PRACTICAL

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Nanostructured powders of Ni-TZP cermet
Elaboration by combustion and structural characterizations
Application : SOFC

1) Objectives

The main objectives of this practical are (1) to fabricate nanostructured powders of cermet based on Ni and Tetragonal Zirconia Polycrystals which will be referred to as TZP by combustion, (2) to characterize the raw powders and to discuss the consequence of a heating treatment in air and in H_2.
The word «cer-met » comes from « CERamic and METal ».
These materials can be used as anodes for SOFCs.

2) see the description of the combustion process in the jointed article

The reaction is an oxydo-reduction using urea $CO(NH_2)_2$ as fuel (high reducing power), O_2 from air as combustive and nitrates as reactives (high oxidizing power) : $Ni(NO_3)_2.6H_2O$, le $ZrO(NO_3)_2.6H_2O$ and $Y(NO_3)_3.4H_2O$.
The combustion of urea is as the following :

$$3/2O_2 + CO(NH_2)_2 \longrightarrow N_2 + CO_2 + 2\ H_2O$$

and is very exothermic (ΔH= -130kcal/mol at 25°C) and is self sustaining.

3) Synthesis of 50Ni/50TZP powders with 150 vol.% of urea for group 1 (200 vol.% for group 2)

For security, the synthesis will be limited to **0.5 cm^3 of cermet**.

a – Calculation of the quantities of reactives to weigh

The cermet will be consisted of 50 vol.% of Ni and 50 vol.% of TZP.
TZP is based on: $(ZrO_2)_{0.97}(Y_20_3)_{0.03}$ or $(ZrO_2)_{0.94}(Y0_{1,5})_{0.06}$
TZP: molar mass: 121,5696 $g.mol^{-1}$, volumic mass: 6 $g.cm^{-3}$
Ni: molar mass: 58,69 $g.mol^{-1}$; volumic mass: 8.9 $g.cm^{-3}$.
Reactives are:
- $Ni(NO_3)_2.6H_2O$ (M= 290.69 $g.mol^{-1}$)
- $ZrO(NO_3)_2.6H_2O$ (M= 339.22 $g.mol^{-1}$)
- $Y(NO_3)_3.4H_2O$ (M= 382.91 $g.mol^{-1}$)

Quantity of urea.

The determination of urea quantity is obtained by the calculation of equivalent valencies for each component, $Ni(NO_3)_2$, $ZrO(NO_3)_2$, $Y(NO_3)_3$.
the valencies of elements are: Ni(+2), N(0), O(-2), C(+4),H(+1), Y(+3), Zr(+4)
Urea molar mass is given as the following : $CO(NH_2)_2$: M= 60 $g.mol^{-1}$

For a complete reaction with 100% of urea, the respective quantities of materials have to verify this equation: $\Sigma\ \upsilon i.ni = 0$
where υi and ni are the valency and the number of moles of each component , respectively.

Urea has a positive valency (reducing power).

b – Operating mode

- First weigh the 3 reactives and crush them in a mortar
- Ten put them in a crucible in silica and mix them on a heating plate pre-heated at 250°C
  Up to the obtention of a green liquid mixture. Then urea is added progressively up to the formation of a green gel.
- As soon as the mixture is starting to boil, one introduces the silica crucible in the pre-heated furnace at around 500°C.
- After some minutes, an exothermic reaction is produced inside the furnace with a large increase of temperature due to the combustion *(Fig. 1).*
  This phenomenon can last for 2 minutes. ENJOY !!
- When the combustion is finished, you can close the door of the furnace and leave the crucible for 5 minutes.

Combustion à 630°C de Ni/TZP

- Fig. 1 : Flame due tocombustion

- Then you take the refractory gloves, the big holders and the protection glasses to take out the crucible.
- Then you leave the crucible on a refractory stone and wait for cooling. You can observe the microstructure of the raw powders (morphology and colour)

4) Microstructural and structural analyses of raw powders of 50Ni/50TZP
With 150 % vol. of urea (group 1)
With 200 % vol. of urea (group 2)

Morphology of the raw powders
Observation of raw powders will be performed using SEM.
The colour of the powders will be discussed versus the synthesis.

Determination of crystalline phases
Scan the XRD diffractogramm from 20 to 80° in 2 theta with Rigaku diffractometer

using $K_{\alpha 1}$ Cu, λ = 1.5406 Å.

You will have JCPDS of Ni (file #4-850), NiO (file #4-835) and TZP (file #17-923).
Determinate the nature of the crystalline phase that you have prepared and index XRD peaks in (hkl).

Determination of TZP grain size
Calculate the crystallite size from the Scherrer formula which will be applied to peak *111* of tetragonal zirconia and to peak *111* of silicon (29°) and the one on the larger Ni peak.

$$L = (0.9\lambda) / (\Delta\theta * \cos\theta_0)$$

avec $\Delta\theta$ (rad) = $(FWHM^2_{échantillon} - FWHM^2_{Si})^{½}$

L (nm) = crystallite size

λ (nm) : incident wavelength

θ (in radian) :Full width at half maximum

θ_0 (in degree) angular position of the peak

The instrumental resolution is measured with a reference Silicon powder (Rectapur Prolabo).

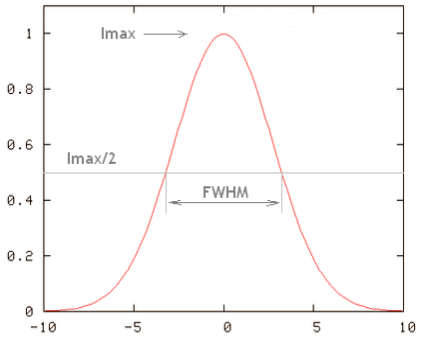


Fig.2 : FWHM: Full Width at Half Max

5) Structural characterizations of 50Ni/50TZP powders with 150 vol.% urea after heat treatments in air and in H_2

Two thermal treatments on raw powders have been performed.
One part was calcined at 1000°C for 1h in air and another part in H_2.
Find below (Fig. 3) the XRD patterns, of as-prepared powder, heat-treated in air and inH_2.

What is the evolution of the reactions on
(i) the nature of phases and crystallization degree as a function of temperature
(ii) the nature of phases as a function of atmosphere

6) Application
In order to use these materials as anode for SOFC, what do you recommend as thermal treatment atmosphere ?
Justify your answer.

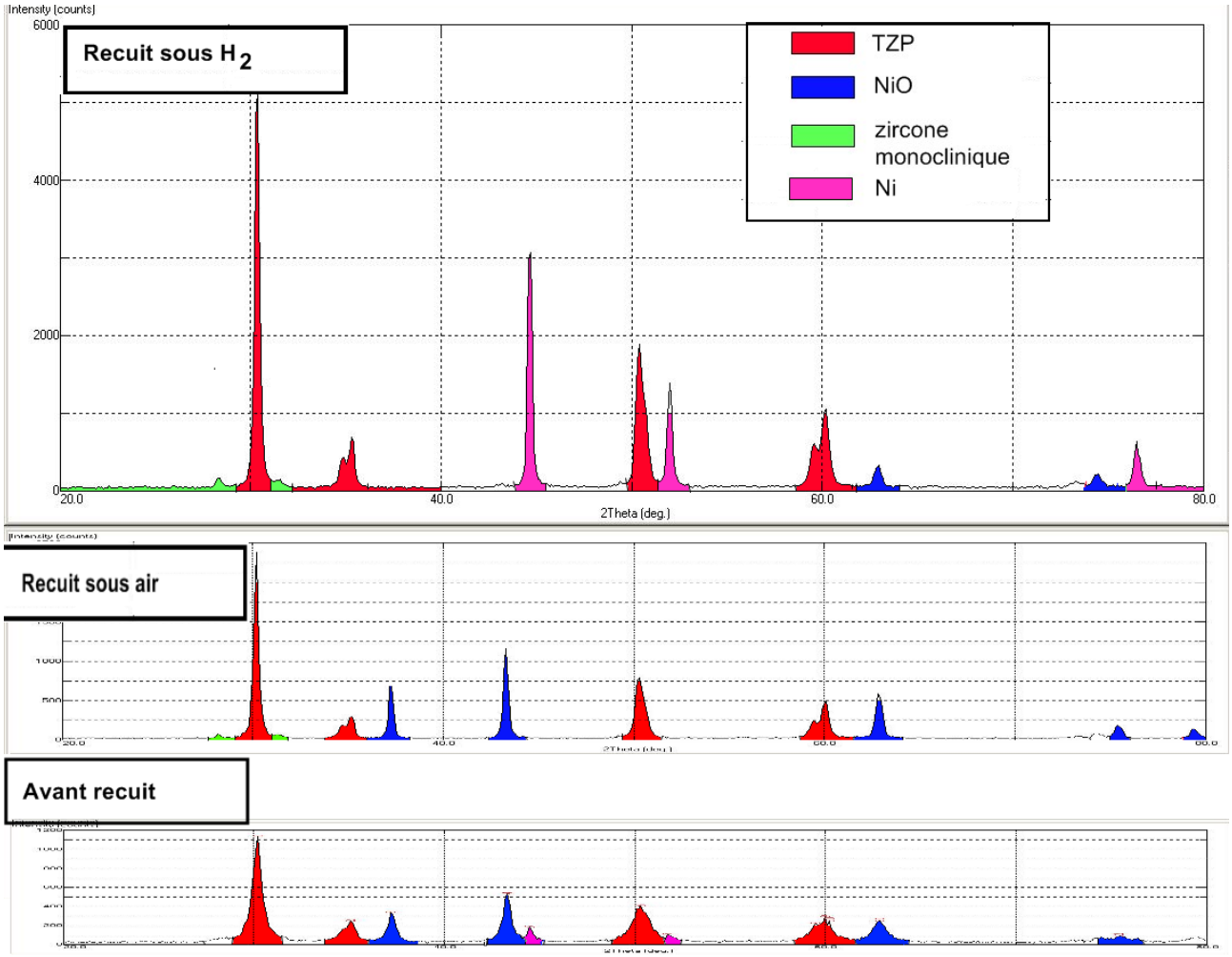
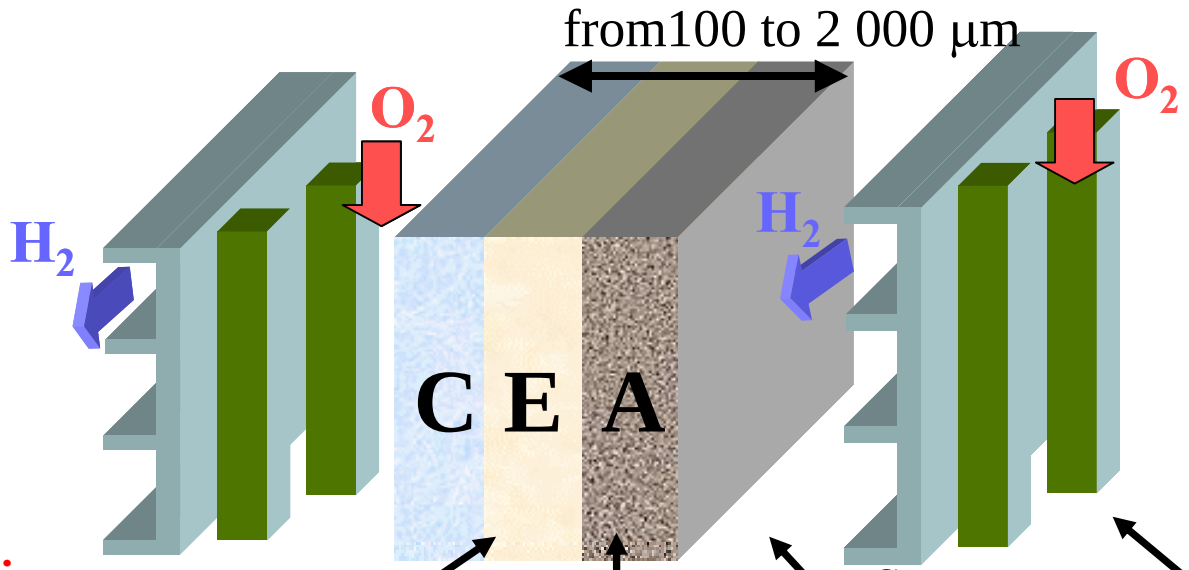


Fig. 3 : Comparison of XRD patterns on the raw powder and after heat treatments in air and in air and in H_2 at 1000°C/1h.

APPLICATIONS

SOFC



Reactions at cathode : $1/2\ O_2 + 2\ e^- \Rightarrow O^{2-}$

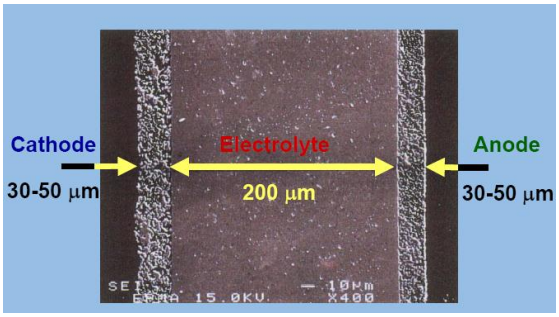
Combustive : air

Reactions at anode : $O^{2-} + H_2 \Rightarrow H_2O + 2e^-$

Fuel : H_2

or CH_4 with *in situ* reforming to give H_2

$$CH_4 + 2H_2O \Rightarrow CO + 3\ H_2$$



Electrical characteristics at 900°C

$U_{theor.} \sim 0.94$ V

$U_{out} \sim 0.7$V

$P \sim 0.2 W.cm^{-2}$

$i \sim 0.3\ A.cm^{-2}$