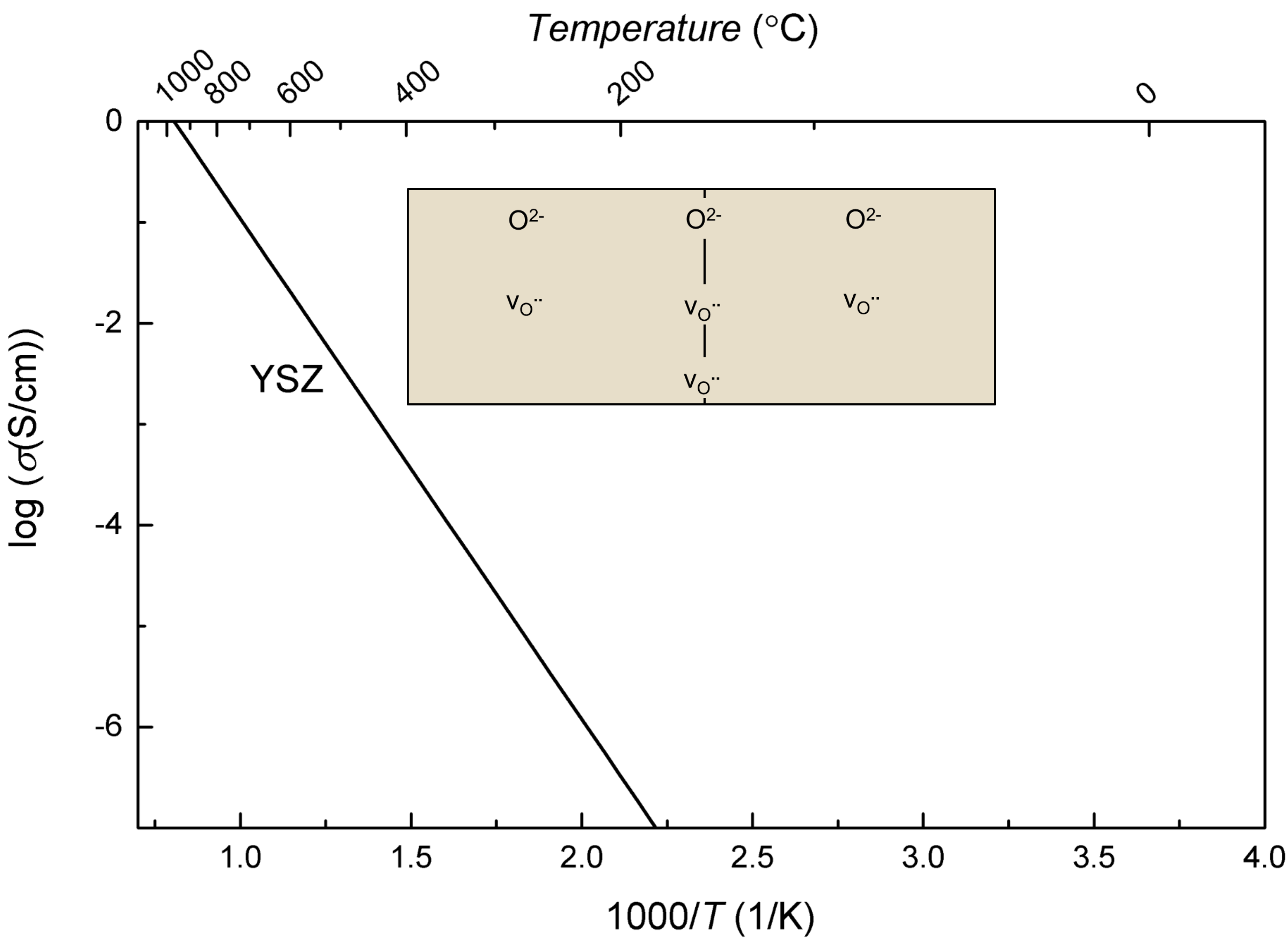


Porous oxide ceramic

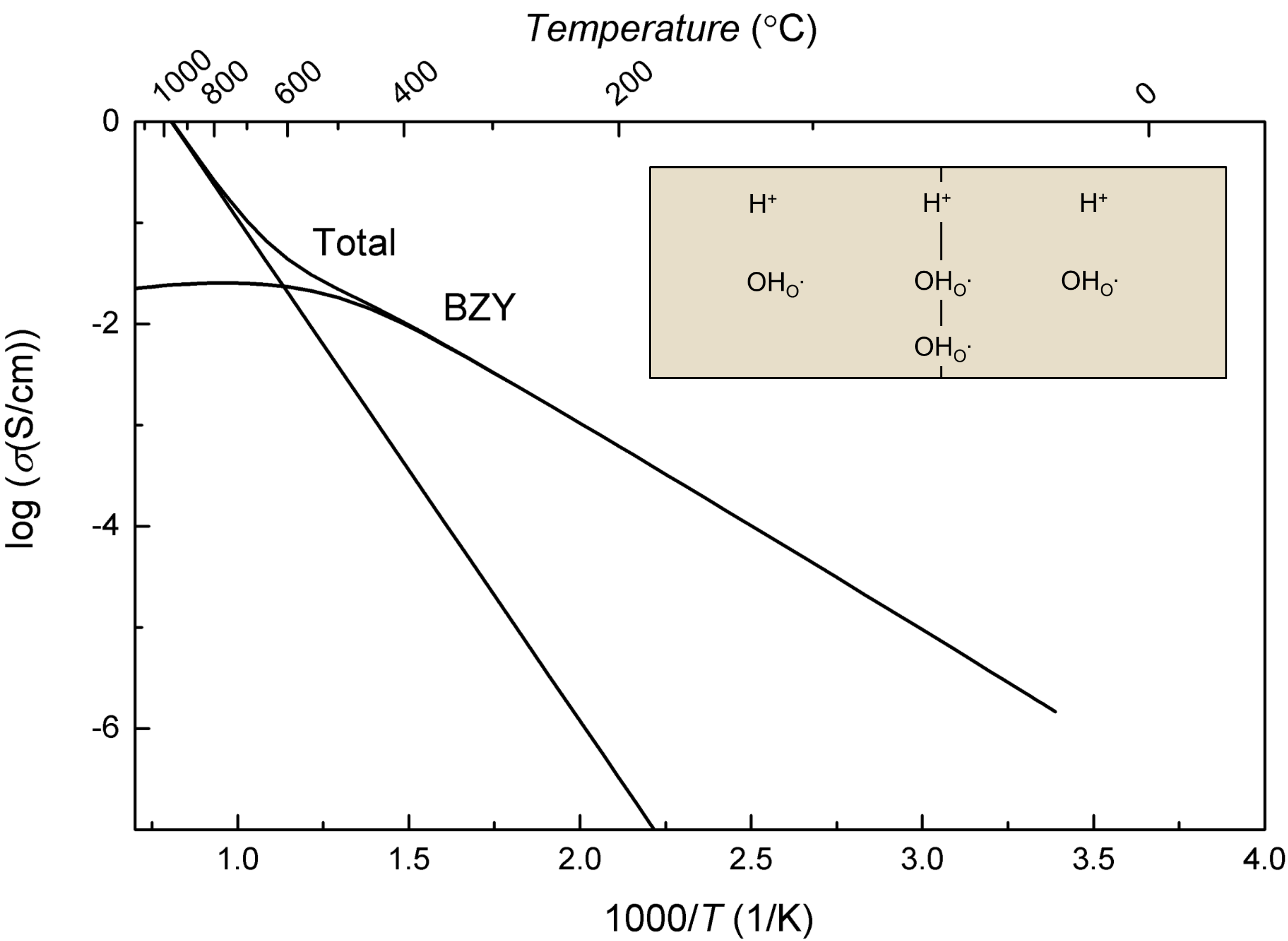
- Surface functionalization
- Acid surface groups. Secondary phases.



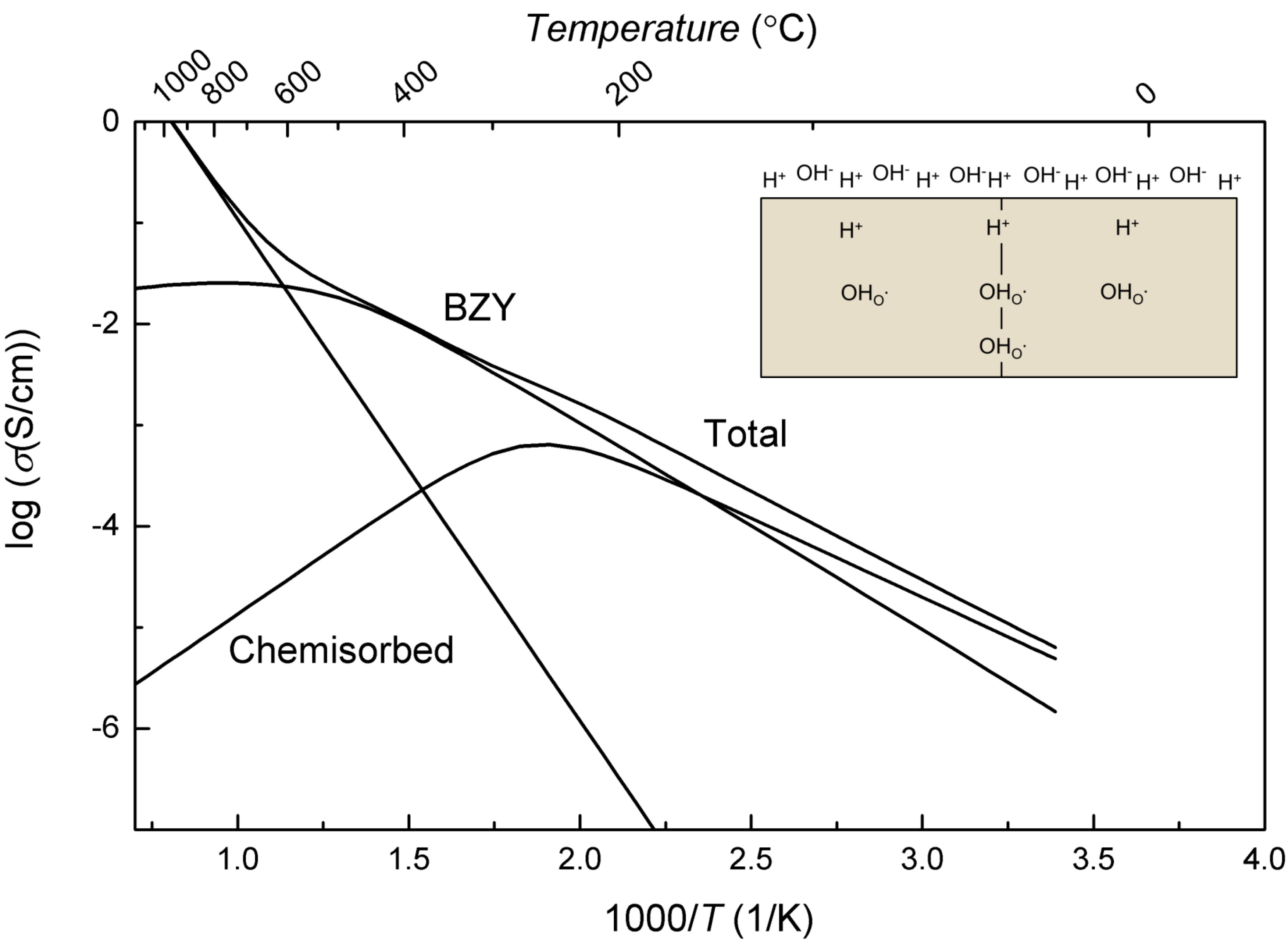
Let's do the same in a conductivity plot...



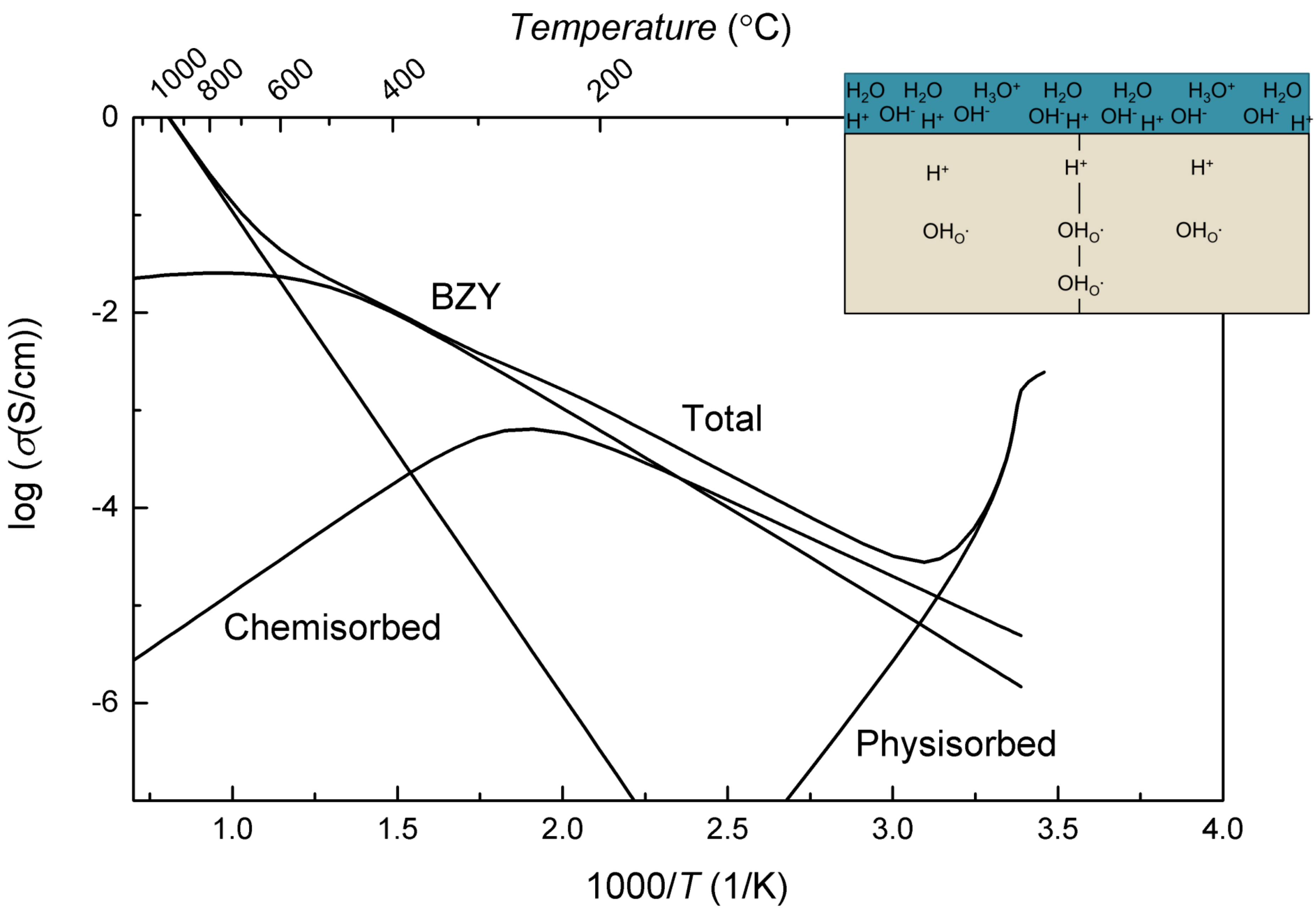
Temperature (°C)
1000
800
600
400
200
0
0
-2
-4
-6
log (σ(S/cm))
YSZ
O2-
O2-
O2-
vO··
vO··
vO··
vO··
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1000/T (1/K)



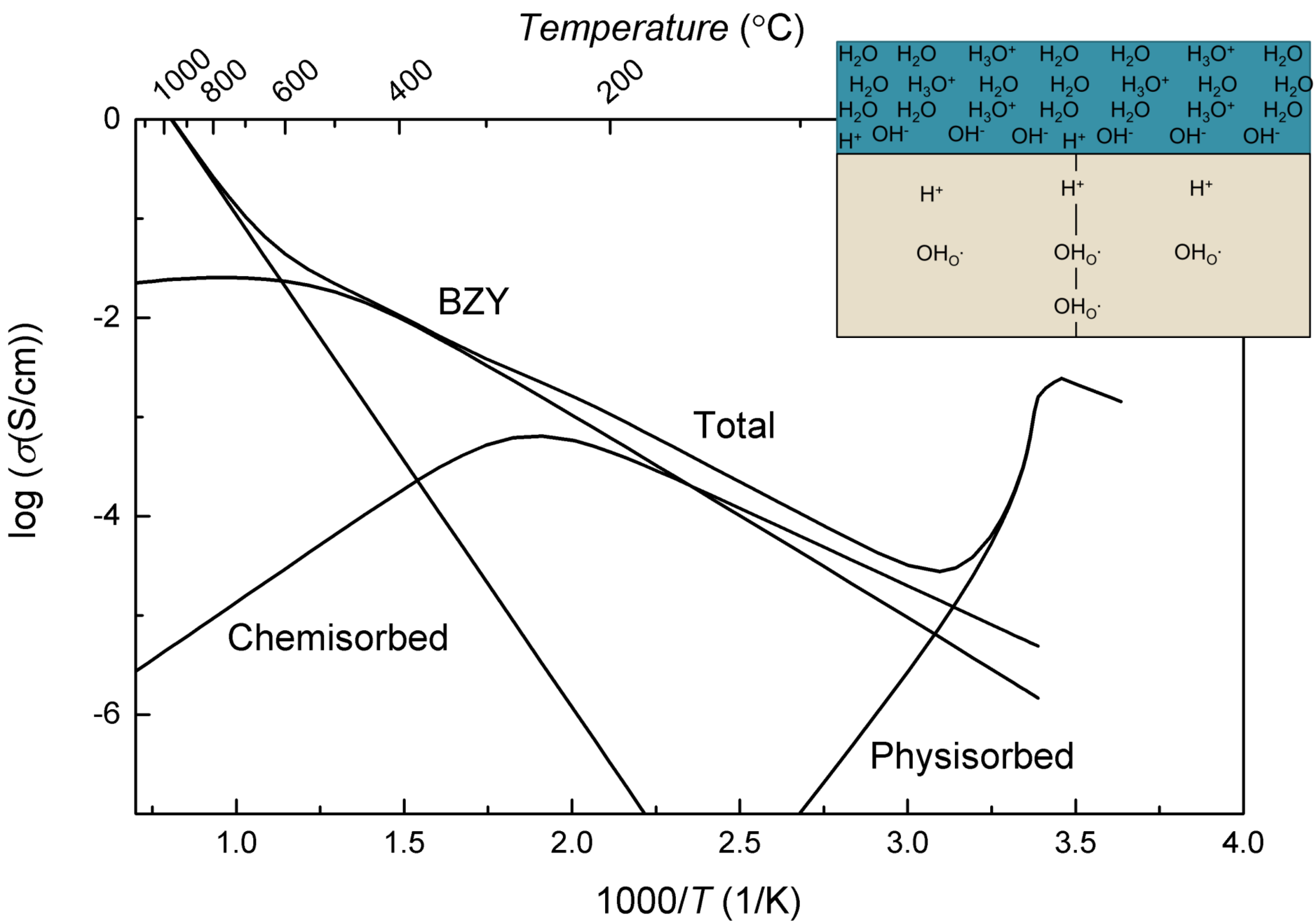
Temperature (°C)
1000
800
600
400
200
0
0
-2
-4
-6
log (σ(S/cm))
Total
BZY
H+
H+
H+
OHO·
OHO·
OHO·
OHO·
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1000/T (1/K)

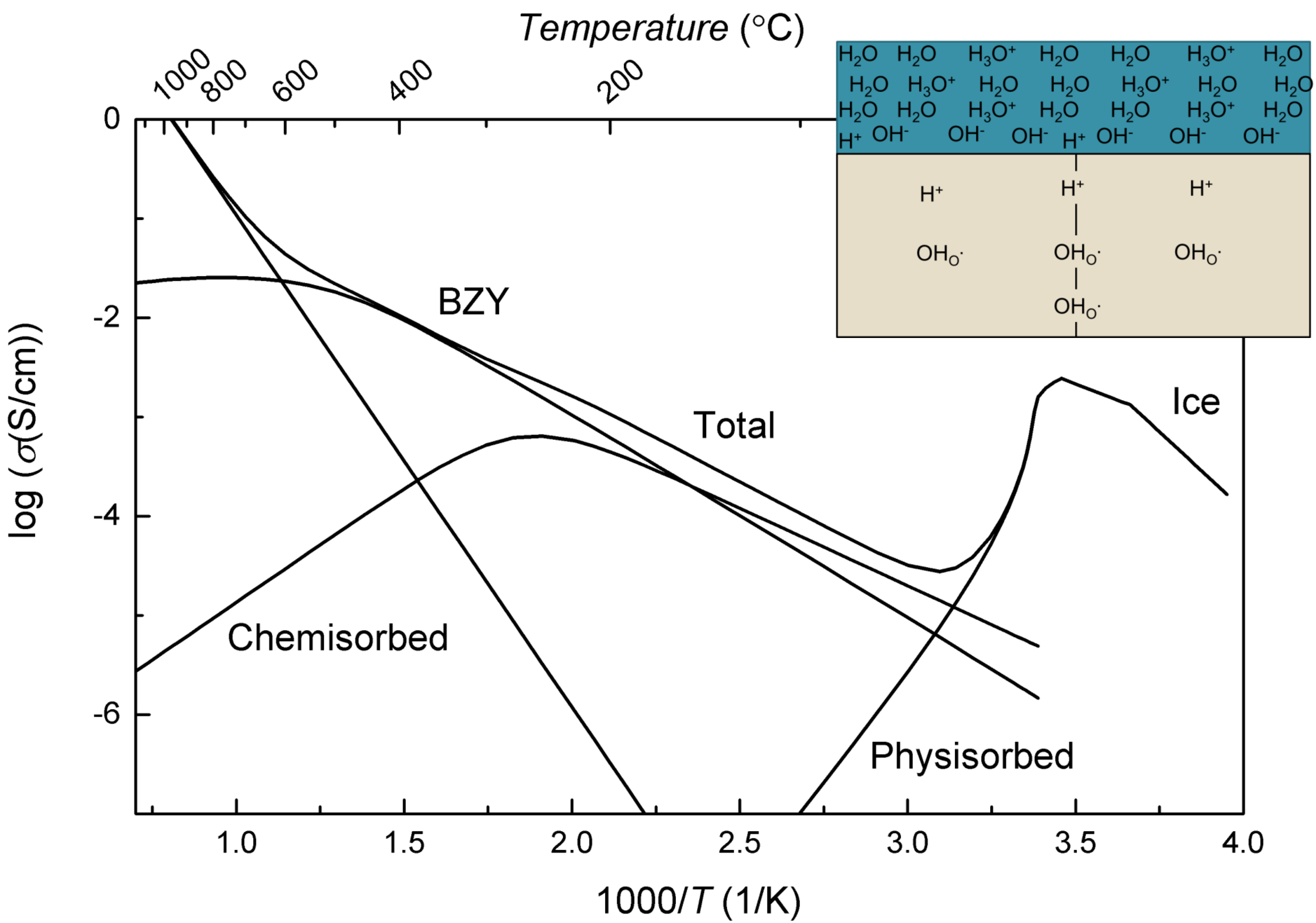


Temperature (°C)
1000
800
600
400
200
0
H+ OH- H+ OH- H+ OH- H+ OH- H+ OH- H+ OH- H+
H+
H+
H+
OHO·
OHO·
OHO·
OHO·
BZY
Total
Chemisorbed
log (σ(S/cm))
0
-2
-4
-6
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1000/T (1/K)

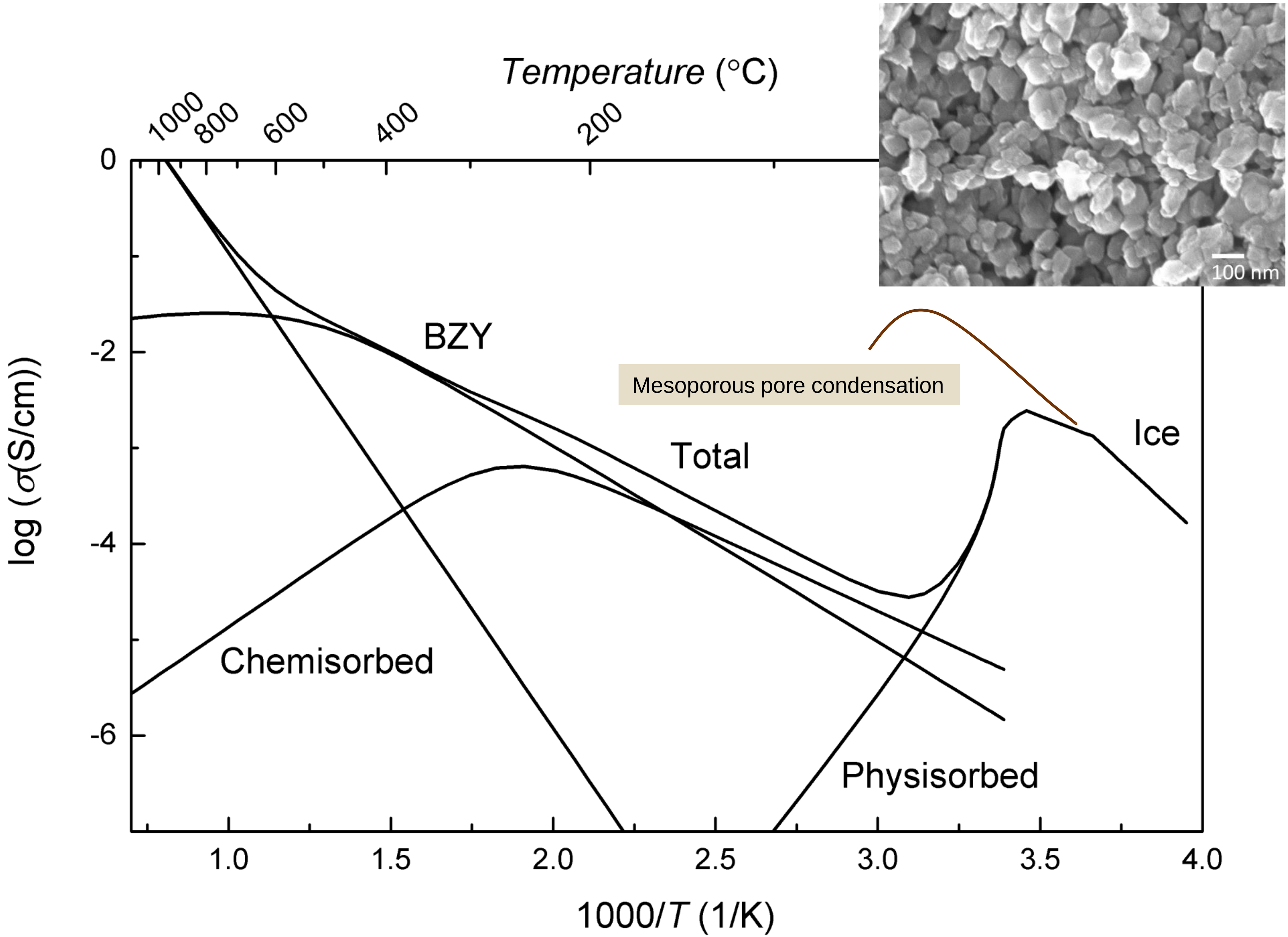


Temperature (°C)
1000
800
600
400
200
0
-2
-4
-6
log (σ(S/cm))
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1000/T (1/K)
BZY
Total
Chemisorbed
Physisorbed
H2O H2O H3O+ H2O H2O H3O+ H2O
H+ OH- H+ OH- OH- H+ OH- H+ OH- OH- H+
H+ H+ H+
OHO· OHO· OHO·
OHO·

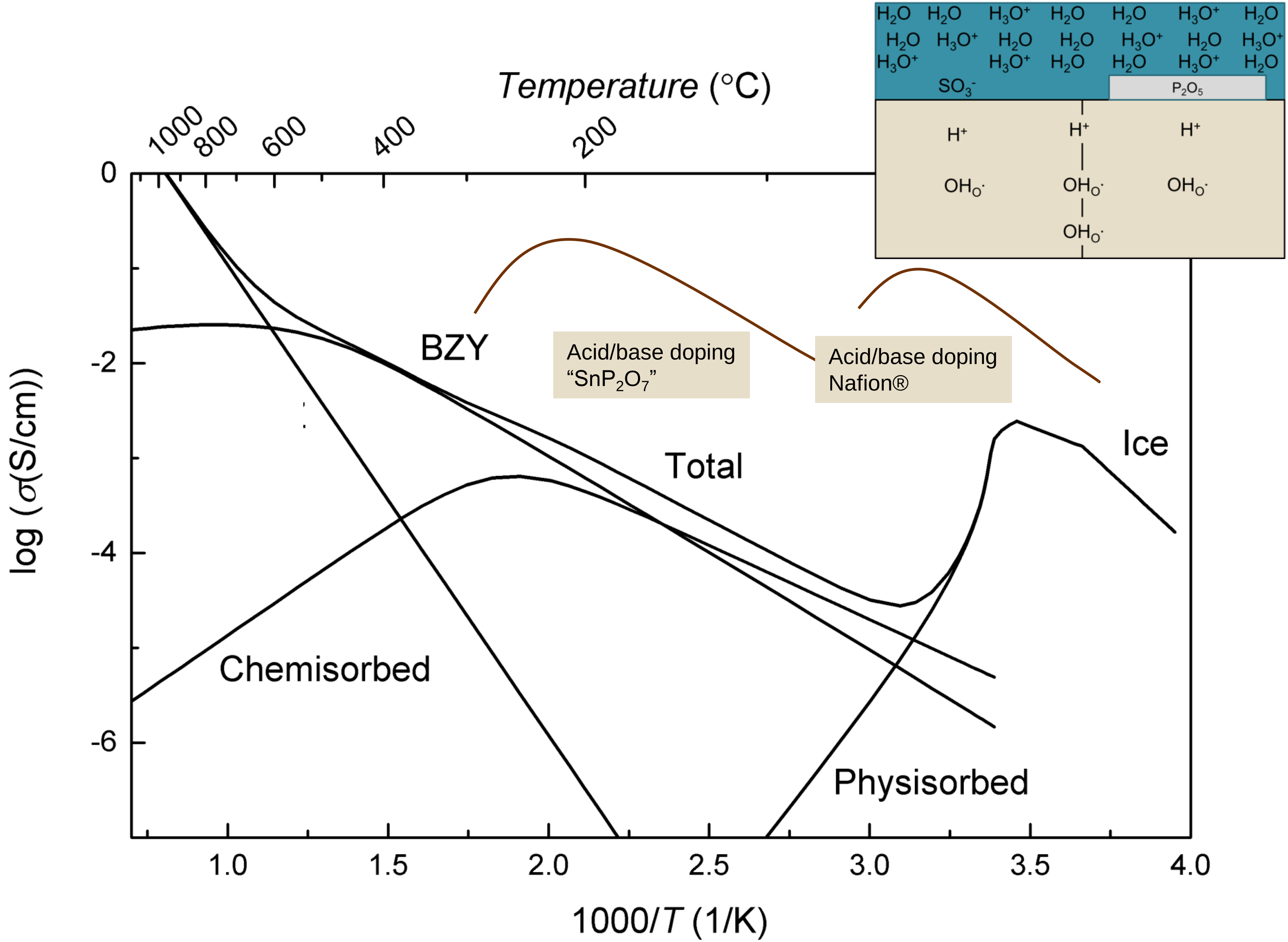

Temperature (°C)
1000
800
600
400
200
0
-2
-4
-6
log (σ(S/cm))
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1000/T (1/K)
BZY
Total
Chemisorbed
Physisorbed
H2O H2O H3O+ H2O H2O H3O+ H2O
H2O H3O+ H2O H2O H3O+ H2O H2O
H2O H2O H3O+ H2O H2O H3O+ H2O
H+ OH- OH- OH- H+ OH- OH- OH-
H+ H+ H+
OHO· OHO· OHO·
OHO·



Temperature (°C)
1000
800
600
400
200
0
-2
-4
-6
log (σ(S/cm))
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1000/T (1/K)
BZY
Total
Chemisorbed
Physisorbed
Ice
H2O H2O H3O+ H2O H2O H3O+ H2O
H2O H3O+ H2O H2O H3O+ H2O H2O
H2O H2O H3O+ H2O H2O H3O+ H2O
H+ OH- OH- OH- H+ OH- OH- OH-
H+ H+ H+
OHO· OHO· OHO·
OHO·



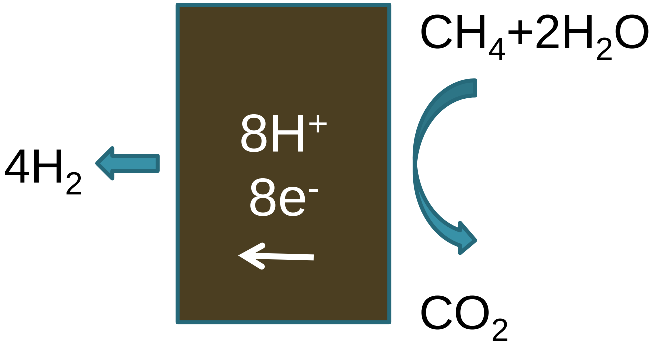
Temperature (°C)
1000
800
600
400
200
0
-2
-4
-6
log (σ(S/cm))
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1000/T (1/K)
BZY
Total
Chemisorbed
Physisorbed
Ice
Mesoporous pore condensation
100 nm



Temperature (°C)
1000
800
600
400
200
0
-2
-4
-6
log (σ(S/cm))
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1000/T (1/K)
BZY
Total
Chemisorbed
Physisorbed
Ice
Acid/base doping
"SnP2O7"
Acid/base doping
Nafion®
H2O
H3O+
SO3-
P2O5
H+
OHO·

Summary

- Solid electrolytes and mixed conductors
- Bulk transport
  - Defect thermodynamics
  - Defect mobilities
- Trapping
- Charge separation
  - Grain boundaries
  - Dislocations
  - Surfaces
  - Electrodes
- Electrodics
- Relationships between solid and liquid, HT and LT



Acknowledgements

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UiO : Universitetet i Oslo

Electra

SINTEF

CoorsTek
MEMBRANE SCIENCES

Marion Technologie

ABENGOA HIDROGENO

FCH
FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

CSIC
Consejo Superior de Investigaciones Científicas

CARBON RECYCLING INTERNATIONAL

FOXCET

The Research Council of Norway

UiO : Department of Chemistry
University of Oslo