Materials and Technologies for Hydrogen Energy – current Gdańsk Tech perspective

on behaf of

Aleksandra Mielewczyk-Gryń

Presentation plan

- A short introduction to research groups working on hydrogen-related topics at Gdańsk TECH
- The major research interests of particular groups
- The current „hot topic” researched by Proton in Solids Research Group

Faculty of Electronics, telecommunication and informatics

POLITECHNIKA GDAŃSKA

Laboratory of Functional Materials

eceramics

Piotr Jasiński (PI) Sebastian Molin

Low TRLs (1-5)

Sylwia Pawłowska, Paweł Kalinowski, Karolina Sycewska, Ahsanul Kabir

Solid oxide cells: SOFC/SOECs

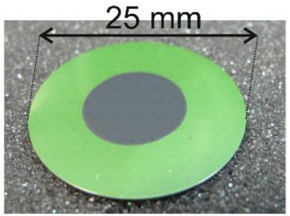
- Novel electrode materials: hydrogen and oxygen electrode;
- Ceramic processing;
- Testing of cells;

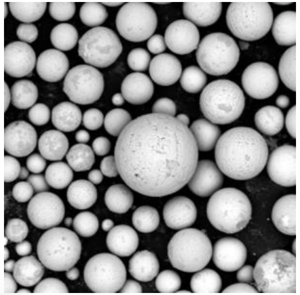
High-temperature corrosion and protective coatings:

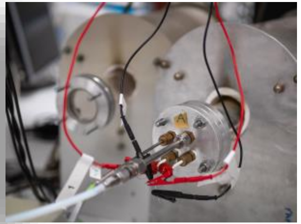
- Dense alloys
- Porous alloys

Electrochemistry

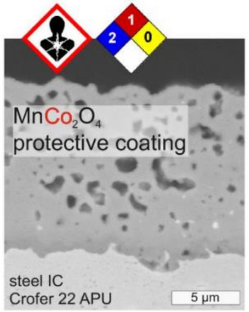
- Bio-interfaces;
- Electrocatalysis;
- Sensors;







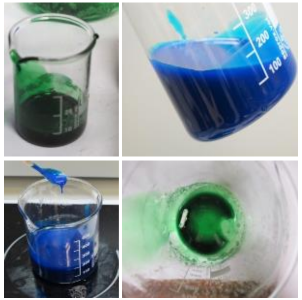
High-temperature corrosion – protective coatings



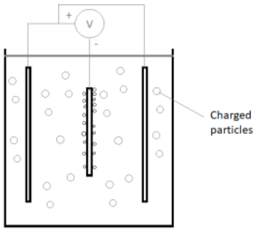
Replacement of $(MnCo)_3O_4$

- it is regarded as a carcinogenic material by the World Health Organization
- processing at all stages requires expensive safety procedures and equipment;
- fluctuating price, during the last 5 years the price of cobalt more than doubled;
- it is not-sustainably mined
- We propose to search for new materials, composed of abundant and cheap elements (Fe, Mn, Cu, Ni, Mg etc.) with protective properties comparable to the Mn-Co spinel.

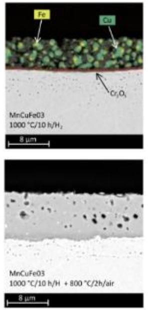
Material synthesis sol-gel method



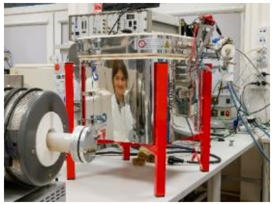
Coating deposition electrophoretic deposition



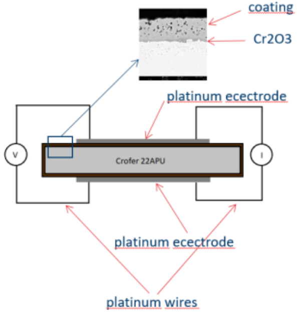
Sintering of the coatings



Oxidation test



Characterization of the coating

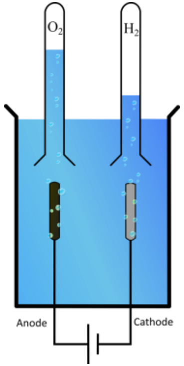


POLITECHNIKA GDAŃSKA | Laboratory of Functional Materials

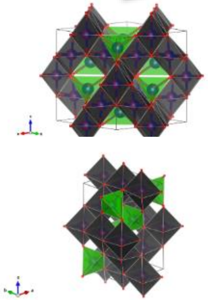
eceramics

Alkaline electrolysis

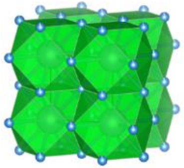
Oxygen Evolution Reaction (OER) electrocatalysts



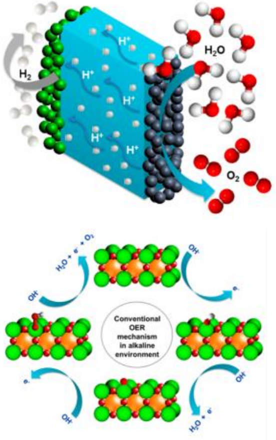
$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$



Spinels
$Mn_xCo_{3-x}O_4$
(x = 0, 0.5, 1, 1.5, 2)



Perovskites
$SrTi_{x-1}Fe_xO_{3-\delta}$
(x= 0.35, 0.5, 0.7, 0.9, 1)



[1] E. Fabbri *Oxygen Evolution Reaction-The Enigma in Water Electrolysis*, ACS Catalysis, 2018

- Material Synthesis
- Structural Studies:
  - SEM
  - BET SSA
  - XRD
  - XPS
  - XAS*
  - TEM
- Electrochemical Studies:
  - CV
  - EIS

Alkaline electrolysis

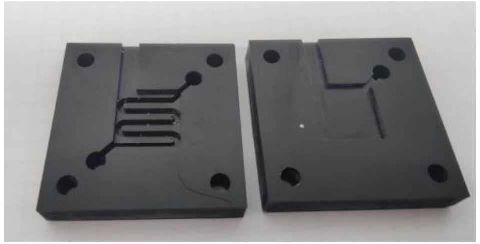
Electrode size upscaling – towards real life performance benchmarks

0.2 cm^2 < 1 cm^2 < 10 cm^2

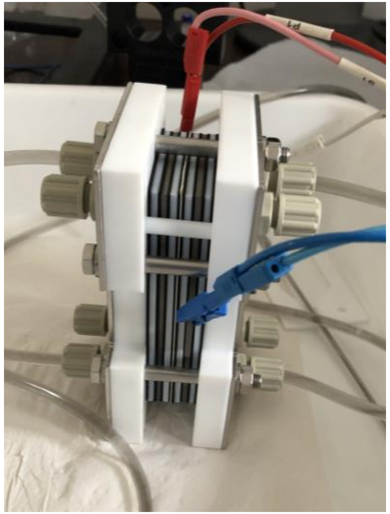
Rotating Disk Electrode

Catalyst screening / activity determination

Ni Foam Electrode



Platform for long-term performance evaluation



Development towards larger scale systems

LMF works on several aspects of materials engineering:

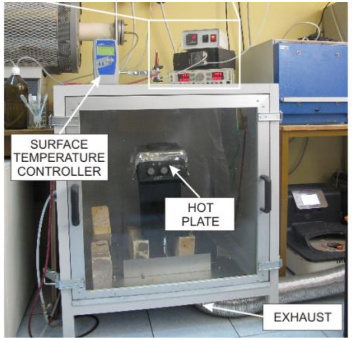
Ceramic deposition technologies:

- Dip-coating
- Spin-coating
- Spray-pyrolysis
- (soon) Electrospinning of nanofibers

} Especially low-temperature methods

New materials:

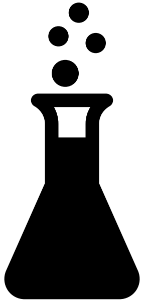
- From powders to devices: SOCs, AECs;



Institute of Nanotechnology and Materials Engineering

Research in the insitutute:

- solid oxide fuel cells and solid oxide electrolyzers materials – both electrolytes and electrodes;
- glasses – luminescent and thermoelectric properties;
- carbon nanotubes and graphen based materials;
- thin films deposition and properties;
- intermetallic compounds and their low temperature properties – superconductors;
- Non destructive testing
- solid state simulations and modeling – MD, DFT, MC.
- „wet” electrochemistry



Maria Gazda – PI
Aleksandra Mielewczyk-Gryń
Tadeusz Miruszewski
Sebastian Wachowski
Wojciech Skubida

Jakub Karczewski - PI
Beata Bochentyn

collaboration P. Jasiński

DIR-SOFC fed with biogas

- Ceria-based anode catalytic layers
- In-situ measurements of electrical parameteres and outlet gases
- Non-equilibrium chemical analysis of outlet gases
- Influence of fuel impurities (H_2S, HCl, siloxanes)

prof. Sea-Fue Wang

TAIPEI TECH

Araceli Fuerte, Ph.D.

Ciemat
Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

GOBIERNO DE ESPAÑA
MINISTERIO DE CIENCIA, INNOVACIÓN Y UNIVERSIDADES

- **Project SONATA „*Anode catalytic materials for direct internal reforming solid oxide fuel cells (DIR-SOFCs)*", 2017/26/D/ST8/00822, NCN**

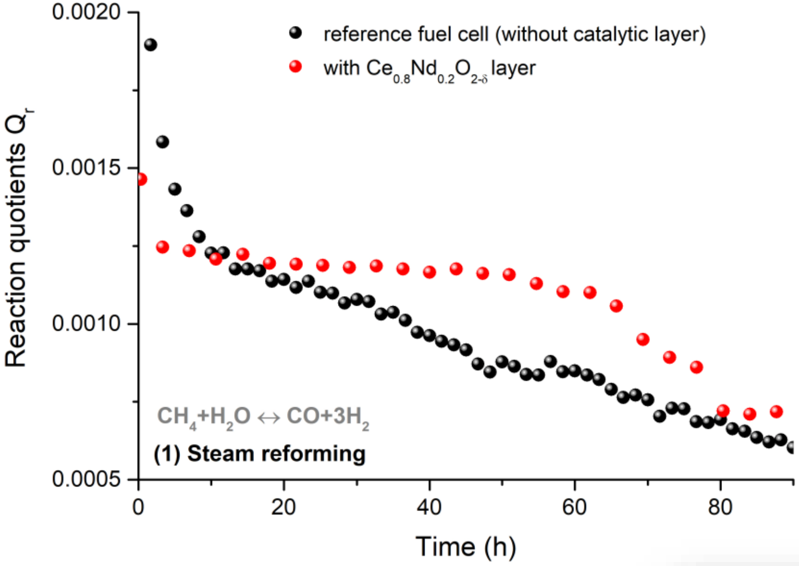
NEW MATERIALS FOR ENERGY CONVERSION RESEARCH GROUP

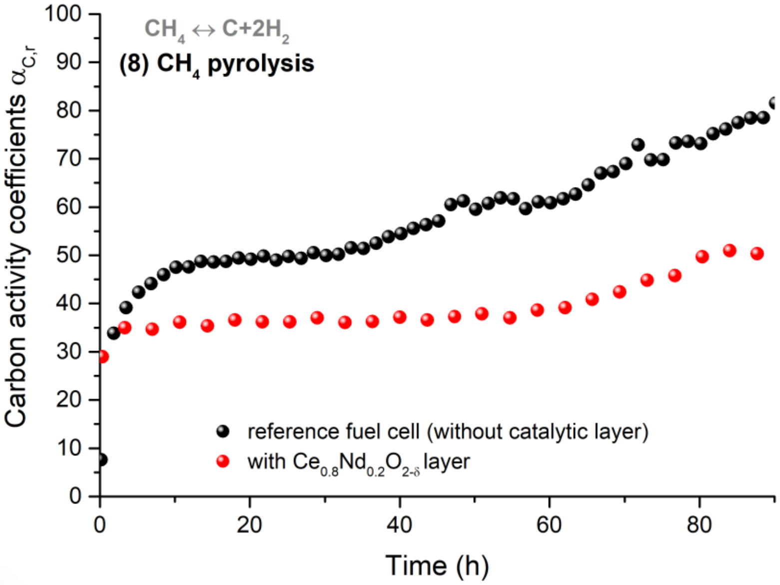
WFOŚiGW w Gdańsku

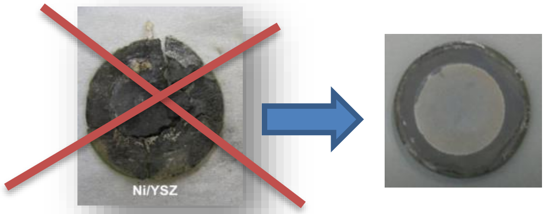
NARODOWE CENTRUM NAUKI

DIR-SOFC fed with biogas

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$
$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$$

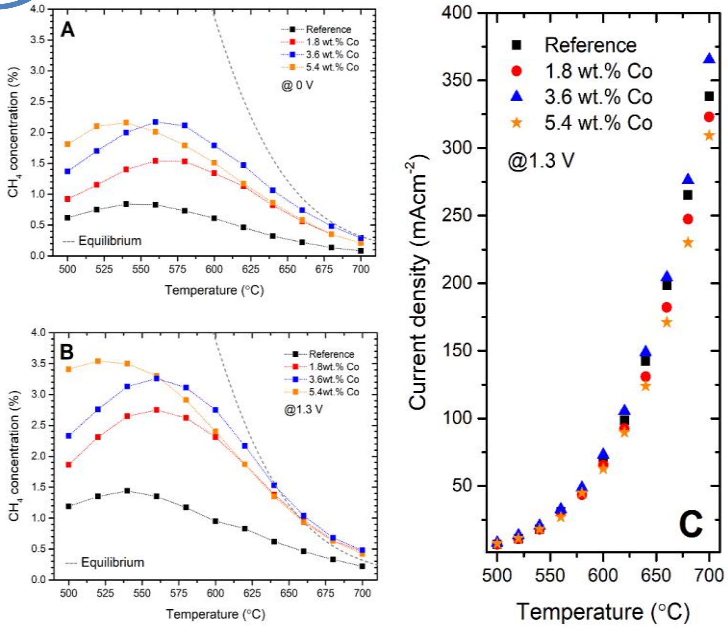


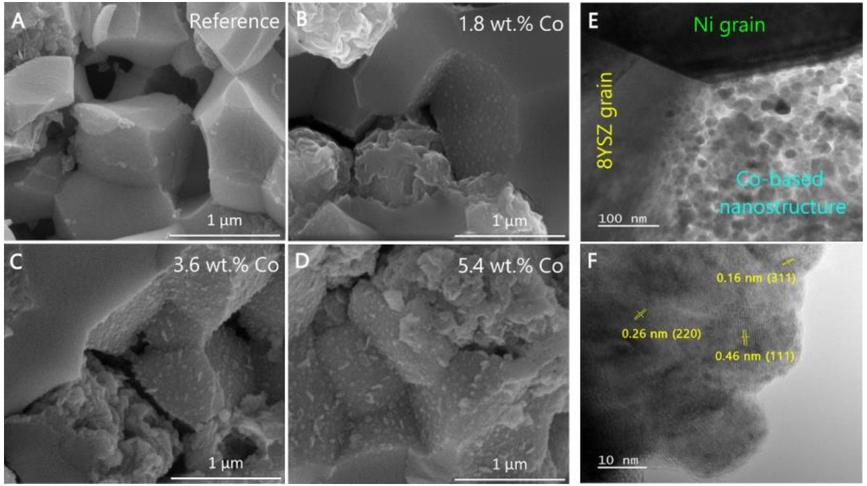


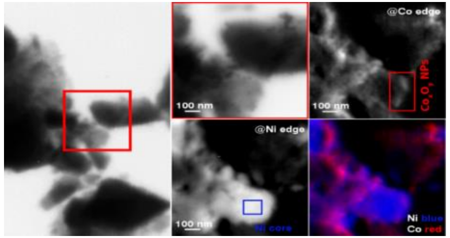


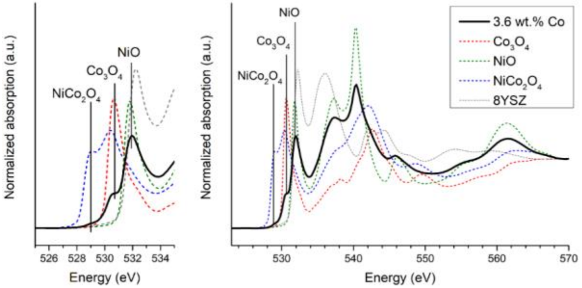
Nanometallic catalysts for SOEC/SOFC

Infiltration of nanometallic catalysts (Co, Cu, Fe, Mn, Ni) into Ni-YSZ matrix









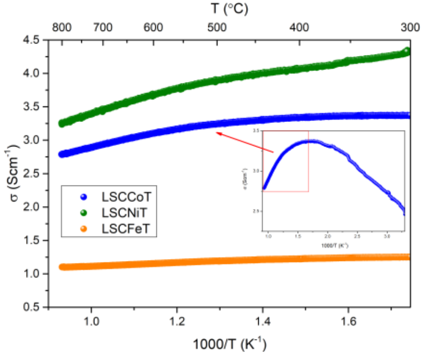
Exsolution of metallic nanoparticles and formation of alloys

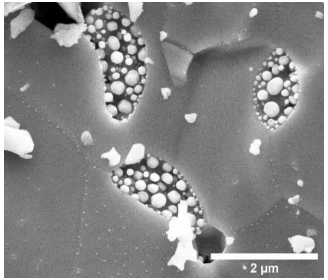
Support: (La,Sr,Ce)(ME,Ti)$O_{3-\delta}$, (Ce,ME)$O_{2-\delta}$, where ME=Co, Cu, Fe, Mn, Ni

Exsolution of mono- and multimetallic nanoparticles

Exsolution with topotactic ion exchange

Experiment vs. DFT calculation





- **Project SONATA „*New fuel electrodes for solid oxide electrolysis cells for syngas production*”, 2015/19/D/ST8/02783, NCN**
- **Project SONATA BIS „*Tailoring multicomponent nanometric alloys formed on active support for designing the stable anodes of Solid Oxide Fuel Cells*”, 2021/42/E/ST5/00450, NCN**

ESRF The European Synchrotron
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NARODOWE CENTRUM NAUKI

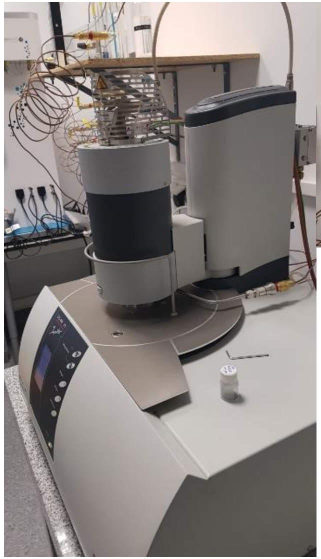
Projects → materials

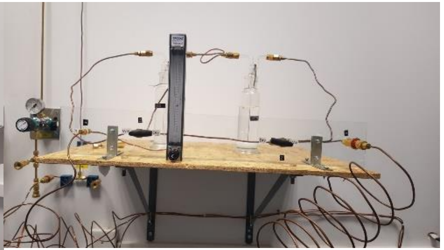
- ❑ GoPHyMICO → barium lanthanide cobaltites hydration
- ❑ FunKeyCat → barium lanthanide cobaltites and ferrrites for positrodes in PCECs
- ❑ Triple Conducting Oxides → materials modification for three charge carriers conductivity
- ❑ High Entropy Oxides for protonic conductivity
- ❑ Positrode Optimization for Protonic Ceramic Electrochemical Cells Technology
- ❑ Entropy stabilized oxides – transport properties
- ❑ Thin films for protonic conductivity
- ❑ Gas flow meters for industrial hydrogen

Methods

Synthesis methods:

- Solid state synthesis
- Molten salt synthesis
- Co-precipitation method
- Mechanosynthesis





Experimental methods:

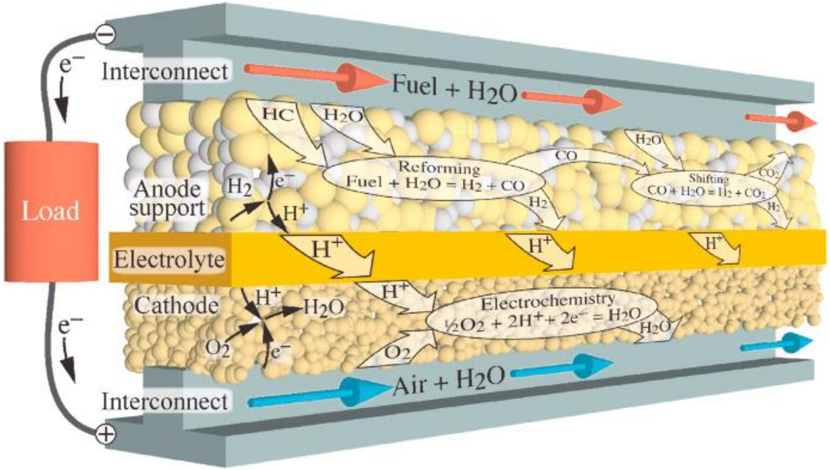
- Impedance spectrometry
- 4 wire DC methods
- Hebb-Wagner polarization method
- ECR method
- Fuel cell and electrolyzer testing
- High temperature X-ray diffraction
- Dilatometry
- Low temperature heat capacity measurements by PPMS system
- High temperature heat capacity measurements
- Water sorption studies
- SEM/SPM
- **Water uptake measurements → thermogravimetry**

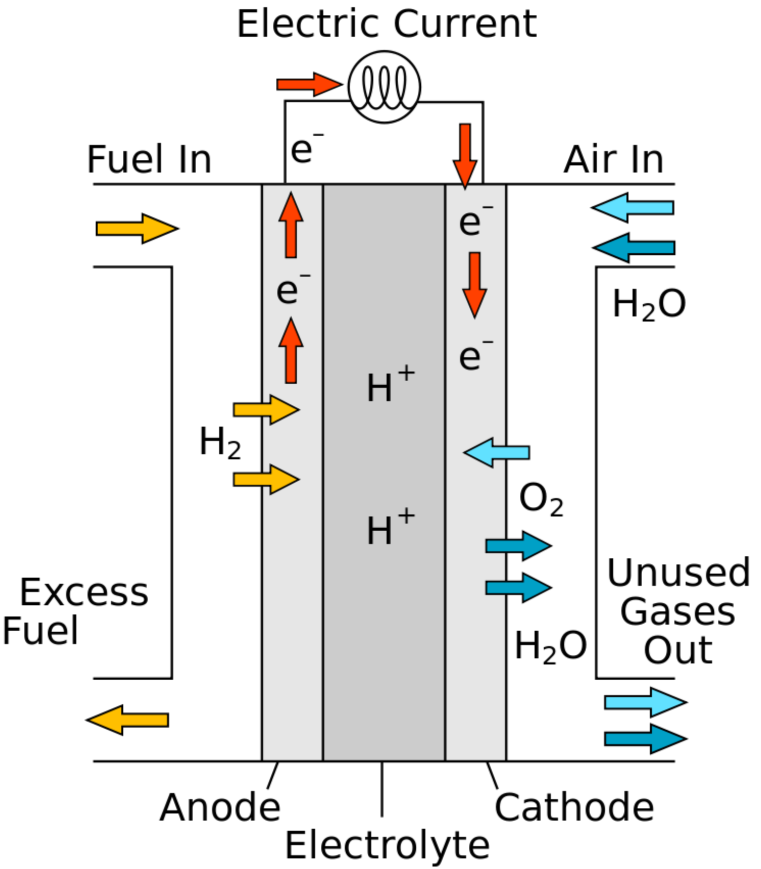
- X-ray absorption spectrometry
- Neutron diffraction
- SR-XRD
- TEM and TEM+SIMS

Motivation

Currently work on following parts of the Protonic Ceramic Electrochemical Cells:

- Positode
- Electrolyte





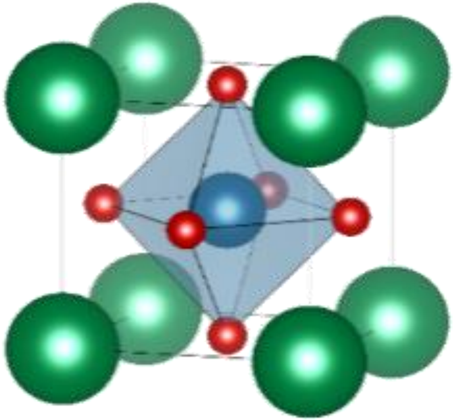
Le et al. Journal of Power Sources Volume 482, 15 January 2021, 228868

High entropy/multiconsitutent materials

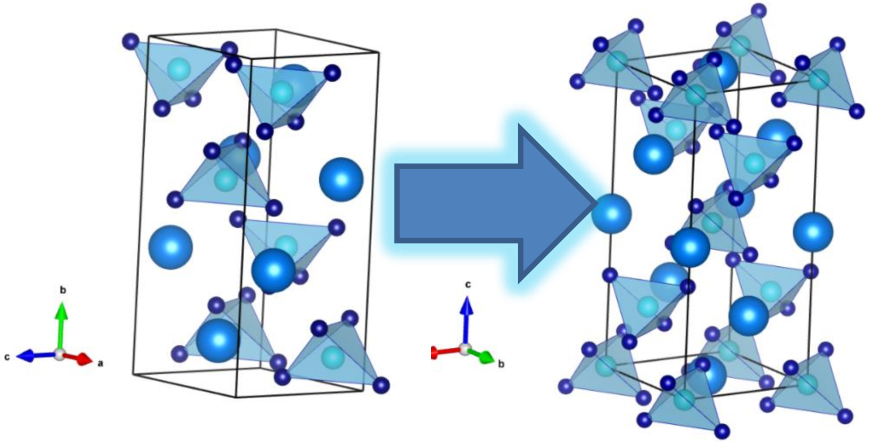
a new „*buzz word*” or real a „*hot topic*” in materials science

Materials based on proton conductors

Barium zirconate - one of the most recognized proton conducting oxides.

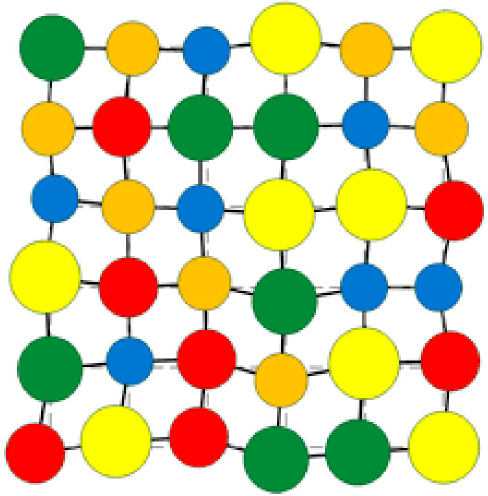


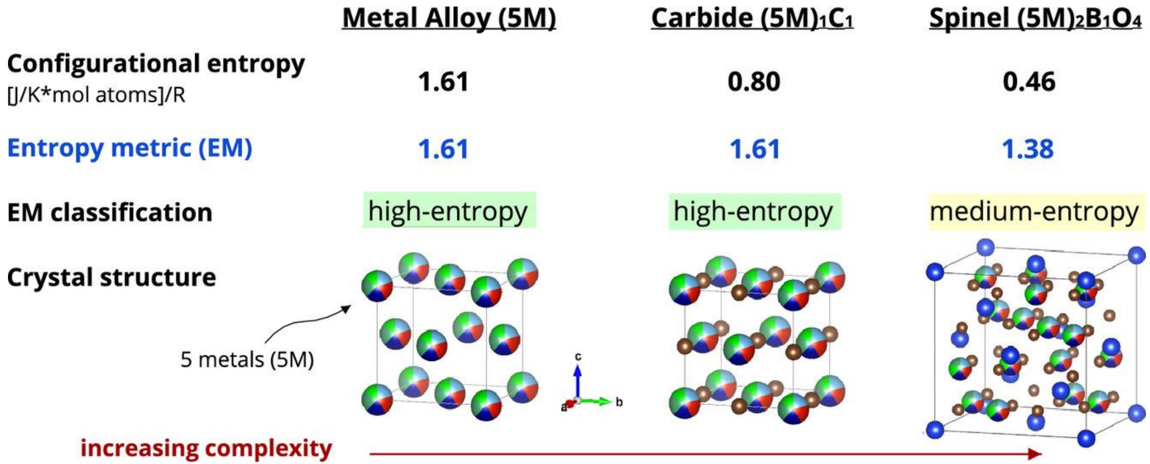
Lanthanum orthoniobate - one the most chemically stable proton conductors.



Configurational entropy in oxides

The total disorder per volume of an oxide seems be lower than in a high-entropy alloy, as the anion sublattice is ordered (apart from point defects). However, the chemically uniform anion sublattice is very important - it hinders the tendency to the segregation of the cations with different electronegativities.

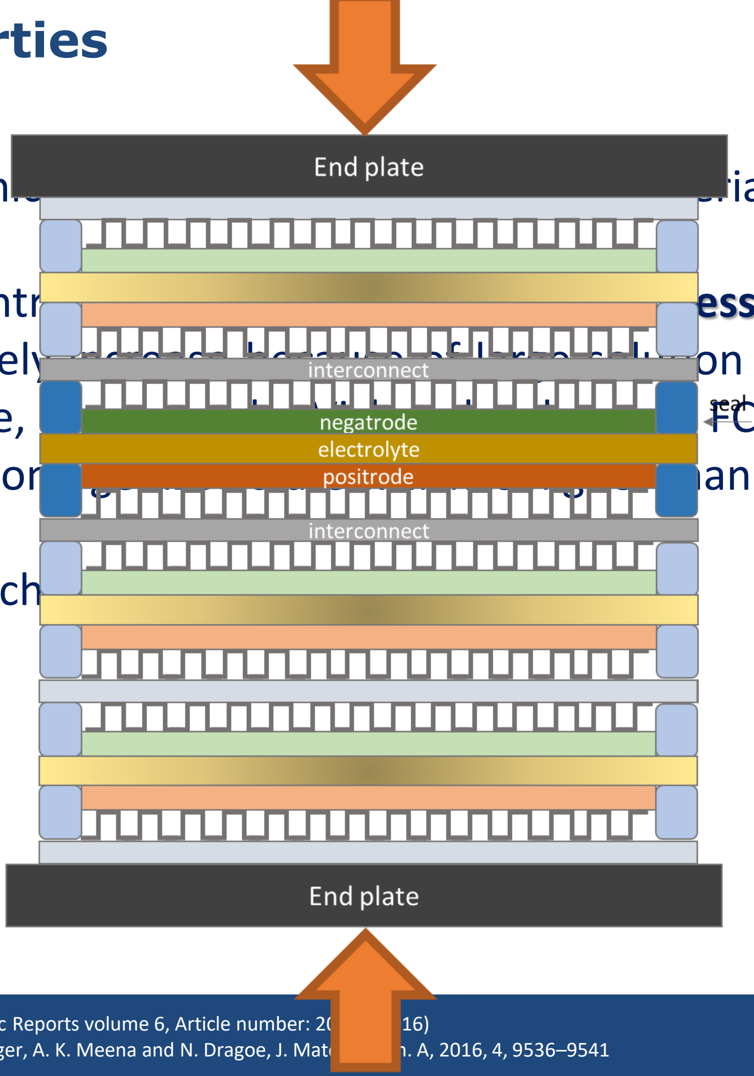




$$EM = \frac{S^{SL}_{config}}{R} \cdot L \qquad S^{SL}_{config} = \frac{-R\sum_{SL}\sum_i a_{SL}[X_i]\ln[X_i]}{\sum_{SL} a_{SL}}$$

E. J. Pickering & N. G. Jones (2016) High-entropy alloys: a critical assessment of their founding principles and future prospects, International Materials Reviews, 61:3, 183-202,
Dippo, O.F.; Vecchio, K.S. *Scr. Mater.* **2021**, *201*, 113974.

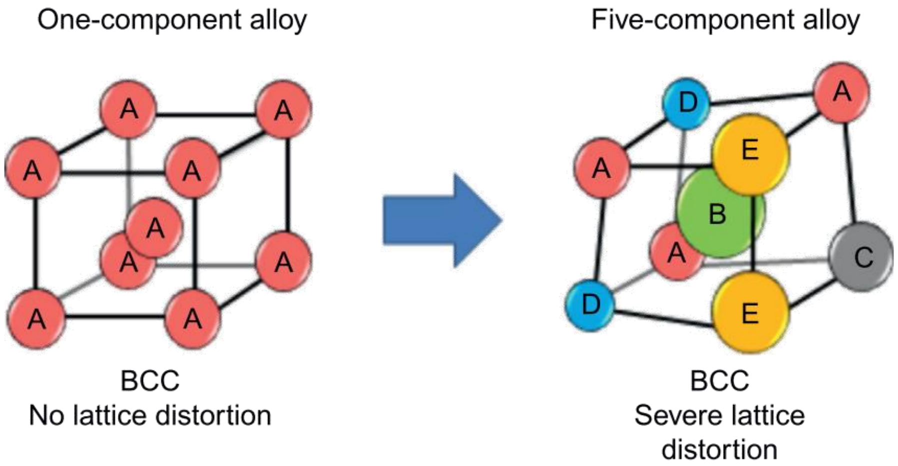
Mechanical properties



Mechan… …rials:

High entr… **…ess Young moduli** etc. Hardness and strength effectively … on hardening in the heavily distorted lattice.For instance, … FCC equiatomic alloy CoCrFeMnNi is 1192 MPa in the hor… …an that 864 MPa obtained by the mixture rule.

Not much…



K. Jin et al. , Scientific Reports volume 6, Article number: 2… …16)
D. Bérardan, S. Franger, A. K. Meena and N. Dragoe, J. Mat… …. A, 2016, 4, 9536–9541

Thermal properties

Category	Composition/Alloy	Thermal conductivity (W/m K)
High Entropy Alloy	CoCrFeNi	12
	AlCoCrFeNi	11
	$Al_2CoCrFeNi$	16
Pure Element	Al	237
	Fe	80
	Ni	91
	Ti	22
	Cu	398
Conventional Alloy	7075 Al alloy	121
	Low Carbon Steel	52
	304 Stainless Steel	15
	Inconel 718	11
	Ti-6Al-4V	6

Thermal properties of high-entropy materials:

High entropy alloys exhibit **lower thermal conductivity** than those of most pure metals, but are similar to those of heavily alloyed conventional metals such as high-alloy steel or Ni-based superalloys.

High-entropy oxides have even lower thermal conductivity, e.g. $Y_{0.2}Nd_{0.2}Sm_{0.2}Eu_{0.2}Er_{0.2}AlO_3$ at room temperature: 4 W/mK

Ming-Hung Tsai, Entropy 2013, 15, 5338-5345; doi:10.3390/e15125338
Z. Zhao et al. Journal of Materials Science & Technology, Volume 47, 15 June 2020, Pages 45-51

Electrical properties

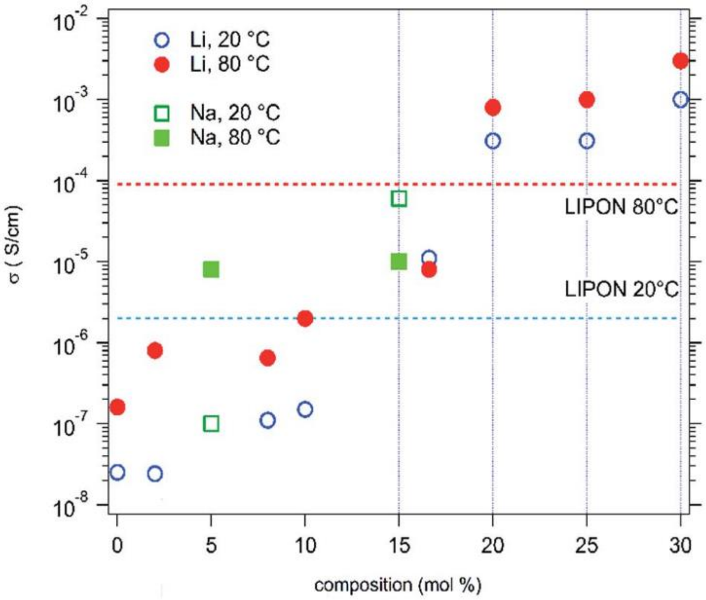


Fig. 5 Ionic conductivities for Li and Na doped HEOx samples.

Electrical properties of high-entropy materials:

- High entropy alloys exhibit high electrical resistivity with a low temperature coefficient of resistivity → the contribution to the resistivity of electron scattering on lattice defects is stronger than the electron-phonon scattering

- The ionic conductivity observed in some lithium substituted oxides was very high, reaching 1 mScm^{-1} at room temperature

K. Jin et al. , Scientific Reports volume 6, Article number: 20159 (2016)
D. Bérardan, S. Franger, A. K. Meena and N. Dragoe, J. Mater. Chem. A, 2016, 4, 9536–9541

High-entropy proton/mixed conductors?

The presence of at least five cationic constituents, related to that disorder and lattice distortions may be expected to influence both concentration of particular charge carriers and their mobility.

$$v_O^{\bullet\bullet} + H_2O_{(g)} + O_O^x = 2OH_O^{\bullet}$$

$$H_2O_{(g)} + 2O_O^x + 2h^{\bullet} = 2OH_O^{\bullet} + \frac{1}{2}O_{2(g)}$$

$$O_O^x = v_O^{\bullet\bullet} + \frac{1}{2}O_{2(g)} + 2e'$$

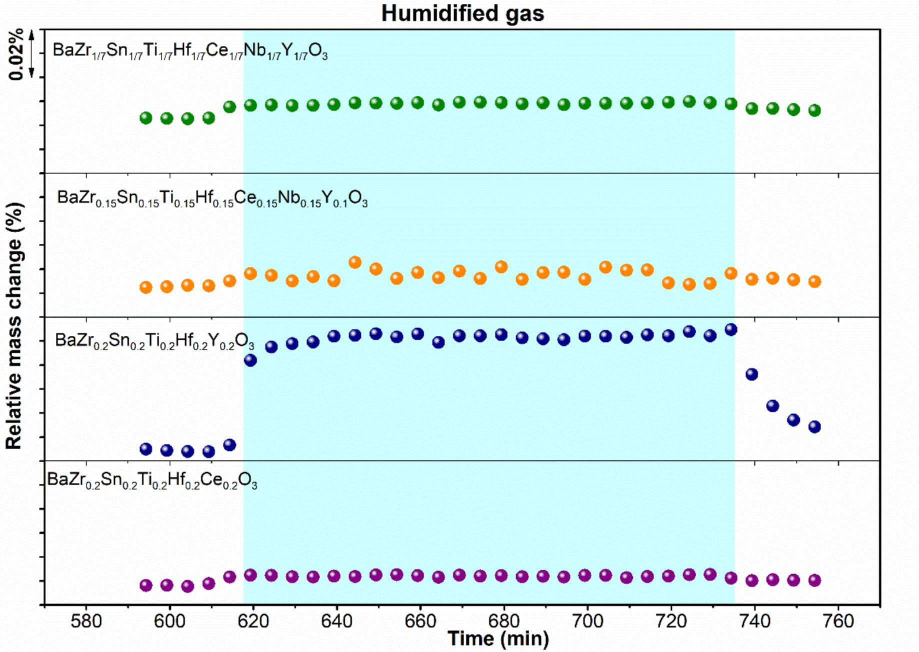
$$\mu(T) \sim \exp\frac{\Delta S_{migr}}{k}\exp\left(-\frac{\Delta H_{migr}}{kT}\right)$$

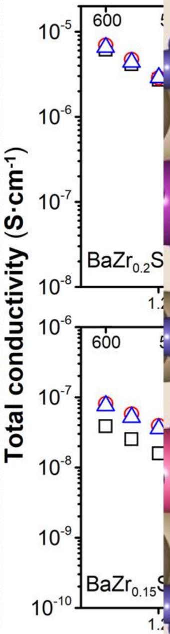
Concentration of ionic and/or electronic charge carriers: aliovalent constituents/intrinsic defects/transition metals presence /hydration/ hydrogenation/reduction/oxidation;

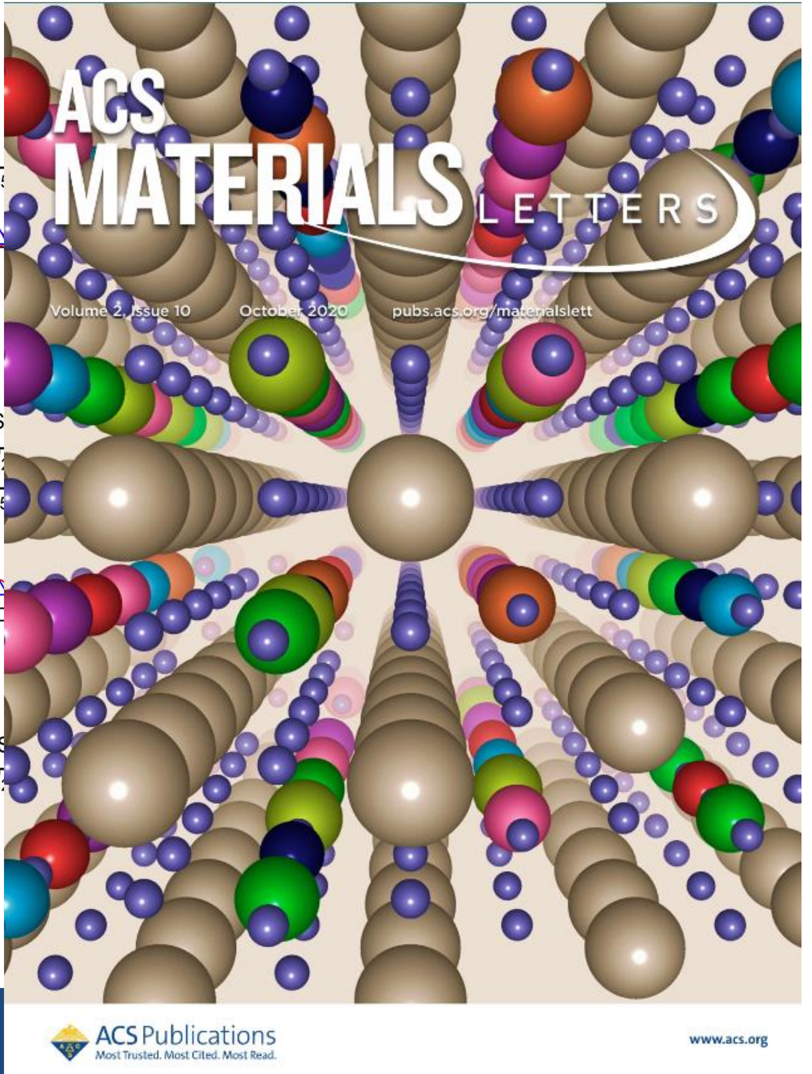
Mobility of ionic and/or electronic charge carriers: disorder may influence migration enthalpy, migration entropy, defect clustering. Migration enthalpy and entropy may be coupled.

D. P. Almond and A. R. West, Solid State Ionics, 1987, 23, 27–35.
K. L. Ngai, Solid State Ionics, 1998, 105, 231–235

Initial Studies

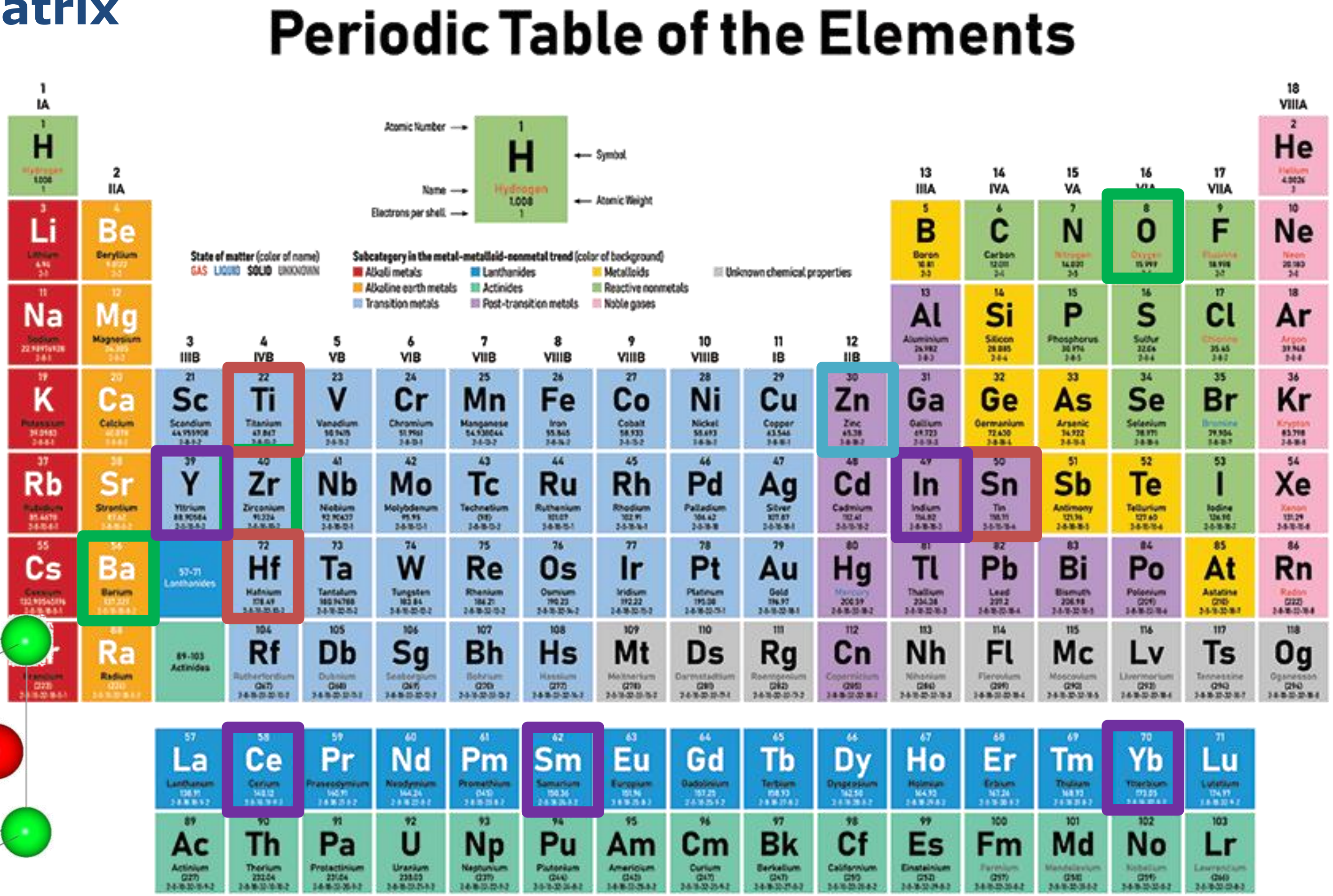


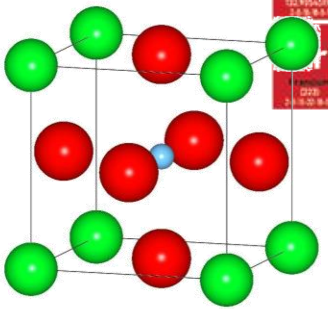




Gazda et al. ACS Materials Lett. 2020, 2, 10, 1315–1321

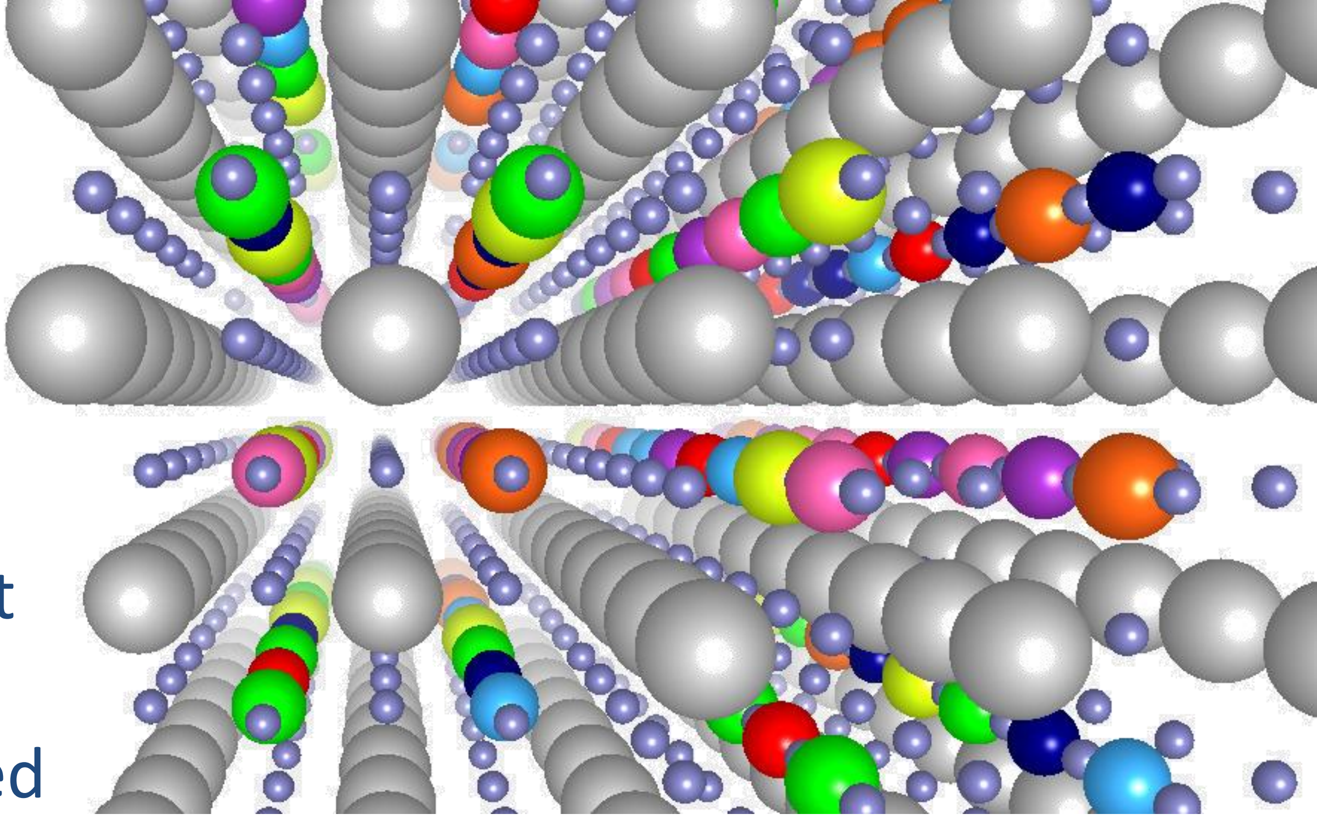
Samples matrix





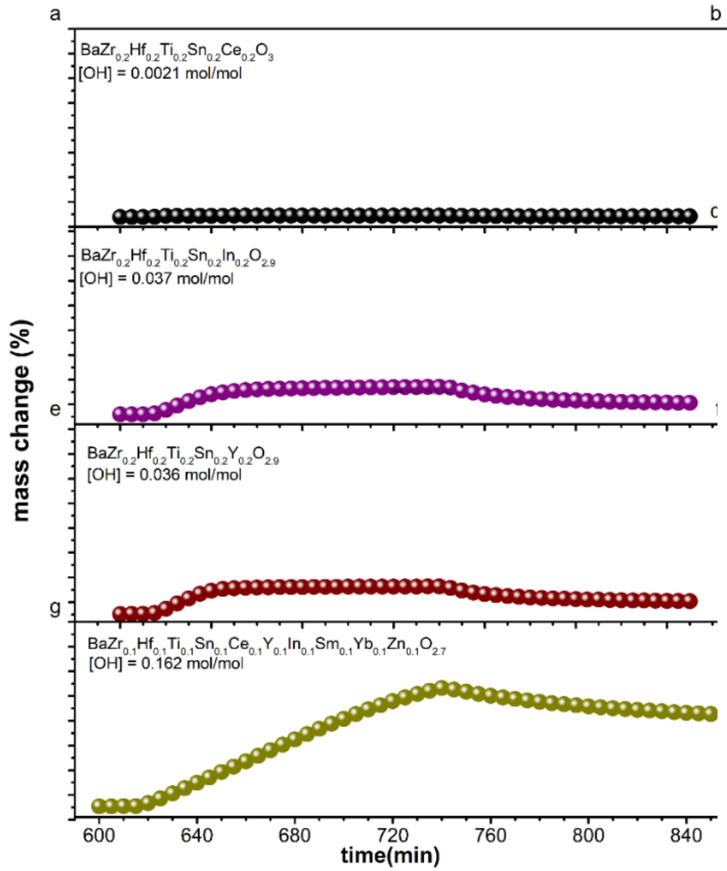
https://www.sciencenewsforstudents.org/article/scientists-say-periodic-table

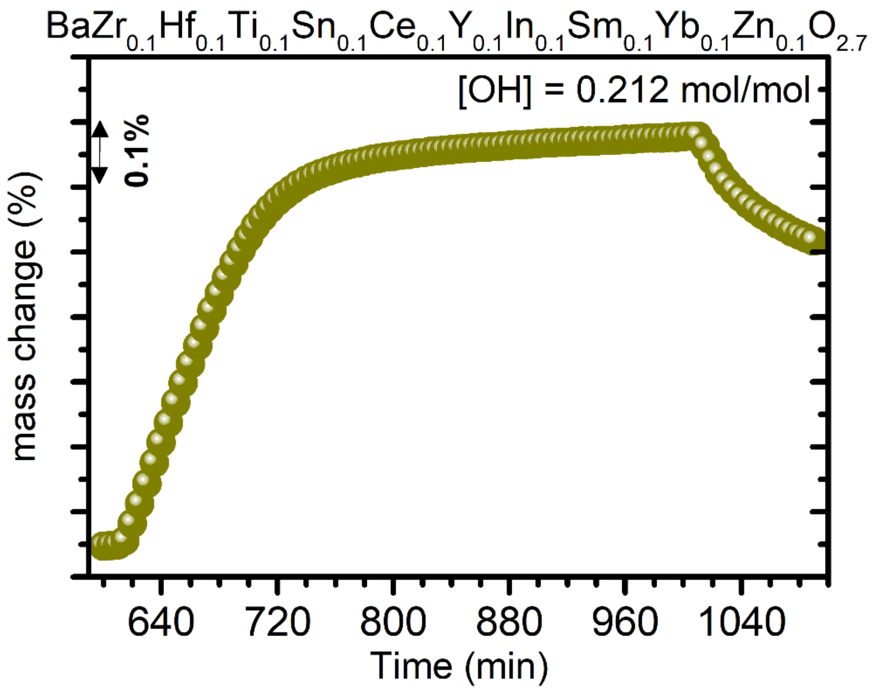
What's In A Name?



- Multiconstutient
- High entropy
- Entropy stabilized

Studies – water uptake



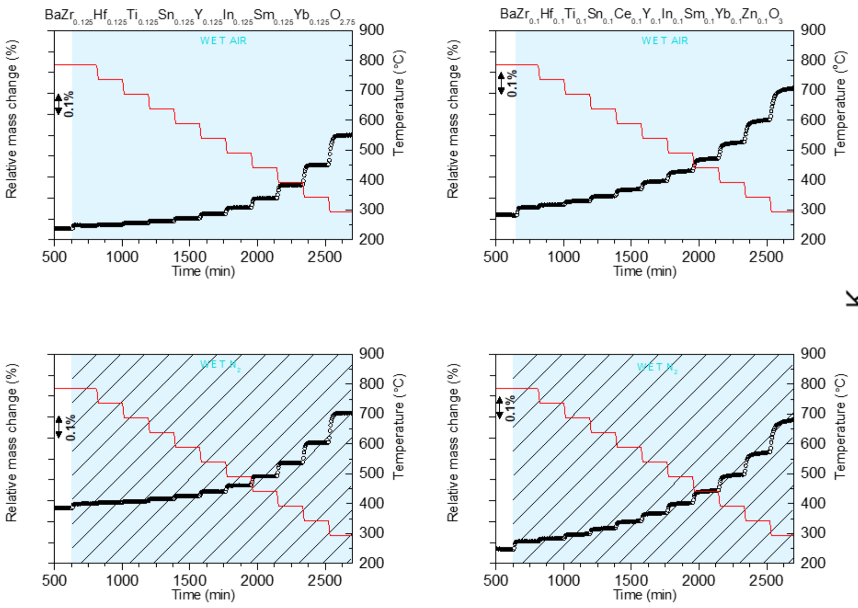


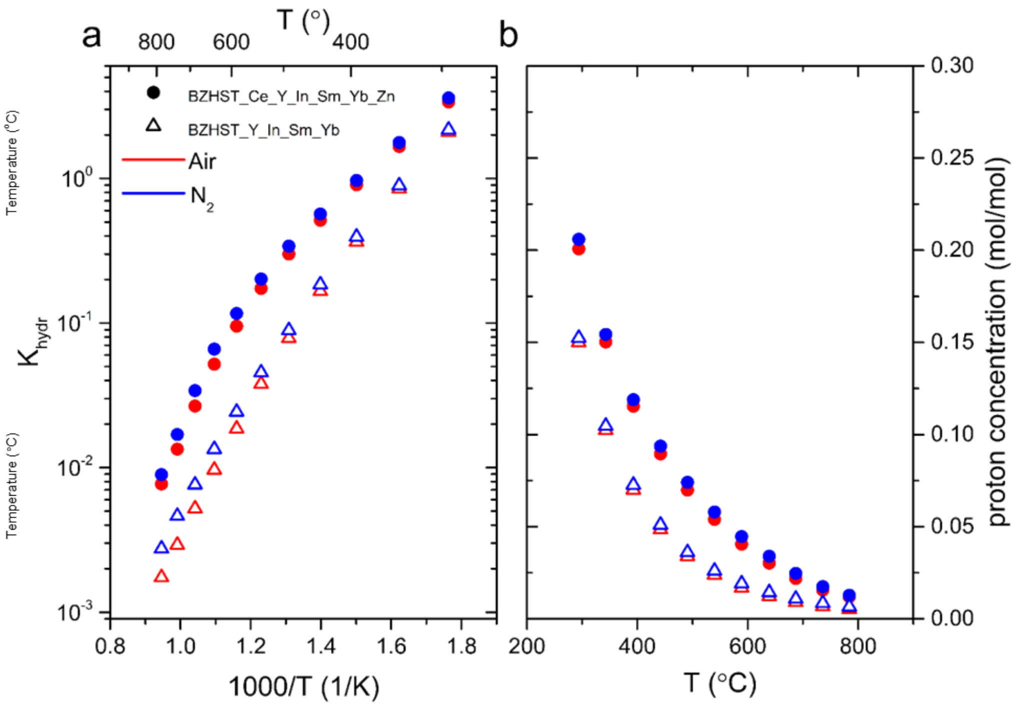
Mielewczyk-Gryń et al. Phys. Chem. Chem. Phys., 2023

Hydration thermodynamics

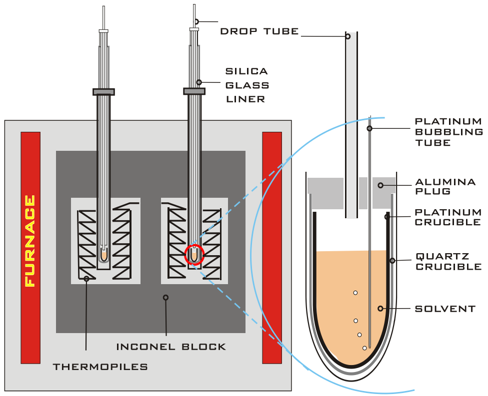
~ ΔH_{hydr} =-40-60kJ/mol

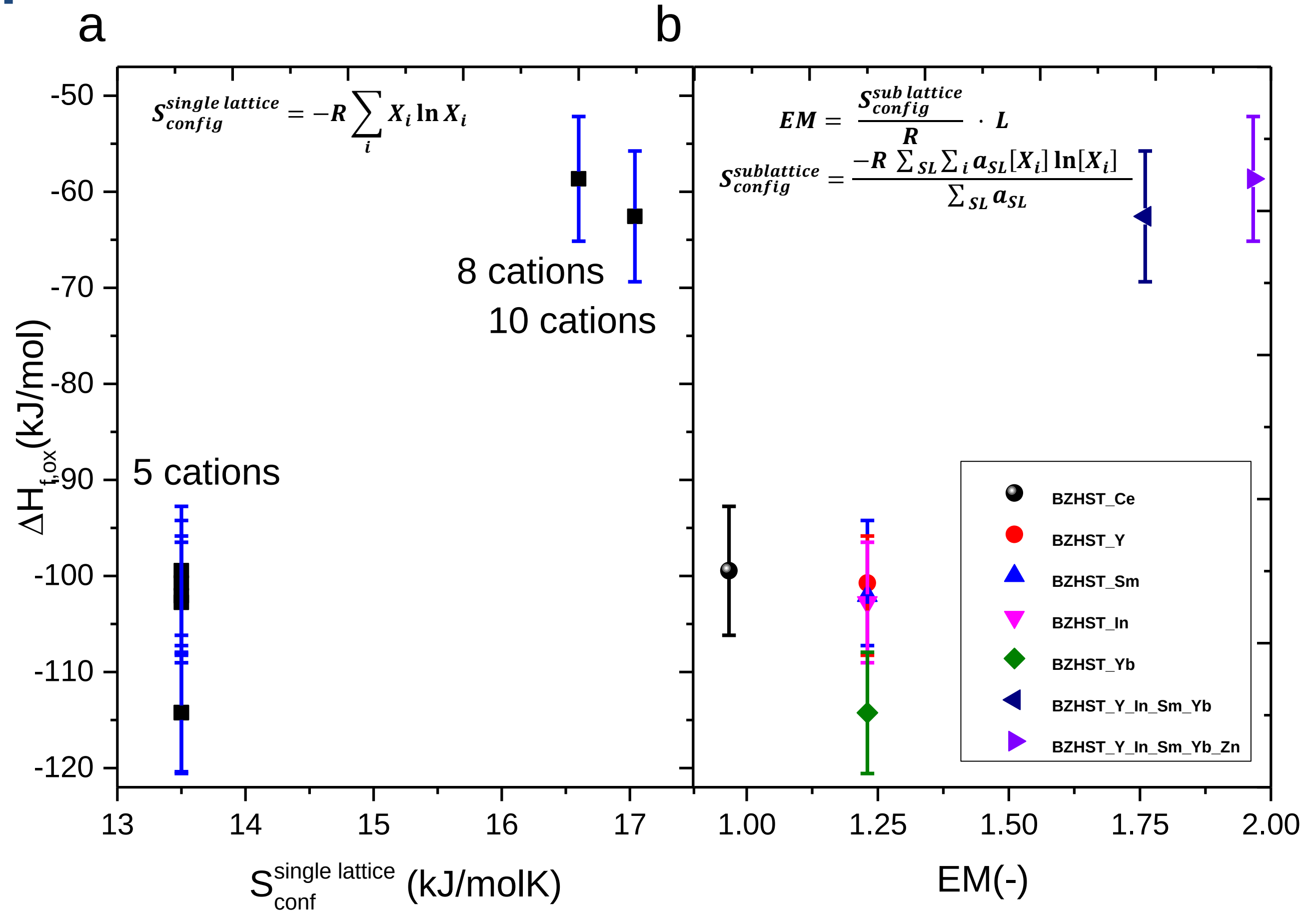
~ΔS_{hydr}=-140 J/mol





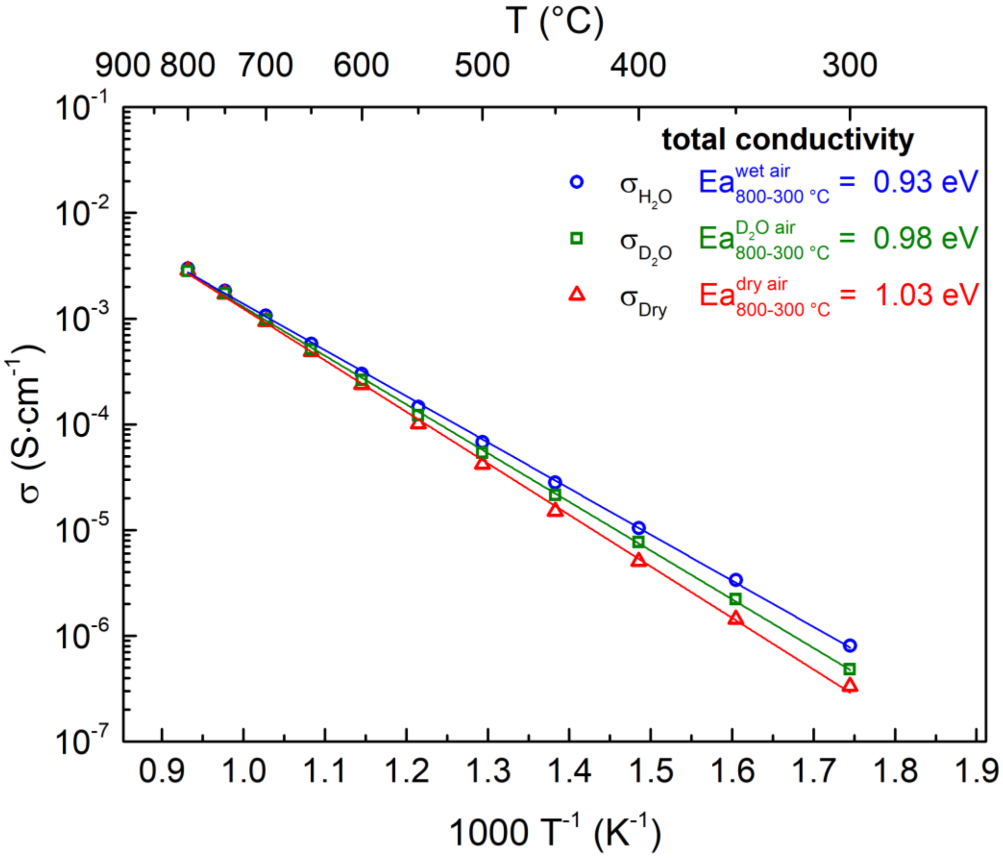
Enthalpy of formation

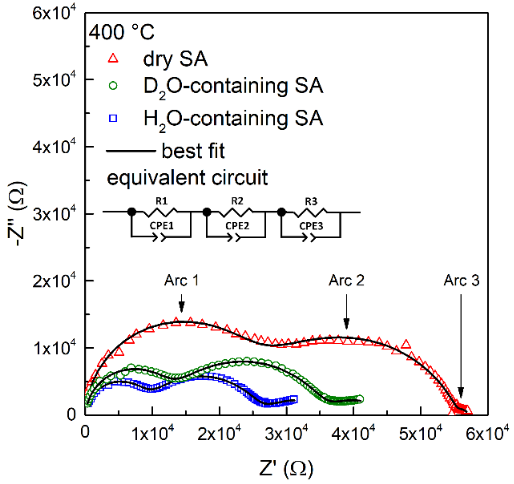


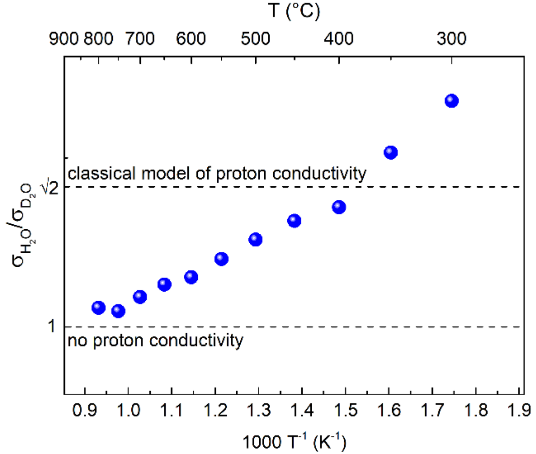


Conductivity

$BaZr_{1/8}Hf_{1/8}Sn_{1/8}Ti_{1/8}Y_{1/8}In_{1/8}Sm_{1/8}Yb_{1/8}O_{3-\delta}$

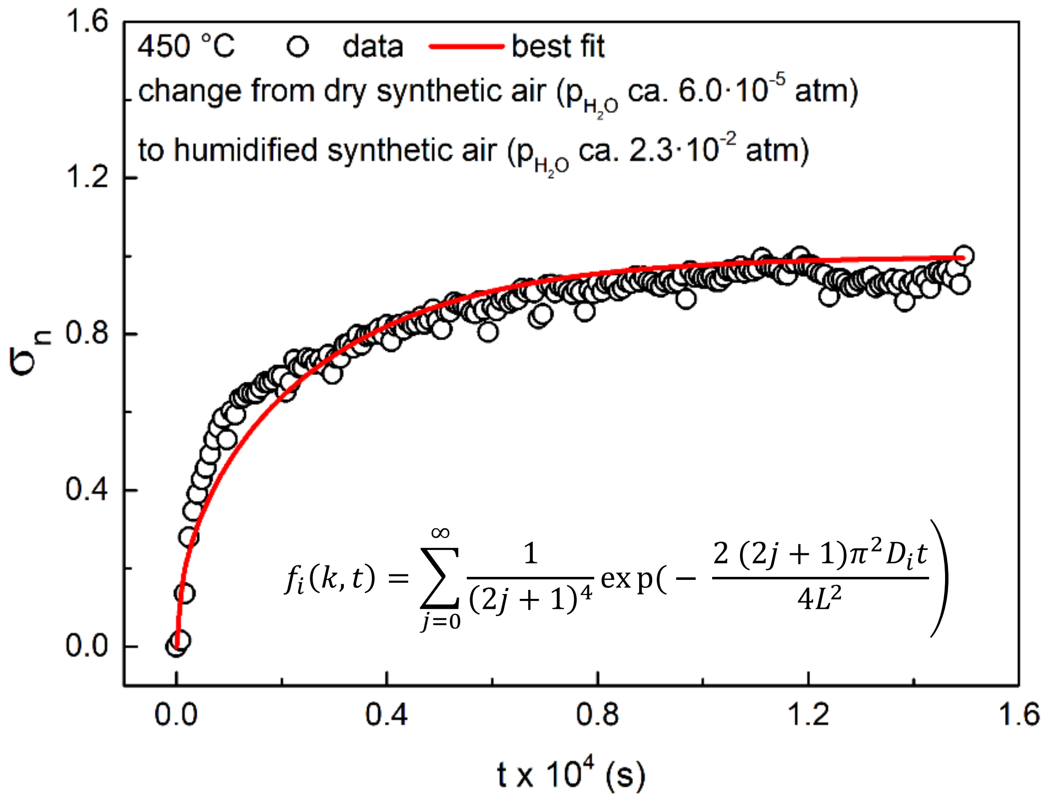






Chemical diffusion of water

$BaZr_{1/8}Hf_{1/8}Sn_{1/8}Ti_{1/8}Y_{1/8}In_{1/8}Sm_{1/8}Yb_{1/8}O_{3-\delta}$

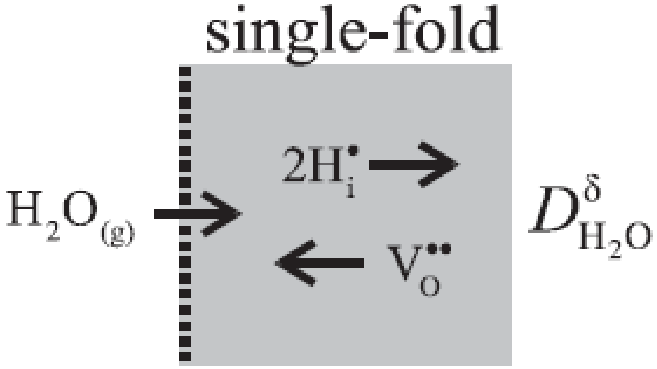


$$H_2O + V_O^{\bullet\bullet} + O_O^X \leftrightarrow 2OH^{\bullet}$$

ambipolar diffusion of $2H^+$ and O^{2-},

$$H_2O \leftrightarrow 2H_{ad} + O_{ad}$$

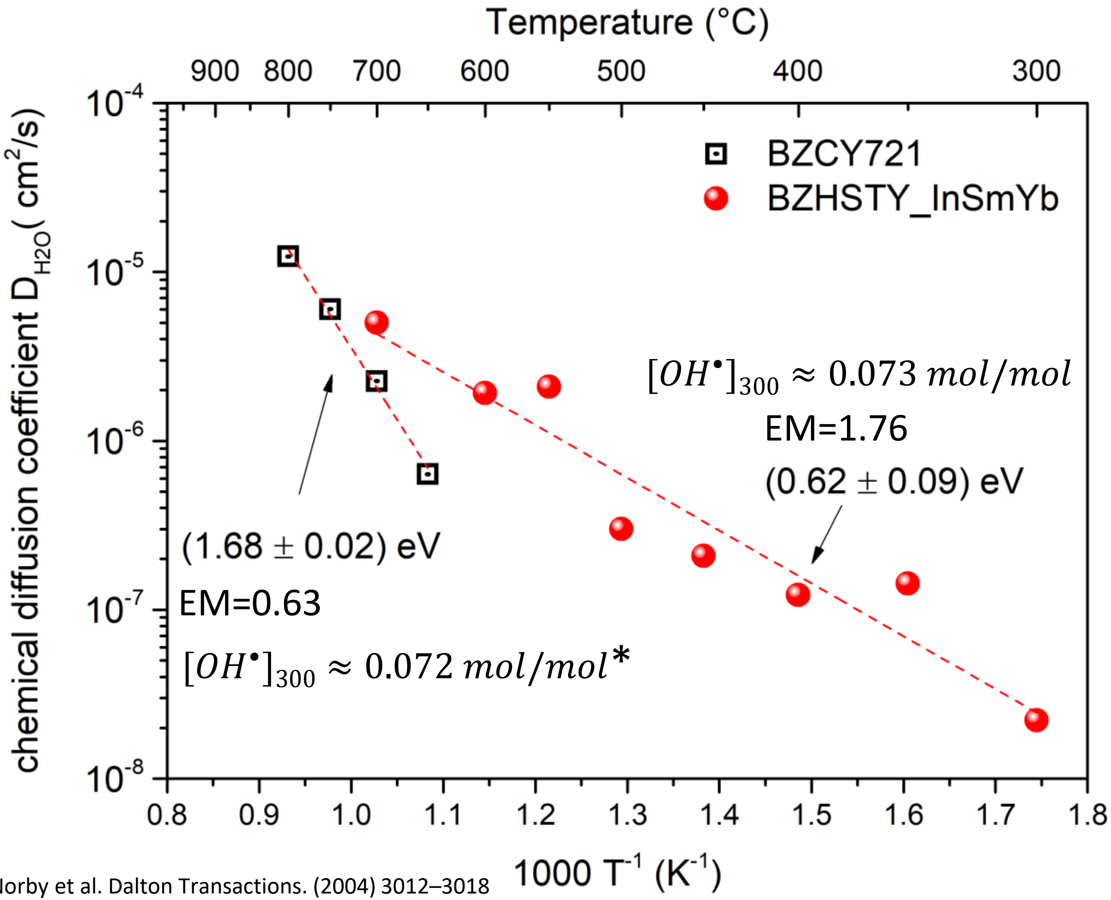
$$2H_{ad} + O_{ad} + V_O^{\bullet\bullet} + O_O^x \leftrightarrow 2OH_O^{\bullet}$$

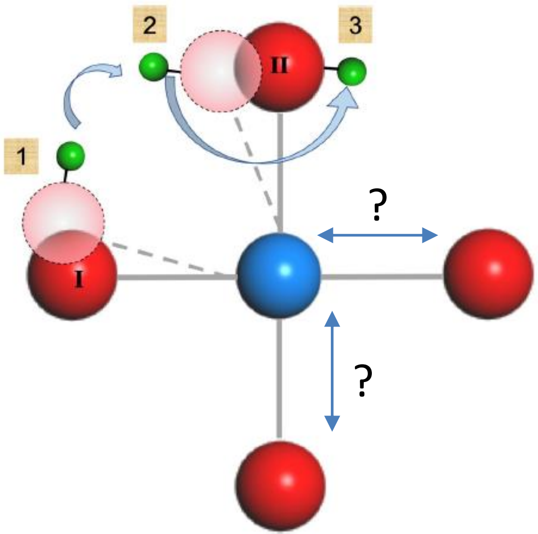


D. Poetzsch et al. (2015) Adv. Funct. Mater 25, 1542–1557

Chemical diffusion of water

Meng et al. J Mater Sci (2019) 54:9291–9312

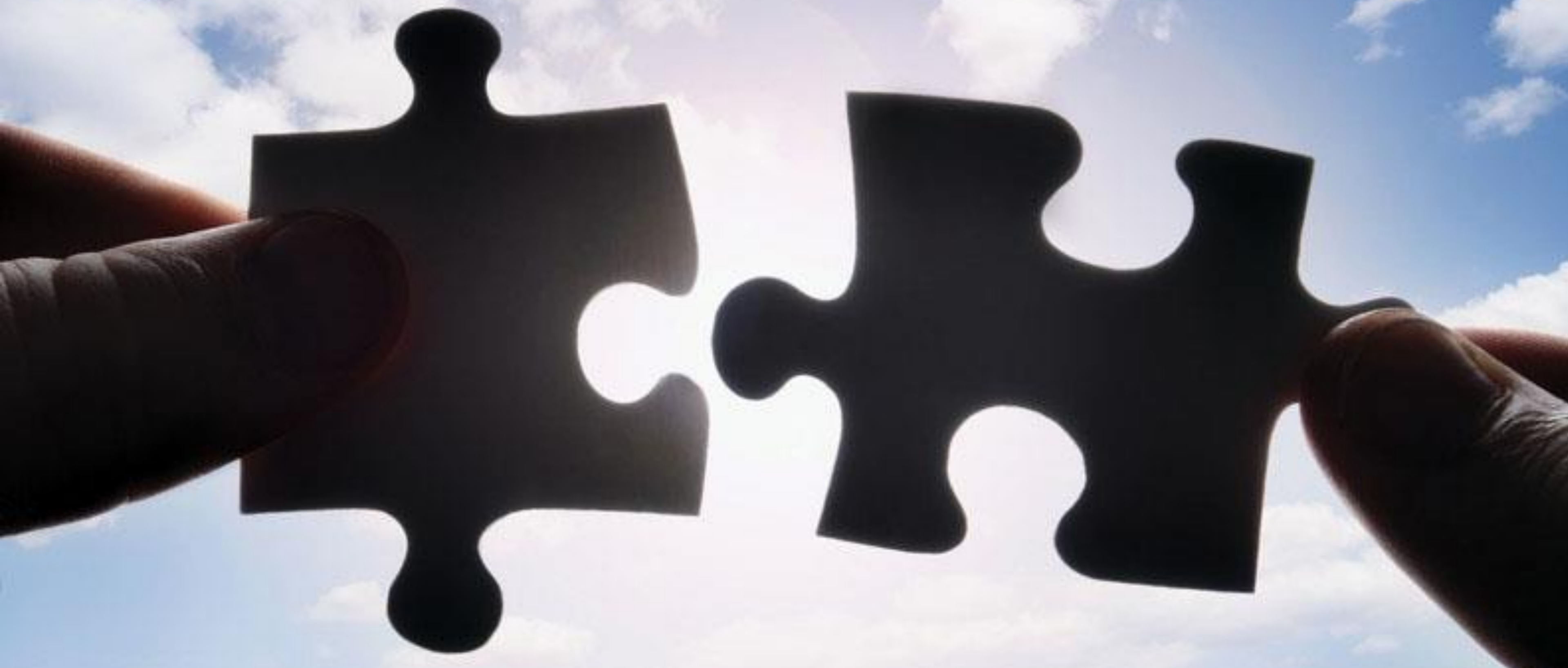




Multicomponent system

Lower activation energy for D_{H2O}

*T. Norby et al. Dalton Transactions. (2004) 3012–3018



Conclusion

Thank you for your kind attention.

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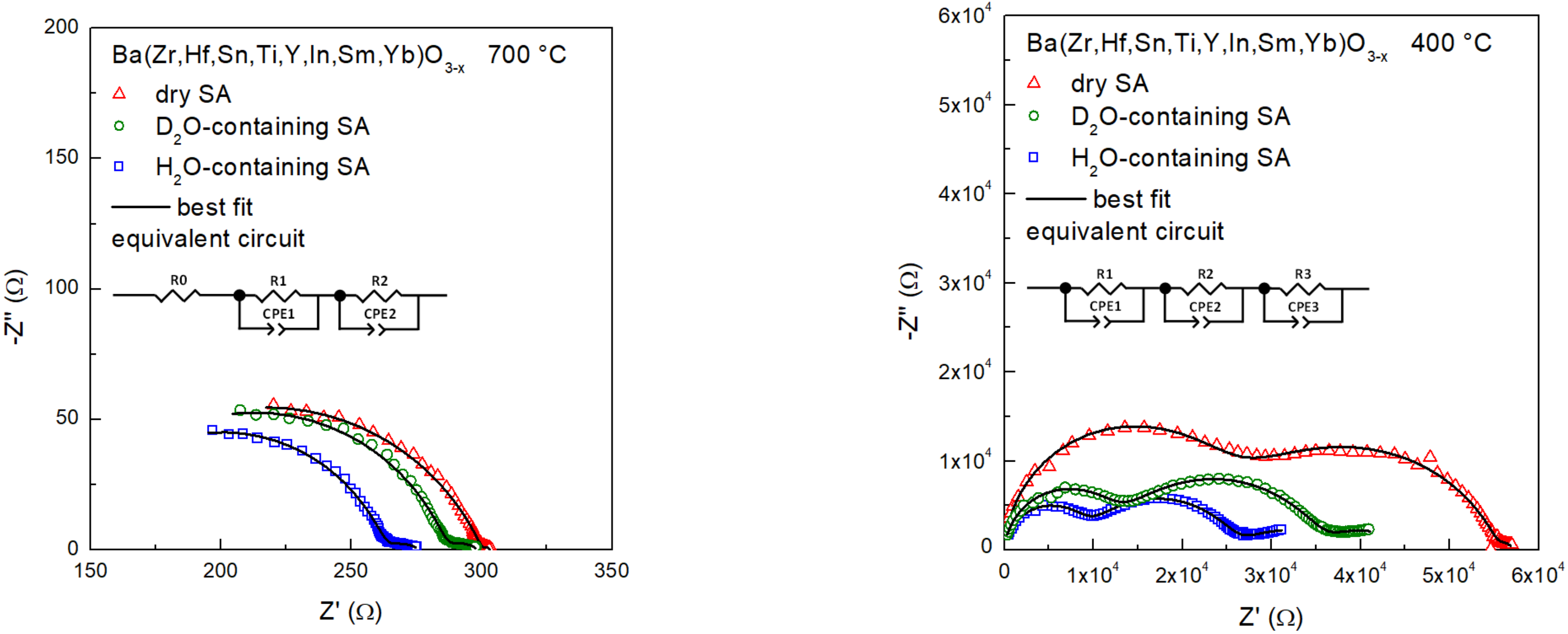

Ba(Zr,Hf,Sn,Ti,Y,In,Sm,Yb)O3-x 700 °C
dry SA
D2O-containing SA
H2O-containing SA
best fit
equivalent circuit
R0
R1
R2
CPE1
CPE2
-Z'' (Ω)
Z' (Ω)
0
50
100
150
200
150
200
250
300
350
Ba(Zr,Hf,Sn,Ti,Y,In,Sm,Yb)O3-x 400 °C
dry SA
D2O-containing SA
H2O-containing SA
best fit
equivalent circuit
R1
R2
R3
CPE1
CPE2
CPE3
-Z'' (Ω)
Z' (Ω)
0
1x10^4
2x10^4
3x10^4
4x10^4
5x10^4
6x10^4