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Uudsete keraamiliste vesinikelektroodide arendamine tahkeoksiidsetele kütuseelementidele ja elektrolüüseritele

Development of novel ceramic hydrogen electrodes for solid oxide fuel cells and solid oxide electrolysis cells

Gunnar Nurk, Kuno Kooser, Indrek Kivi, Sara Paydar, Alar Heinsaar, Mait Ainsar, Priit Möller, Freddy Kukk, Karl Markus Villemson, Ove Korjus, Enn Lust

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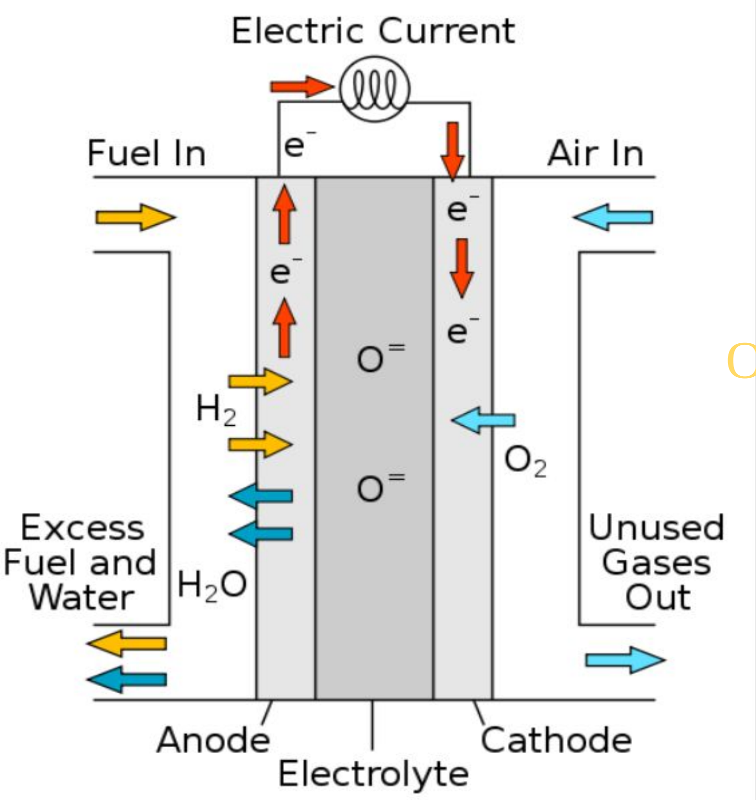
Solid oxide fuel cell (SOFC)

- 550 °C ≤ *T* ≤ 1000 °C
- Fuel flexibility
- High efficiency (~65%)
- No Pt or Ru catalysts
- Scalable, modular
- Better tolerance against impurities compared to low temp. fuel cells

$H_2 + O^{2-} \rightarrow H_2O + 2e^-$

$CO + O^{2-} \rightarrow CO_2 + 2e^-$



$O_2 + 4e^- \rightarrow 2O^{2-}$

$Ni - Zr_{1-x}Y_xO_{2-\delta}$
$Ni - Ce_{0.9}Gd_{0.1}O_{2-\delta}$
$La_{x-1}Sr_xTiO_{3-\delta}$

$Ce_{1-x}Gd_xO_{2-\delta}$
$Zr_{1-x}Y_xO_{2-\delta}$

$La_{1-x}Sr_xCoO_{3-\delta}$,
$La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$
$La_{1-x}Sr_xMnO_{3-\delta}$

Reversible Solid Oxide Fuel Cell

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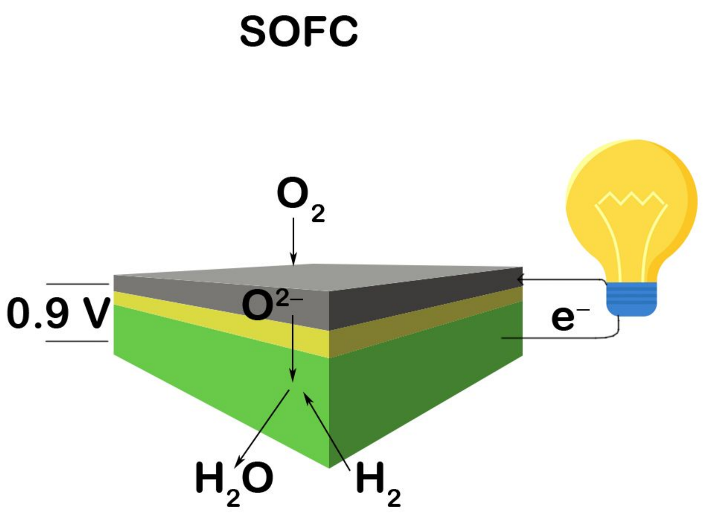
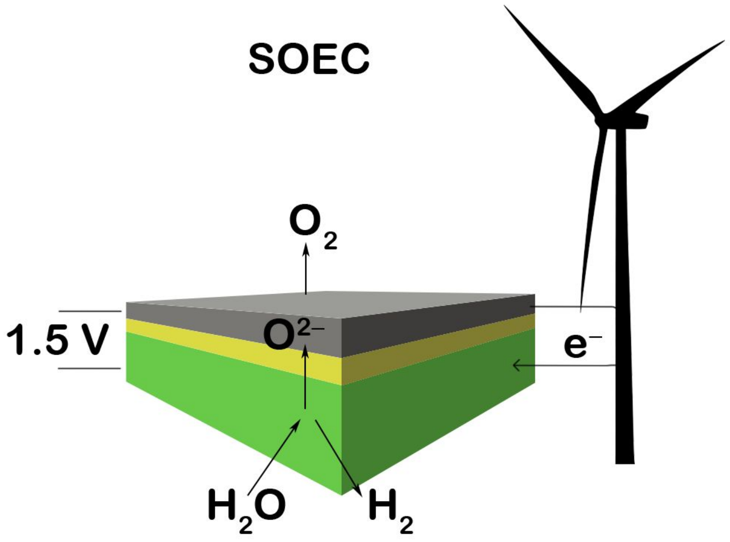




$H_2 + O^{2-} \longrightarrow H_2O + 2e^-$

$O_2 + 4e^- \longrightarrow 2O^{2-}$

$H_2O + 2e^- \longrightarrow H_2 + O^{2-}$

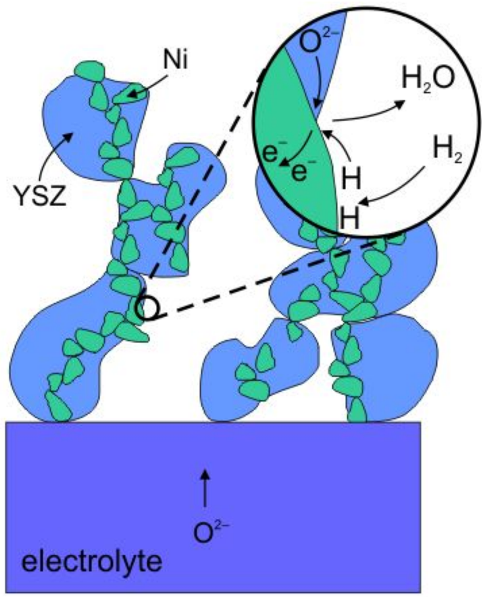
$2O^{2-} - 4e^- \longrightarrow O_2$

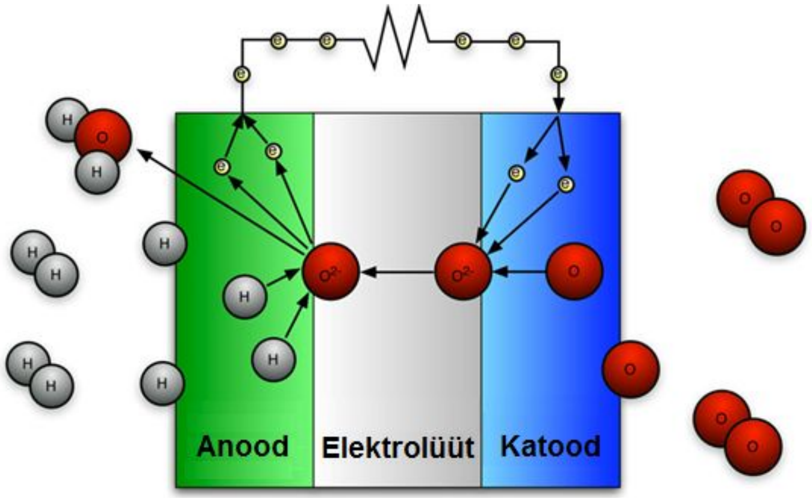
$H_2 + O^{2-} \rightarrow H_2O + 2e^-$

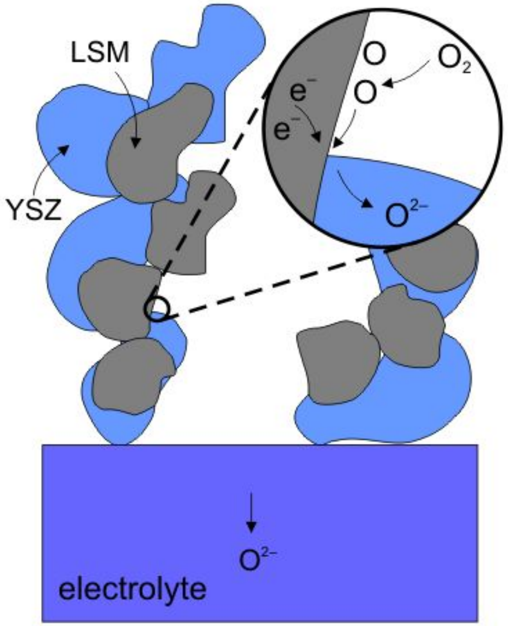
$CO + O^{2-} \rightarrow CO_2 + 2e-$

550 – 900 °C

$\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$







Anode materials:
Ni - YSZ ($(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$)
Ni – GDC ($Ce_{0.8}Gd_{0.2}O_{2-\delta}$)
LST – GDC ($La_{0.2}Sr_{0.8}TiO_{3-\delta}$ - $Ce_{0.8}Gd_{0.2}O_{2-\delta}$)

Electrolyte materials:
YSZ – ($(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$)
GDC - $Ce_{0.8}Gd_{0.2}O_{2-\delta}$

Cathode materials:
LSM - $La_{1-x}Sr_xMnO_{3-\delta}$
LSC - $La_{1-x}Sr_xCoO_{3-\delta}$

Limitations of Ni-cermet electrodes

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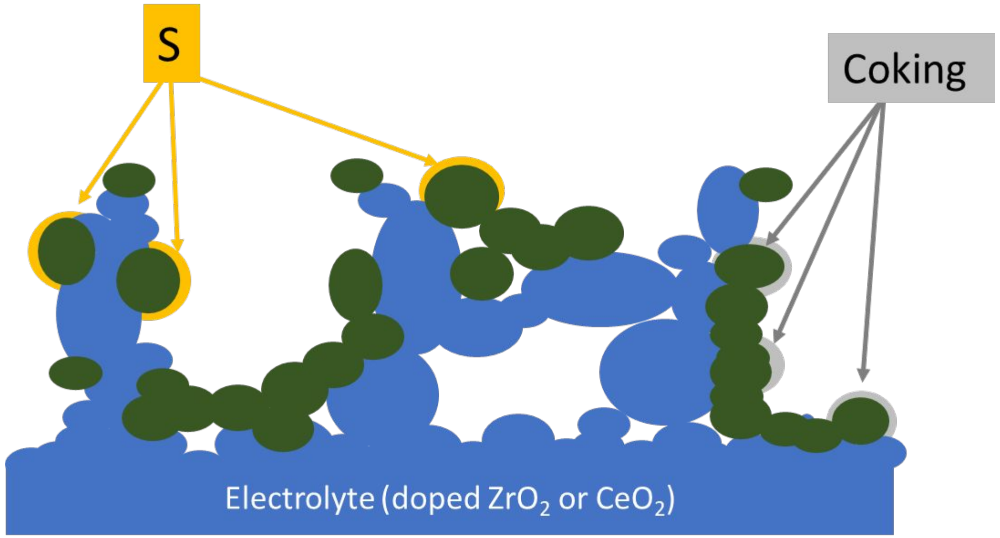
Poor sulphur tolerance of Ni-cermets **Starting from ~ 1 ppm of H_2S**

- **Adsorption of S on Ni at lower concentrations**
- **Formation of Ni_xS_y phases at high S concentrations**

Ni - coarsening in electrolysis mode

Poor redox stability



Sulphur tolerant and redox stable electrode materials

↓

Lower complexity

↓

Lower system cost

Limitations of Ni-cermet electrodes

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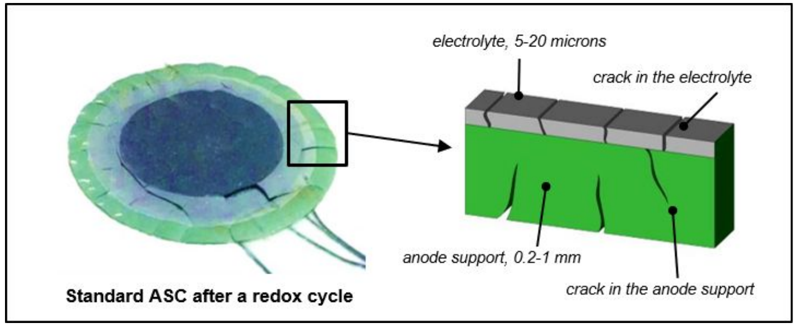
Poor redox stability of Ni-cermet

Re-oxidation if p_{O2} ↑
Volume of Ni particle grows approx. 66 vol%



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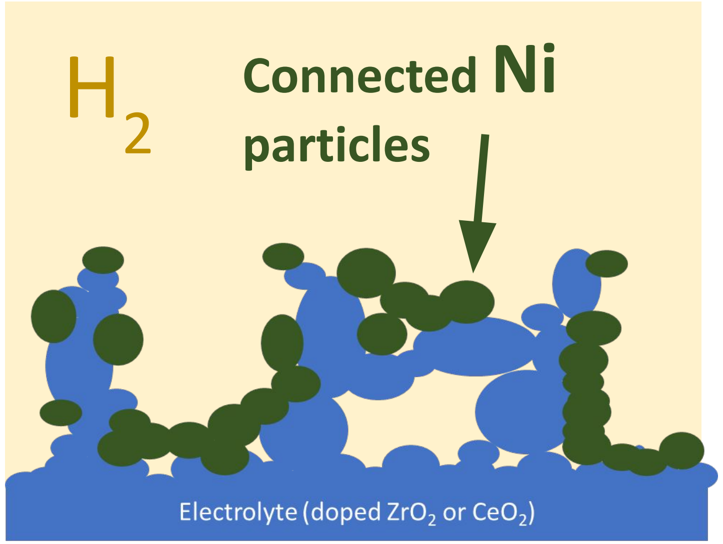
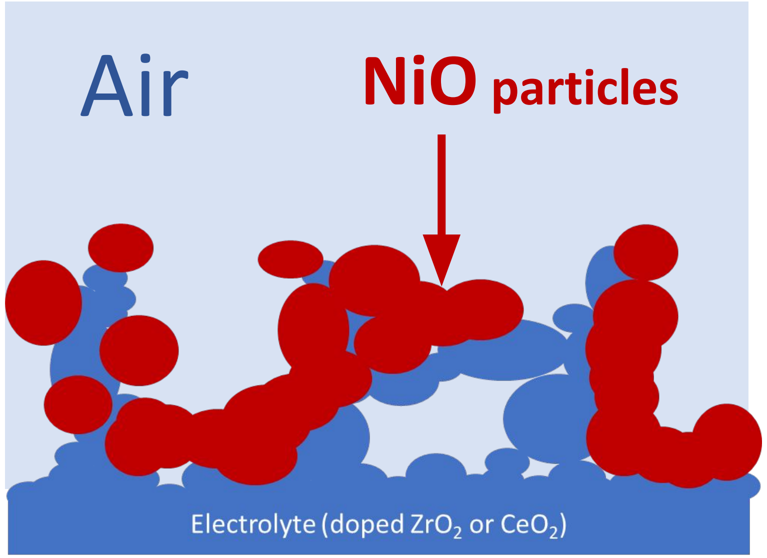




Safety gas (H_2) is needed in SOEC feed gas

Electrode materials with **better sulphur tolerance and redox stability are needed**

One possibility is to use mixed ion-electron conductive (MIEC) complex oxides:

Good redox stability - only very small changes of volume if pO_2 changes from 0.2 bar to 10^{-25} bar

Very good sulphur tolerance

Reaction centres can be everywhere on the MIEC surface – potentially very good activity

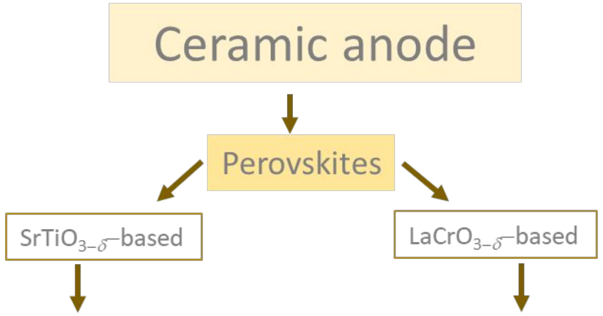
Potential to renew the catalyst using reoxidation process

Mixed ion-electron conductive (MIEC) complex oxides

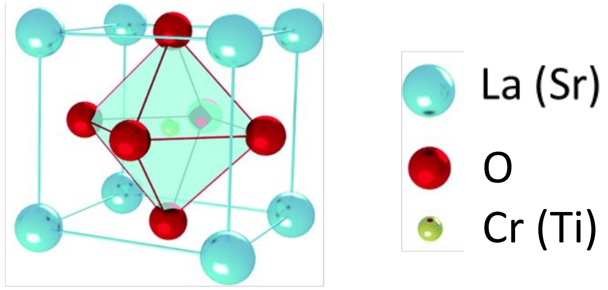
Expectations for hydrogen electrode material:

- stable at high temperatures at high and low pO_2
- chemically compatible with electrolyte
- thermomechanically compatible with electrolyte
- good electronic and ionic conductor
- catalytically active
- components should not be very rare and expensive

Most prominent group of materials is **perovskites**

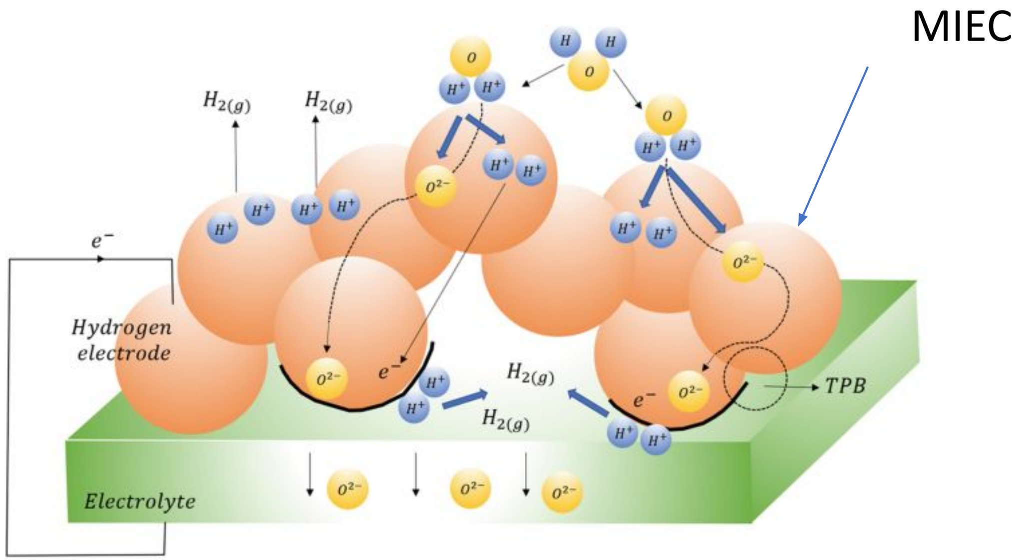


$La_{0.25}Sr_{0.25}Ca_{0.4}Ti_{1-x}Ni_xO_{3-\delta}$ $La_{0.75}Sr_{0.25}Cr_{0.5-x}Mn_{0.5-y}Ni_{y+x}O_{3-\delta}$

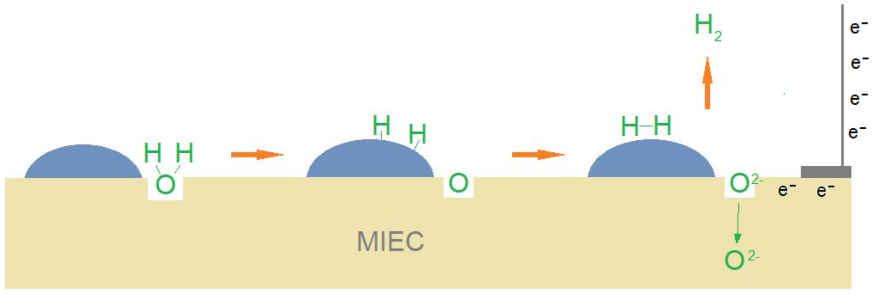


Chen et al., RSC advances, 2018

General simplified understanding about mechanisms during water electrolysis



Cavaliere, P. (2023). Solid Oxide Water Electrolysis. In: Water Electrolysis for Hydrogen Production. Springer, Cham. https://doi.org/10.1007/978-3-031-37780-8_8



Conditions which should be fulfilled for electrolysis:

Sites for adsorption of water molecules

Oxide ion vacancies

Catalyst for adsorption and recombination of hydrogen atoms

Cathodically polarized electrode

Transport of H_2O to reaction site

Transport of H_2 away from reaction site

Design of mixed ion-electron conductive (MIEC) material

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To fulfil requirements perovskite host lattices are doped in A and B site

Stability ?!

Host lattice components

A-site dopant,
to create n-type conductivity

$La^{3+}_{0.25}Sr^{2+}_{0.25}Ca^{2+}_{0.4}Ti^{(3+;4+)}_{1-x}Ni^{(2+)}_{x}O_{3-\delta}$

A-site is deficient
to suppress the Sr segregations

A-site dopant,
to reduce lattice parameter for increasing the electronic conductivity of material

B-site dopant for improving the catalytic activity and for creating oxide ion vacancies

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Several compositions have been studied

$(La_{1-x}Sr_x)_yCr_{0.5-z}Mn_{0.5-w}Ni_{z+w}O_{3-\delta}$

$La_{0.25}Sr_{0.25}Ca_{0.45}Ti_{0.95}Ni_{0.05-x}Co_xO_{3-\delta}$

$La_{0.25}Sr_{0.25}Ca_{0.45}Ti_{0.95}Ni_{0.05-x}V_xO_{3-\delta}$

$La_{0.25}Sr_{0.25}Ca_{0.45}Ti_{0.95}Ni_{0.05-x}Mn_xO_{3-\delta}$

$La_{0.25}Sr_{0.25}Ca_{0.40}Ti_{0.90}Ni_{0.05-x}Sn_xO_{3-\delta}$

$La_{0.25}Sr_{0.25}Ca_{0.45}Ti_{0.95}Ni_{0.05-x}Mo_xO_{3-\delta}$

$La_{0.21}Sr_{0.26}Ca_{0.48}Ti_{0.95}Fe_{0.05}O_{3-\delta}$

Very different phase purities and stabilities

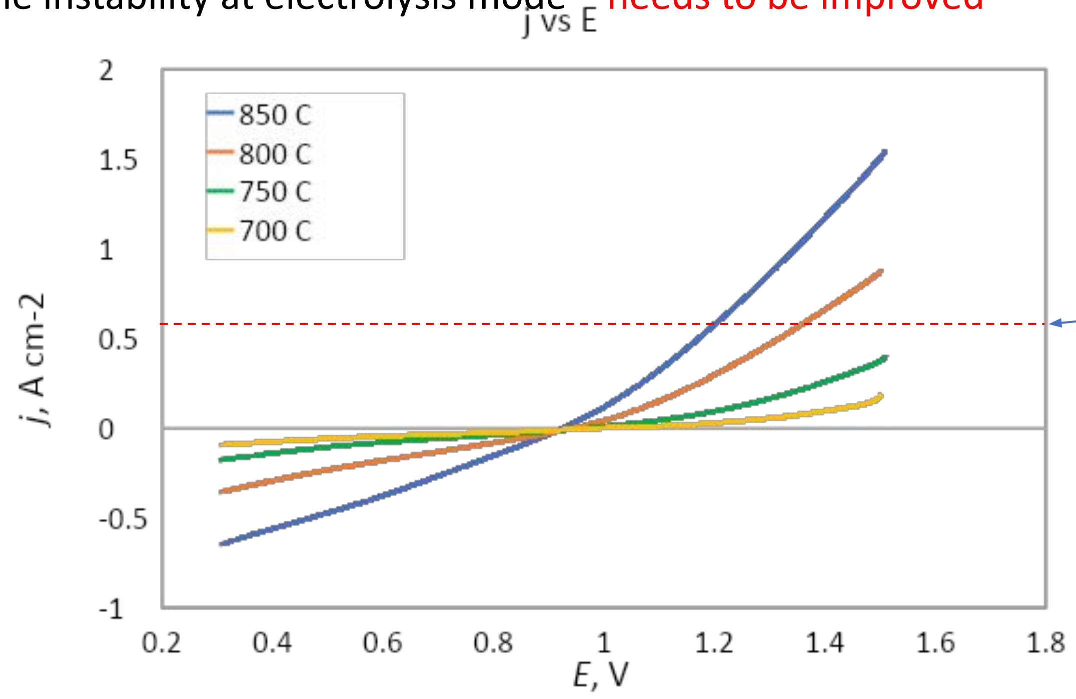
Small amount of dopant has significant influence on properties

Properties of $La_{0.21}Sr_{0.26}Ca_{0.48}Ti_{0.95}Fe_{0.05}O_{3-\delta}$

Good stability at fuel cell mode

Cheap components

Some instability at electrolysis mode – needs to be improved



Best Ni-cermet based systems are stable at approximately 0.5 to 0.6 A cm^{-2}

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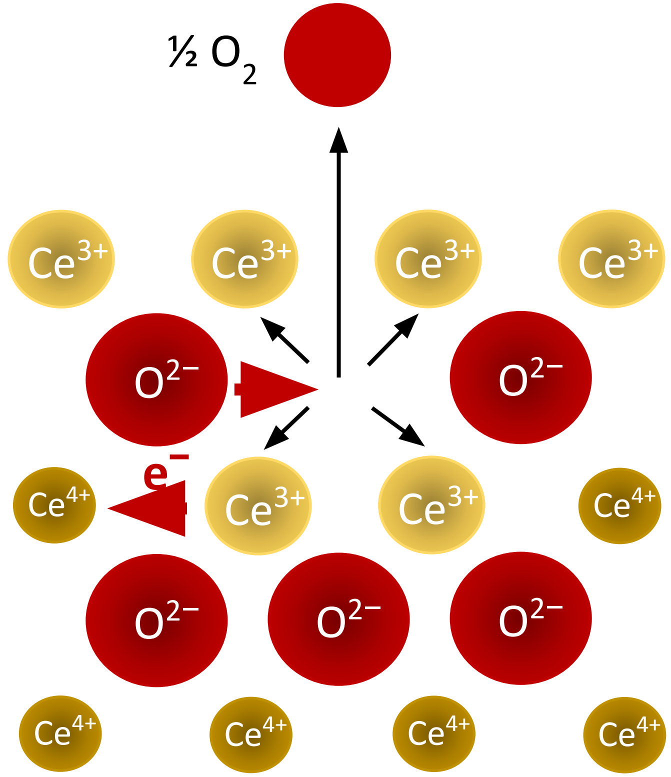
Why MIEC hydrogen electrode is less stable at electrolysis mode, at cathode conditions?

Basic processes during reduction and cathodic polarization of oxide:

Lattice expansion (formation of oxide ion vacancies, change of cation radius).
Changes of ionic and electronic conductivity

Close to material surface there are more oxide ion vacancies because of space charge effect.

Cathodic polarization might increase the concentration of oxide ion vacancies over the critical limit.



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Conclusive remarks:

General aim of MIEC electrode material research is to find ceramic electrode composition with good redox stability and high stability against impurities and at cathodic conditions to make SOFC and SOEC systems less complex and cheaper.

Some novel redox stable ceramic materials at electrolysis mode are comparable with conventional Ni-cermets.

Stability of materials at high polarizations and current densities at electrolysis conditions should be improved

Thank you!

Eesti Teadusagentuur
Estonian Research Council

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