Nanostructured catalysts for todays energy challenges

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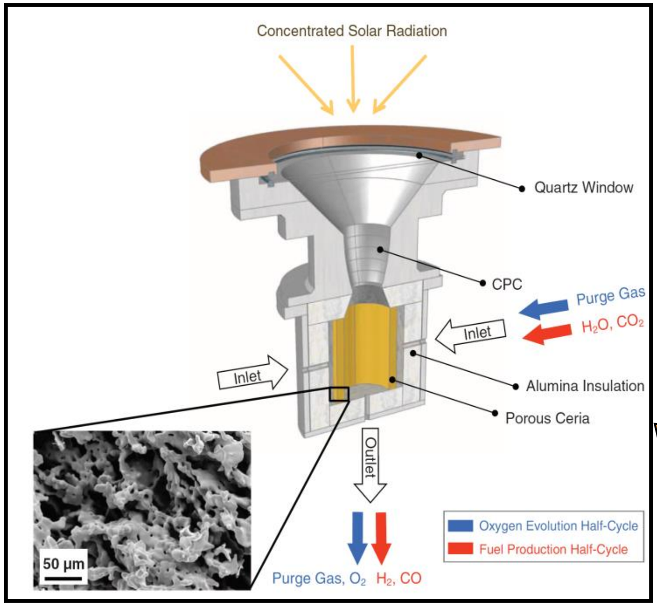
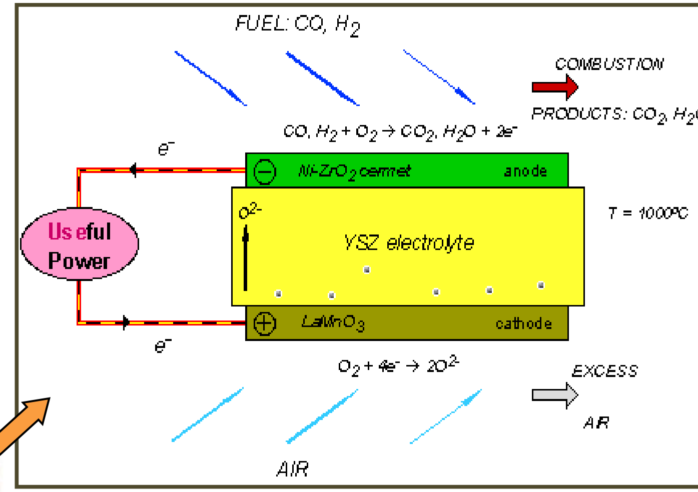
Thermal Splitting of Water



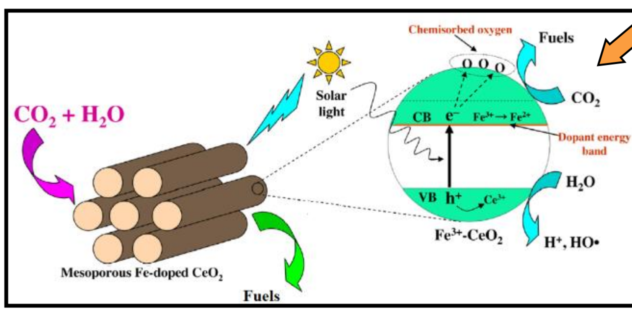
W.C. Chunch et al. Science 330 (2010) 1797

SOFC: Solid Oxide Fuel Cell



Taken from http://www.spice.or.jp/~fisher/sofc.html

Photocatalysis



Y. Wang et al. Appl. Catal. B 147 (2014) 602

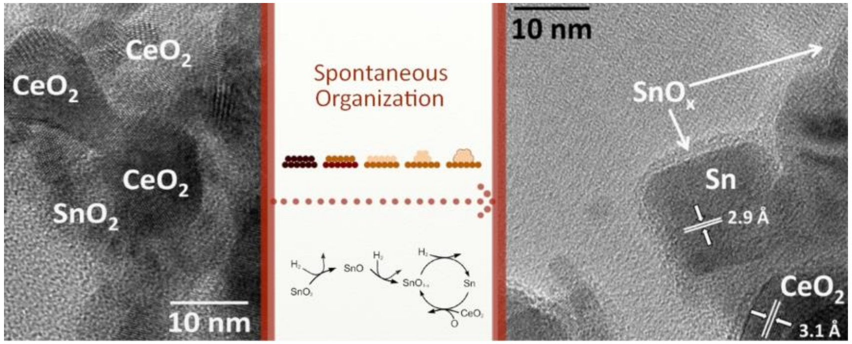
Catalytic processes for use of renewable resources :

- CO_2 methanation
- Alcohols reforming
- CH_4 dry reforming

Main Researches

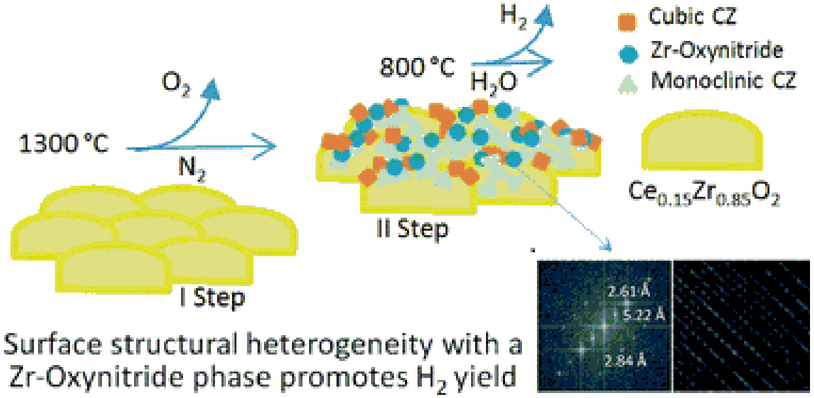
- Development of catalysts and materials for IT-SOFC anodes
- Catalysts for dry-reforming of methane and biogas conversion
- Carrier oxides for two step thermal water splitting reaction

Case Hystories



Bardini L. et al.; Appl. Catal. B 197 (2016),254.

CeO_2-Sn@SnOx electrocatalysts for IT-SOFC anodes



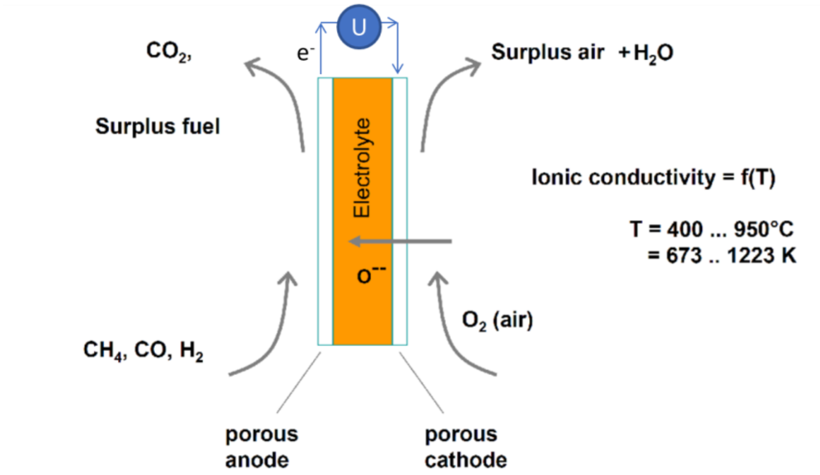
Pappacena, A. et al., Catal. Sci. Tech. 6 (2016), 399;
Pappacena, A. et al., J. Phys. Chem. C 121 (2017) 17746.

Ceria-Zirconia Solid Solutions in Thermochemical Water Splitting Cycles

CeO_2-Sn@SnOx electrocatalysts for IT-SOFC anodes

CATALYSIS for ENERGY and ENVIRONMENT

Solid Oxide Fuel Cell



Membrane properties:
- gas tight
- high ionic conductivity
- low electronic conductivity

Electrode properties:
- porosity
- mixed electronic-ionic conductivity
- mechanical and chemical compatibility with other cell components
- Catalytic and electrocatalytic activity
- Thermal stability

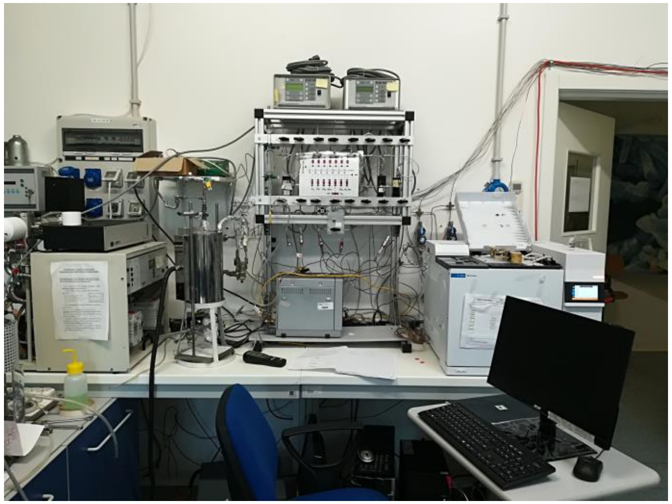
Ceria Properties:
- Good ionic conductivity and good oxygen storage capacity at temperatures as low as 600° C .
- Poor catalytic activity and electronic conductivity.

Tin has been tested to improve ceria properties

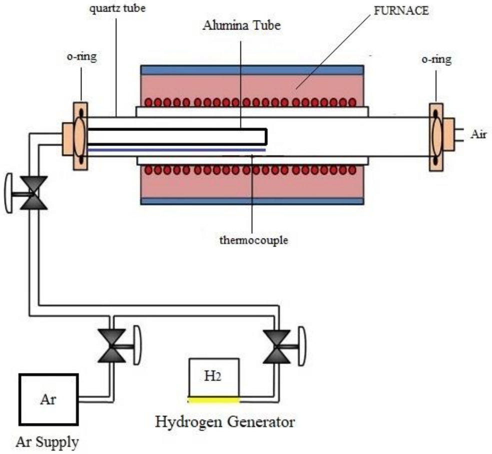
Laboratory Facilities

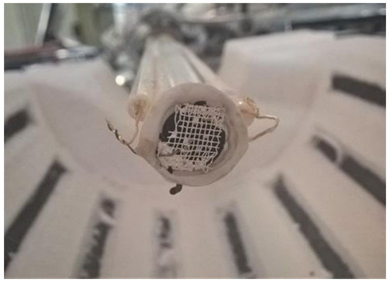
CATALYSIS for ENERGY and ENVIRONMENT

Catalytic test plan



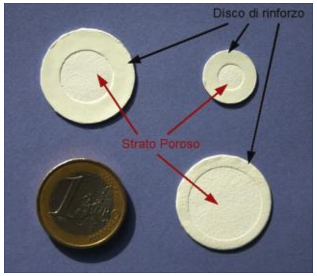
Cell test system

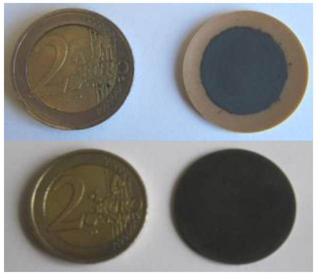




Anodic chamber interfaced with a Micro Gas-Chromatograph and with a Polarograph and Electrochemical Impedence Spectrometry Analyser

Cell preparation

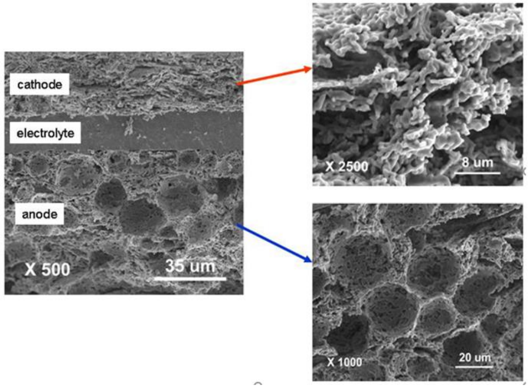




Tape casting

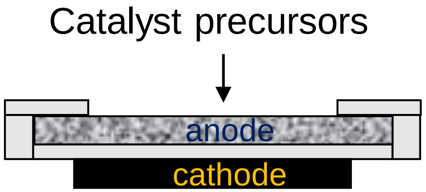
Pressing

Structure of Cells



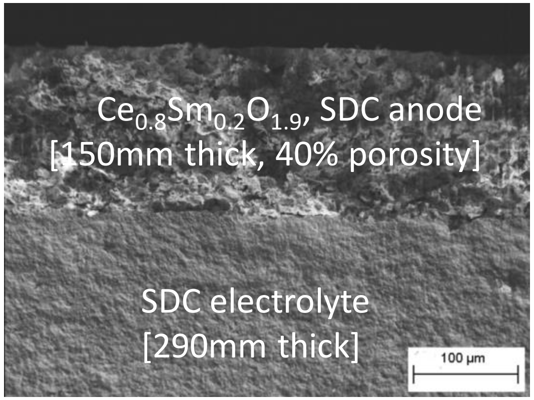
S.P. Jiang Mat. Sci. Eng. A418 (2006) 199-200
M. Vohs et al. Adv. Mater. 21 (2009) 943-945

Impregnated Anode



CeO_2-Sn@SnOx electrocatalysts for IT-SOFC anodes

Electrolyte supported Cells



50wt% $(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-x}$ /
50wt% $Ce_{0.8}Gd_{0.2}O_{1.9}$, cathode
[20mm thick]

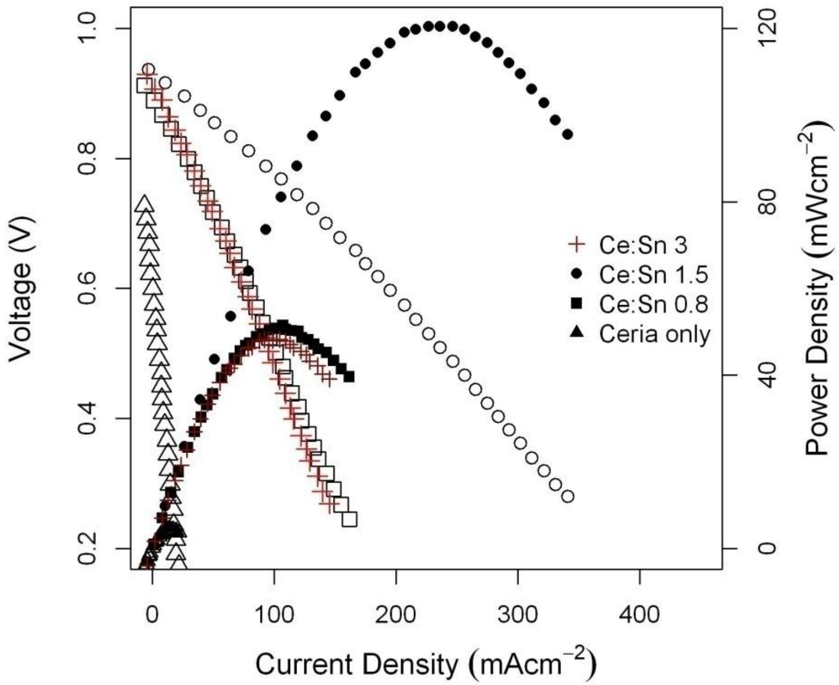
1. Infiltration of ceria precursor and calcination at 873K
2. Infiltration of tin oxide precursor and calcination at 873K

↓

Tin oxide on ceria WITHOUT solid solution

Cells	Ceria (weight%)	Tin (weight %)	Ce/Sn (mol /mol)
A	20	0	-
B	0	12	-
C	20	6	3
D	20	12	1.5
E	10	12	0.8

V-J /Power curves for different Ce:Sn molar ratios



- Power 20mW/cm^2 for Sn alone
- 10x Power increase if Ce:Sn = 1.5
- Power drop with other Ce:Sn values

Possible reasons (not mutually exclusive):

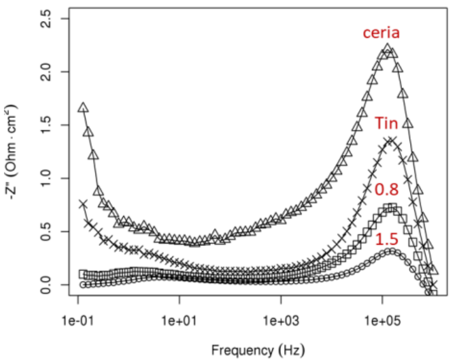
Excess tin segregates

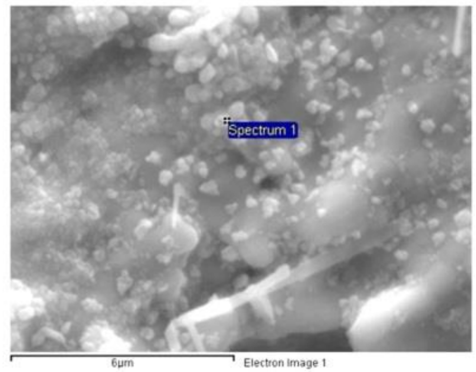
Area of TPB is reduced

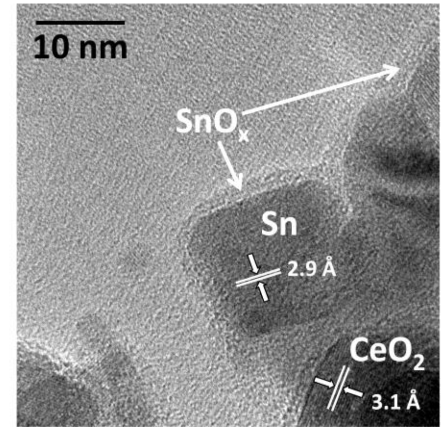
It is important to maximize Ce-Sn interaction without having excess tin

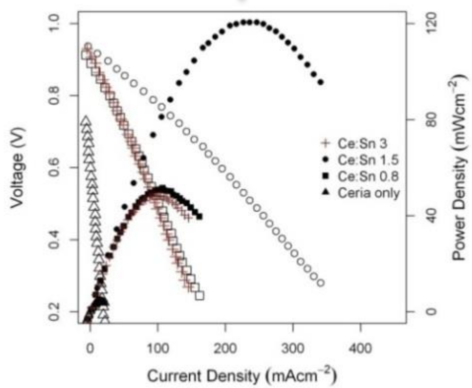
CeO_2-Sn@SnOx electrocatalysts for IT-SOFC anodes

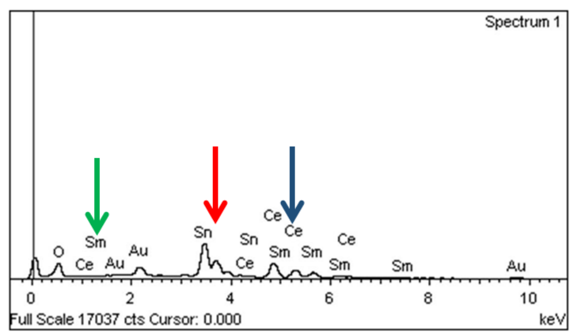
Layout of the investigation

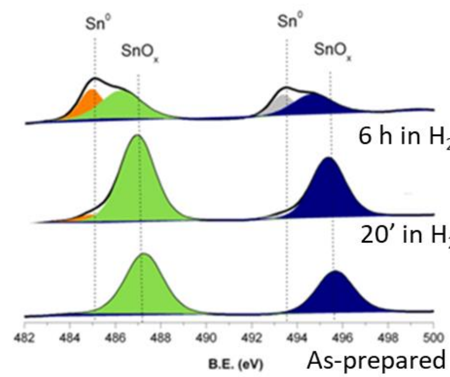










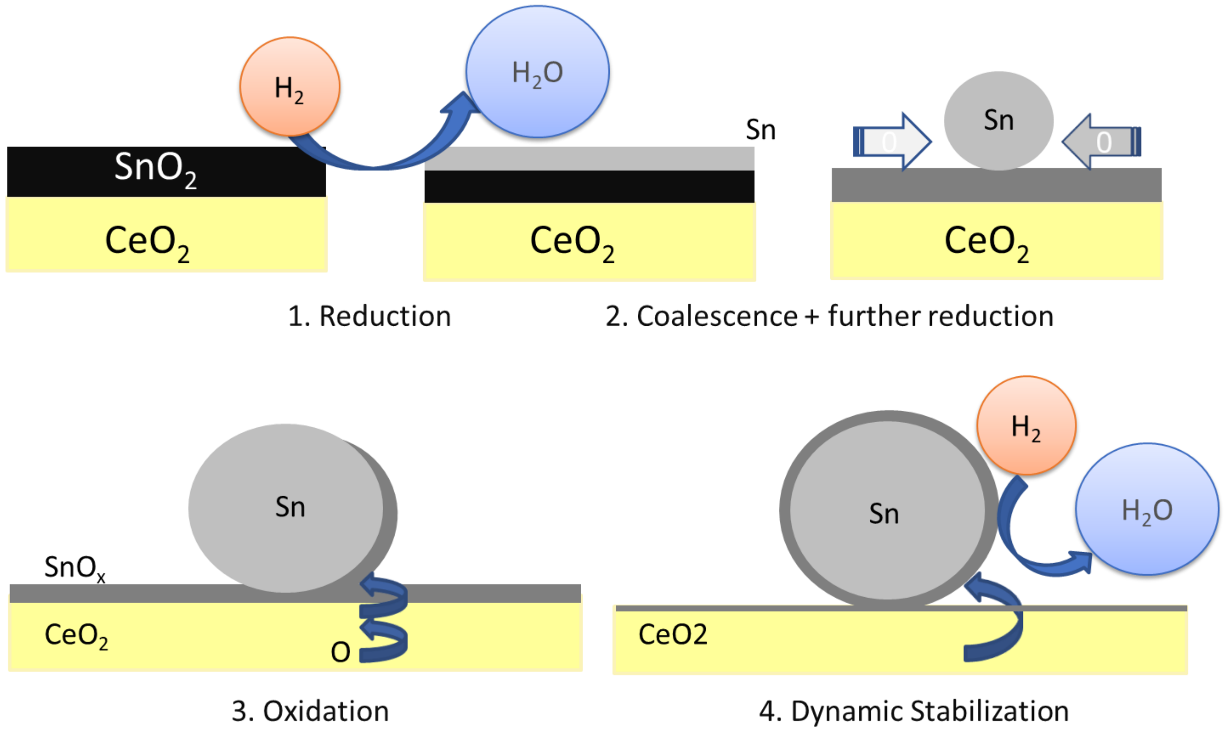


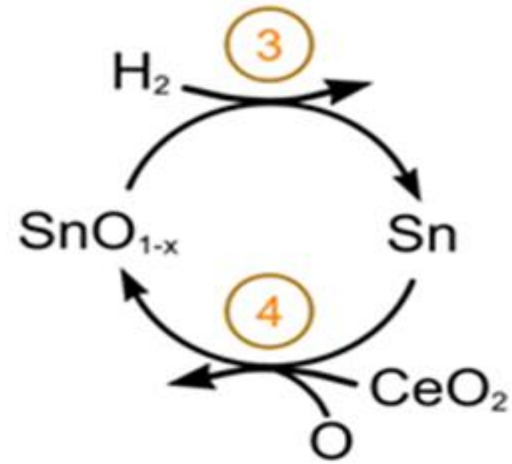
Electrochemistry
testing in H_2 at 600° C

SEM
After cell testing in H_2

HRTEM & XPS
on powder

In situ formation of the active phase

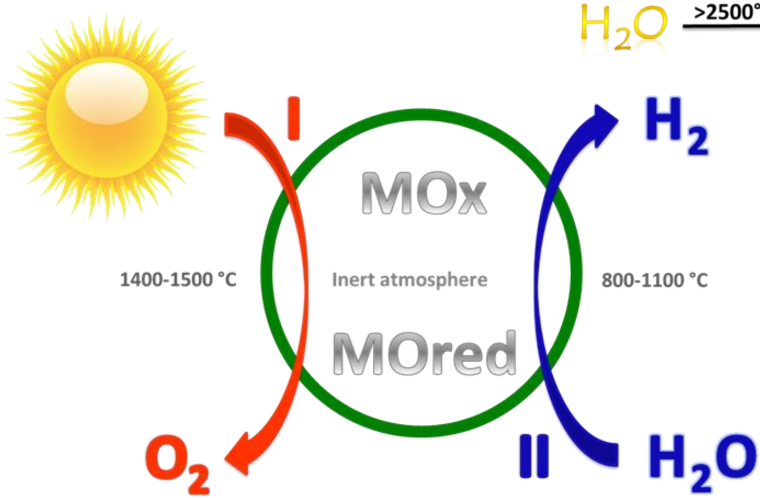




The interaction between CeO_2 and SnO_x leads to an electro-catalytically active interface and to the stabilization of molten tin 400K above its melting point in form of core-shell Sn@SnO_x nanoparticles

Ceria-Zirconia Solid Solutions in Thermochemical Water Splitting Cycles

$$H_2O \xrightarrow{>2500°C,\ 1\ bar} H_2 + \frac{1}{2}O_2$$



Drawbacks

1. Reduction at hight temperatures
2. Sublimation of Ceria → decrease of reactivity

I Endothermic step:

$CeO_2 \rightarrow Ce_2O_3 + ½O_2$
ΔH =198 kJ/mol at 2027 °C

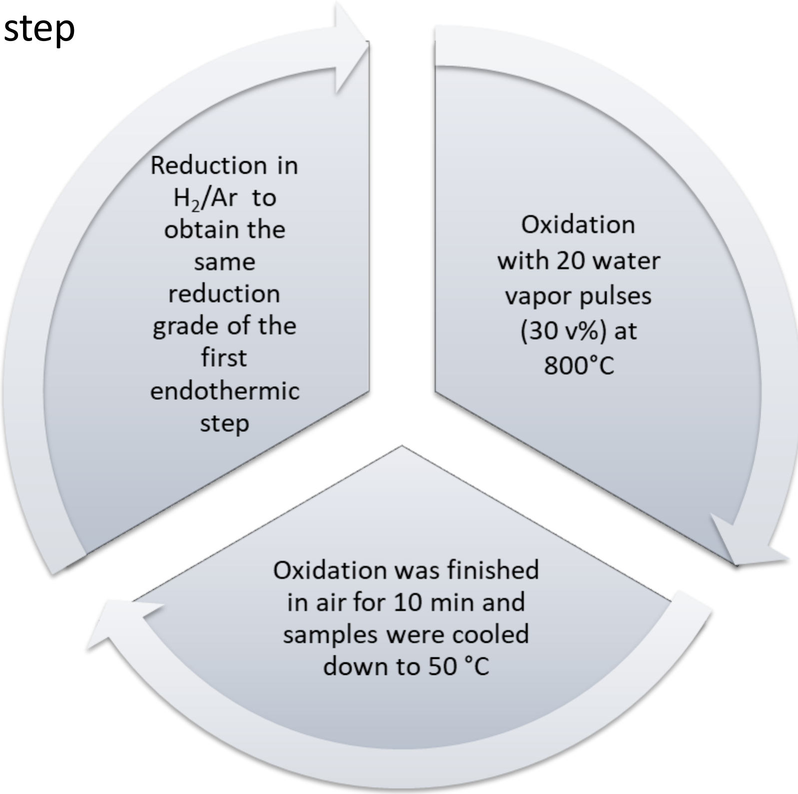
Zirconia doping decreases temperature at 1300-1500 °C

II Exothermic step:

$Ce_2O_3 + H_2O \rightarrow CeO_2 + H_2$
ΔH = -125 kJ/mol at 400-800 °C

Investigated $Ce_{0.15}Zr_{0.85}O_2$ (CZ15) and $Ce_{0.80}Zr_{0.20}O_2$ (CZ80) solid solutions after thermal treatments in N_2 or air at 1300°C.

II step

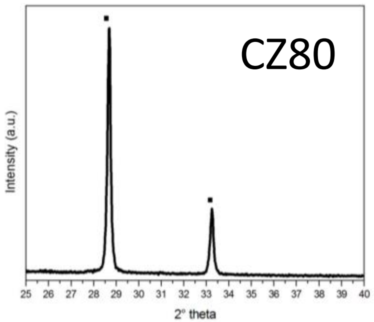


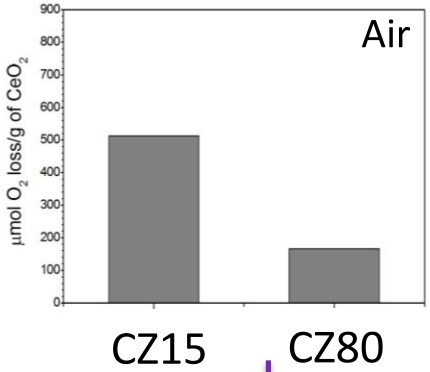
Objectives of the study

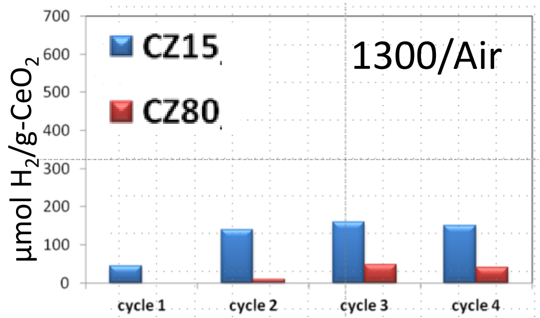
- The effect of thermal treatment atmosphere (N_2 and air) in the structure of materials.
- Relationship between structural changes of these materials and their activity in the water splitting .

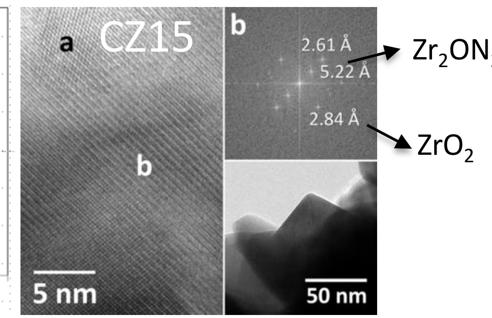
Ceria-Zirconia Solid Solutions in Thermochemical Water Splitting Cycles

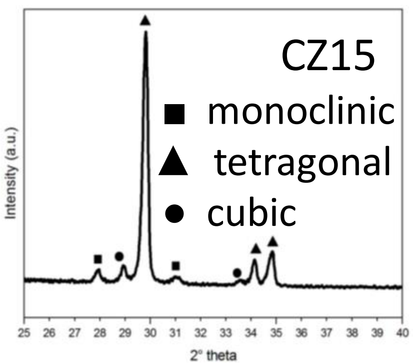
Layout of the investigation

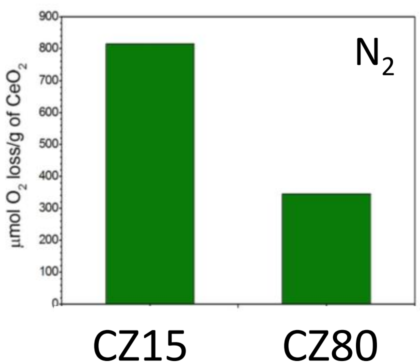


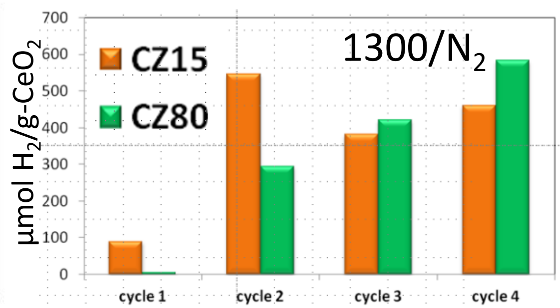


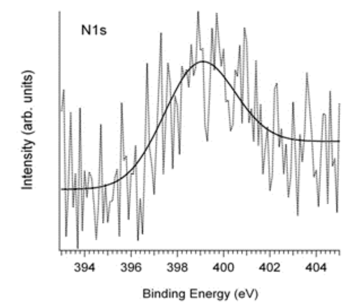












XRD
After 4 h in N_2 and Air

TGA
in N_2 in 80'

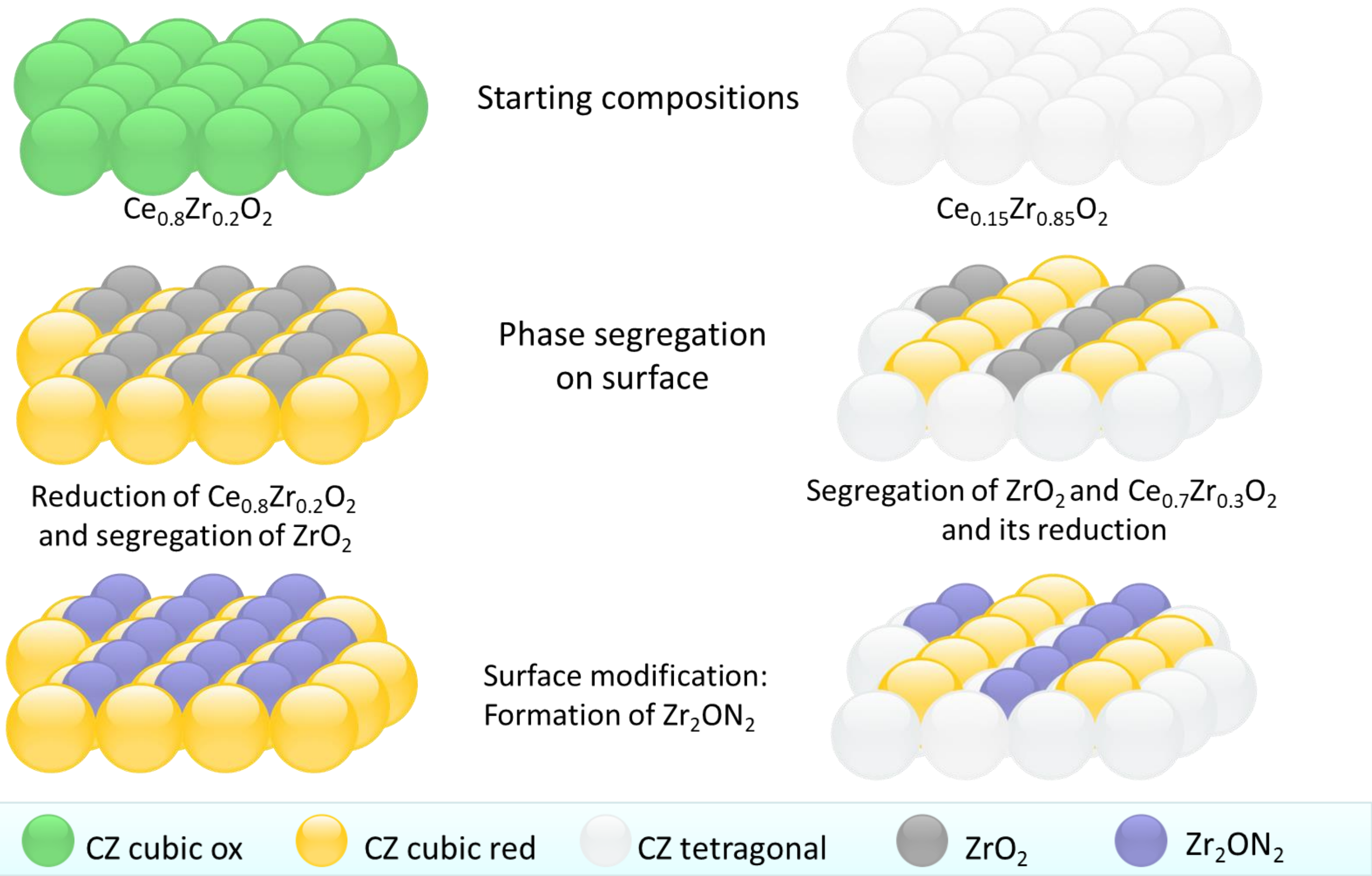
Autochem II Analyser
-Reduction in 5% H_2/Ar
-Oxidation by water vapor/Ar pulses

HRTEM & XPS
after 4h in N_2

Ceria-Zirconia Solid Solutions in Thermochemical Water Splitting Cycles

CATALYSIS for ENERGY and ENVIRONMENT

In situ formation of the active phase



Oxynitride phase favors the WSR

Surface heterogeneity drives the ceria-zirconia water splitting reactivity

Conclusions

- In the fields of energy applications it is important to study the evolution of catalysts and electrocatalysts under operating conditions since the active phase often is formed in situ.

- The future approach would be engineering the trasformations of the materials during the reaction

- **Direct utilization of bio-fuels in solid oxide fuel cells for sustainable and decentralised production of electric power and heat (PRIN 2017-DIRECTBIOPOWER):** development anode electrocatalysts for direct utilization of biofuels in SOFC tailoring exsolved perovskites characterized by active transition metals (Ni, Co, Fe..)

Aknowledgments

Post Doc: PhD Alfonsina Pappacena, PhD Marzio Rancan (UNIPD), PhD Luca Bardini

Students: Andrea Felli, Rudy Calligaro

Faculty: Prof Alessandro Trovarelli, Prof. Carla de Leitenburg, Prof. Jordi Llorca (UPC), Prof. Lidia Armelao (UNIPD)

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