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Recent developments of Y-doped $BaZrO_3$ (BZY) as proton conducting electrolyte for fuel cells and steam electrolysers

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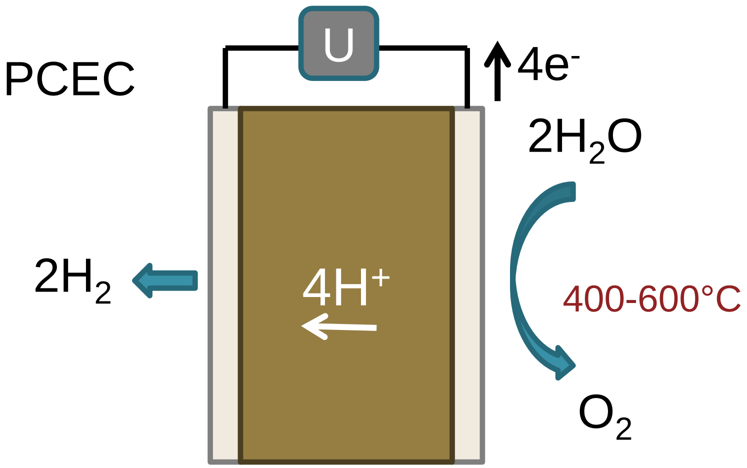
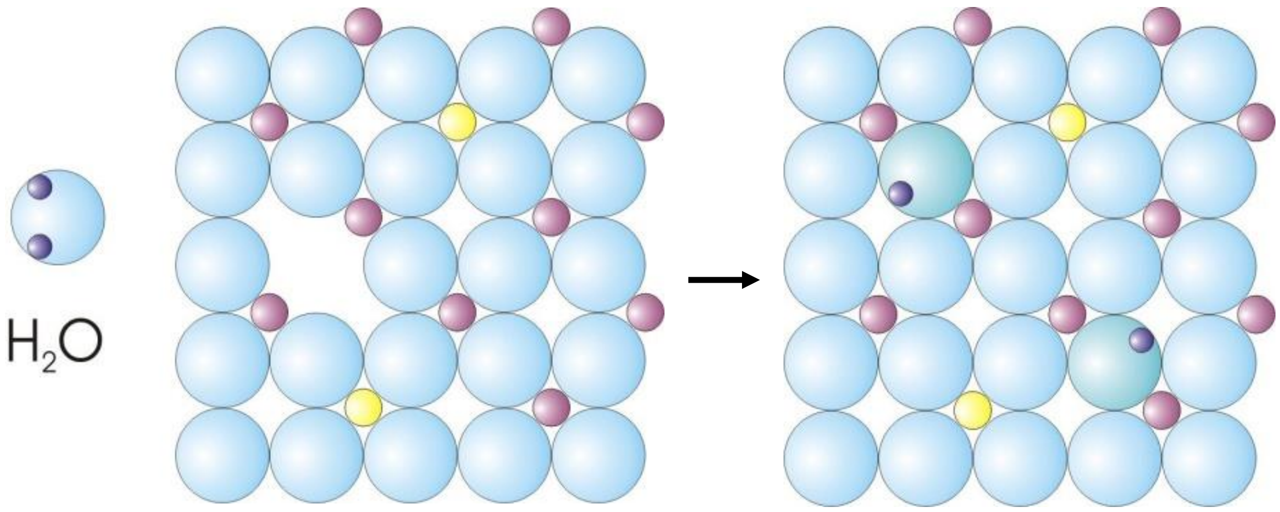


Proton conducting ceramics are acceptor-doped oxides

Hydration in presence of steam (H_2O) gives proton conduction

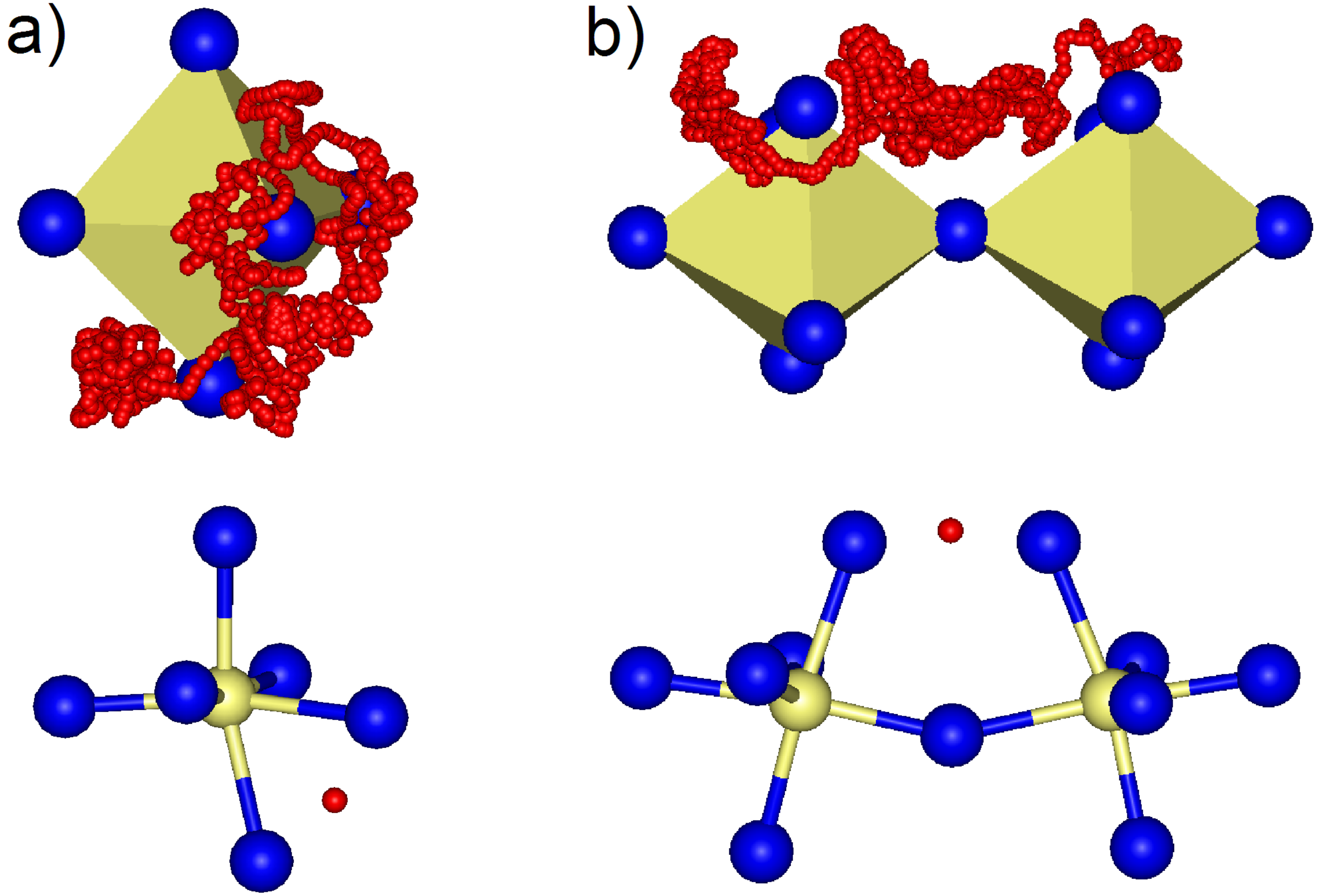


$$H_2O(g) + v_O + O^{2-} = 2OH^-$$

$$H_2O(g) + v_O^{\bullet\bullet} + O_O^x = 2OH_O^{\bullet}$$

Protons migrate by rotation and jumps

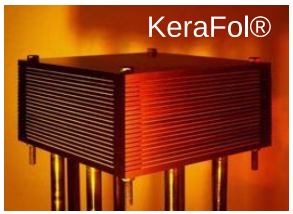
a) Intra- and b) inter-octahedral proton diffusion paths in a perovskite, by MD:



From K.-D. Kreuer, 2008

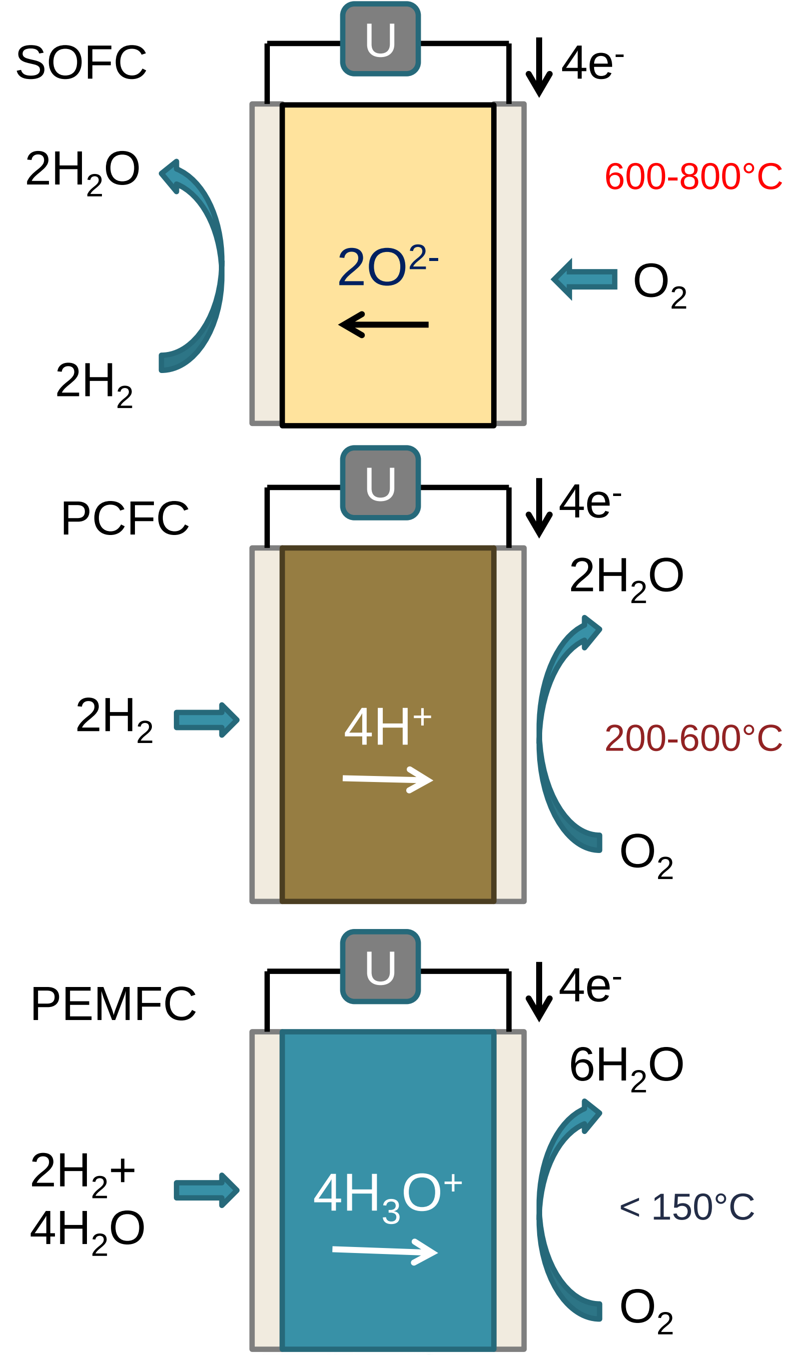
Solid-state fuel cells

- Examples with H_2 as fuel
- Solid Oxide Fuel Cell



- Proton Ceramic Fuel Cell

- PEM Fuel Cell



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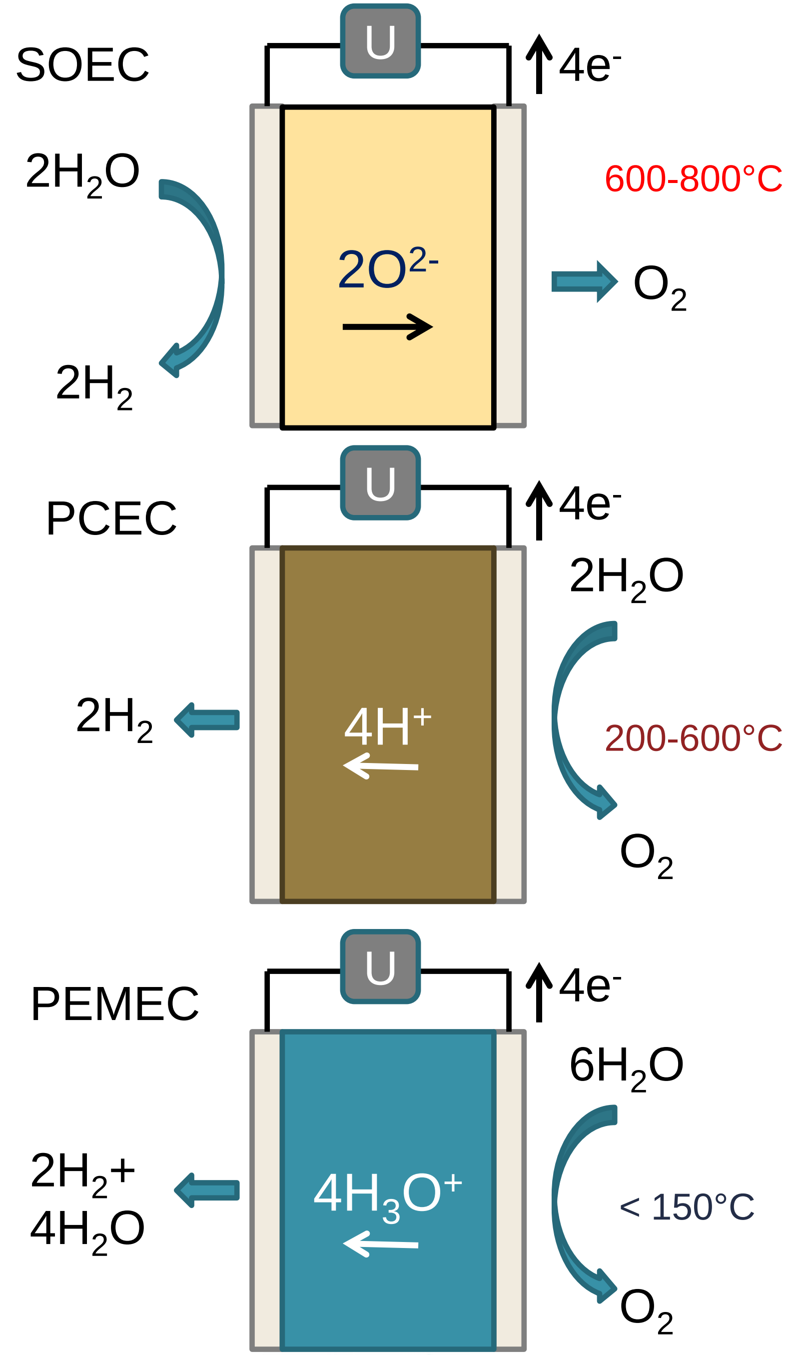
Solid-state electrolyser cells

- Solid Oxide Electrolyser Cell

- Proton Ceramic Electrolyser Cell

- PEM Electrolyser Cell



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Protia – CoorsTek Membrane Sciences Group, Norway

- Spin-off from University of Oslo and NTNU
  - Commercialisation of proton ceramic materials and processes
  - Lab facilities integrated with University of Oslo and SINTEF Oslo
  - Focus on processes for natural gas upgrading
  - Norwegian venture capital 2008-2012
  - Coors / CoorsTek / Ceramatec 2013-2014
  - Renamed and Part of CoorsTek Membrane Sciences Group 2015
    - USA, France, Norway

CoorsTek Amazing Solutions®

Dr. Grover W. Coors

MEMBRANE SCIENCES GROUP

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Three main Protia processes

- Steam electrolysis to hydrogen

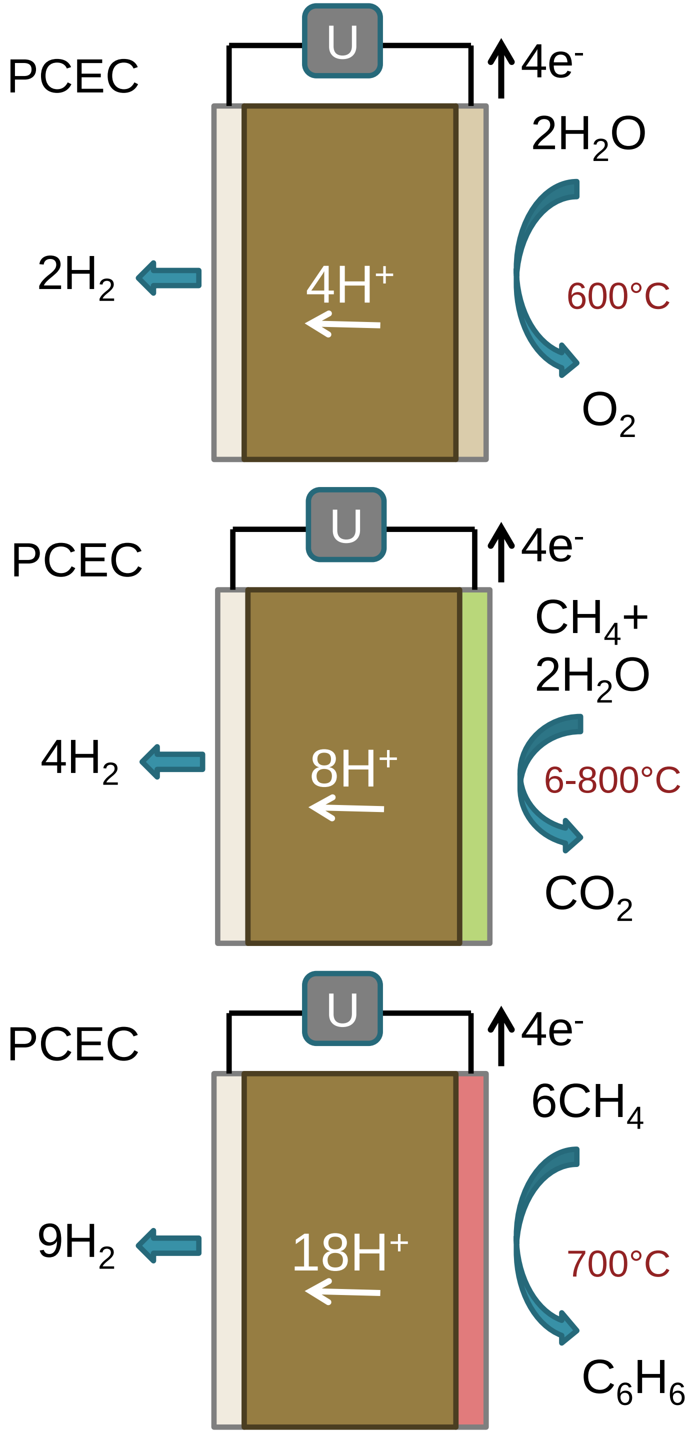
  $2H_2O = 2H_2 + O_2$

- Direct reforming to compressed hydrogen

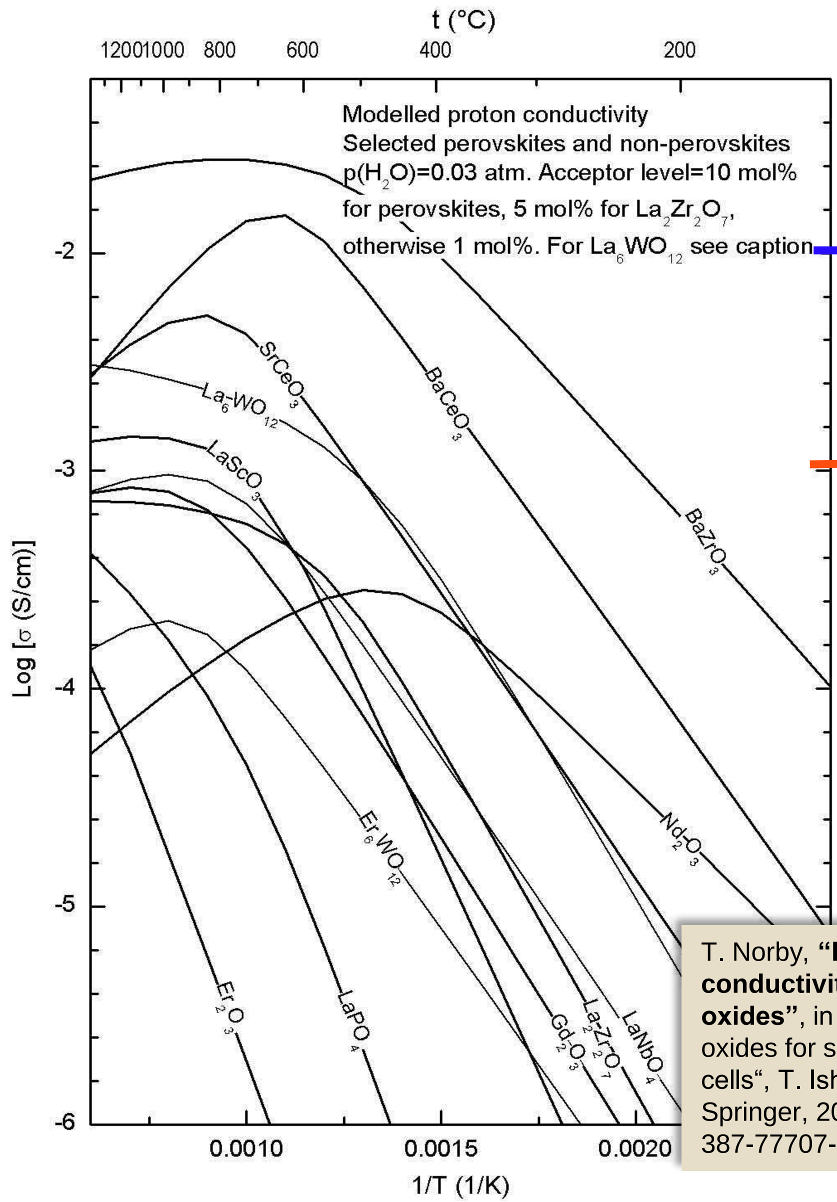
  $CH_4 + 2H_2O = CO_2 + 4H_2$

- Direct dehydro-aromatisation

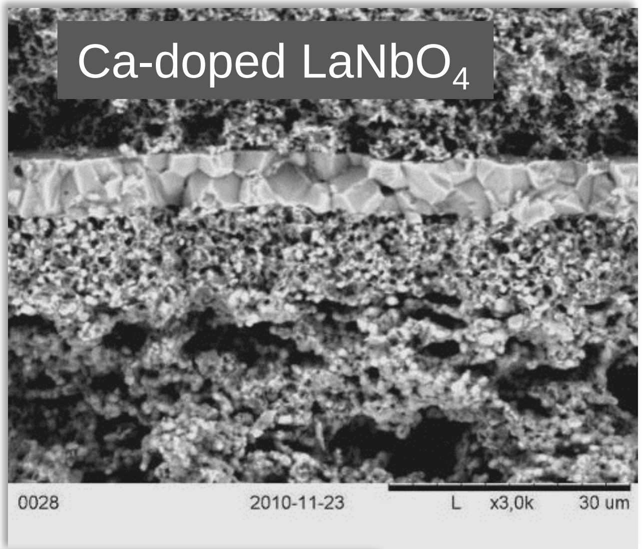
  $6CH_4 = C_6H_6 + 9H_2$



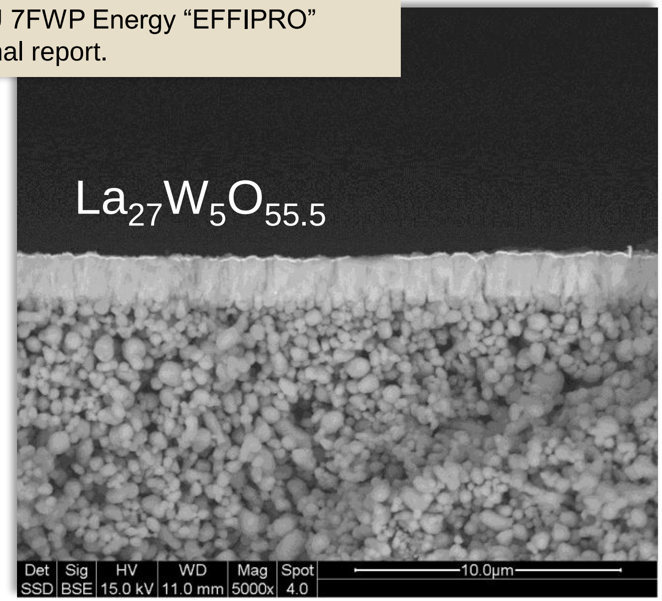
Proton conductivity in acceptor-doped oxides



T. Norby, **"Proton conductivity in perovskite oxides"**, in "Perovskite oxides for solid oxide fuel cells", T. Ishihara, ed., Springer, 2009, ISBN 978-0-387-77707-8.

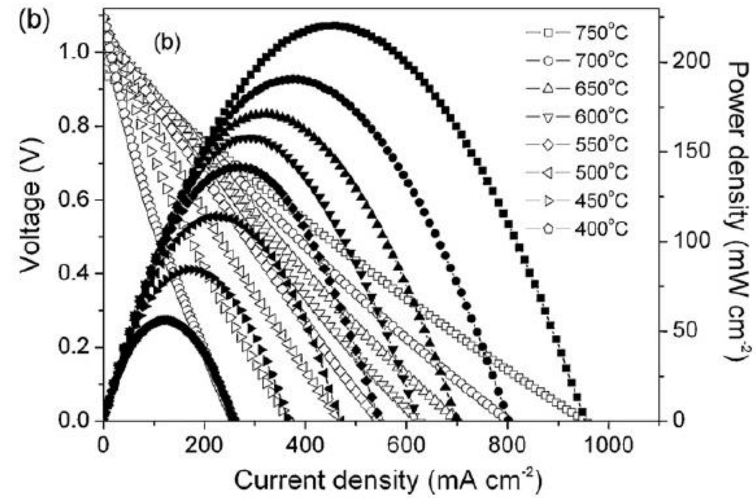


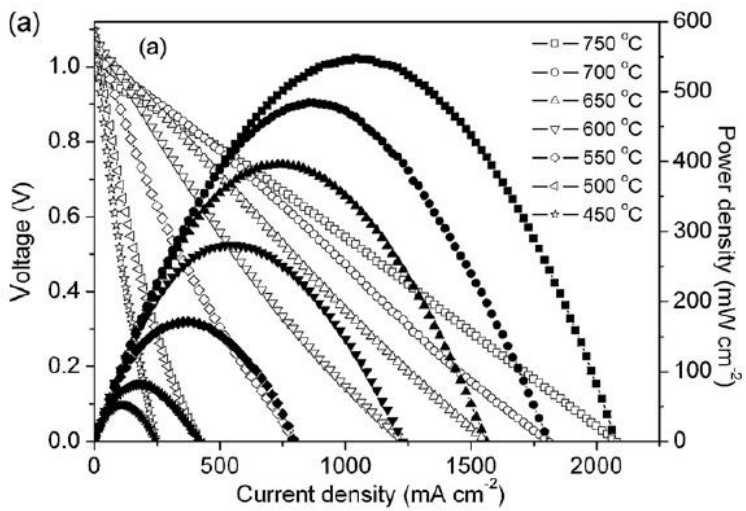
EU 7FWP Energy "EFFIPRO" Final report.



Leading material: $BaY_xCe_yZr_{1-x-y}O_{3-d}$

- Example: $BaY_{0.2}Ce_yZr_{0.8-y}O_{3-d}$
- 40 µm electrolyte
- Ni-electrolyte cermet anode
- $(Ba,Sr)(Co,Fe)O_3$ cathode
- Wet H_2 vs air





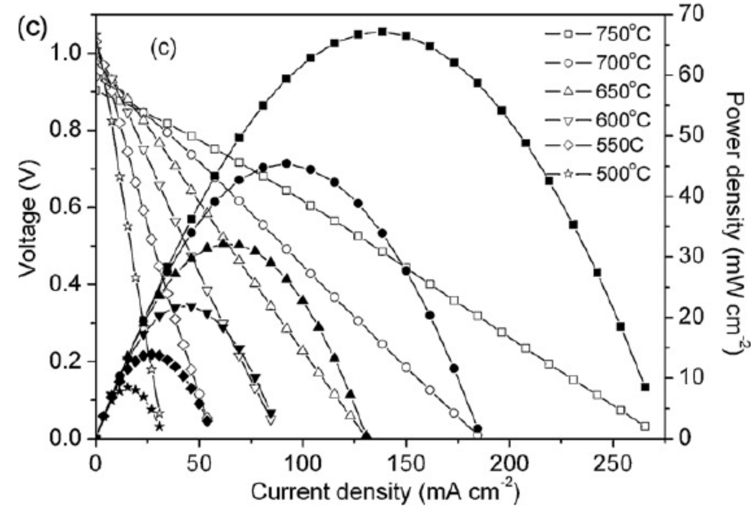
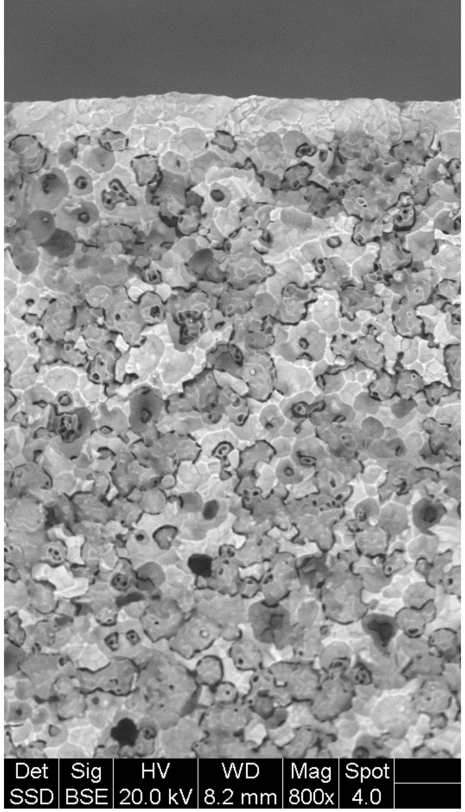


Fig. 7. *I–V* curves of the cells with various BZCY*y* electrolytes and the BSCF cathode: (a) $y = 0.0$; (b) $y = 0.4$; (c) $y = 0.8$.

Y. Guo, et al., J. Power Sources (2009), doi:10.1016/j.jpowsour.2009.03.044

Anode-supported tubular BZCY

- CoorsTek/Protia/SINTEF
- Reaction sintering:
  $BaCO_3$/$BaSO_4$+ ZrO_2 + CeO_2 + Y_2O_3 (+NiO)
- Slip-cast/extrude BZCY-NiO composite
- Spray/dip/spin BZCY electrolyte precursor
- Co-sinter
- Reduce NiO to Ni in H_2
  - Sufficient porosity for PCFC&PCEC with H_2
- 30 cm, 10 mmØ, 1 mm wall, 20 µm BZCY
- Developments:
  - DC conductivity – bulk and grain boundaries
  - Chemical expansion
  - O_2 side electrodes
  - Segmented in series tubes
  - Overall fabrication procedures



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International workshop on BZY, Oslo, March 2015

RCN NANO2021 FOXCET

International Workshop on BZY

March 24-27, 2015

Oslo Science Park (Forskningsparken), Gaustadalleen 21, Oslo, Norway

Tuesday March 24th

- 2000 Invited speakers welcome at dinner in downtown restaurant (TBA)

Wednesday March 25th; Oslo Science Park - CIENS Top Centre

- Start 0830 Welcome, coffee
    - R. Bredesen: Welcome

International workshop on BZY, Oslo, March 2015

- BZY workshop sessions:

  General, proton conductivity

  Structure and stability

  Defects, tranport, modelling

  Grain boundaries

  Fabrication

  Electrodes

  Applications

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20 years of BZY

- «Fundamentals»
- Grain boundary resistance
- Sintering aids
- Solid state reactive sintering
- Space charge
- Proton trapping

1981

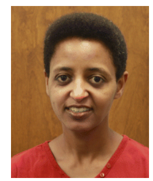
H. Iwahara et al.

1993

K.-D. Kreuer et al.

1997

S. Haile et al.



1999

Bohn and T. Schober

2000

JTS Irvine et al.

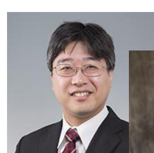
2005

P. Babilo and S. Haile

2007

2010

R. O'Hayre et al.



F. Iguchi et al.

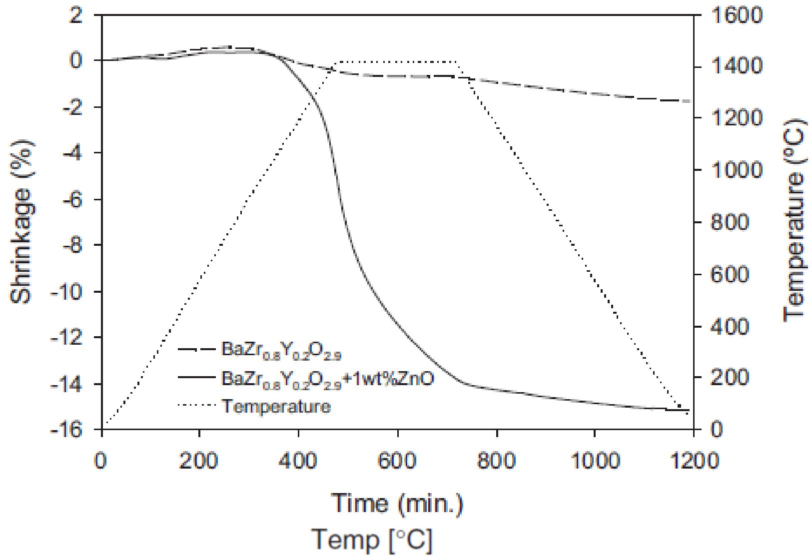
S. Kim et al.

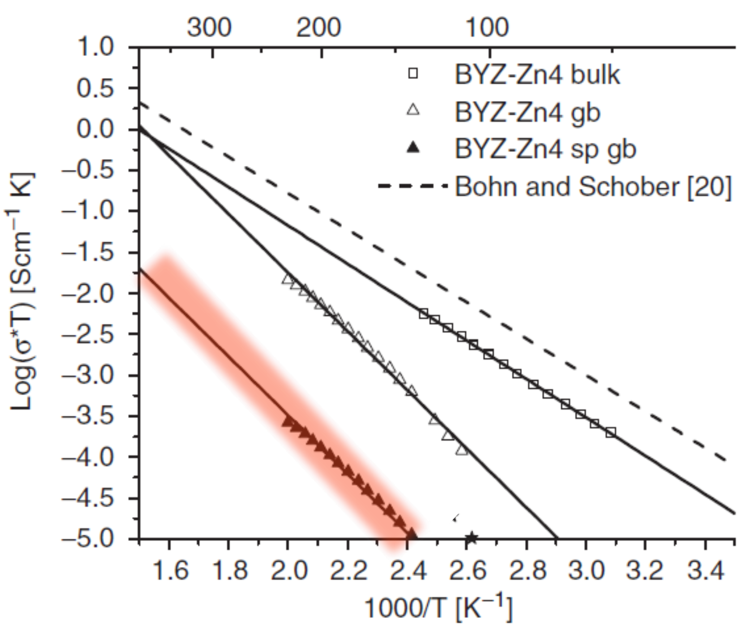
C. Kjølseth et al.

2013

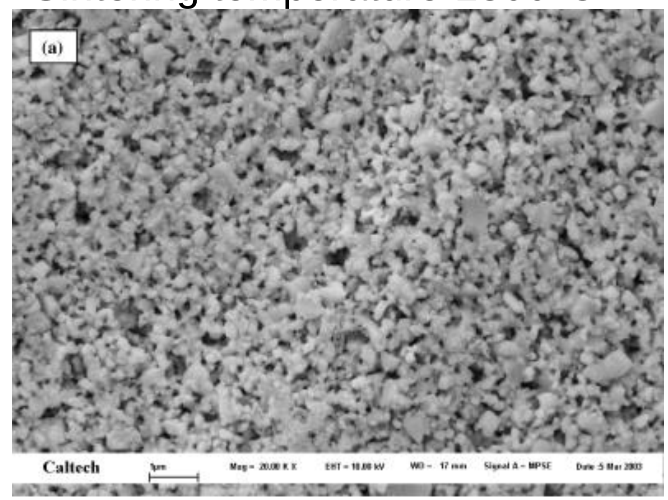
Y. Yamazaki et al.

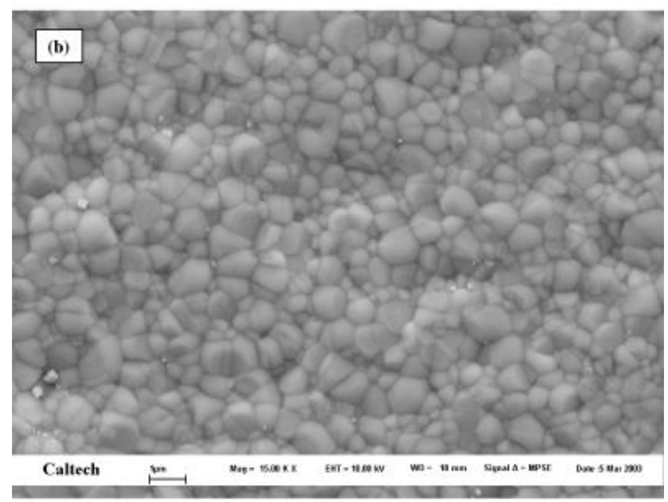
BZY sintering aids – started with ZnO





Sintering temperature 1300°C

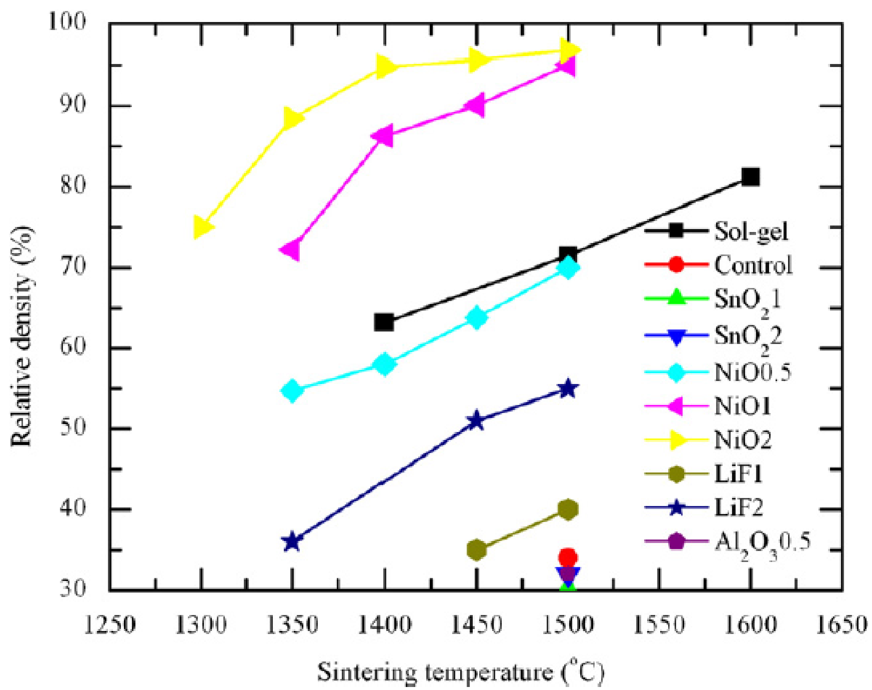


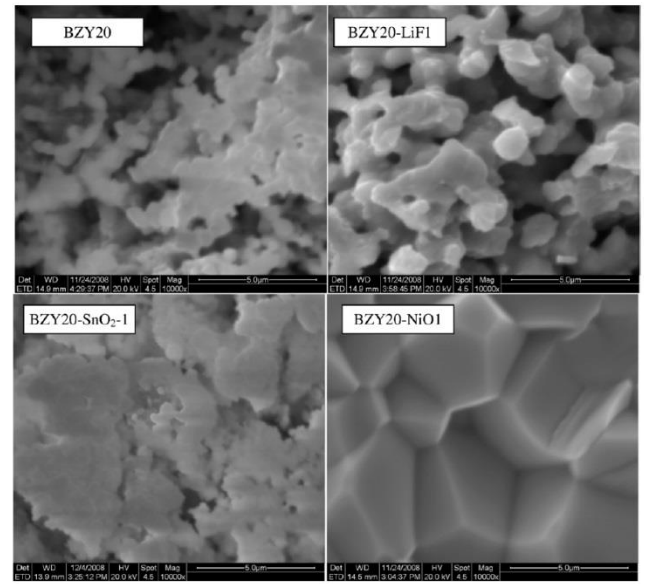


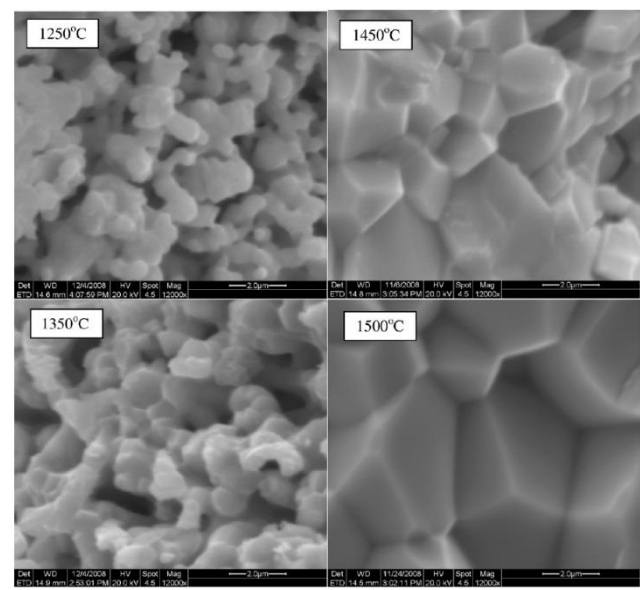
Tao and Irvine / *Adv. Mater.* (2006) **18**, 1581–1584

Babilo and Haile / J. Am. Ceram. Soc., **88** 2362–2368 (2005)

Sintering aids for BZY; almost everything has been tried…

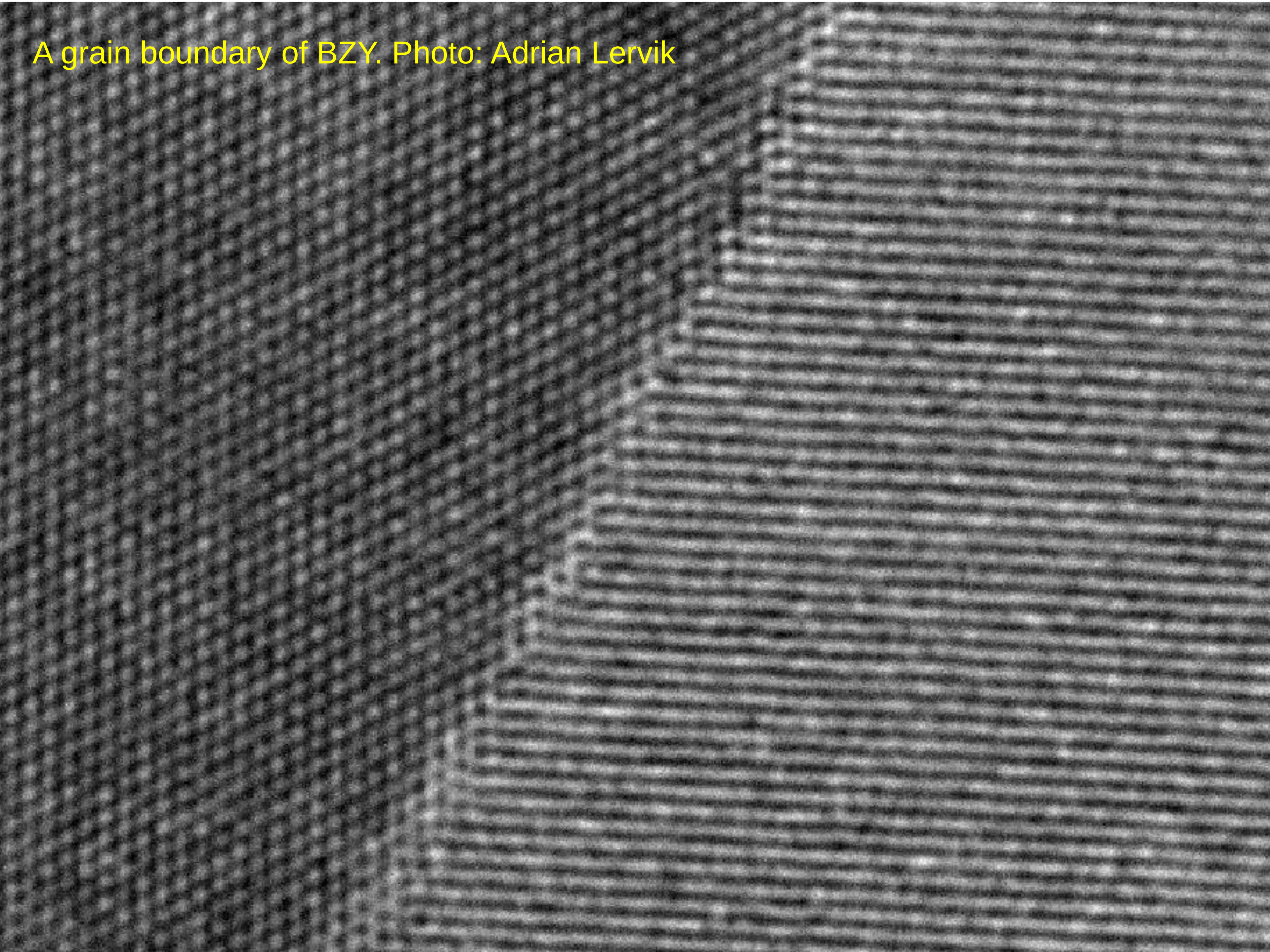




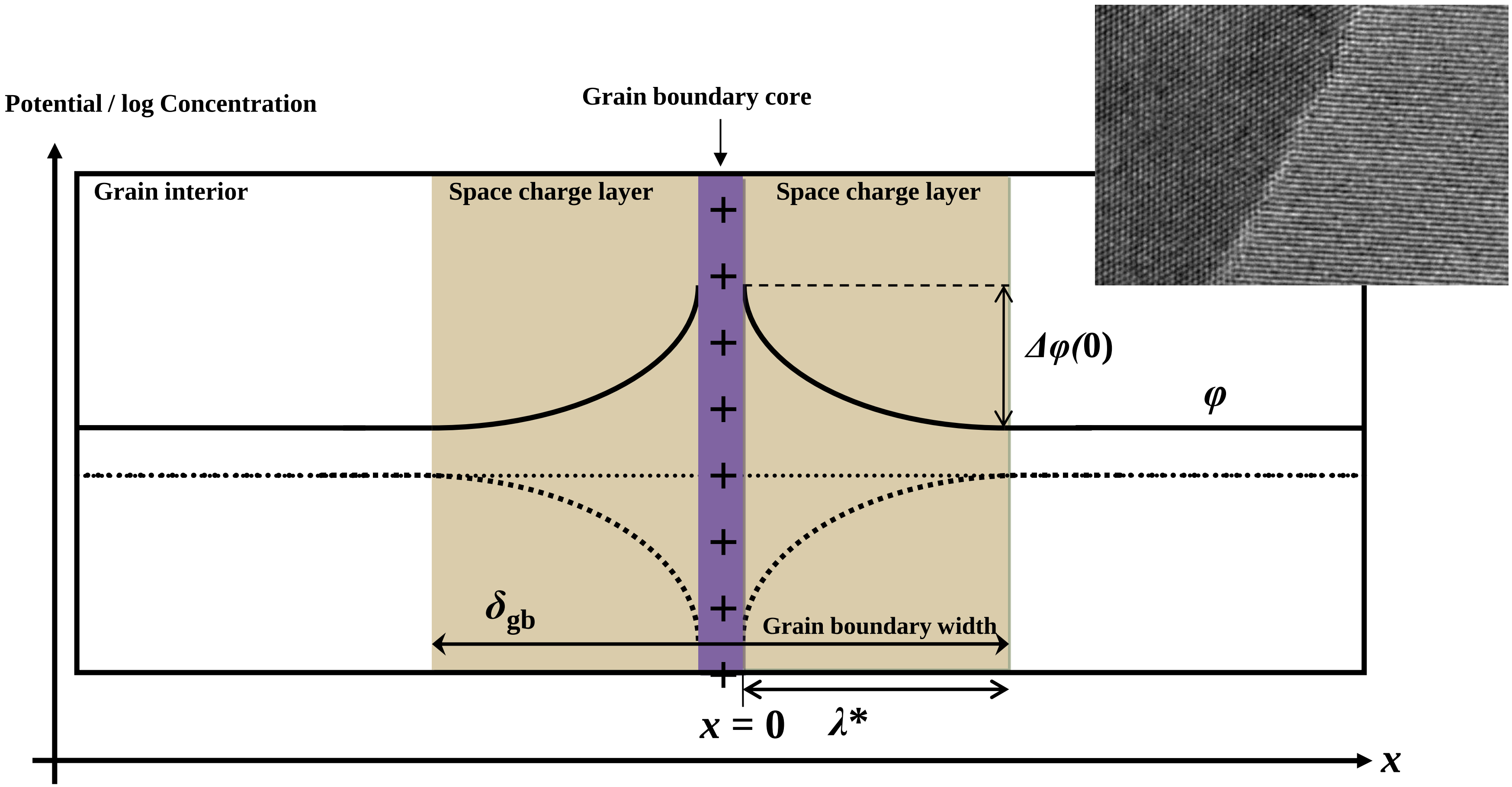


- Various sintering additives have been tested, transition metal oxides in particular
- NiO yields the best result (?)

J. Tong et al. / *Solid State Ionics* **181** (2010) 496–503


A grain boundary of BZY. Photo: Adrian Lervik

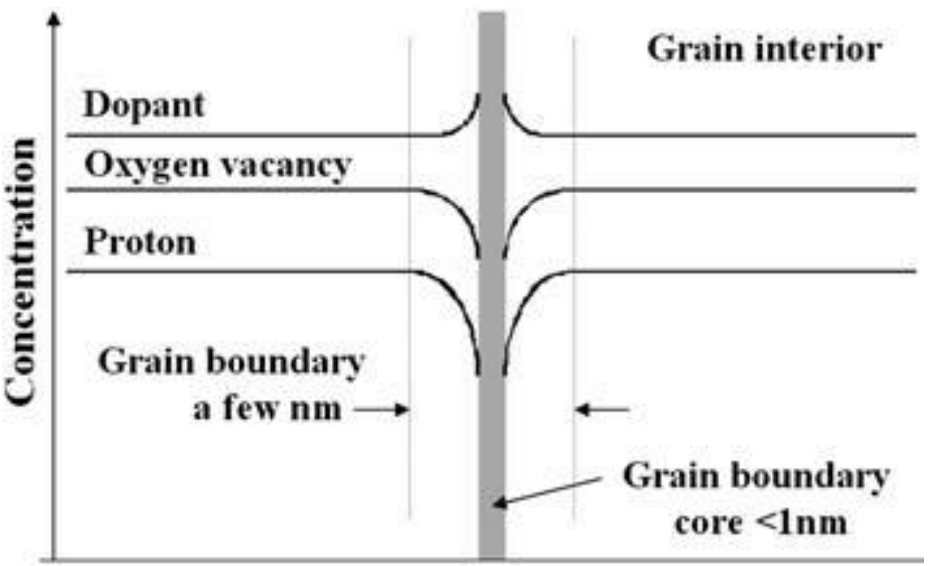
Schematic overview of a charged grain boundary



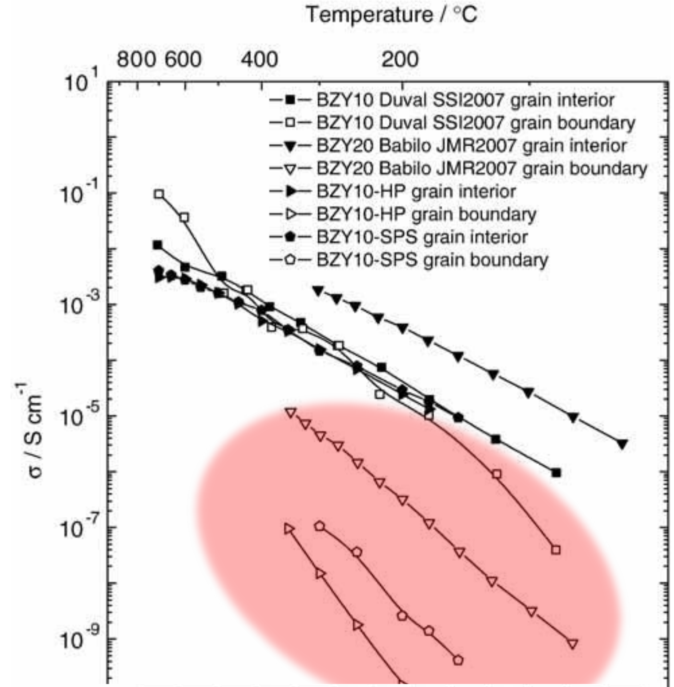
Kjølseth, C.; Fjeld, H.; Prytz, Ø.; Dahl, P. I.; Estournès, C.; Haugsrud, R.; Norby, T. *Solid State Ionics* 2010, 181, 268–275.

Space charge effect in BZY gb's

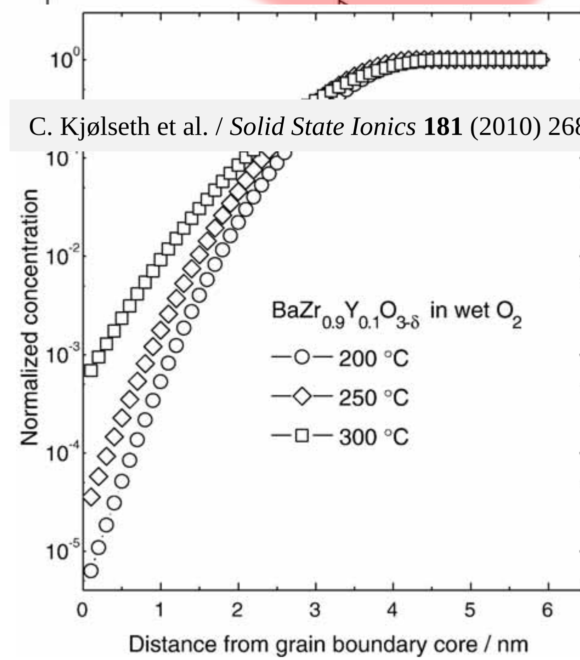
- Positive grain boundary core yields adjacent charge compensating regions, *i.e.* **space charge layers**:
- Decreasing concentration of protons, oxygen vacancies, and electron holes in the vicinity of core
- Increasing amount of acceptors and electrons



F. Iguchi et al. / *J. Mater. Chem.*, (2010), **20**, 6265–6270

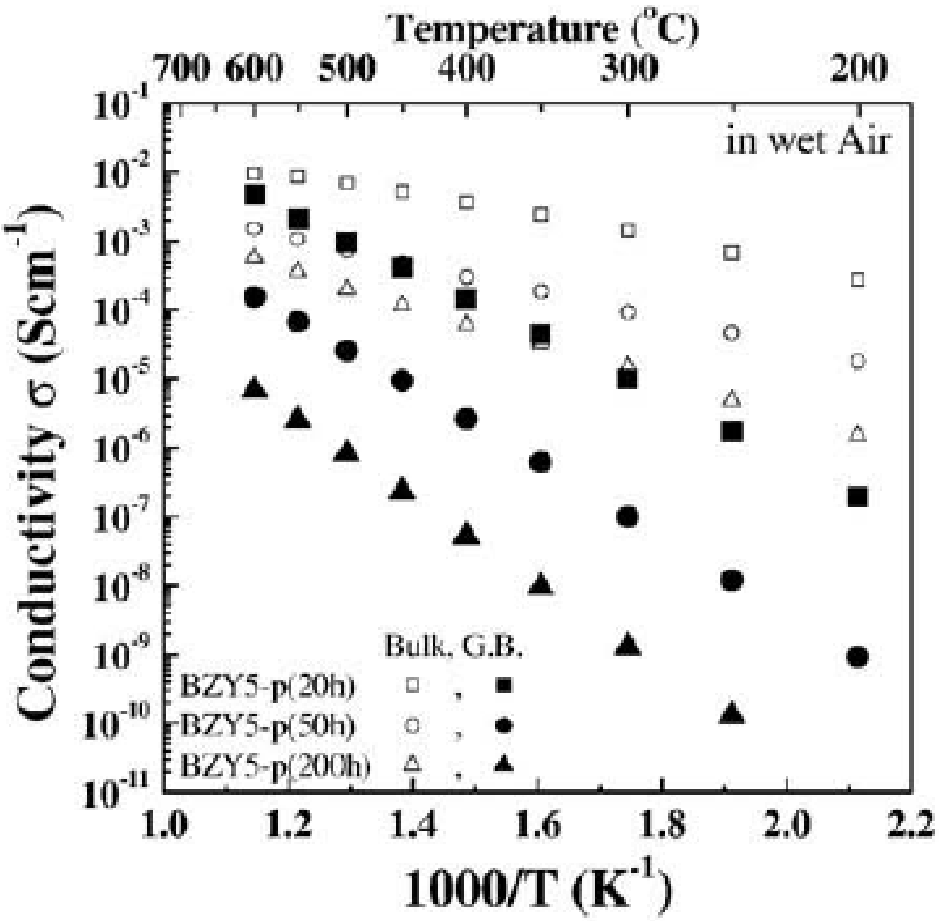


C. Kjølseth et al. / *Solid State Ionics* **181** (2010) 268–275



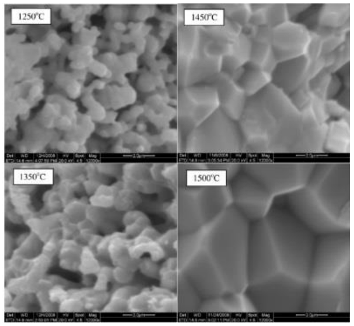
Proton conductivity varies with fabrication procedures

- Grain size
- Ba loss
- Sintering aid loss
- Dopant distribution
- Sintering aid distribution



F. Iguchi et al. / Solid State Ionics **180** (2009) 563–568

What we think happens in $BaZr_{1-x}Y_xO_{3-2x}$

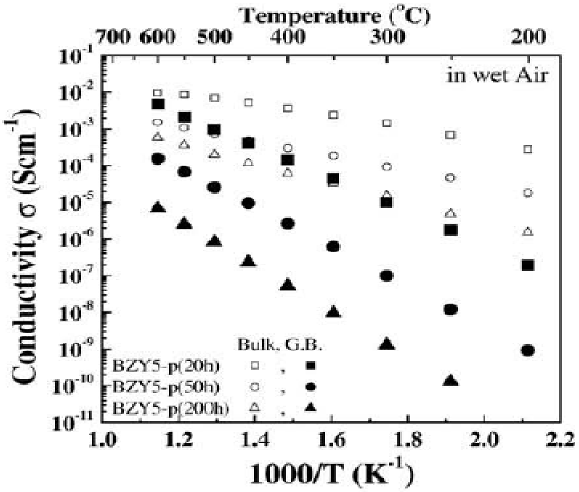


- High T and sintering aid like NiO necessary
  - Dense, large grained material
- Ni ends up as $BaY_2NiO_5(l)$, Ni_i^*, or Ni(s)
- Ba loss by evaporation, leads to Y_{Ba}^*

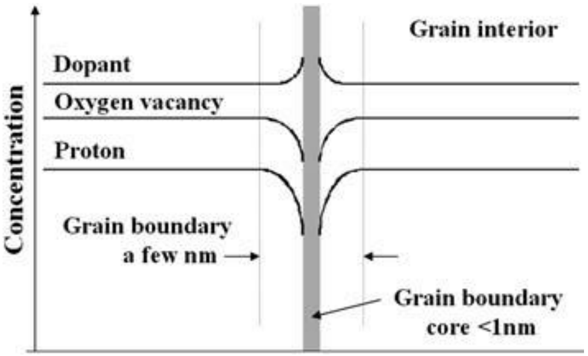
- **Effective acceptor dopant content becomes critically low**

- Grain boundaries positive from oxygen vacancy accumulation
- Well chosen sintering procedure counteracts this by accumulating the dopant Y too

- **Space charge depletion of charge carriers varies by orders of magnitude**

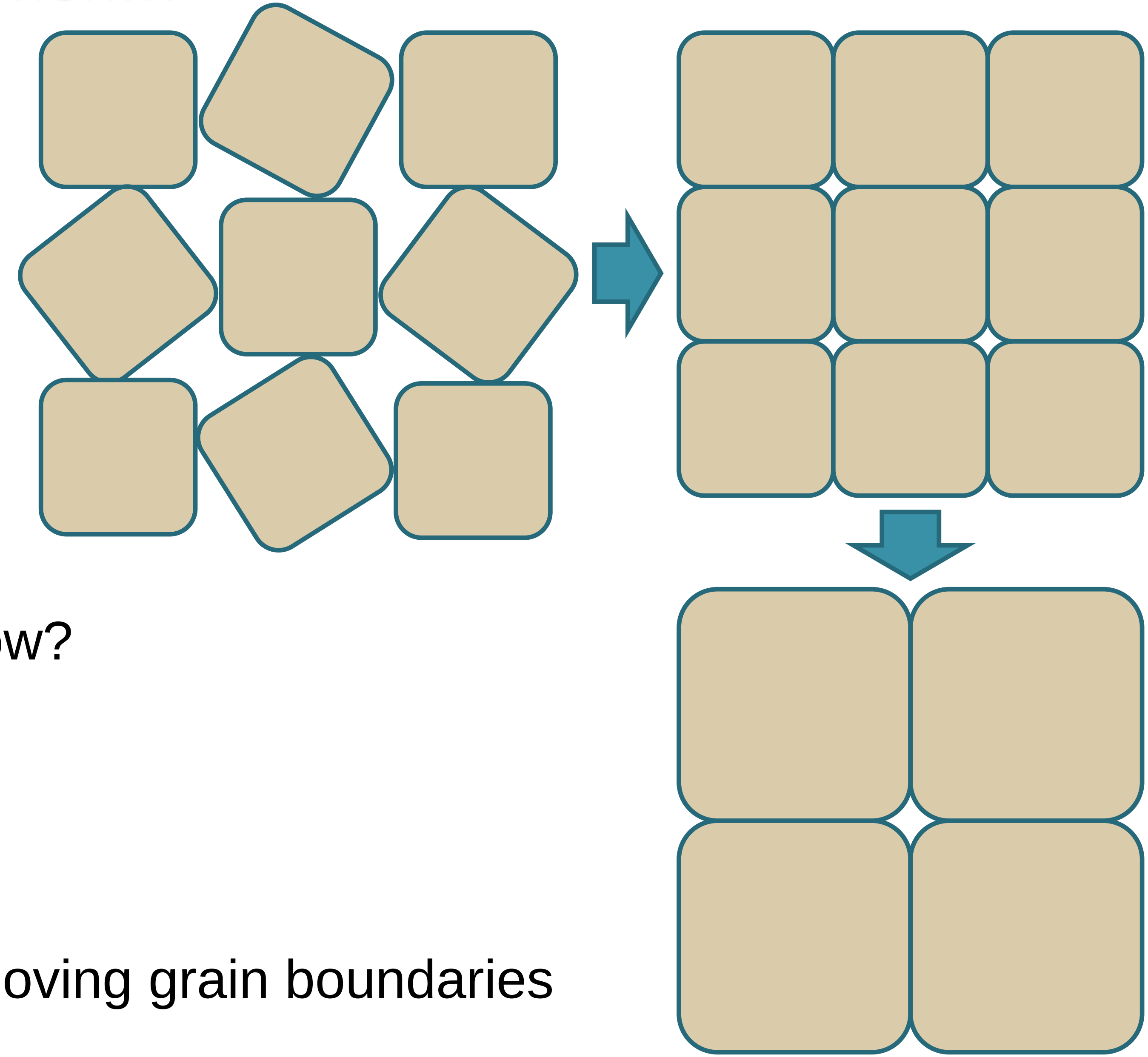


F. Iguchi et al. / Solid State Ionics **180** (2009) 563–568



What happens when…

- BZY sinters?



- BZY grains grow?

Stationary vs moving grain boundaries

Summary

- Proton conducting ceramics are pure H transporters
- Electrochemical processes with H more efficient
- BZY and similar most promising materials
- Challenges
  - Sintering
  - Chemical expansion
  - Grain boundary resistance
- Now focus on
  - Correctly interpreting the complexity of effects!
  - What happens during fabrication; sintering and grain growth?