UiO : **Department of Chemistry**
University of Oslo

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The chemistries of proton ceramic electrochemical cells

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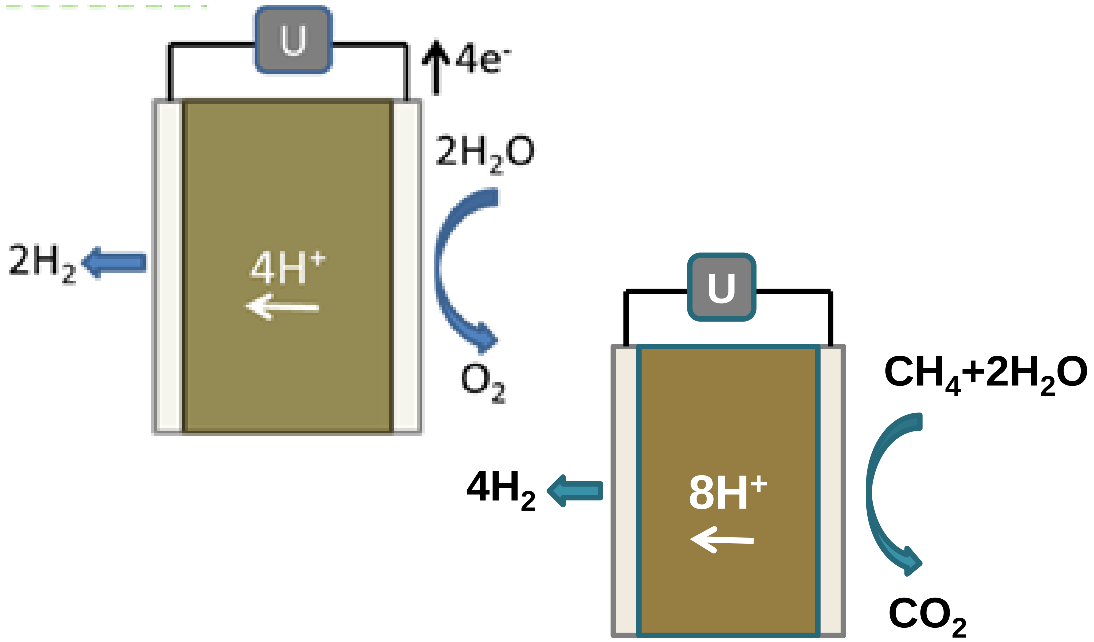

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FERMiO
Oslo Innovation Centre

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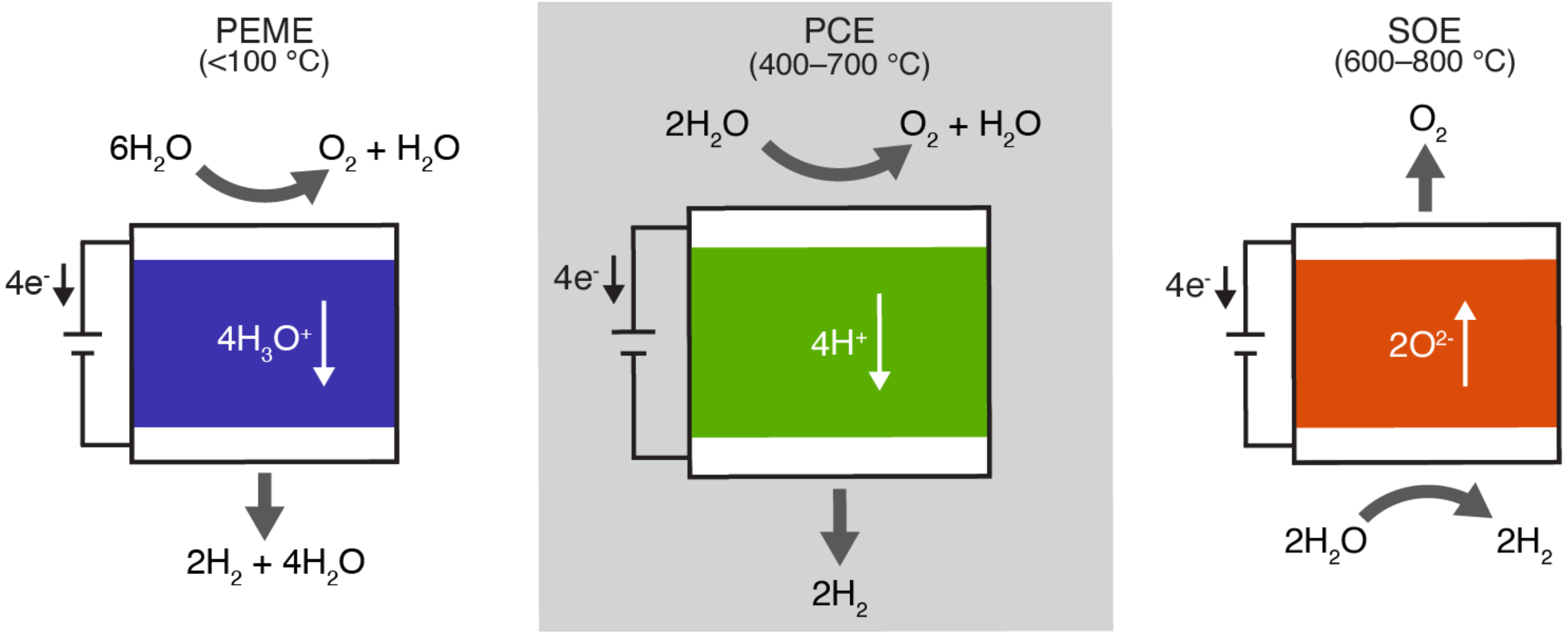
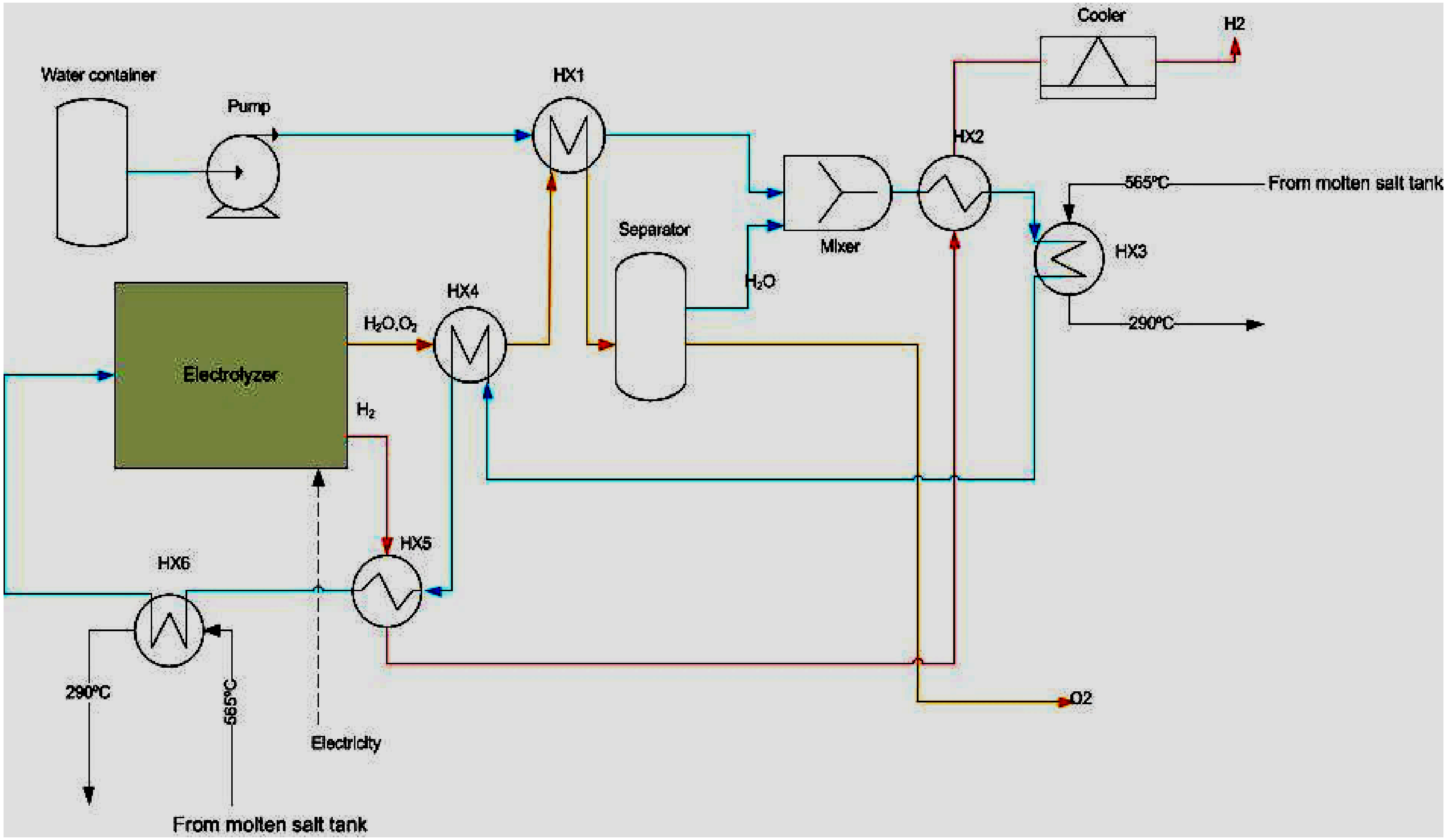
Electrochemical cells need as a minimum

positrode
electrolyte
negatrode

Examples: PEM water and PCE and SOE steam electrolysers
Application and technology determine conditions



Proton ceramic steam electrolysis coupled with thermal energy sources:
Example of solar-thermal molten salt plant



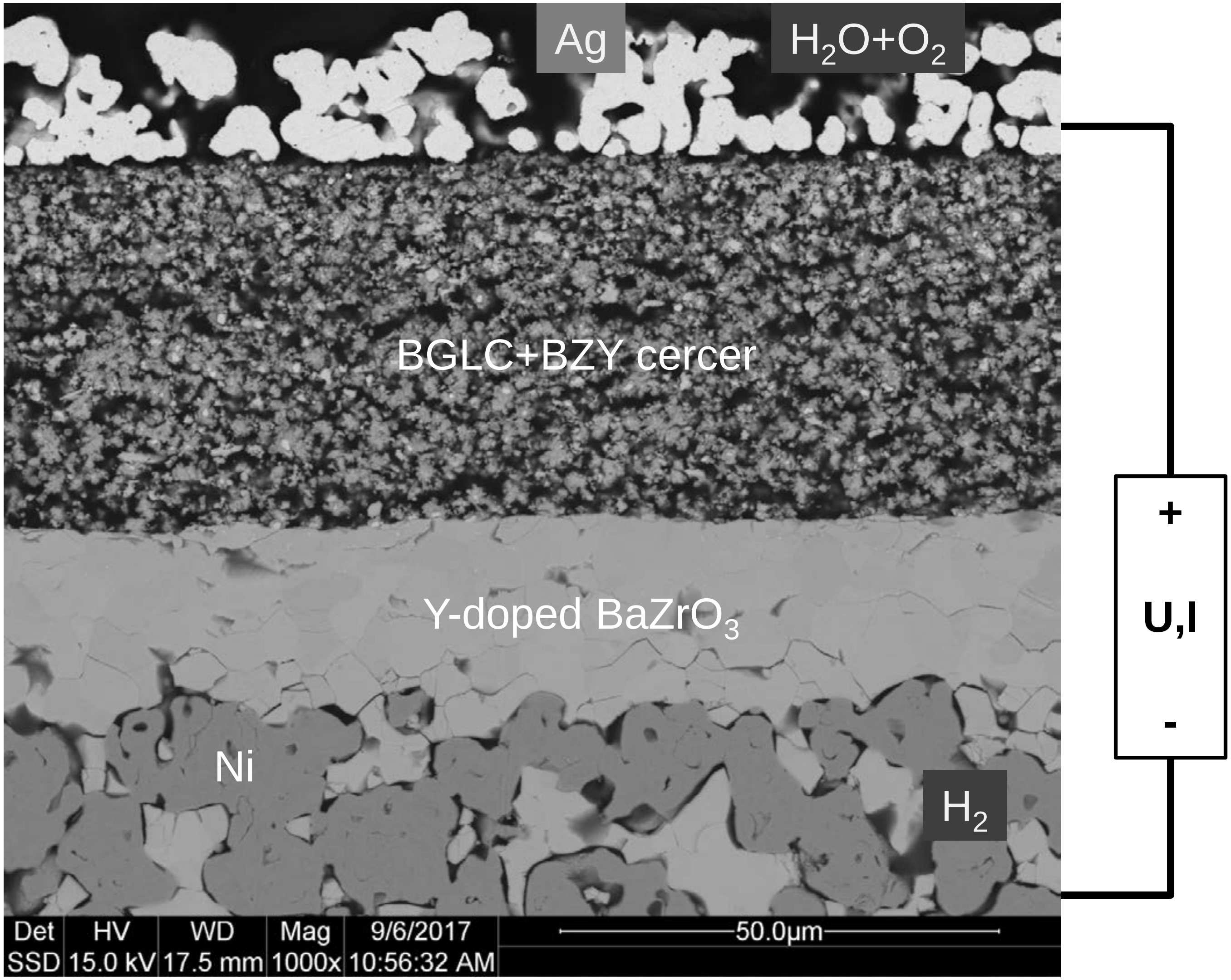
The chemistries of PCECs – example of BGLC-BZY-Ni

Current collector

Positrode

Electrolyte

Negatrode



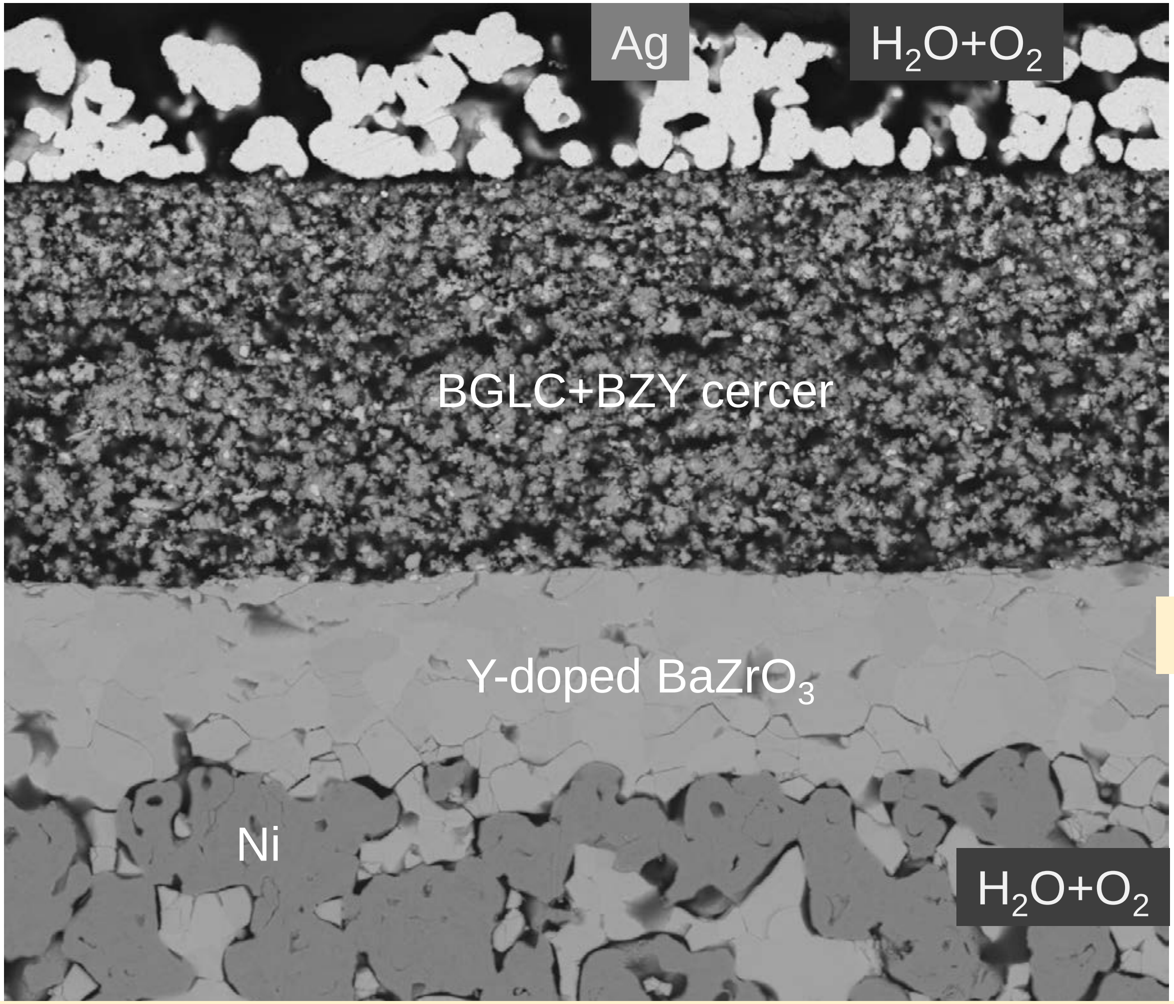
PCECs synthesis and fabrication – 1100 -1600°C in air

Current collector

Positrode

Electrolyte

Negatrode



Ag

BaO
Gd_2O_3
La_2O_3
CoO

$BaCO_3$ or $BaSO_4$
ZrO_2
Y_2O_3

NiO

Phases and interfaces: Why do they form? Wanted or not?

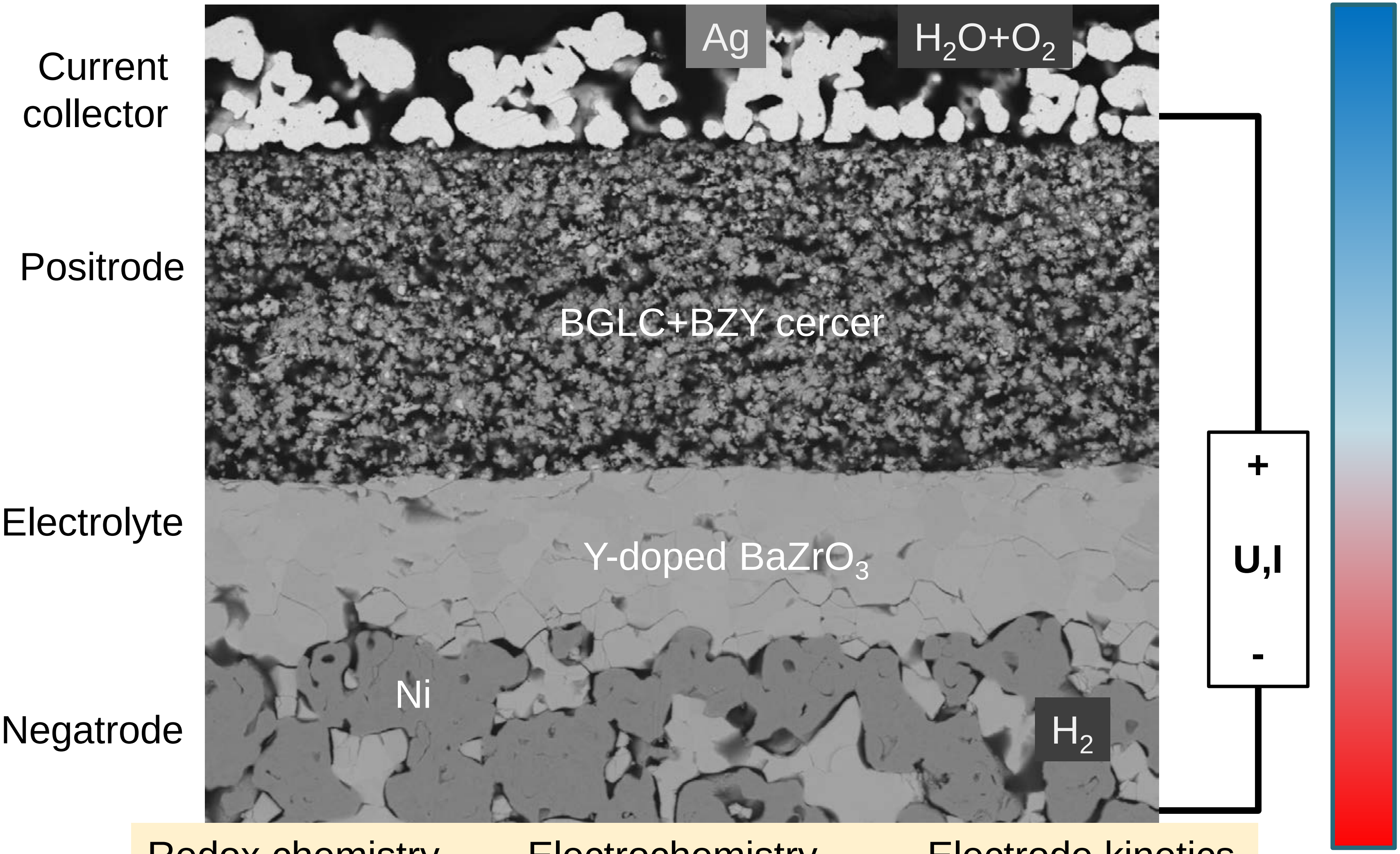
Thermodynamics: Acid – base. Phase diagram Balanced kinetics

Phases and interfaces

- The **phases** formed are preferably coexistent
- They would then be neighbours in a (binary, ternary, quadrernary…multinary) phase diagram
- They would spontaneously form from an atomic mix of the cations – a PCEC soup
- Solid solutions; defects.

- The **interfaces** are grain boundaries (unnecessary), phase boundaries (necessary - wanted), and surfaces.
- Two and three phase boundaries (2pb, dpb, 3pb, tpb)
- Interfaces impose
  - Function – ionic and electronic separation
  - Interface energy – destabilises the system; phase stability may change. E.g. $BaZrO_3 + CO_2 = BaCO_3 + CeO_2$
  - Charge separation – space charge – affects carrier concentrations; fuction or dysfunction

PCECs – chemical and electrical gradients – 600°C



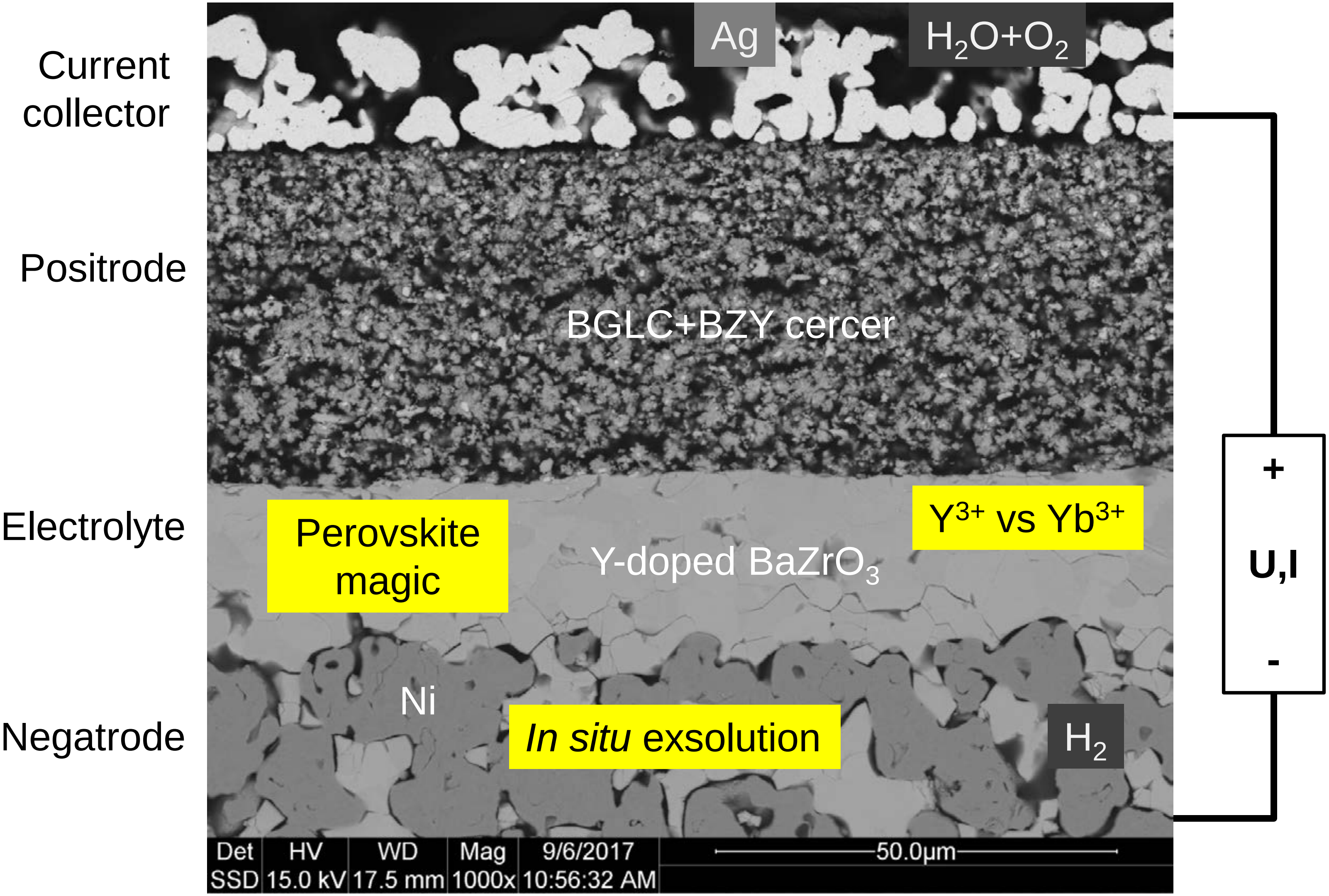
Redox chemistry Electrochemistry Electrode kinetics

Electrochemical driving forces - everything wants to move – are we in control?

Similarities to living organisms?

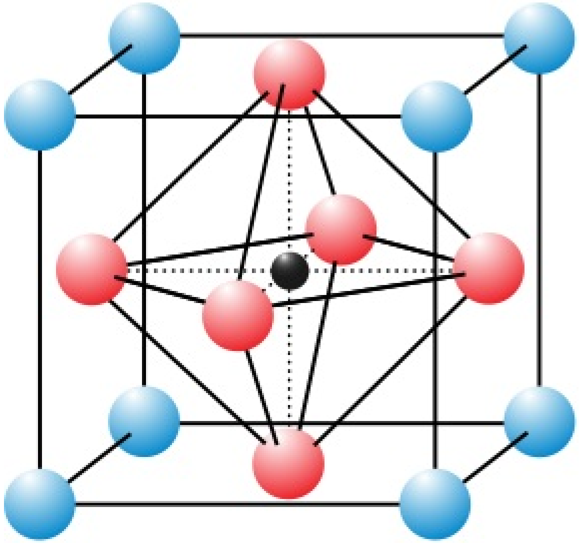
How do they do it?

Three selected chemistries of PCECs



Perovskite magic

- High solid solubilities: High doping and defect concentrations
  - Low energy of defects
- Large A site cations
  - Oxide sublattice dynamics
- Acid-base
  - Stabilisation
  - Differentiation
- Structure variety
  - Cubic when you need it – layered when you don't
- Transition metal variety
  - B – O – B covers all imaginable electronic properties
- More?



In situ exsolution

- Phase separation
- Reduced solid solubility
  - Reduced temperature
  - Changed redo-ox
    - Reducing conditions
    - Oxidising conditions
    - Polarisation
    - Kinetic demixing
- Continuous or cyclic
- Fresh
- Mechanically robust

Simplest example: Ni-YSZ

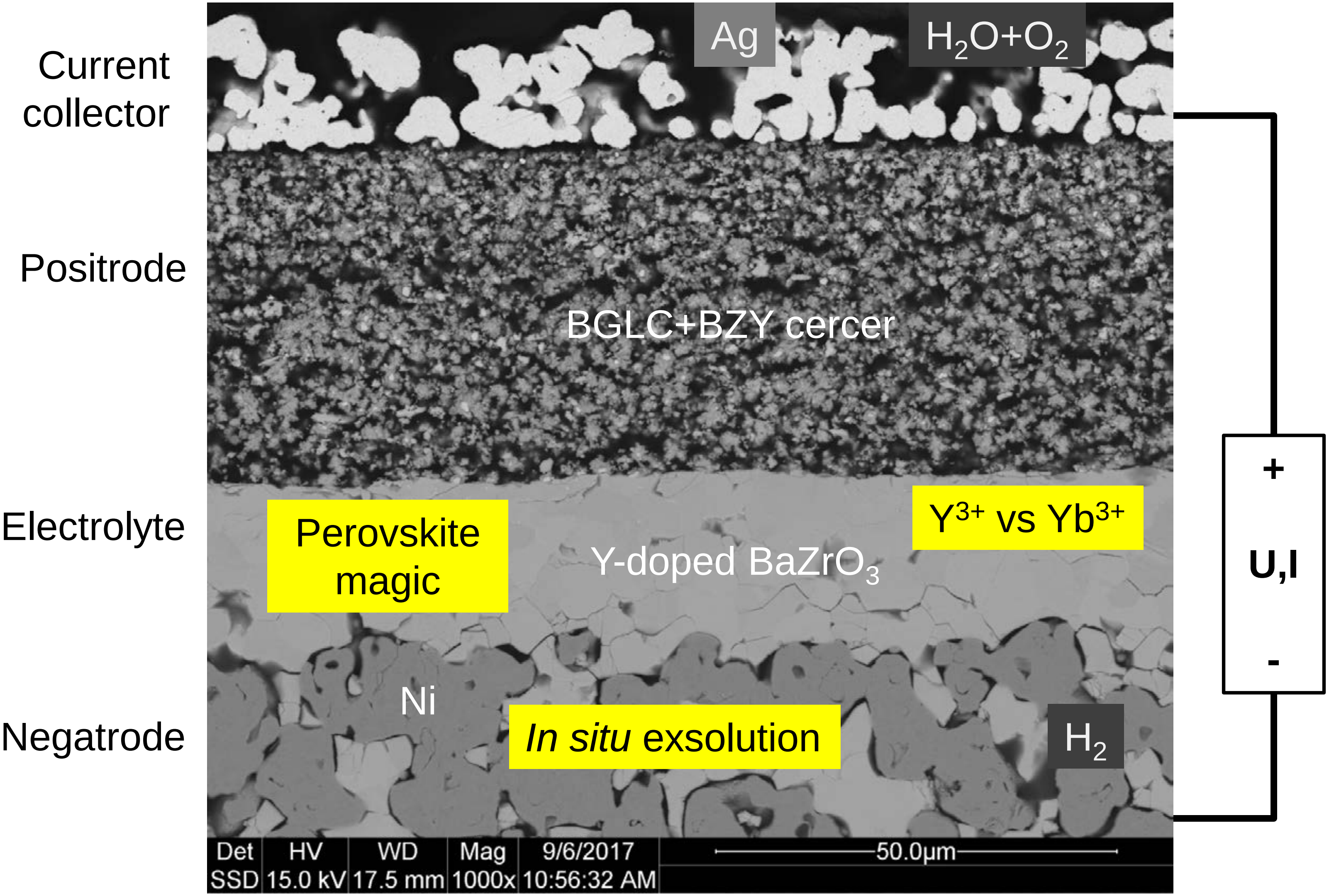
Ni^{2+} dissolves in YSZ during sintering of NiO-YSZ composite electrode in air

Ni exsolves operando in H_2

The same applies to Ni-BZY

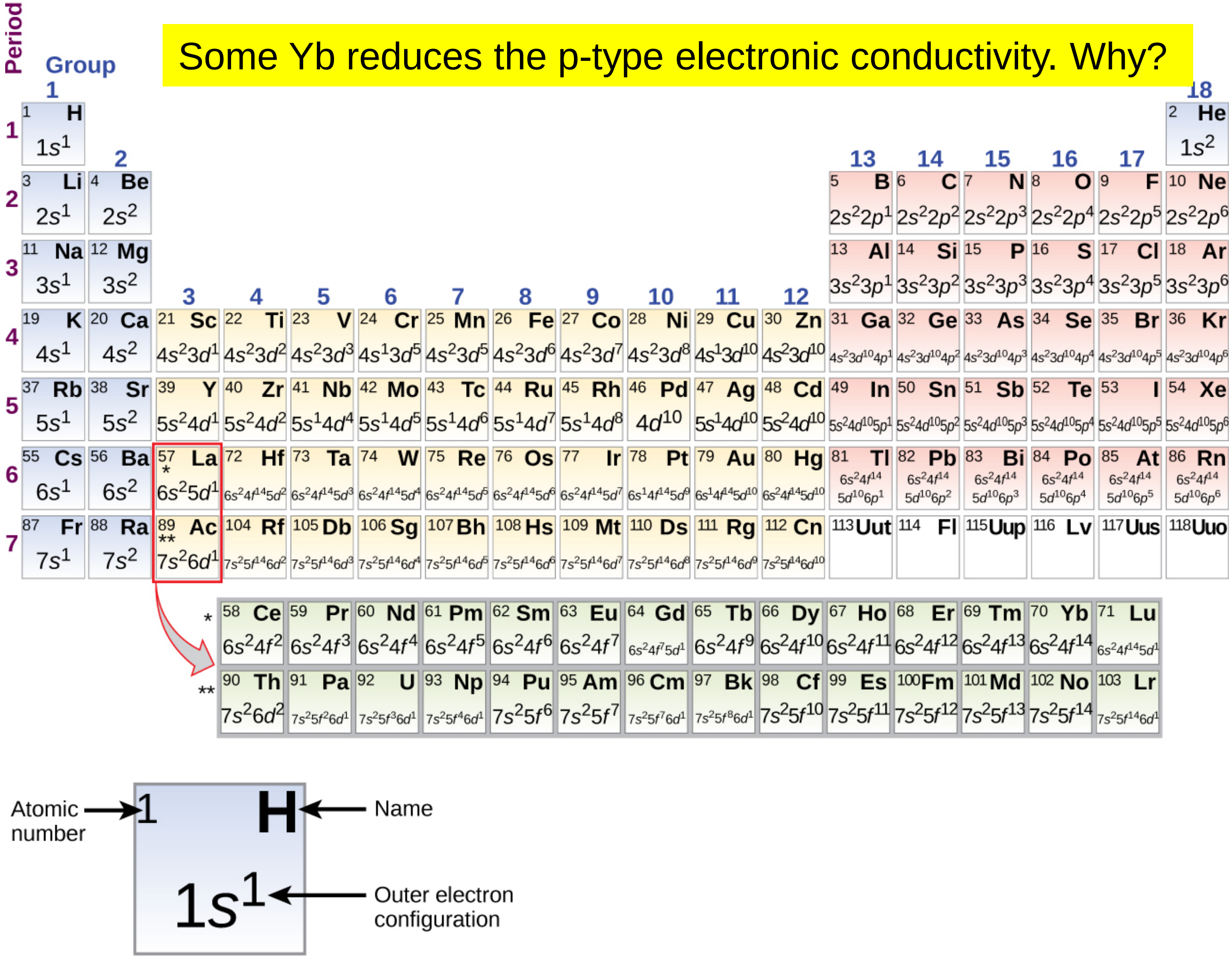
The race is on for positrodes

Three selected chemistries of PCECs



Y^{3+} vs Yb^{3+} in $BaZrO_3$ BZY BZYYB BZYb

Some Yb reduces the p-type electronic conductivity. Why?



Period \ Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
3	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
4	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $4s^23d^1$	22 **Ti** $4s^23d^2$	23 **V** $4s^23d^3$	24 **Cr** $4s^13d^5$	25 **Mn** $4s^23d^5$	26 **Fe** $4s^23d^6$	27 **Co** $4s^23d^7$	28 **Ni** $4s^23d^8$	29 **Cu** $4s^13d^{10}$	30 **Zn** $4s^23d^{10}$	31 **Ga** $4s^23d^{10}4p^1$	32 **Ge** $4s^23d^{10}4p^2$	33 **As** $4s^23d^{10}4p^3$	34 **Se** $4s^23d^{10}4p^4$	35 **Br** $4s^23d^{10}4p^5$	36 **Kr** $4s^23d^{10}4p^6$
5	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $5s^24d^1$	40 **Zr** $5s^24d^2$	41 **Nb** $5s^14d^4$	42 **Mo** $5s^14d^5$	43 **Tc** $5s^14d^6$	44 **Ru** $5s^14d^7$	45 **Rh** $5s^14d^8$	46 **Pd** $4d^{10}$	47 **Ag** $5s^14d^{10}$	48 **Cd** $5s^24d^{10}$	49 **In** $5s^24d^{10}5p^1$	50 **Sn** $5s^24d^{10}5p^2$	51 **Sb** $5s^24d^{10}5p^3$	52 **Te** $5s^24d^{10}5p^4$	53 **I** $5s^24d^{10}5p^5$	54 **Xe** $5s^24d^{10}5p^6$
6	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La** * $6s^25d^1$	72 **Hf** $6s^24f^{14}5d^2$	73 **Ta** $6s^24f^{14}5d^3$	74 **W** $6s^24f^{14}5d^4$	75 **Re** $6s^24f^{14}5d^5$	76 **Os** $6s^24f^{14}5d^6$	77 **Ir** $6s^24f^{14}5d^7$	78 **Pt** $6s^14f^{14}5d^9$	79 **Au** $6s^14f^{14}5d^{10}$	80 **Hg** $6s^24f^{14}5d^{10}$	81 **Tl** $6s^24f^{14}$ $5d^{10}6p^1$	82 **Pb** $6s^24f^{14}$ $5d^{10}6p^2$	83 **Bi** $6s^24f^{14}$ $5d^{10}6p^3$	84 **Po** $6s^24f^{14}$ $5d^{10}6p^4$	85 **At** $6s^24f^{14}$ $5d^{10}6p^5$	86 **Rn** $6s^24f^{14}$ $5d^{10}6p^6$
7	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac** ** $7s^26d^1$	104 **Rf** $7s^25f^{14}6d^2$	105 **Db** $7s^25f^{14}6d^3$	106 **Sg** $7s^25f^{14}6d^4$	107 **Bh** $7s^25f^{14}6d^5$	108 **Hs** $7s^25f^{14}6d^6$	109 **Mt** $7s^25f^{14}6d^7$	110 **Ds** $7s^25f^{14}6d^8$	111 **Rg** $7s^25f^{14}6d^9$	112 **Cn** $7s^25f^{14}6d^{10}$	113 **Uut**	114 **Fl**	115 **Uup**	116 **Lv**	117 **Uus**	118 **Uuo**

*	58 **Ce** $6s^24f^2$	59 **Pr** $6s^24f^3$	60 **Nd** $6s^24f^4$	61 **Pm** $6s^24f^5$	62 **Sm** $6s^24f^6$	63 **Eu** $6s^24f^7$	64 **Gd** $6s^24f^75d^1$	65 **Tb** $6s^24f^9$	66 **Dy** $6s^24f^{10}$	67 **Ho** $6s^24f^{11}$	68 **Er** $6s^24f^{12}$	69 **Tm** $6s^24f^{13}$	70 **Yb** $6s^24f^{14}$	71 **Lu** $6s^24f^{14}5d^1$
**	90 **Th** $7s^26d^2$	91 **Pa** $7s^25f^26d^1$	92 **U** $7s^25f^36d^1$	93 **Np** $7s^25f^46d^1$	94 **Pu** $7s^25f^6$	95 **Am** $7s^25f^7$	96 **Cm** $7s^25f^76d^1$	97 **Bk** $7s^25f^86d^1$	98 **Cf** $7s^25f^{10}$	99 **Es** $7s^25f^{11}$	100 **Fm** $7s^25f^{12}$	101 **Md** $7s^25f^{13}$	102 **No** $7s^25f^{14}$	103 **Lr** $7s^25f^{14}6d^1$

Atomic number → 1 **H** ← Name

$1s^1$ ← Outer electron configuration

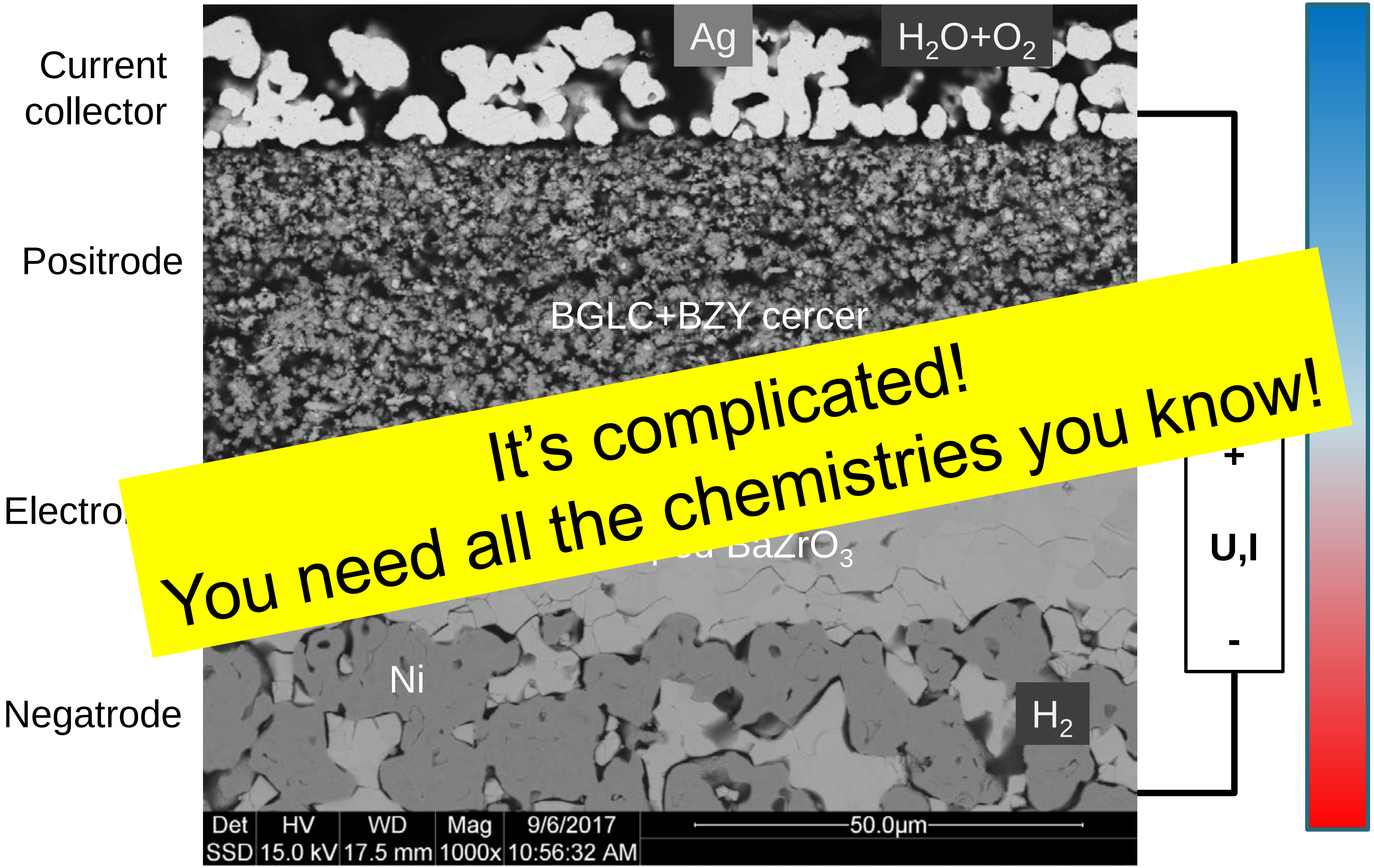
Y vs Yb

- Y^{3+} [Kr]
- r_{3+} = 88 pm

- Yb is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^0 6s^2$
- $[Xe]4f^{14}5d^0 6s^2$

- Yb^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{13} 5s^2 5p^6$
- $[Xe]4f^{13}$
- r_{3+} = 86 pm

Conclusions



It’s complicated!
You need all the chemistries you know!

Acknowledgements

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FCH
FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

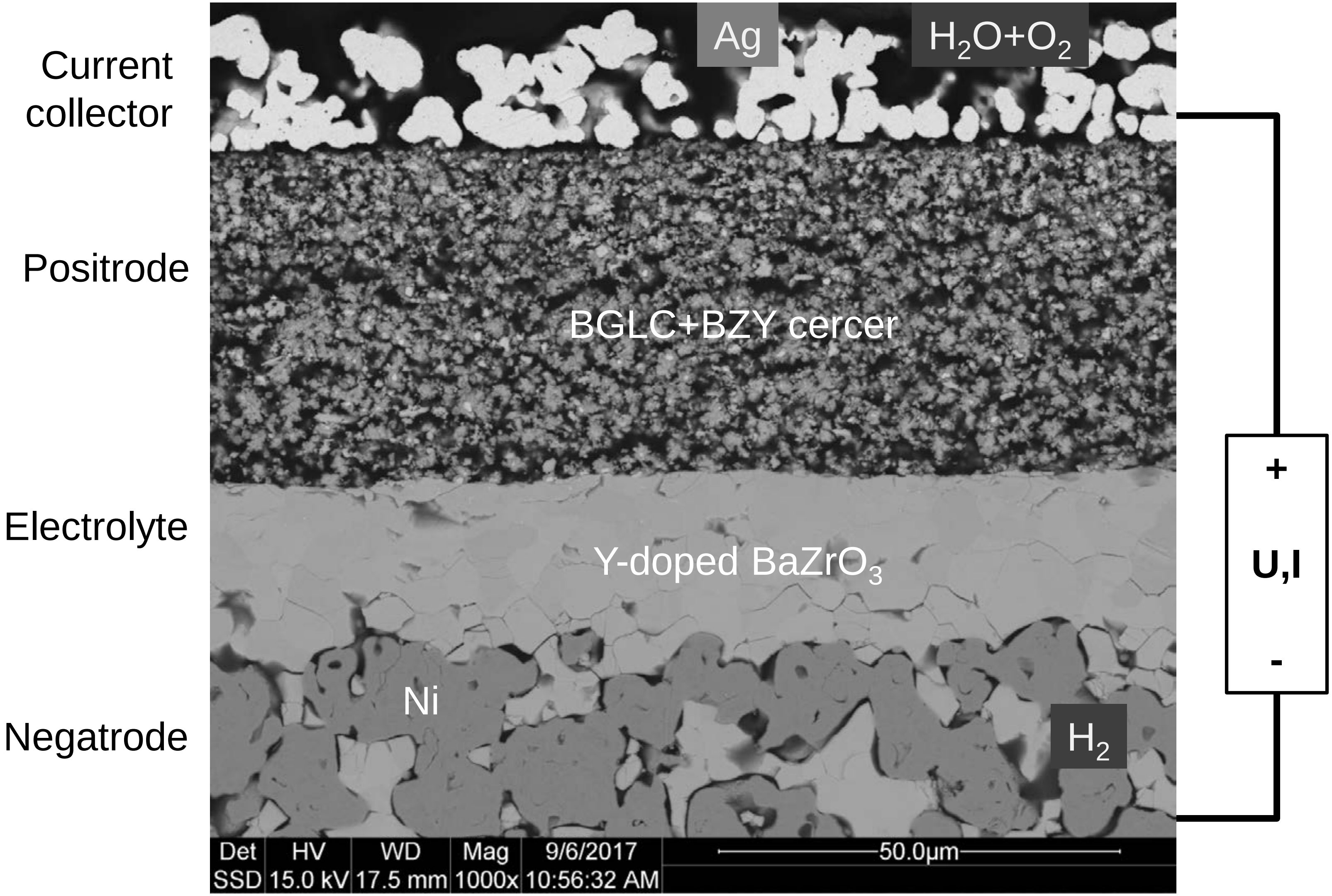
Electra

The Research Council of Norway

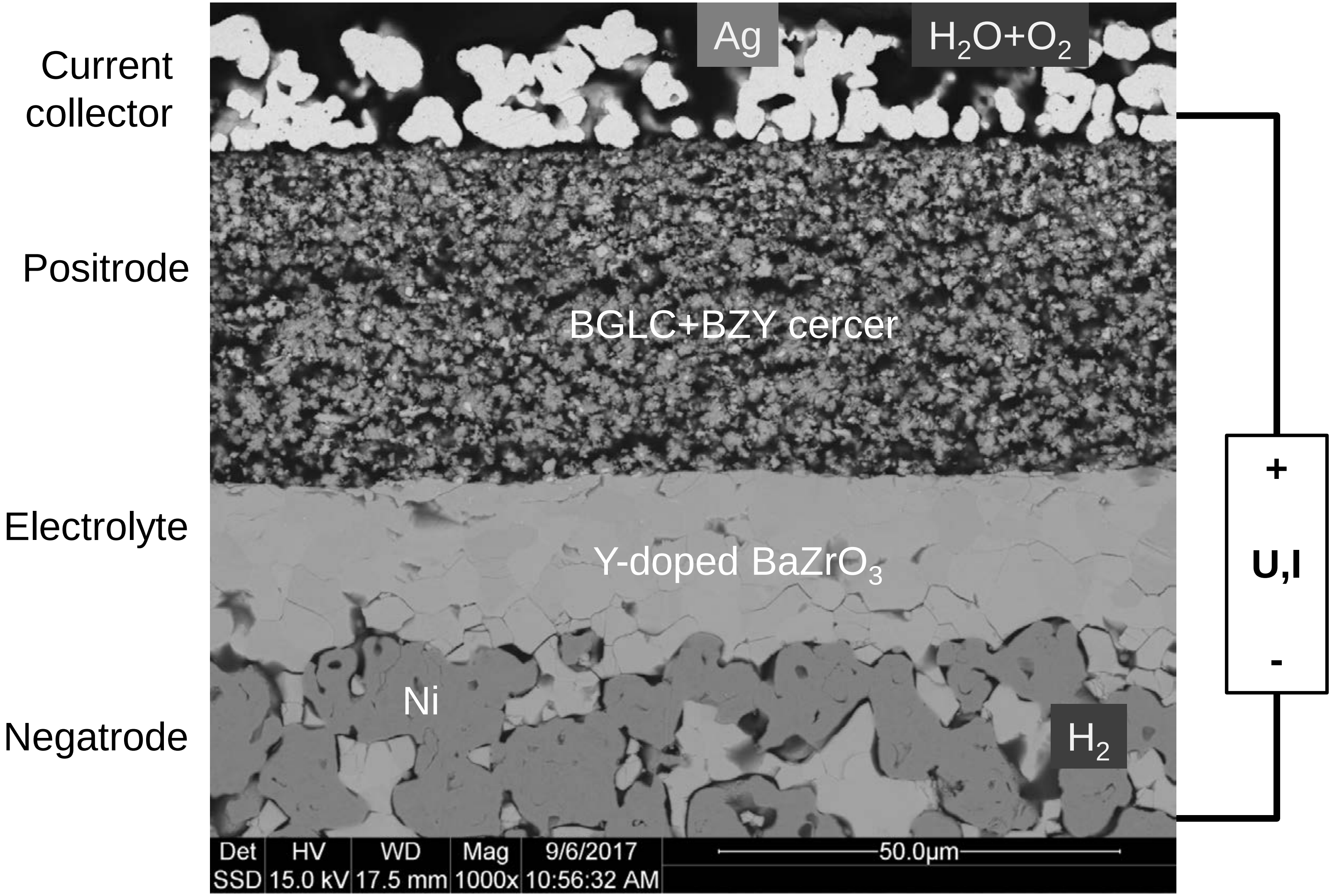
FOXCET

Backup slides

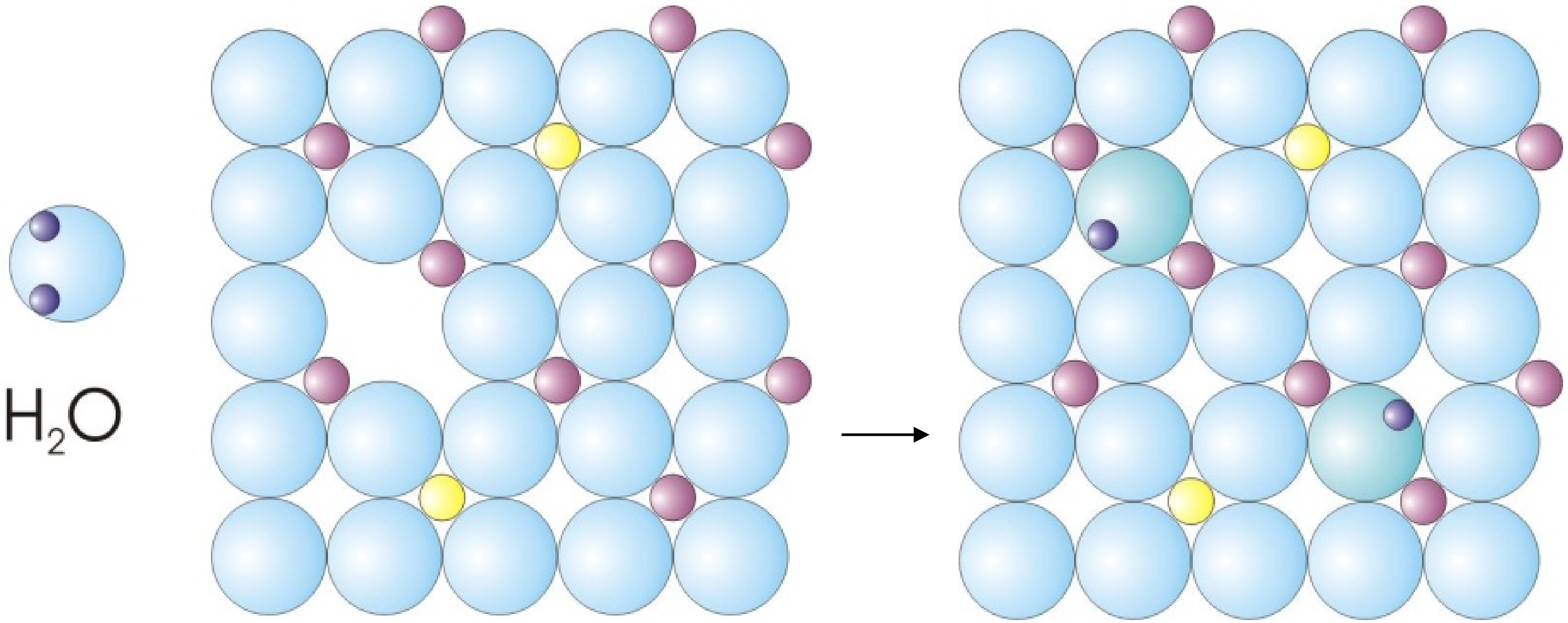
The chemistries of PCECs



The chemistries of PCECs



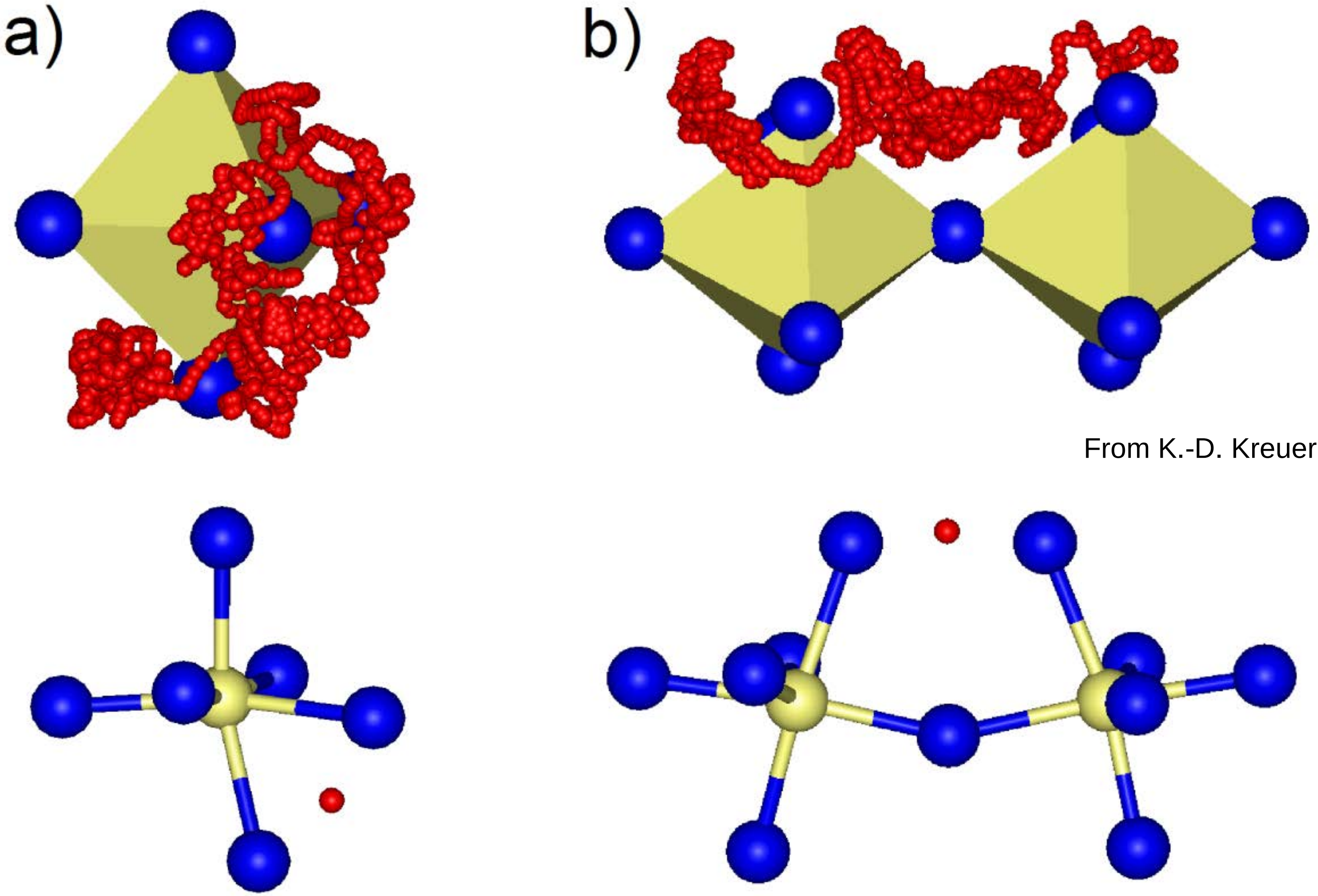
Proton conducting oxides by hydration of oxygen vacancies



$$H_2O(g) + v_O + O_O^{2-} = 2OH_O^-$$

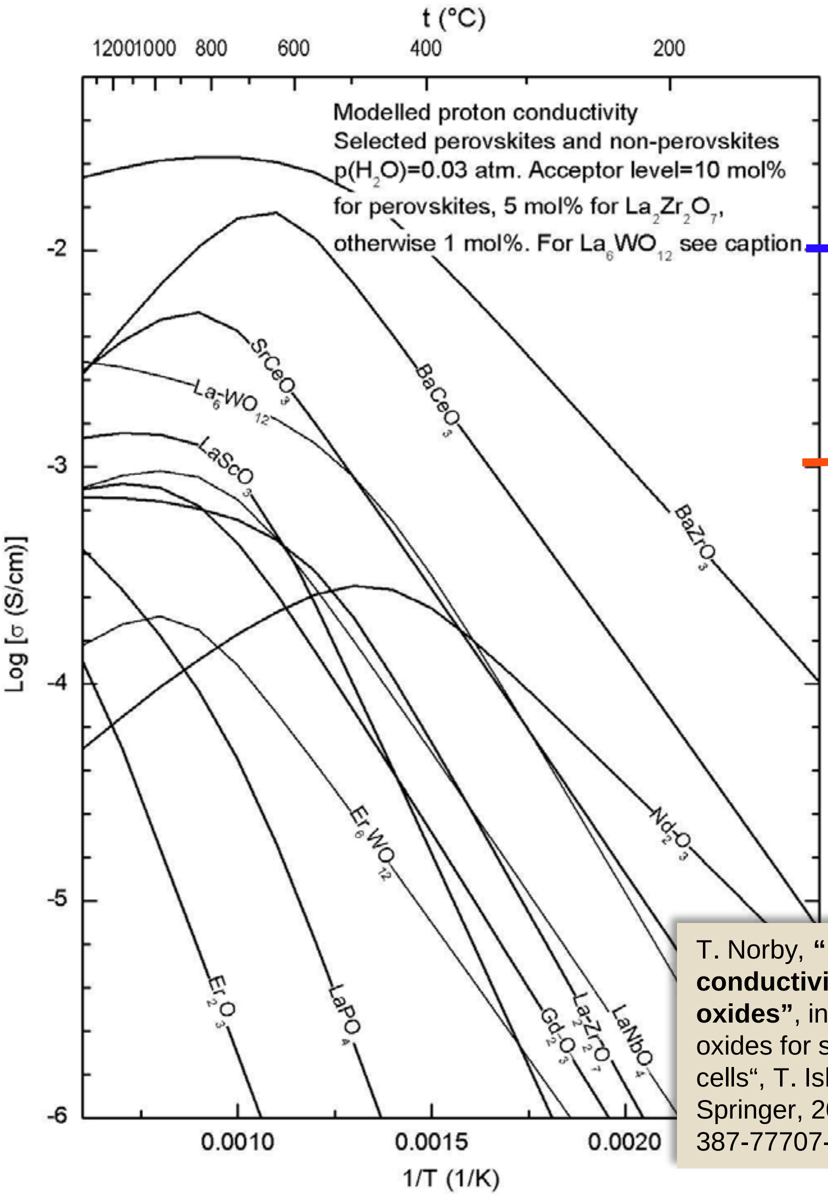
$$H_2O(g) + v_O^{\bullet\bullet} + O_O^x = 2OH_O^{\bullet}$$

Protons transport: rotation and hydrogen bond jumps



From K.-D. Kreuer, 2008

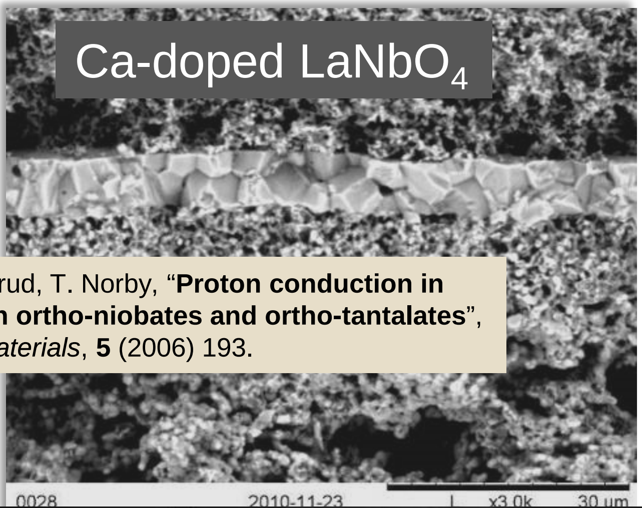
Proton conductivity in acceptor-doped oxides



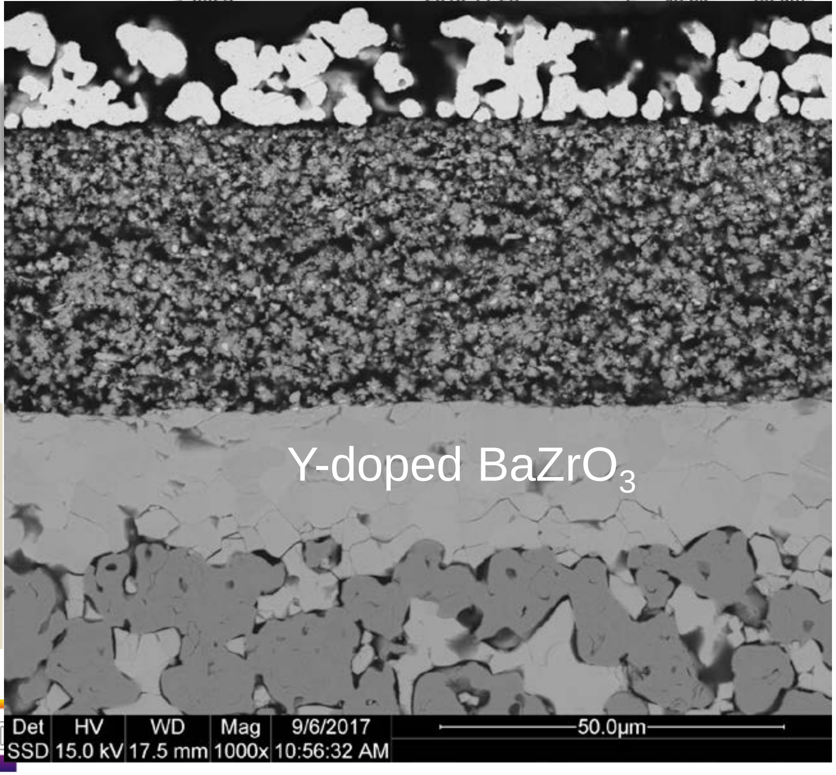
0.1 Ωcm^2
10 µm

0.1 Ωcm^2
1 µm

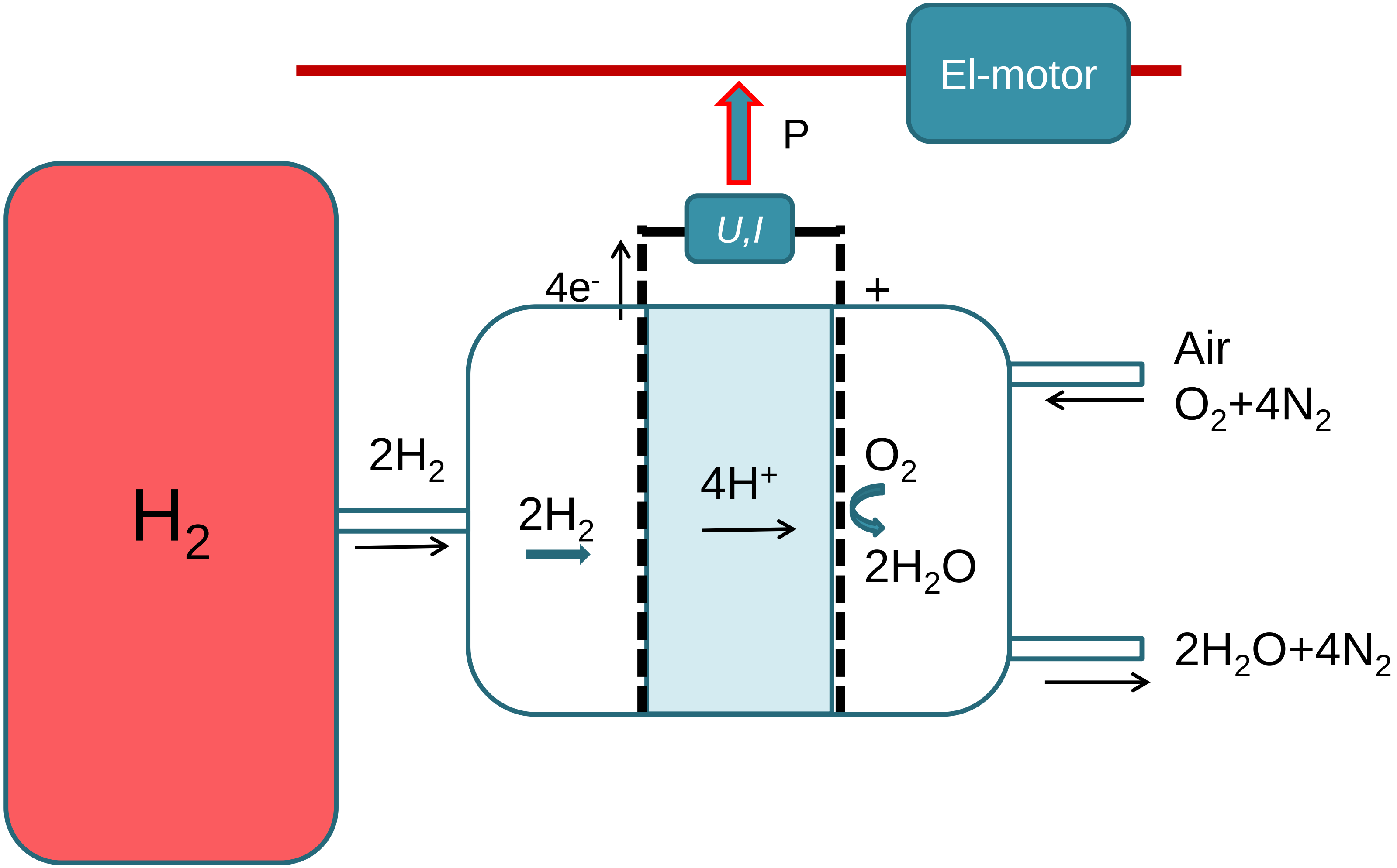
T. Norby, **“Proton conductivity in perovskite oxides”**, in “Perovskite oxides for solid oxide fuel cells“, T. Ishihara, ed., Springer, 2009, ISBN 978-0-387-77707-8.



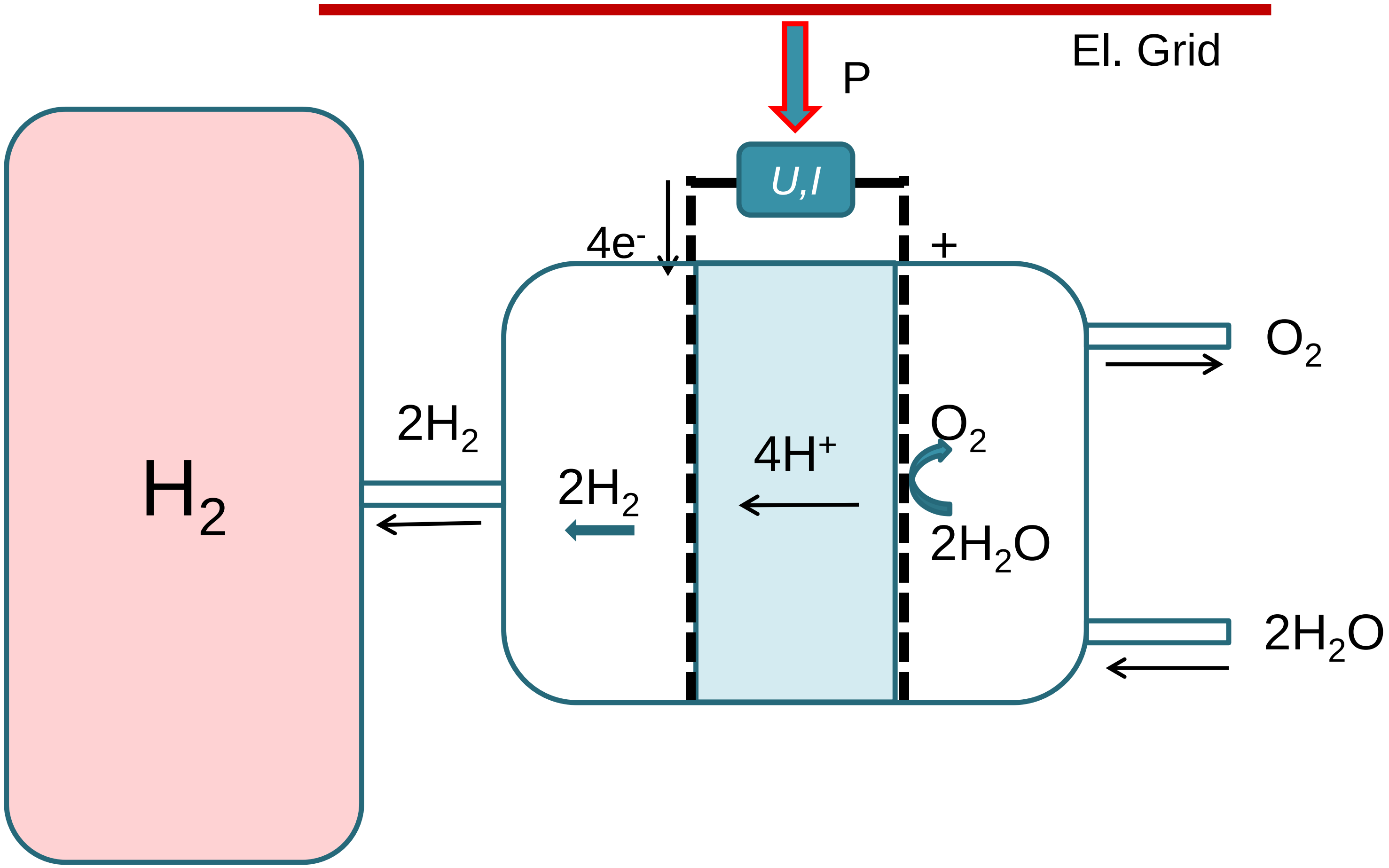
R. Haugsrud, T. Norby, “**Proton conduction in rare earth ortho-niobates and ortho-tantalates**”, *Nature Materials*, **5** (2006) 193.



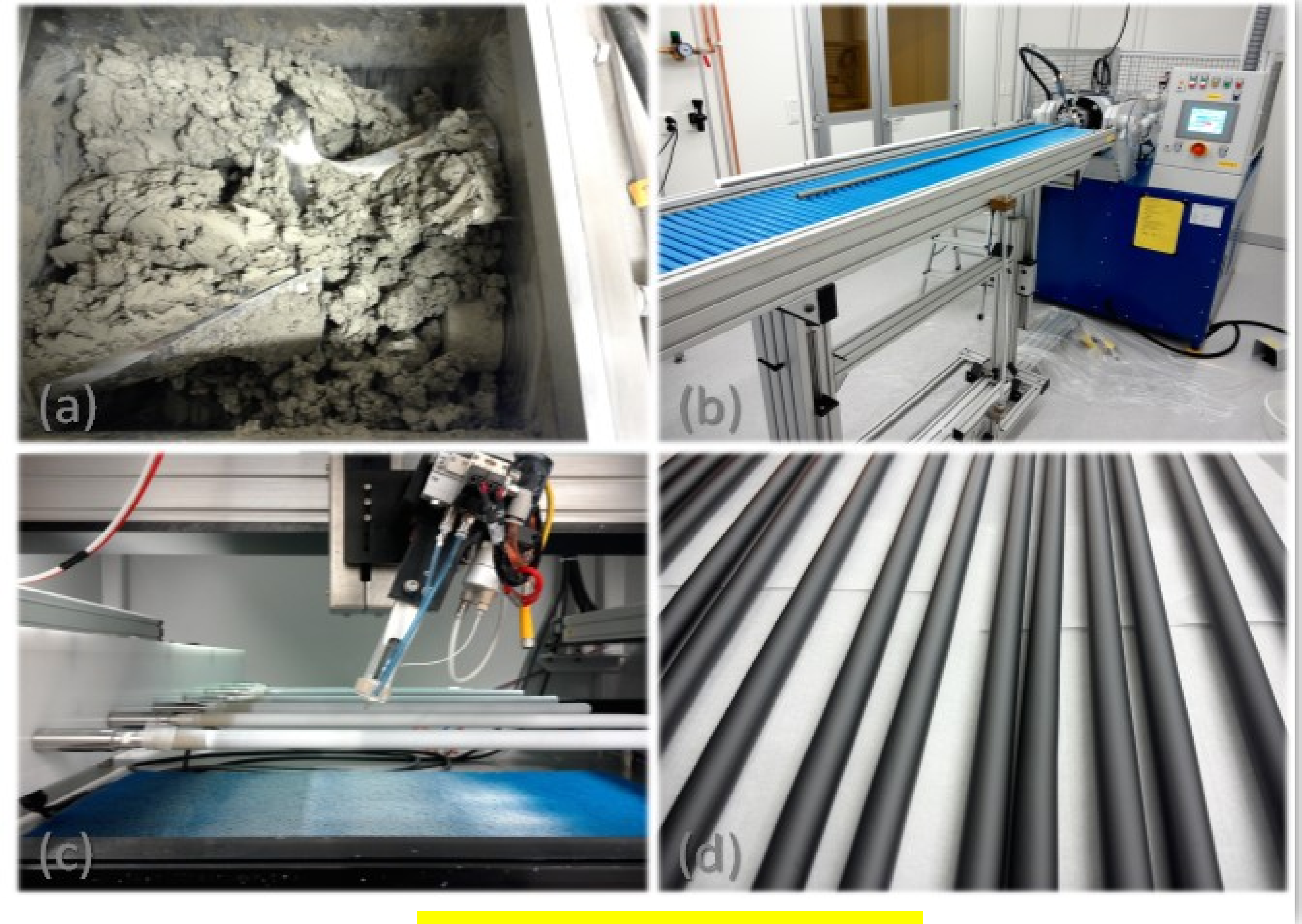
Fuel cell



Electrolyser and electrochemical compressor



ELECTRA and GAMER EU projects: Production of tubes



Courtesy of Marie-Laure Fontaine, SINTEF